



Hydrothermal Conversion of Biomass

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Glossary

Hydrothermal: denotes an aqueous system under pressure and elevated temperature, i.e., above 100 °C and 0.1 MPa, in which the water is mainly present in liquid form.

Carbonization: converting fresh biomass into a char-like material by a thermochemical process.

Liquefaction: converting a solid into a liquid by a thermochemical process, and not just by melting.

Gasification: converting a solid or a liquid into a gaseous product by a thermochemical process, and not just by evaporation.

Pyrolysis: decomposing a solid or liquid organic material by heating it to above ca. 300 °C in the absence of oxygen.

Bio-oil: crude oil-like liquid from biomass liquefaction or pyrolysis.

HTL oil: bio-oil from a hydrothermal liquefaction process.

HTG gas(es): gas(es) formed by a hydrothermal gasification process.

HTC char: solid carbon-rich material formed by a hydrothermal carbonization process.

Hydrolysis: breaking chemical bonds by the action of liquid water.

Definition of the Subject

The term “hydrothermal” originates from the fields of geochemistry and mineralogy and denotes hot, liquid water courses (aquifers) in the deeper crust or on the ocean floor. In a technical context, “hydrothermal” is used as a synonym for hot, pressurized liquid water (or hot compressed water). In its pure form, hot compressed water is used in thermal power plants for supercritical steam cycles. This enables reaching higher thermal efficiencies compared to using steam below the critical point of water. Supercritical steam cycles are operated at a pressure above the critical pressure p_c and at a temperature above the critical temperature T_c of pure water, respectively. Strictly speaking, such a steam cycle contains supercritical water and not steam. In this chapter the following definitions are used:

- Hydrothermal: liquid water at a pressure above 0.1 MPa and at a temperature above 373 K
- Subcritical water: liquid water at a pressure above the saturation pressure and at a temperature below 647 K (i.e., the critical temperature T_c)
- Supercritical water: water at a pressure above 22.1 MPa (i.e., the critical pressure p_c) and at a temperature above 647 K
- Near-critical water: water in the vicinity of (often below) the critical point p_c and T_c

Referring to the conversion of biomass under such hydrothermal conditions, the following terms are used:

- Hydrothermal carbonization (HTC). During hydrothermal carbonization, typically conducted

at conditions below the critical point, the thermochemical phases of “heating up” and – at least partially – of “pyrolytic decomposition” are occurring. Moreover, the presence of liquid water enhances hydrolytic reactions as well as dehydrations. Its goal is the provision of a solid fuel (bio-char) similar to lignite.

- Hydrothermal liquefaction (HTL). HTL is carried out in near-critical water (typically below the critical point) and at pressures considerably higher than for HTC. Similar to HTC, the thermochemical phases of “heating up” and – at least partially – of “pyrolytic decomposition” are occurring. The presence of liquid water leads to the hydrolysis of the biomass. The goal of HTL is the provision of a liquid fuel (bio-oil).
- Hydrothermal gasification (HTG). HTG is typically carried out in supercritical water, during which the thermochemical phases of “heating up,” of “pyrolytic decomposition,” and of “gasification” are occurring. The goal of HTG is the conversion of the biomass into a combustible gas.

Introduction

Processing fresh biomass means processing a large amount of water. If the biomass is to be converted at high temperatures, it is usually (partially) dried before processing to increase the energy efficiency by avoiding excessive evaporation of water. Nevertheless, the action of *liquid* water on woody biomass has been known for long in the pulping of wood. Together with the pulping chemicals, water breaks up the structure of the wood and allows the recovery of the valuable cellulose fibers. This is an example of a well-established mild hydrothermal process used in industry. Geochemical transformations involving hot liquid water are other examples of such hydrothermal processes in nature that led to the formation of our fossil coal, oil, and gas reservoirs. Making such geochemical transformations amenable to industrial processing in the context of energy utilization has been the subject of intense research since the early twentieth century.

An important argument for selecting hydrothermal technologies is the water content of the feedstock to be converted. Wet biomass and sludges require a substantial amount of energy for their drying, a precondition if they are to be used as a solid fuel for combustion. If such wet feedstocks are converted thermally with conventional (non-hydrothermal) technologies, the net energy gain is very low or it can even become negative; i.e., if the water content in the biomass is too high, even an additional fuel might be required. Also biochemical technologies are well suited to convert wet fermentable biomass, because they operate at a temperature at which only insignificant amounts of water evaporate. Hydrothermal processes are thus particularly suited for biomass with a water content of ca. 40–85% and bear much potential for its efficient and environmentally friendly conversion into fuels and chemical products.

Fundamentals

The aim of the following sections is a discussion of the fundamental relationship governing biomass conversion within a hydrothermal medium. First, the thermodynamic context and the phase behavior are explained. Then, the different hydrothermal conversion pathways and the main chemical reactions are presented.

Thermodynamics and Phase Behavior

The density of water under the conditions of HTC and HTL resembles the one of liquid hydrocarbons. At near-critical and even more at supercritical conditions, the density decreases further and has a value similar to a compressed gas at the same pressure. The specific enthalpy increases monotonically with temperature and pressure. The specific heat capacity, on the other hand, takes on much higher values near the critical point than liquid water at ambient conditions. The dynamic viscosity decreases steadily from HTC to HTG conditions. The relative static permittivity ϵ_r , as a measure for the polarity of a solvent takes on much lower values than water at ambient conditions ($\epsilon_r = 78$). At HTC conditions, it corresponds to glycerol at

ambient conditions. At HTL conditions, ϵ_r corresponds to acetone, and at HTG conditions, ϵ_r lies in the range of weakly polar to nonpolar solvents such as diethyl ether and n-hexane, respectively [1]. This change in solvent properties makes oily compounds, formed under HTL and HTG conditions, well soluble in hot compressed water. Ionic species are not solvated beyond the critical point and precipitate as salts. Organic acids are mainly present in their protonated state.

Liquid water under hydrothermal conditions exhibits already at relatively low temperatures a chemical reactivity that is much higher than water vapor. Liquid, subcritical water is able to solvate also ionic species and enables thus a whole palette of reaction mechanisms that do not happen in the vapor phase. The most prominent of these reactions is hydrolysis (i.e., the splitting of a chemical bond by the attack of a water molecule). Both at HTC and HTL conditions, the ionic product of water is several orders of magnitude higher than at ambient conditions. The much higher concentration of protons and hydroxide ions at such conditions accelerates in particular hydrolytic reactions without the need of adding an acid or a base. Under supercritical conditions, the ionic product decreases to very small values (Table 1).

Because in a hydrothermal medium there are many reactions going on, the selectivity of uncatalyzed conversions is generally low, leading to a mixture of many different chemical compounds. Only by using catalysts (during

liquefaction or gasification) or by choosing very high temperatures (for the gasification) can a desired, narrow product spectrum be obtained.

During the hydrothermal conversion of biomass, numerous solid, liquid, and gaseous compounds are formed as intermediates or as end products. These compounds may form solutions, emulsions, or suspensions with water, or they may be present as separate solid, liquid, or gaseous phase (see Fig. 2). The thermodynamics of such a multi-component and multiphase system are very complex. For this reason, there is no comprehensive model yet available to calculate the thermodynamic parameters of such mixed systems with acceptable accuracy. For thermodynamic calculations of hydrothermal systems, usually the following two approaches are used:

- The fluid phase is taken as pure water and all calculations are performed with the physical properties of pure water. The physical properties of water, such as density, molar volume, internal energy, enthalpy, specific heat capacities, viscosity, and compressibility, are available with good accuracy over a wide range of temperatures and pressures [5, 6].
- The fluid mixture is described using specific equations of state (EOS) and mixing rules.

For nonelectrolyte systems, a cubic equation of state is often used, similar to van der Waals' equation for real gases:

Hydrothermal Conversion of Biomass,

Table 1 Selected properties of pure water at ambient conditions and at conditions typical for hydrothermal

	Ambient conditions	HTC	HTL	HTG ^a	HTG ^b
Temperature in °C	25	200	330	400	600
Pressure in MPa	0.1	2	20	30	30
Density in kg/m ³	997	865	667	357	87
Spec. enthalpy in kJ/kg	105	852	1,506	2,153	3,447
Heat capacity in J/(kg K)	4,181	4,493	6,268	25,868	3,169
Dyn. viscosity in Pa s	$8.9 \cdot 10^{-4}$	$13.4 \cdot 10^{-5}$	$7.8 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$
Dielectric constant	78	35	17	6	1.4
Ion product in mol ² /kg ²	$1.0 \cdot 10^{-14}$	$7.0 \cdot 10^{-12}$	$1.8 \cdot 10^{-12}$	$1.7 \cdot 10^{-15}$	$9.5 \cdot 10^{-23}$

Dyn dynamic, *Spec* specific

^aNear-critical

^bSupercritical

carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) [2, 3]

- Peng-Robinson [7]
- Redlich-Kwong-Soave with the mixing rules of Schwartzentruber and Renon [8]
- Duan (based on Lee and Kesler's equation of state) [7]

Hydrothermal electrolyte systems can be described up to high pressures and temperatures with the semiempirical method of Helgeson-Kirkham-Flowers (HKF) [7].

The main difficulty for the application of such equations of state (EOS) to any mixture is the lack of the required temperature-dependent binary interaction parameters. These parameters can only be obtained from experimental data of pressure, temperature, volume, and composition, which in turn have been determined only for simple binary and a few ternary mixtures at hydrothermal conditions.

Hydrothermal systems with electrolytes (i.e., salts) exhibit a particularly complex phase behavior including miscibility gaps. Such mixtures of one or several salts with water can be categorized roughly into a "type 1" and a "type 2" behavior. There are several subcategories for each of these two main categories [9]. For type 1 systems, the solubility of the salt in water increases monotonically with temperature, whereas for type 2 systems, the solubility of the salt decreases monotonically up to the critical point of water, or it may pass through a maximum. An example for this behavior is sodium sulfate (Na_2SO_4) in water (H_2O). Beyond the solubility curve, type 2 systems form a solid salt phase, which is in equilibrium with a saturated supercritical fluid phase. Since the solubility of type 2 salts in supercritical water is very low, the two phases are merely solid salt and supercritical water. These solid salt phases typically form "sticky" deposits on vessel walls and may thus lead to blockages. Type 1 systems, on the contrary, form a liquid salt phase saturated with water, which is in equilibrium with a supercritical water phase. Only at high temperatures do type 1 systems also form a solid salt phase. Such systems do normally not lead to sticky deposits and blockages. An example is sodium chloride (NaCl) in water. The description of ternary and higher systems is even more

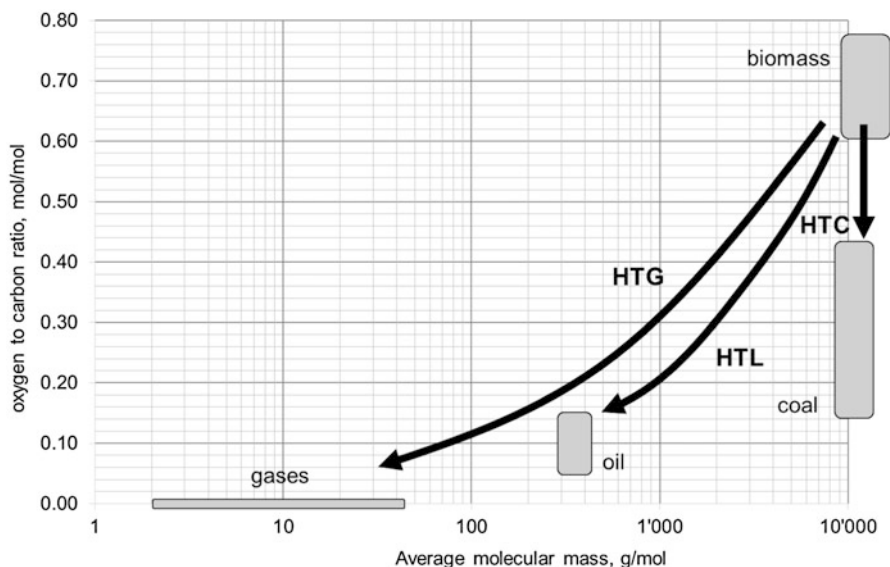
complex. In such systems liquid-liquid immiscibility was also reported [10].

For hydrothermal gasification (HTG) performed under suitable reaction conditions, a mixture of water and gases can be obtained whose composition corresponds to the thermodynamic equilibrium and which can be described satisfactorily by a cubic equations of state (EOS). Often the conversion of the biomass and the intermediates will not be complete. Also the gaseous products will usually not equilibrate fast enough to the thermodynamically stable compounds without a catalyst. In that case, a sound design of a hydrothermal gasification process can only be performed if the reaction kinetics are known. Such kinetics must account for the variability in the composition of the feedstocks as well as for the breadth of reactivities of the different intermediates. Kinetic models and their parameters have only been derived for a limited number of model substances and loosely for some real mixtures. Mass transport in the often concentrated multiphase systems aggravates the challenge for designing hydrothermal processes. Therefore, it is not surprising that to date no plant has been designed considering rigorously all pertinent aspects of reaction engineering.

Hydrothermal Conversion Paths

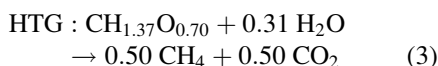
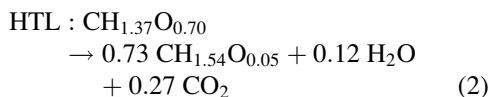
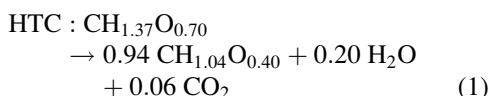
All three hydrothermal conversion paths (i.e., HTC, HTL, and HTG) aim at reducing the molecular size of the feedstock and/or at realizing a low oxygen content in the final product. The latter corresponds also to an increase in heating value of the products. This relationship is visualized in Fig. 1. As the water content of all three final products (bio-char from HTC, bio-oil from HTL, and methane- or hydrogen-rich gas from HTG) is reduced considerably compared to the feedstock, a further increase of the specific energy content compared to the starting material is realized.

To be able to compare the three conversion paths, simplified stoichiometric equations are discussed below. The starting material is beech wood (dry ash-free), represented by its elemental composition $\text{CH}_{1.37}\text{O}_{0.70}$. HTC is represented by Eq. (1), HTL by Eq. (2), and HTG by Eq. (3):



Hydrothermal Conversion of Biomass, Fig. 1 Reduction of the oxygen content and of the molecular size (typical ranges) for hydrothermal processes (the

rectangle in the upper right corner represents the initial biomass, e.g., wood, and the bar for the HTG path encompasses hydrogen to propane)



These three equations are based on idealized conversion pathways:

- HTC: A complete conversion of the carbon to HTC char and gas is assumed (i.e., no carbon left in the aqueous phase, and only CO₂ formed as gaseous product).
- HTL: A complete conversion of the carbon to HTL oil and gas is assumed (i.e., no carbon left in the aqueous phase, and only CO₂ formed as gaseous product).
- HTG: A complete conversion of the carbon to gases is assumed (i.e., only CH₄ and CO₂ are formed as gaseous products).

The elemental composition of the HTC char, CH_{1.04}O_{0.40}, corresponds to a bio-char formed under typical HTC reaction conditions, i.e., 220 °C and 4 h reaction time [11]. The elemental composition of the HTL oil corresponds to the oil from the Hydrofaction process (section “Processes and Installations” of section “Hydrothermal Liquefaction (HTL)). For HTG it was shown that wood can be converted to a gas with approximately equal amounts of methane and carbon dioxide and only minor amounts of hydrogen when using an appropriate catalyst [12].

The theoretical carbon efficiency, i.e., the fraction of the carbon in the starting material transferred to the energy-rich product, decreases from 94% for the ideal HTC to 73% for the HTL to 50% for the HTG (Eqs. 1, 2, and 3). In reality, however, these values are not attained because a significant fraction of the carbon is lost as dissolved organic carbon (DOC) in the aqueous phase, in particular for HTC and HTL. For example, HTC of wood shavings led to a carbon distribution of 78% in the char, 17% in the aqueous phase, and 5% in the gas [13].

For the HTG the practical carbon efficiencies are close to the theoretical ones because only

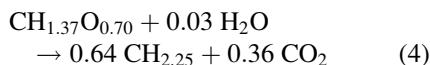
small amounts of dissolved organic carbon (DOC) are formed. Furthermore, the small amount of higher hydrocarbons (C₂₊ such as ethane and propane) in the gas can be used energetically and thus contributes to the carbon efficiency.

All three hydrothermal conversion paths lead to a disproportionation of the carbon in the biomass. Referring again to the simplified stoichiometry in Eqs. (1), (2), and (3), a fraction of the initial carbon with a mean oxidation number of -0.03 is converted to a lower (-0.24 in HTC char, -1.44 in HTL oil, -4 in methane) and the other fraction to the highest oxidation number ($+4$ in CO₂).

Focusing on the main products (i.e., HTC char, HTL oil, methane), the oxygen content decreases and the hydrogen content increases from HTC to HTL to HTG. Methane is the fully hydrogenated product with an oxygen content of zero. Conversely, the amount of carbon dioxide increases from HTC to HTG. While during HTC only 17% of the oxygen bound in the biomass is converted to CO₂, this number increases to 77% for HTL and reaches 143% for HTG (i.e., some of the water is consumed and its oxygen ends also up as CO₂).

These ideal stoichiometric relationships also highlight water to be formed during HTC and HTL. For HTG water is consumed as a hydrogen donor to yield the fully hydrogenated product methane. The stoichiometry depicted in Eq. (3) can only be reached at temperatures well below 500 °C for thermodynamic reasons (see Fig. 18). To obtain useful conversion rates and yields at these relatively low temperatures, catalysts are needed (section “Main Influencing Parameters” of section “Hydrothermal Gasification”).

For HTL the ideal conversion can be taken even further. The ultimate goal is to obtain an oxygen-free oil with an elemental composition close to typical liquid hydrocarbons (e.g., n-octane). This leads to the “perfect” HTL of beech wood according to Eq. (4):



In this case a small amount of water would be consumed to yield the fully hydrogenated product “CH_{2.25}” (the liquid oil), and no water would be

produced. The oxygen in the biomass would be removed exclusively by decarboxylation. This ideal case should be targeted as the ultimate limit. However, to date no catalysts are available that can selectively produce liquid alkanes under these hydrothermal conditions.

Main Chemical Reactions

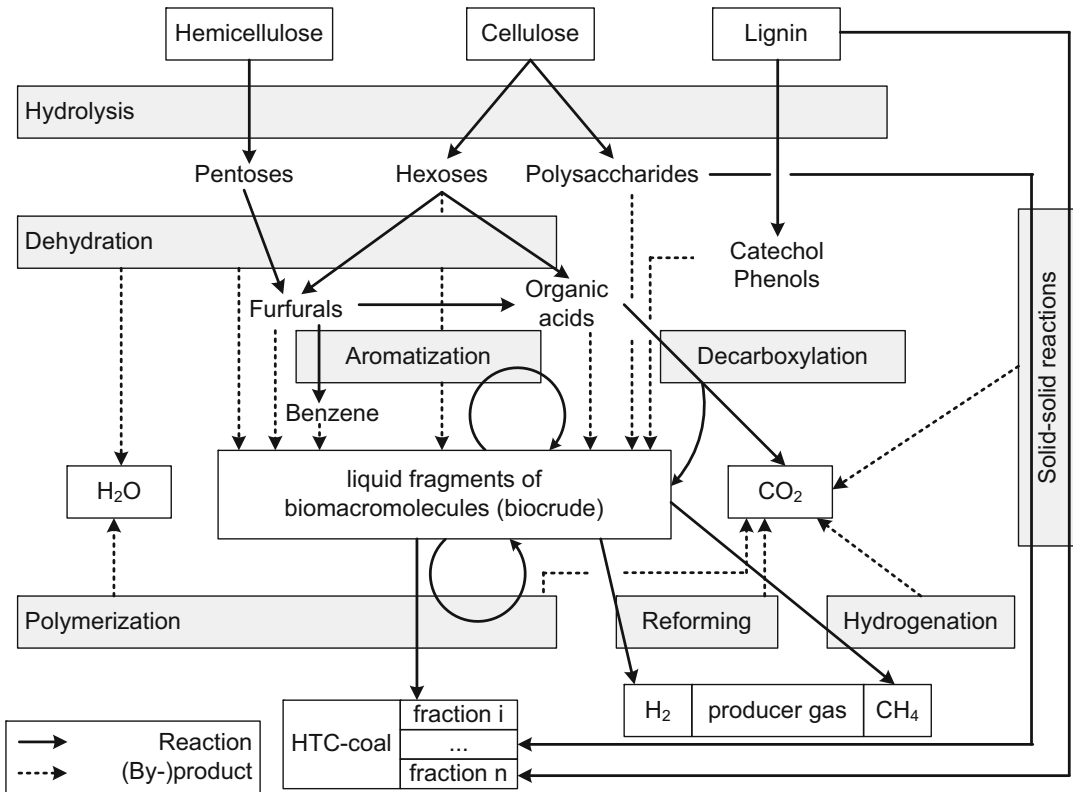
Even from a simple molecule such as glycerol, a large number of more or less stable intermediates and final products are formed upon hydrothermal conversion [14]. With biomass the number of possible degradation pathways and products merely explodes due to the complex molecular structure of biomass (e.g., lignin, cellulose, hemicellulose) and the diversity of chemical functions. Nevertheless, it is possible to group all the different reaction paths into eight typical classes of reactions to simplify the system. The main reaction classes are depicted in Fig. 2.

Hydrothermal Carbonization (HTC)

The carbonization of organic material is a natural geochemical process that led to the formation of the coal reservoirs. In technical processes these natural processes can be strongly accelerated and the distribution of the products can be influenced.

Ernst Berl [15] was able to show already in 1933 that without any or with only small amounts of caustic soda, cellulose was transformed into a coal-like solid under hydrothermal conditions (310–330 °C, 18–20 MPa). Upon addition of larger amounts of caustic soda, a liquid, tarry product similar to crude oil was formed. He postulated the formation of a “protosubstance” first from cellulose, which could be transformed to either oil or asphalt, depending on the conditions (Fig. 3). Berl also conducted experiments under supercritical conditions (400 °C) and reported the formation of a limpid oil with a pungent and gasoline-like odor that hardly darkened over time [15].

More recently, starch was converted to carbon nanostructures under mild hydrothermal conditions [17], which was later extended to using plant material [18]. This work triggered a whole bunch of



Hydrothermal Conversion of Biomass, Fig. 2 Reaction pathways for lignocellulosic biomass under hydrothermal conditions (grouped into eight

reaction classes, *gray boxes*, according to [4] and complemented by the conversion of furfurals to organic acids)

activities in research and development of hydrothermal carbonization technologies [19, 20]. These new developments were, however, performed under milder conditions than the early work of Berl [15].

When discussing HTC, a differentiation has to be made between work with chemically pure and well-defined substances (e.g., sugars, starch) for the synthesis of defined carbon nano- and microstructures and the carbonization of biomass, characterized by a complex mixture of diverse chemical structures. Furthermore, process engineering and energy aspects come to the fore when applying HTC to the production of HTC char from biomass, while these aspects are not relevant for producing pure carbon microstructures.

Main Influencing Parameters

In the following, the main influencing factors for the hydrothermal carbonization are analyzed. The

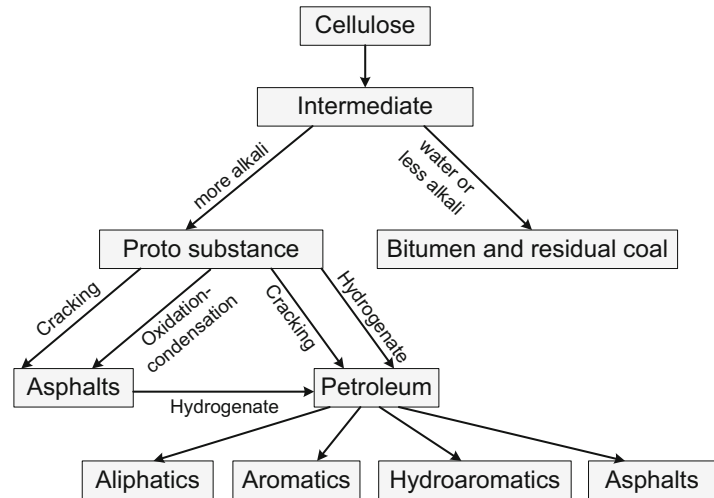
reactor design, the mixing behavior in the reactor, and the heating rate have a minor significance for the reaction engineering; therefore, they are not discussed here. The reactor design is, however, crucial for an energy-efficient process and a high availability (section “Processes and Installations” of section “Hydrothermal Carbonization (HTC)”).

Temperature

The temperature has a marked effect on the HTC; a higher temperature accelerates the rate of the decomposition and polymerization reactions, and the degree of coalification increases (i.e., the maximum carbon content of the HTC char increases with temperature, Table 2). Most of the HTC processes operate at temperatures below 250 °C (section “Processes and Installations” of section “Hydrothermal Carbonization (HTC)”). This means that HTC chars with up to 75% of carbon

Hydrothermal Conversion of Biomass,

Fig. 3 Hydrothermal reaction pathways from cellulose to coal, bitumen, asphalt, or crude oil (After [16])



Hydrothermal Conversion of Biomass, Table 2 Maximum carbon content and higher heating value (HHV) of the HTC char as a function of temperature [13, 21]

Temperature	Carbon content	HHV
Up to 200 °C	Up to 70 wt-% (db)	Up to 29 MJ/kg (db)
Up to 300 °C	Up to 80 wt-% (db)	Up to 33 MJ/kg (db)
Up to 350 °C	Up to 85 wt-% (db)	Up to 35 MJ/kg (db)

db dry basis

and a heating value of ca. 31 MJ/kg (dry basis) can be obtained. These maximum values can be reached only for practically ash-free substrates (e.g., wood), because both the carbon content and the heating value are reduced by the ash content; this can reduce the carbon content of the HTC char to below 30% for substrates with a high ash content such as sewage sludge.

The temperature influences also the properties of the hydrothermal medium itself. This in turn has an influence on the heat and mass transport phenomena; however, their influence is most pronounced for the faster reactions during HTL and in particular HTG.

Pressure, Fluid Density

These two physical parameters are not very relevant for HTC. But the pressure must be high enough to ensure the presence of a liquid

(aqueous) phase. The saturation pressure of pure water is 1.56 MPa at 200 °C and its density 865 kg/m³. Most of the processes discussed in Table 5 operate at a pressure that is slightly above the saturation pressure for the respective process temperature.

Total Solids Content of the Feed and Ratio of Water to Biomass

The water content of the feed plays an important role for providing a liquid aqueous phase in the reactor. If, for instance, the water content of the biomass is low and the head space in the reactor is large, all water can evaporate and remain in the head space. In this case no liquid phase exists, which is called “vapo-thermal” conditions. A large ratio of water to biomass, on the other hand, leads to a large fraction of organics dissolved in the aqueous phase and thus to a lower yield of HTC char [22]. Therefore, an optimum range exists for the ratio of water to biomass. Most processes operate within a window of 1–4 for the mass ratio of water to biomass dry solids.

Particle Size

Because the HTC is characterized by a slow conversion, the particle size has no significance for the reaction engineering. It does, however, play an important role in a continuous HTC process for the reliable conveying and loading of the reactor. For this reason continuous processes operate on

particles up to 2 cm size, while for larger particles, batch processes are preferred (Table 5).

Residence Time

Typical residence times for HTC are in the range of 1–72 h [23]. It is possible to describe the influence of temperature and residence time on the HTC conversion with Eq. (5) [24]:

$$f = 50 t^{0.2} e^{-\frac{3500}{T}} \quad (5)$$

The parameter f (also called reaction intensity) describes the conversion, defined by the remaining oxygen content of the char, t is the reaction time in seconds, and T the temperature in Kelvin. As the reaction intensity f correlates with the higher heating value, the knowledge of the reaction conditions t and T enables the estimation of the attainable heating value of the HTC char.

When using Eq. (5), one must be aware that the right-hand side of the equation is dimensional and it does not go to $f = 1$ for t going to infinity. The energy yield of the HTC (i.e., heating value of the char to the heating value of the biomass) shows a slightly negative correlation with f . According to this relationship, carrying out the HTC at f values above 0.35 does not seem to make sense from an energy point of view [25].

pH Value of the Feed

Key to a good carbonization is an acidic pH value. Under very acidic conditions (pH < 3, e.g., pH = 1.5), a significant acceleration of the carbonization was observed [26]. It is, however, questionable whether such a strong reduction of the pH value makes sense from a process engineering point of view. Adding an acid generates costs and increases the rate of corrosion. Nevertheless, most HTC processes foresee an addition of an acid, depending on the biomass (Table 5). Because some substances released during the carbonization, such as CO₂ or NH₃, have a buffering effect, the calculation of the economic acid dosage is not straightforward. As an example, the addition of citric acid to sewage sludge did not result in measurable differences of the HTC char compared to the one obtained without acid added [27].

Additives

Besides acids, only few other additives are used in HTC. As an example, one process adds sodium hydroxide, depending on the biomass. Since most biomasses contain already acids and salts, some processes recycle a part of the acidic process water, together with the dissolved organics, and mix it to the feed. In laboratory experiments, a catalytic effect of silver, copper, and iron salts was observed [17], which has, however, not gained any importance for practical HTC processes.

Characteristics and Use of the Products

Characteristics of the HTC Coal

HTC produces two types of “coal”:

- Coke (primary coke or char), formed from the primary biomass structure by dehydration and decarboxylation reactions
- Coke (secondary coke), formed by polymerization of hydrolysis products

The primary coke’s structure is very similar to the original biomass structure, especially in the case of woody biomass. The secondary coke has nothing in common with the biomass structure and usually forms spheres with a diameter of 20 nm up to a few micrometers, which can be hollow [18]. These spheres are presumably formed by the formation of a second, water-insoluble organic phase in the form of droplets [11]. The coke spheres can be produced from very different substances (e.g., glucose, xylose, maltose, starch, glycerol, 5-HMF, and from vegetable material). For example, a temperature of about 180 °C is sufficient for sugars. On the other hand, the formation of coke only occurs at about 210 °C from pure cellulose [11]. As the temperature increases, these spheres grow into larger structures. This leads to the formation of a coherent, holey “coke carpet” at supercritical temperatures. Lignin also forms similar holey structures over a wide temperature range [11].

In the case of the HTC of biomass, both types of coke formation usually take place; i.e., the woody biomass is transformed to char and the

hydrolysis products form secondary coke, which is usually observed on the surface of the biomass char [28]:

- For wood, only slight hydrolysis takes place under typical HTC conditions (180–220 °C). Accordingly, the fraction of secondary coke is small.
- In the case of non-lignified biomass, a substantial portion of it can be hydrolyzed and converted to secondary coke [18].

The comparison between primary coke from beech wood and secondary coke from glucose and lignite shows that at a comparable reaction intensity f coke species with a similar chemical composition are obtained (reference: dry and ash-free), although morphology and structure differ greatly (Table 3). Contrary, secondary coke from glycerol, prepared under the same reaction conditions, has a significantly higher carbon content and a lower oxygen content than that of glucose (Fig. 4) [14].

Figure 4 shows the elemental composition of HTC carbons in a graph in which the respective hydrogen to carbon (H/C) ratio is plotted over the oxygen to carbon (O/C) ratio. In addition, the values for the secondary coke from glycerol and glucose obtained at higher temperatures are also shown. Accordingly, the composition of HTC carbons, which are derived from various substrates and are obtained under different reaction conditions, extends over a wide range of H/C and O/C values. Many are located near lignite.

For demanding carbonization parameters (i.e., high temperatures and long reaction times), the composition moves into the range of bituminous coal. HTC coals are porous and have oxygen-containing groups on their surface (phenols, lactones, carboxylic groups). These two characteristics determine many of their physical-chemical properties and applications [30]. A large proportion of the inorganic fraction from biomass substrates remains as ash in the HTC coal. As a result, the ash content of the HTC coal is practically always higher than or equal to that of the starting substrate. Especially for sewage sludge, this

results in a very high ash content of the coal of up to 54%, and the carbon content can drop below 30% [31]. The majority of the heavy metals in sewage sludge are found also in the HTC coal [27]. As expected, in HTC coal, the share of the volatile and the solid carbon increases compared to the starting material. Also the calorific value of the HTC coal increases due to the higher carbon and the lower oxygen content. Using Eq. (6), the higher heating value HHV can be calculated from the carbon content [13]:

$$HHV \text{ (in MJ/kg)} = (440.8\%C - 2,204.2)/1,000 \quad (6)$$

An advantage for their thermal utilization is the greatly improved dewatering ability of the HTC coals compared to the starting substrate. As a result, subsequent drying requires significantly less thermal energy than the direct drying of the original substrate.

Use

HTC coals can be used energetically and as a raw material. Both options are briefly discussed below.

The energetic use is essentially the provision of a transportable and storable solid biofuel with an increased energy density compared to the starting material. In order to assess its combustion properties, parameters such as the specific calorific value, the ash content, the ash softening point, the N, S, and Cl content, the heavy metal content, the bulk density, and the particle size distribution are needed. These parameters are dependent on the starting material, the HTC process conditions, and the subsequent processing (drying, grinding, pressing) [32].

For the use as a raw material, applications are proposed [30, 33] which largely correspond to those for amorphous carbon and soot of fossil origin:

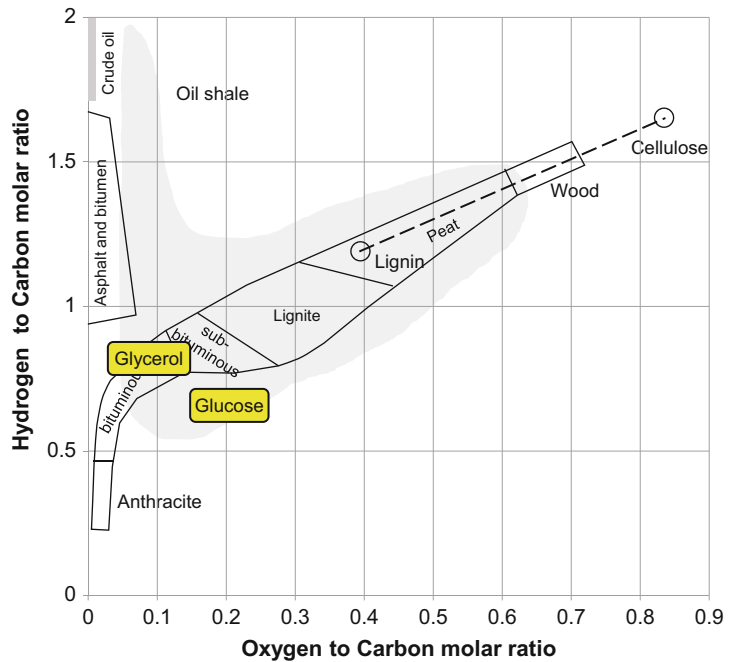
- Functional carbon materials (including adsorbents for the purification of gases and water, filter material, carbon electrodes, nano-carbon structures, catalysts, storage materials for gases)

Hydrothermal Conversion of Biomass, Table 3 Comparison between the various types of HTC coal and lignite [11, 14, 24, 29]

	Primary coke	Secondary coke	Lignite
Reaction conditions	250 °C, 4 h	300 °C, 0.5 h	ca. 40 °C, > 10 ¹⁰ h
Reaction intensity	0.42	0.50	ca. 0.50
Starting material	Beech wood	Glucose	Plant biomass
C content in wt.% (daf)	71.8	71.6	65–75
H content in wt.% (daf)	5.2	4.3	3.5–6.5
O content in wt.% (daf)	23	24.6	12–30
N content in wt.% (daf)	≈0	0	Up to 2
S content in wt.% (daf)	≈0	0	Up to 3
H/C molar ratio	0.86	0.72	0.64–1.1
O/C molar ratio	0.24	0.26	0.12–0.4
Ash content in wt.% (db)	<1	0	5–39
HHV in MJ/kg (db)	28.8	27.5	19–22.5
Typical usage/suitability	Solid fuel Soil conditioner	Carbon black printing black electrodes adsorbent (solid fuel)	Solid fuel

daf dry ash-free, db dry basis

Hydrothermal Conversion of Biomass, Fig. 4 Classification of the HTC coals according to their molar H/C and O/C ratios (gray area, according to [23, 26]); also highlighted are cokes formed from glucose and glycerol at higher temperatures (rectangles); according to [14]



- Soil improver (i.e., “Terra Preta”) and carbon sequestration in soil
- Phosphorus recycling from the HTC coal or from the process water
- Carbon additive (i.e., carbon black, printing black (ink pigment), concrete aggregate, road coverings)
- Raw material for the chemical industry

By-Products: Process Water

The process water from HTC can contain a considerable portion of the carbon and nitrogen of the starting substrate (Table 4). In addition to a large amount of low molecular weight carboxylic acids (including acetic acid, glycolic acid, formic acid), the process water also contains dissolved phenols, furfurals, phthalates, pyridine, pyrazines, and other organic substances [13]. BTX (i.e., benzene, toluene, and xylene) and PAH (polycyclic aromatic hydrocarbons) were not detected [34]. When the process water is recycled within the HTC process the content of organic ingredients increases strongly [22]. As a result, in the ideal case, a separate acidification of the feed stream is not needed. The pH of the process water varies according to the starting substrate, the ratio of biomass to water, and the addition of acids or bases. For various non-acidified substrates, pH values between 3.7 and 7.2 have been found [13]; e.g., pH values in the range of 5.0–7.0 were measured after HTC of sewage sludge [27]. When acidifying the sewage sludge to a pH value of 2, the process water reached a pH value of 3.0–3.5. Protein-containing biomasses tend to yield higher pH values because the released ammonia buffers the pH. For acidified, low-nitrogen substrates, the pH of the process water remains at low values [35].

Phenols are of particular importance for the recycle of the process water to a sewage treatment plant; e.g., up to 666 mg/L of phenols were measured in the process water of HTC from sewage sludge [27]. Therefore, studies have

focused on the biodegradability of the HTC process water.

It was shown that the process water from sewage sludge is readily biodegradable after dilution. The safe compliance with the permissible concentration values at the outlet of the sewage treatment plant due to the greatly increased load of the introduced HTC process water is, however, still unsolved. One possibility is a pretreatment of the HTC process water by membranes [32].

A further challenge are the very fine coke particles suspended in the HTC process water, which are not retained during the dewatering, ending up in the filtrate [36].

The HTC process water would be very well suited as a feed for the HTG due to its chemical composition. However, the organic concentration is too low for an economically meaningful operation, which would require concentrating it to an organic content of at least about 100 g/L (section “Processes and Installations” of section “Hydrothermal Gasification”).

Processes and Installations

Table 5 gives an overview of the HTC processes developed mainly in Germany. According to this, the currently largest plants can process approx. 10,000 t/a of wet biomass. The plant concepts are usually modular so that by replicating a basic module the plant capacity can easily be adapted to the specific requirements of a regional solution. The SlurryCarb process, which has been primarily developed for the processing of sewage sludge and household refuse, has been demonstrated in the USA and Japan in larger plants, which are currently not operated due to economic problems.

Process Example

Since the process conditions of HTC do not allow large variations, the different methods (Table 5) differ mainly in the operating mode, the reactor design, and the heat management. An example of an innovative and thermally integrated reactor concept has been developed and demonstrated [48]. As another example of a thermally integrated full-scale process, the AVA-CO₂ process is presented below (Fig. 5). The wet biomass is initially introduced into a mixing tank. Biomass streams

Hydrothermal Conversion of Biomass, Table 4 Sum parameters and compounds found in HTC process waters [13, 27]

pH		3.7–7.2
TOC	In mg C/L	9,000–36,100
COD	In mg O ₂ /L	24,200–68,500
BOD ₅	In mg O ₂ /L	10,000–42,000
Nitrate-N	In mg N/L	2.9–178
Ammonium-N	In mg N/L	3.4–2,187
Phosphate	In mg P/L	0.2–149
Phenols	In mg/L	292–666
Conductivity	In mS/cm	11–14

Hydrothermal Conversion of Biomass, Table 5 Hydrothermal carbonization processes

Process	AVA-CO ₂	SlurryCarb	CarboREN	REVATEC	Carbon solutions	TerraNova	KELAG/TFC	Loritus/ Ingelia	Grenol	Antaco
Reference	[21, 37]	[38]	[39]	[40]	[31]	[35]	[41, 42]	[43, 44]	[45]	[46]
Temperature in °C	220	230	200	187–200	n. s.	200	190–230	180–220	200	200
Pressure in MPa	2.2	$\geq p_{sat}(T)$	2	1.2–2.0	n. s.	2.0–2.5	2.0–2.5	1.7–2.4	2	2.5
Time in h	2–4	0.17	1.5–3.0	4–8	1.0–1.5	2–4	3–4	8–16	2–6	4–10
Type	Multi batch	Cont.	Cont.	Sequential batch	Cont.	Cont.	Sequential batch	Cont.	Cont. ($d_p \leq 2$ cm) semi-cont. ($d_p > 2$ cm)	Cont.
Reactor	Standing cylinder, mixing by steam injection	Standing cylinder	Standing “cooker”	Unmixed standing cylinder	n. s.	Stirred tank	Two nested cylinders	Stirred tank	Tubular	Tubular
Feed/DM in reactor in %	Various 25–50	Sewage sludge, MSW ($d_p < 1.3$ cm) 20–30	Plant residues, industrial sludges 15–25	Various 50	n. s.	Sewage sludge 23	Sewage sludge, green waste ($d_p \leq 2.5$ cm) n. s.	Bio-waste, sewage sludge 5–45	Various 20 (cont.) 40–50 (semi-cont.)	n. s.
Additives	Recycled process water retentate	n. s.	H ₂ SO ₄ , CO ₂ , NaOH (depending on biomass)	n. s.	n. s.	Mineral acid	n. s.	Citric acid (depending on biomass)	Acid (depending on biomass), recycled process water	n. s.

(continued)

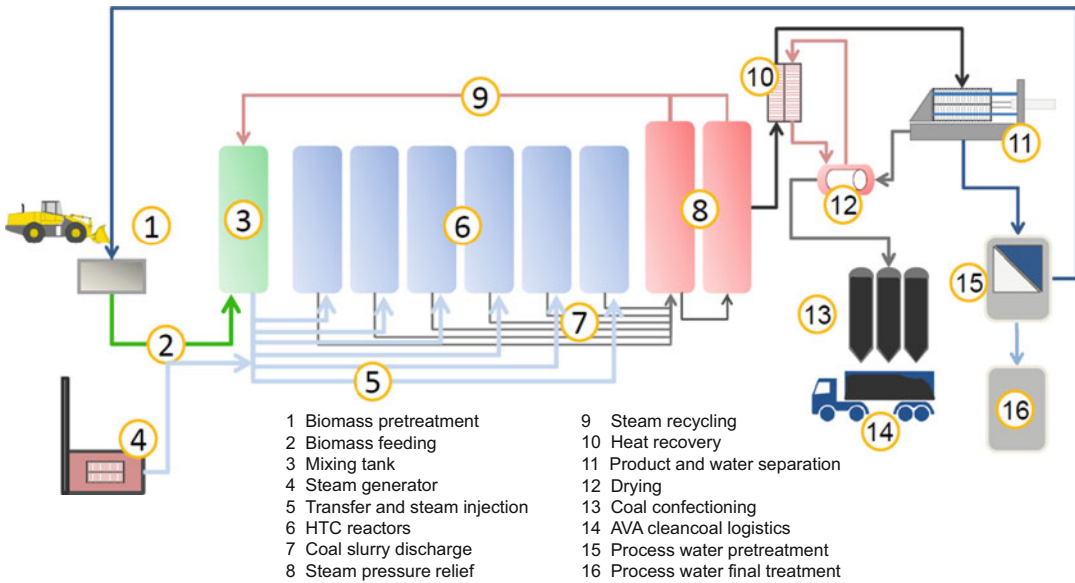
Hydrothermal Conversion of Biomass, Table 5 (continued)

Process	AVA-CO ₂	SlurryCarb	CarboREN	REVATEC	Carbon solutions	TerraNova	KELAG/TFC	Loritus/Ingelia	Grenol	Antaco
Heat recovery	Steam recovery	Heat exchanger product stream-feed stream	Mechanical vapor recompression using vapor from dryer to heat reactor	Thermal oil loop	n. s.	Heat carrier loop between heat exchanger product stream-feed stream	Integrated in reactor	Steam recovery and thermal oil loop	Heat exchanger with thermal oil loop	Heat carrier loop between heat exchanger product stream-feed stream
Largest plant in t/a ^a	8,400	ca. 180,000	1,440	ca. 450	10,000	1,200	10,000	1,100	3,000	n. s.
Carbon efficiency (effective) in %	58 (sewage sludge) > 90 (spent grains)	n. s.	85–95	n. s.	60–85	81 (sewage sludge)	n. s.	n. s.	80–85	n. s.
Thermal efficiency in %	59 (sewage sludge) ca. 80 (spent grains)	n. s.	84 (lop)	ca. 79	n. s.	75 (sewage sludge)	n. s.	n. s.	n. s.	n. s.

From [32, 37, 47]

n. s. not specified, *cont.* continuous operation, d_p mean particle size, p_{sat} saturation pressure, T temperature, *DM* dry mass, *MSW* municipal solid waste

^aWet biomass; assumed operating hours: 7,200 h/a or 300 d/a



Hydrothermal Conversion of Biomass, Fig. 5 Schematic of AVA-CO2’s HTC process [37]

containing cellulose, hemicellulose, and proteins (e.g., manure, horse dung, sewage sludge, digestate, food wastes, green cut, diapers, spent grains) are regarded as well-suited feedstock; wood is an unsuitable feedstock [21]. Recycled steam from the expansion tanks is blown into this mixing vessel, which preheats and mixes the biomass introduced. This heated reaction mass is then pumped into several standing HTC reactors and brought to reaction temperature with additional steam. The number of HTC reactors is based on the desired system capacity. After a batch has been processed, the coal slurry from this reactor is discharged into a large expansion tank.

The steam for the heating and mixing of the mixing vessel is then withdrawn from this expansion tank. The still hot coal slurry is cooled in a heat exchanger and dewatered in a chamber filter press. A large part of the organic matter in the filtrate is separated from the remaining process water in a membrane unit, and the retentate is recycled to the feed stream. The HTC coal from the filter press is dried with waste process heat and brought into the desired final shape.

Such a production plant would typically process 36,000 t of wet biomass (30% dry mass content). To this end, six HTC reactors per day

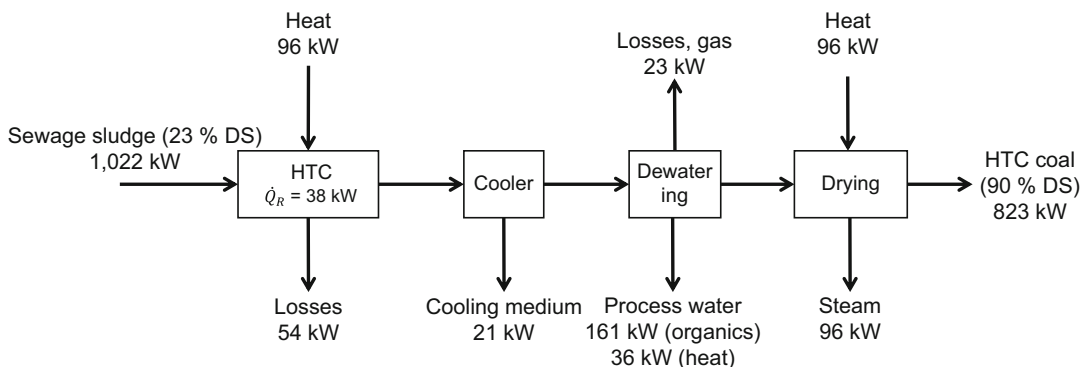
would process four batches of 1.5 t dry mass each. At 7,200 h/a this plant would produce 8,040 t of dry mass HTC coal per year [21].

Energy Balance

HTC is a process for the production of a solid biofuel from wet biomass. This means that its energy balance is an important evaluation parameter compared to other types of biomass utilization. A distinction must be drawn between a static balance of laboratory batch tests and the dynamic balances obtained from process data of a continuous system at steady state.

Static balances are usually based on laboratory data. Laboratory systems, however, are characterized by high surface to volume ratios; this increases the heat losses and makes a representative balancing difficult. In addition, in laboratory studies, small heat and material flows are often neglected; this is no longer appropriate when balancing a larger continuous plant. The results of static balances are therefore often given as energy recovery in the HTC coal. These values are typically in the range of 50–90% and depend, among others, on the biomass and the experimental conditions [13].

The remaining 10–50% of the energy content of the biomass is found in the process water as



Hydrothermal Conversion of Biomass, Fig. 6 Energy flow of the HTC of sewage sludge and subsequent drying of the HTC coal to 90% dry mass (the numbers are taken from a pilot plant [49] and were calculated for a planned

production plant [35]; in addition, the process requires 45 kW of electrical energy; \dot{Q}_R heat of reaction (i.e., specific heat of reaction times mass flow rate of sewage sludge) DS dry solids)

dissolved organic material, as the reaction heat and to a smaller part in the process gas.

Dynamic balances are usually determined for continuously operated plants. The methodical problem arises that no consensus has yet been found on the amount of the heat of reaction for HTC [26]. This relatively small amount of heat of reaction from real substrates, together with the heterogeneity of the feedstock to be used, makes an accurate determination difficult. All HTC processes have a heating and heat recovery system to ensure energy-efficient operation. For example, in Fig. 6 the energy flows for the HTC of sewage sludge are shown.

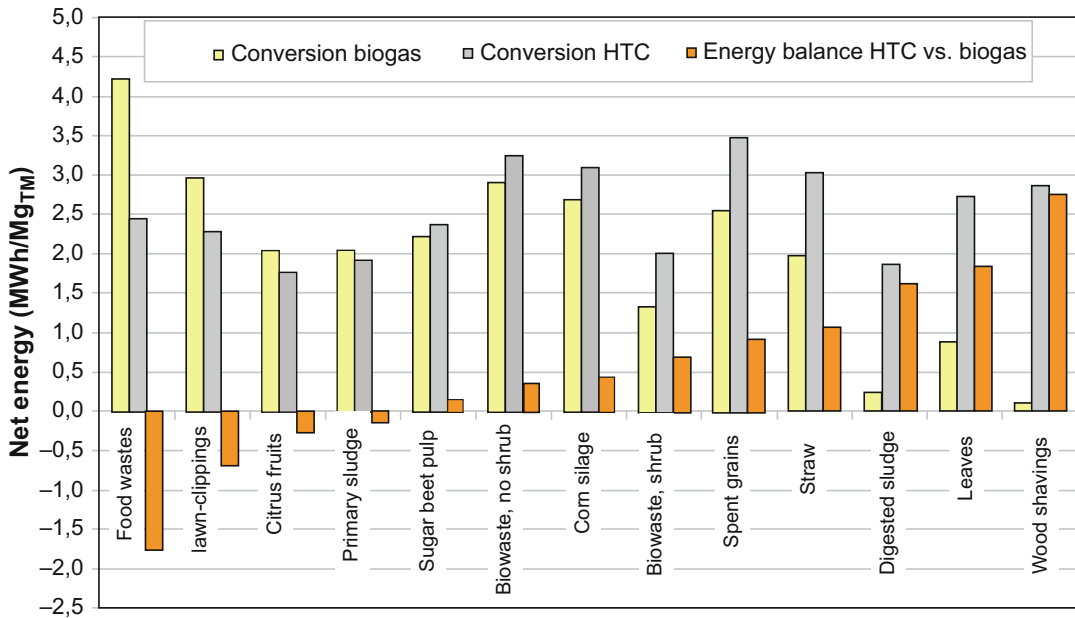
The reaction heat was estimated to be 3.7% of the calorific value of the sludge [49]. This corresponds to 533 kJ/kg (dry mass), calculated based on the throughput of sewage sludge (1.1 t/h with 23% dry mass). The reaction system involves a heat recovery from the hot reactor output to the cold feed stream (not shown in Fig. 6). A considerable portion of the energy input is lost with the dissolved organic matter in the process water from the mechanical dewatering. In this example, an external heat supply of 375 kWh/t of dry mass or about 12% of the calorific value of the HTC coal is necessary in order to maintain the process. This heat requirement could be reduced by a better insulation of the HTC reactor. The drying of the coal from 60% to 90% dry mass again requires as much heat as the thermal energy

required for reactor heating. The resulting steam is not used in this process, but could be decoupled as low temperature heat. In this example, the chemical efficiency is 81% (i.e., the ratio between the calorific value of the HTC coal to the calorific value of the sewage sludge).

The thermal efficiency, as defined in Table 5, is 74% without and 68% with drying of the HTC coal.

A feature of HTC is the high carbon recovery in the HTC coal, which for most substrates is in a range of 62–78%. 17–31% of the remaining carbon end up in the process water and 4–9% in the gas. For very dilute substrates (e.g., waste food, primary sludge), practically the same amount of carbon is found in the process water as in the coal. In the case of primary and sewage sludge, some 26% of the carbon is also recovered in the gas phase. HTC conversions should therefore be run with as concentrated substrates as possible in order to maximize the transfer of the carbon into the HTC coal and to minimize the treatment effort for the process water. Substrates with a high proportion of animal proteins (e.g., food waste) also tend to form an oily phase, which is undesirable in the subsequent dewatering [35].

The two utilization paths of wet biomass, HTC and anaerobic fermentation to biogas, can be compared over the entire process chain – in each case in combination with a thermal utilization of the products HTC coal (in a biomass power plant) and



Hydrothermal Conversion of Biomass, Fig. 7 Comparison of substrate usage in a biogas plant and in an HTC plant, in each case in combination with a biomass power plant; the net energy was calculated (electricity plus heat) (According to [33], the respective

right-hand bar shows the difference between the biomass conversion via anaerobic digestion or HTC; when the net energy that can be provided by HTC exceeds the one by anaerobic digestion, this is shown in the graph with the right bar in the positive area)

biogas (in a CHP plant) [33]. The useful energy available from both paths is shown in Fig. 7 for different substrates. Accordingly, the anaerobic fermentation to biogas can provide a higher useful energy for well-fermentable substrates (e.g., waste food, lawn clippings, citrus fruits) than HTC. The latter, in turn, is more suitable for poorly fermentable substrates (e.g., wood shavings, foliage, digested sludge, straw, and spent grains).

Hydrothermal Liquefaction (HTL)

Precursors of hydrothermal biomass liquefaction were the various coal liquefaction processes (e.g., high pressure hydrogenation according to Friedrich Bergius). However, due to the differences between coal and biomass, an independent development line for biomass was followed. For example, experiments with cellulose show that the reaction conditions, especially the pH, determine whether coal or oil is produced from cellulose (section “Hydrothermal Carbonization (HTC)”).

The first continuous hydrothermal liquefaction process was the LBL process in the 1980s [50]. Often its predecessor, the PERC process, is also regarded as the first process of this kind [50]. In the PERC process, however, the water content was so small that it is not sensible to speak of a hydrothermal environment in the proper sense. Various process variants have been developed based on the LBL process. Neither of these modifications, however, have been able to master all the technical hurdles and at the same time to show economic viability [51].

At about the same time, the HTU process (“HydroThermal Upgrading”) was developed [52]. Initially intended as a method of converting biomass into an energy carrier of higher energy density, this approach developed into an independent process for the hydrothermal liquefaction of wet biomass in the 1990s. A pilot plant was also built and operated; the planned commercial implementation, however, has so far not been reported.

Main Influencing Parameters

In the development of all liquefaction processes, the main goals are an economic production of a high-quality HTL oil and a trouble-free operation of a plant with a commercially relevant throughput.

Crucial for this is to maximize the yield for a given investment. This is achieved primarily by adopting the highest possible biomass concentration in the feed. From a chemical point of view, small amounts of water are enough to allow the desired reactions to proceed. However, the water serves primarily to produce a pumpable biomass slurry. But the more water is pumped through the plant instead of biomass, the more energy has to be used to heat it up and the less HTL oil is produced. Therefore, HTL processes aim to achieve a dry matter content of over 20% in the feed. By adding a portion of the HTL oil to the feed, the water content can be further reduced with only a minor impact on the fluidity; this has been implemented as an extreme case in the PERC process.

Asking for the highest possible biomass content in the feed often works against the second requirement for trouble-free operation. Reliable pumping of high-viscosity biomass slurries with solid particles (dry mass > 20%) at high pressures has hitherto only been tackled by few and has not yet been demonstrated over economically relevant periods.

The most important influencing parameters for hydrothermal liquefaction are discussed below.

Dry Matter Content in the Feed

With an increasing dry mass fraction in the feed, the HTL plant can be exploited more efficiently as the oil production rate is proportional to the biomass supplied (i.e., more oil per hour per invested money unit).

Although the chemical reactions do not change fundamentally at high concentrations, their kinetics are strongly influenced by the concentration. Condensation (polymerization) reactions are kinetically often of higher order with respect to the reactants and are thus promoted by higher feed concentrations. The consequence is an increased formation of heavy tars and coke [53]. These undesirable side reactions can be suppressed in the presence of hydrogen donors. Therefore,

partial recycling and mixing of a stream of the liquefied biomass with the cold feed was proposed (CatLiq process) [54]. The pH of the reacting medium also has a considerable influence; acidic conditions favor coke formation [53]. It has also been found, for example, in the HTU process that more water-soluble organics and less oil are formed at feed concentrations below 25% by weight (dry mass) [52].

Temperature

The temperature influences the oil yield as well as the reaction kinetics. Therefore, in Fig. 8, oil yields are depicted as a function of the final temperature [55]. Although the absolute yields vary considerably, a temperature window of approx. 300–350 °C can be identified in which maximum yields are achieved. However, this is to be considered with caution because the influence of the temperature also depends on the heating rate and most of the experiments were carried out with a slow heating rate.

Residence Time

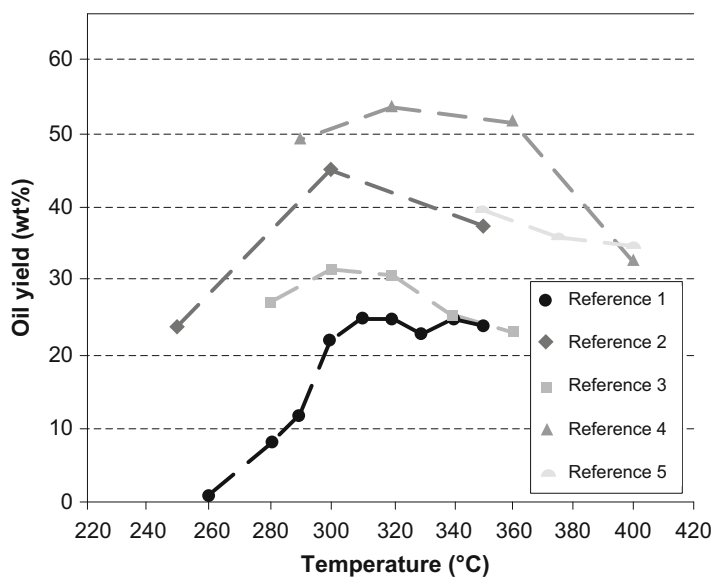
The initial decomposition of wood under hydrothermal conditions occurs very rapidly at about 250 °C (i.e., within a few minutes [28, 56]). These initial decomposition reactions yield predominantly reactive, water-soluble intermediate products, which also react relatively quickly to stable water-soluble end products as well as gases on the one hand and to an oil fraction on the other hand.

Parallel to these rapid reactions, much slower decomposition reactions occur, such as the dehydration of the solid residue or the further reaction of oil components to heavy tars and coke.

Thus, the residence time plays an important role in maximizing the yield of light oil. If it is too long, the high molecular weight oil components as well as the coke will increase, which then have to be converted into light fractions again by means of hydro-treating. For example, for poplar wood a maximum oil yield at 350 °C was already found after approx. 1 min, while at 370 °C the maximum was apparently already reached during the heating phase of 90 s [57].

Gas formation also increases with the residence time, with a particularly strong rise being

Hydrothermal Conversion of Biomass,
Fig. 8 Oil yield as a function of peak reaction temperature (Various sources, taken from [55])



observed beyond the critical temperature [58]. Under subcritical conditions, the gaseous products are predominantly formed from the decomposition of the water-soluble components (carboxylic acids, aldehydes); carbon dioxide is the main product followed by carbon monoxide and methane as well as hydrogen at higher temperatures [28, 53, 58].

Pressure, Fluid Density

The pressure affects the oil yield only at values close to the saturation pressure [55]. At high pressures well beyond the saturation pressure (approx. 20–30 MPa), the influence of pressure on the oil yield is negligible [28].

Particle Size

Since the liquefaction predominantly involves reactions between water and a solid, they take place at the surface of the solid and can thus depend on its specific surface area; this is inversely proportional to a characteristic length of the particle. In general, the smaller the particles are, the greater the specific surface area available for attacking the water molecules. Therefore, a markedly reduced oil yield was found for large wood particles (approx. 1 cm) compared to ground wood with a particle size of 0.4–0.8 mm [28].

pH Value of the Feed

Cellulose forms mainly liquid, oil-like products under alkaline conditions and charcoal-like products at acidic, neutral, or only slightly alkaline conditions [16]. In the second case, the small amount of alkalinity should be rapidly neutralized by the carboxylic acids formed and also lead to acidic conditions. The pH value of the feed is therefore decisive, which reaction pathway the hydrothermal transformation will take. For this reason, in most cases, a basic alkali salt or even a strong base is added for better liquefaction.

Additives/Catalysts

There are numerous studies on the influence of homogeneous and heterogeneous additives in the hydrothermal liquefaction of biomass. Alkali salts (e.g., Na_2CO_3 , K_2CO_3 , KHCO_3), acids (e.g., HCOOH , H_2SO_4), or strong bases (e.g., NaOH , KOH) are often used as homogeneous additives. The heterogeneous additives are usually substances such as zeolites, ZrO_2 , Pd/C , $\text{CoMo/Al}_2\text{O}_3$, Raney nickel, Ru/C , and Pt/C , which may be catalytically active. However, the catalytic effect of these additives under the conditions of hydrothermal liquefaction has so far generally not been demonstrated or systematically investigated. As one example, the inefficiency of ZrO_2

(monoclinic, nanocrystalline) for the liquefaction of dried distillers grains with solubles (DDGS) was shown [59]. The catalysts based on an active metal generally require hydrogen (H_2) as a reagent. It is split on the metal into atomic hydrogen, which is thought to saturate the free radicals of the biomass fraction during liquefaction. Since some of these metals also catalyze the gasification of organic molecules to form H_2 and CO_2 , the required hydrogen can theoretically also be obtained directly by partial gasification of the biomass. The aqueous phase reforming (APR) process is based on this idea [60]. Only a low gasification activity may be permitted such that the yield of HTL oil does not decrease in favor of increased gas formation.

Reactor Design, Mixing Behavior

Most laboratory tests for hydrothermal liquefaction are carried out in small autoclaves. These are usually not mixed and only a few are shaken or stirred. Since HTL is a solid-liquid reaction, the mass transport of water to the solid biomass and the transport of the liquefied products is a central step; this is especially true with high feed concentrations. A slow mass transport can thus influence the product distribution if, for example, water is not available fast enough for hydrolysis reactions and thus other pathways (e.g., pyrolysis) are preferred.

In this context, percolation systems are also to be discussed in which the solid biomass remains in the reactor and the hot pressurized water flows over the biomass filling. For example, at low flow rates, more hemicelluloses are extracted from the wood than at high flow rates [61].

The mixing behavior is also important for the distribution of solid, aqueous, and oil phase in the reactor. If the reactor contents are not actively mixed, heavy phases (i.e., solid, catalyst, minerals) can separate from the lighter phases (i.e., water, oil) and thereby affect the yields. Also, the mixing of the liquid phases with the reaction gas influences, especially in the case of hydrogen, the distribution of the resulting products.

Heating Rate

The heating rate influences the residence time at a certain temperature and thus the reaction kinetics. Since the early reactions between the solid biomass and the hot pressurized water are rapid, at a slow heating rate, they have elapsed before reaching the final temperature. In this case, the final temperature and the associated holding time would only affect the subsequent reactions of the liquefaction products. Only with a very fast (quasi-instantaneous) heating rate can the final temperature be related to the kinetics of the early liquefaction reactions.

Such a rapid heating rate is very difficult to realize experimentally. This is probably best achieved by the sudden injection of a concentrated biomass slurry into an autoclave preheated with hot pressurized water. But even then the temperature will drop rapidly by the cold material slurry before the heating can bring the mixed contents back to the desired final temperature [62].

With an inductive heating of an autoclave, heating rates of up to 140 K/min are achieved. Thus, a clear dependence of the oil yield on the heating rate can be shown (Fig. 9) [63]. At the same time, the solid residue decreases from 20% at a heating rate of 5 K/min to 9% at 140 K/min. On the other hand, the cooling rate has no influence on the oil yield.

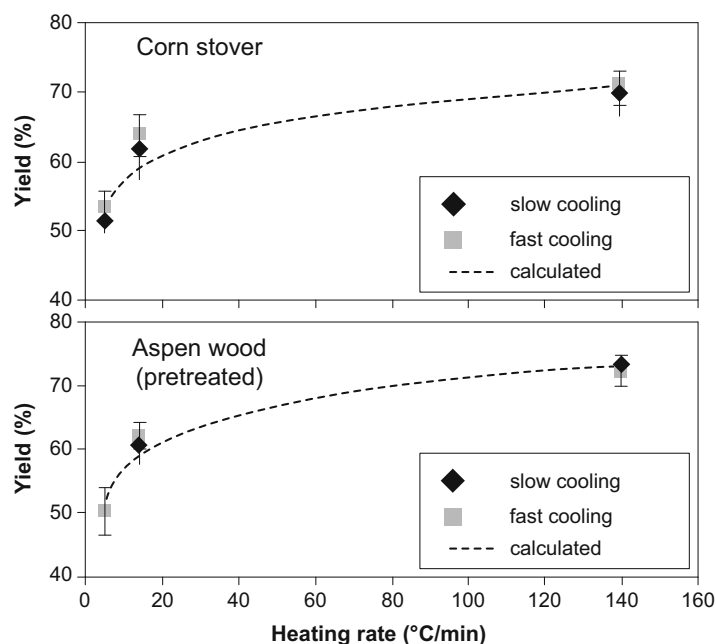
A process engineering solution for fast heating rates in a continuous process is to mix the cold feed stream with a hot recycle stream from the process. This requires the installation of a pump that can withstand high temperatures and pressures. The feed stream is diluted by the recycle flow, the more the higher the desired heating rate and the recycle flow ratio is selected. Such a variant is therefore only suitable for very concentrated feed streams (dry mass > 20%) [64].

Product Characteristics and Use

Properties

The product oils resulting from the hydrothermal liquefaction are not stable; they are – from a thermodynamic point of view – all intermediate products on the way to the stable end products

Hydrothermal Conversion of Biomass,
Fig. 9 Liquid yield (including aqueous phase) as a function of the heating and cooling rates (Adapted from [63])



methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and hydrogen (H_2). The latter are only formed in small amounts at the relatively low temperatures of HTL. Only at significantly higher temperatures ($> 600\text{ }^\circ\text{C}$) are the oils gasified to the stable end products (section “Hydrothermal Gasification”).

The majority of the substances contained in the HTL oils cannot be analyzed by gas chromatography (GC) because they are not volatile enough or would decompose before evaporating. For comparison, only about 40% of a pyrolysis oil contains GC-detectable substances. The proportion in HTL oils is probably similar. More than 100 substances have already been identified as volatile organic components of an HTL oil [65, 66]. They can be assigned to the following classes: carboxylic acids, furfurals, aliphatic and alicyclic ketones, phenols, and aromatic aldehydes. At the relatively low temperatures of HTL, most substituents on aromatic structures are not cleaved. Therefore, HTL oils have a low content of benzene, toluene, ethylbenzene, and xylene (BTEX); this is consistent with a low yield of nonpolar, hexane-soluble substances [28].

The average molecular weight of the organic components in HTL oils of Douglas spruce

according to the LBL process is, for example, 310–470 g/mol [67]. For the HTU process, 300–400 g/mol has been reported [68, 69]. HTL oils are very viscous and have a high proportion of phenols. They are, in contrast to the pyrolysis oils, immiscible with water. The most important properties are shown in Table 6 in a comparison to flash pyrolysis oils and crude (fossil) oil. Accordingly, the organic portion of the HTL oil has a significantly lower oxygen content and a higher carbon content than the pyrolysis oil. The higher degree of oxidation of the pyrolysis oil explains its good miscibility with water. Due to the low oxygen content and high carbon content of the HTL oil, this also has a significantly higher calorific value than the pyrolysis oil. The high pour point of the HTL oils is consistent with the high viscosity; e.g., the oil from the HTU process is only flowable above $80\text{ }^\circ\text{C}$. The high proportion of oxidized compounds in the pyrolysis oil (acids dissolved in the water, aldehydes, ketones, alcohols) causes increased corrosivity and poor thermal stability. From the point of view of further workup, the low oxygen content of the HTL oils represents an advantage since this reduces the effort for the further removal of oxygen to achieve a defined fuel quality.

In comparison to pyrolysis oils, HTL oils have a lower water and oxygen content, a higher viscosity, and a higher calorific value [75]. Also HTL oil from algae has a slightly lower density and a much higher nitrogen content than HTL oil from wood. The nitrogen in the feed is thus largely converted into

the HTL oil. Crude oil differs from HTL oil from algae mainly by a lower oxygen content (Table 6).

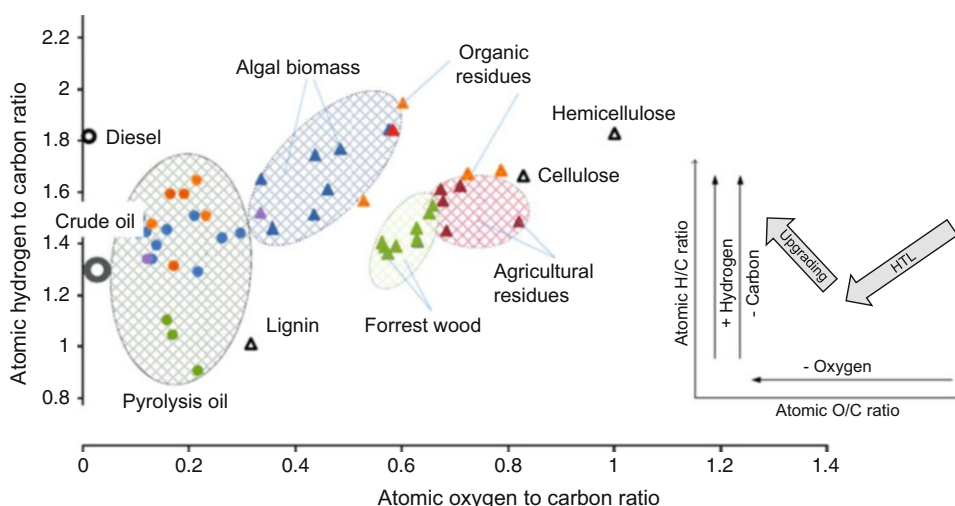
HTL oils can easily be compared with each other in a graph in which the hydrogen to carbon (H/C) ratio is plotted versus the oxygen to carbon (O/C) ratio (Fig. 10). Here, the triangles represent

Hydrothermal Conversion of Biomass, Table 6 Comparison of HTL oils, pyrolysis oil, and crude oil

		HTL oil		Pyrolysis oil	Crude oil
Origin		Douglas fir (LBL)	Nannochloropsis sp. (PNNL)	var. woods	
Water content	wt. %	3–14	2.8–7.8	15–30	< 3
pH		ns	ns	2.0–3.5	ns
Density	kg/m ³	1,150	943–960 (40 °C)	1,100–1,300	801–1,000 (15 °C)
Dynamic viscosity	Pa s	15 (61 °C)	0.11–0.34 (40 °C)	0.016–0.1 (50 °C)	0.001–19.4 (38 °C)
HHV	MJ/kg (db)	33.2–38.4	37.3–38.3	16–23	43.3–46.1
Ash content	%	ns	ns	0.01–0.2	0.001–0.05
Flash point	°C	ns	ns	45–100	<10
Carbon content	wt. % (db)	78.5–85.1	77.0–79.2	55–64	85–90
Hydrogen content	wt. % (db)	6.2–10.3	10.0–10.6	5.2–7.0	10–14
Oxygen content	wt. % (db)	6.6–15.3	5.3–8.0	28–40	0–1.5
Nitrogen content	wt. % (db)	0–0.5	4.0–4.7	0.07–0.39	0.1–0.5
Sulfur content	wt. % (db)	ns	0.3–0.5	0–0.8	0.1–3.0
Solids content	wt. %	1.0–17.8	ns	0.01–1	ns
Pour point	°C	23–60	ns	–36–9	–60–15

Data from [51, 70–74]

db dry basis, *LBL* Lawrence Berkeley Laboratory (process), *PNNL* Pacific Northwest National Laboratory, *ns* not specified, *var.* various, *HHV* higher heating value, *wt.* weight



Hydrothermal Conversion of Biomass, Fig. 10 Classification of the HTL oils according to their H/C and O/C ratios (triangles represent the original

biomass and filled circles are the HTL oils obtained therefrom; hatched areas regroup the same biomass species and the HTL oils obtained, according to [76])

the starting biomass and the circles represent the HTL oils. Accordingly, oxygen is removed during HTL and hydrogen is largely retained. A composition such as diesel oil with an H/C ratio of 1.8 and an O/C ratio of practically zero would be ideal. This is not achieved with HTL since dehydration reactions also slightly decrease the H/C ratio. An increase in this ratio is achieved in practice by a subsequent “upgrading” by hydrogenation under pressure.

Use

HTL oils are particularly suitable for thermal use as storable liquid fuel of high energy density. In untreated form, they can be used as biogenic substitutes for large diesel engines in ships, heavy oil burner systems, or similar. For motor vehicles and airplanes, the oils must be “upgraded” in order to achieve the respective fuel standards and qualities.

In order to use the existing infrastructure in petroleum refineries as optimally as possible, the liquefaction processes are often used to achieve an oil quality allowing their processing in a way compatible with the petroleum cuts (e.g., petrol, diesel, kerosene, “drop-in fuels”).

By-Products: Gas, Aqueous Phase, and Coke

The HTL produces little gas. This mainly contains carbon dioxide (CO₂); e.g., the process gas from the CatLiq process (with DDGS) consists of 95% CO₂, 1.6% H₂, small amounts of N₂, CO, and CH₄, and traces of higher alkanes and alkenes [75]. As the temperature rises, more CO and CH₄ [58] is produced, and significantly higher amounts of gas are measured above the critical temperature [53, 58]. For example, in the case of the Hydrofaction process [77], up to 40% of the feed-dry mass is recovered as gas, whereas in the HTU process, only 18–31% are gaseous (Table 8). In pilot tests with DDGS in the CatLiq process, ca. 12% of the feed carbon was recovered in the gas [75]. For other feedstock, significantly less carbon was present in the gas and the carbon was distributed over the other phases [64].

The aqueous phase from the liquefaction of DDGS by the CatLiq process still contained 33 g/L of total organic carbon (TOC). The

composition of a part of this organic carbon is shown in Table 7. Further identified components in the aqueous phase are piperidone, aniline, various cyclopentenones, and n-heptanoic acid. However, the sum of all these components makes up only 18% of the TOC. Therefore, other unidentified organic substances in the process water are to be assumed.

The process water from the HTL is slightly acidic in most cases due to the carboxylic acids formed (Table 7). For the HTU process, pH values of 3–5 are given [52]. In the case of protein-containing biomasses, some of the organic acids are neutralized by the cleaved ammonia; this increases the pH value.

An aqueous stream with such an organic load must not be introduced into the sewer system without treatment. The organic fraction can also be used for material or energy use. Such a stream would be very well suitable for HTG due to its chemical composition. However, the organic concentration is too low for an economic operation; concentration of the organic content to at least about 100 g/L would be required (section “Processes and Installations” of section “Hydrothermal Gasification”).

In most, if not all, HTL processes, a solid fraction is formed which consists mainly of carbonized organic material (“coke”). This coke may be mixed with precipitated salts and oxides and suspended in the oil phase; this makes its separation considerably more difficult. For example, in the HTU method, the proportion of the coke-like fraction in the total oil is indicated as 33% [69].

Hydrothermal Conversion of Biomass, Table 7 Low molecular weight components in the aqueous phase from the CatLiq process [75]

Methanol	252 mg/L
Ethanol	290 mg/L
1-Propanol	40 mg/L
Butanol	40 mg/L
Acetone	110 mg/L
Acetic acid	3,320 mg/L
Propionic acid	727 mg/L
Butyric acid	305 mg/L
Valeric acid	230 mg/L
Isovaleric acid	241 mg/L

Hydrothermal Conversion of Biomass, Table 8 Mass balance of the HTU process [52, 68, 78, 79]

Feedstock	Wood pellets	Wood	Sugar beet pulp	Onion waste
Biomass	100% (daf)	100% (daf)	100% (daf)	100% (db)
Temperature	350 °C	ns	330 °C	ns
Residence time ^a	6 min		10 min	
Feed DM content	12%		22%	
Products (daf)				
HTU oil	42.5%	45%	41%	37.5%
CO ₂	18%	23%	24%	31.3%
CO ^b		2%	1.5%	
Dissolved organics ^c	39.5%	12%	12.5%	31.3%
H ₂ O ^d		18%	21%	

daf dry ash-free, *db* dry basis, *DM* dry mass, ns not specified

^aReactor residence time

^bIncluding small amounts of H₂ and CH₄

^cAcetic acid, ethanol, others

^dReaction water

In other HTL processes, which foresee the addition of alkali salts, the coke content should be considerably lower.

Processes and Installations

Subsequently, selected processes of hydrothermal liquefaction are discussed (Table 9).

PERC Process

In the PERC (Pittsburgh Energy Research Center) process, wood flour is mixed with recycled product oil and pumped through a tube reactor (Fig. 11). This mixture remains for about 10–30 min in the reactor at temperatures of 300–340 °C and a pressure of about 20 MPa. Depending on the reaction conditions selected, the oil fractions are between 40% and 55% by weight, based on the dry mass of the organic material employed. The solid residue is only about 1%. Up to 10% of the organic compounds are water soluble. The rest of the wood is converted to carbon dioxide and water. The recycled oil serves as a hydrogen donor during the reaction (Fig. 11).

LBL Process

The LBL (Lawrence Berkeley Laboratory) process is a further development of the PERC process (Fig. 12, Table 9). Wood chips are first dissolved in dilute sulfuric acid at 180 °C under mild

conditions. This slurry with a dry matter content of up to 33% is then adjusted to a pH of approx. 8 with sodium carbonate and heated to 330–360 °C in a heater at 10–24 MPa. To prevent solid deposits, the heater is equipped with rotating scraping elements. Before entering the reactor, either CO or a CO/H₂ mixture is added to the reaction mixture. The reactor is configured in the one process variant as a stirred tank and in another option as a tube reactor. The residence time in the reactor is 10–60 min. After cooling, first the gases, and then the process water are separated.

In contrast to the PERC process, the oil is not recycled here and mixed with the feed. The oil fraction is further separated in a vacuum distillation. The properties of the LBL oil are summarized in Table 6. The LBL process was demonstrated in a plant with a throughput of 25 kg/h. But this process has never been scaled up to commercial size due to technical difficulties and poor prospect of economic viability.

HTU Process

In the HTU process (HydroThermal Upgrading, Table 9), the biomass slurry is brought to a pressure of 12–18 MPa, heated, and liquefied in a tube reactor at 300–350 °C (i.e., slightly below the critical temperature) for 5–20 min. A special attention has been given to the conditioning of the biomass into a pumpable pulp [52]. For a

Hydrothermal Conversion of Biomass, Table 9 Comparison of the hydrothermal liquefaction processes developed up to the pilot scale [50, 76, 79–83]

	LBL	HTU	CatLiq	Hydrofaction
Temperature in °C	340 (330–360)	300–350	280–350	390–420
Pressure in MPa	10–24	12–18	22–25	28–30
Reactor residence time in min	10–60	5–20	5–10	ca. 20
Additives	Na ₂ CO ₃ , CO	None	K ₂ CO ₃ , ZrO ₂	K ₂ CO ₃ , recycled process water, HTL oil
Reactor type	Stirred tank/tubular	Tubular	Tubular (fixed bed)	Tubular
Oil yield in wt.% (db)	25–33	41–45 ^a 28–30 ^b	30–35	40
HHV of oil in MJ/kg (db)	33.2–38.4	30–35 ^a (LHV)	37.7 35.8 (LHV)	40.9 (40–42)
Fraction of feed HHV recovered in the oil (%)	n. s.	78 ^a 52 ^b	73.2/64.7	80–85
Fraction of the feed carbon recovered in the oil (%)	n. s.	≥ 50	58 ± 3	60–70
Largest installation in kg/h (location)	25 Albany (USA)	100 Apeldoorn (NL)	20 Turkey	20 Aalborg (DK)
Features	“Scraped surface” heater, prehydrolysis in dilute sulfuric acid, pH 1.8, 180 °C, 45 min	Heating rate > 60 K/min. (lab scale); First, mild hydrothermal pretreatment of wood chips to obtain a pumpable feed	Recycle of hot stream before the reactor and mixing with cold feed stream	Fast heating rate (400 K/min) by two sequential induction heaters; pressure relief after cooling by capillary letdown; Feed conditioning to a pumpable slurry with a high solids content

db dry basis, n. s. not specified, LHV lower heating value, HHV higher heating value

^aIncluding the heavy, coke-like fraction from the HTU process

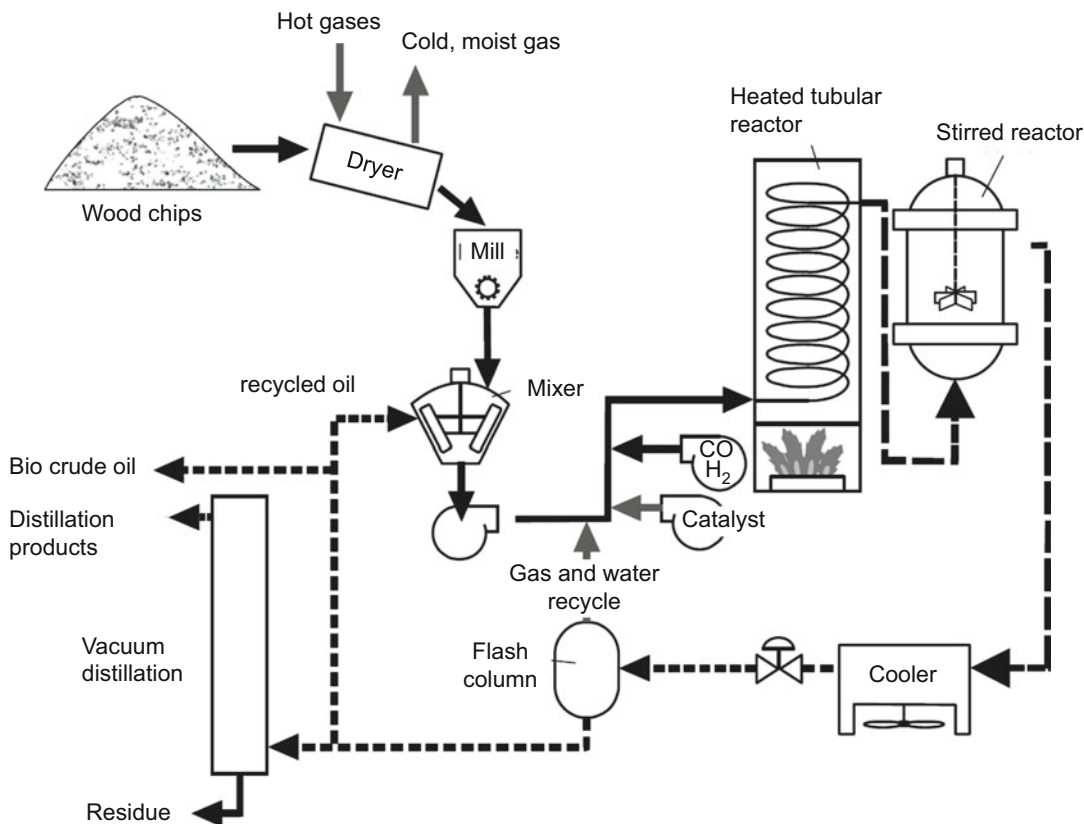
^bThe light oil fraction only

high oil yield and a good economy, the dry mass fraction in the feed must be above 20% by weight. No additives are mixed to the biomass and the reactor contains no catalyst. In fact, the HTU process does not distinguish itself from the other processes by any specific feature.

After a first cooling step, the light gases are separated from the liquid phase (emulsion/suspension) under pressure. The liquid phase is further

cooled and expanded allowing dissolved gases to be separated (Fig. 13).

The main product stream is an emulsion of water and “biocrude” with suspended solids, from which the oil phase can be separated relatively easily. The liquid product oil is highly viscous and separates from the water phase. The HTU oil still contains 10–18% oxygen – and thus only half as much as in the case of flash



Hydrothermal Conversion of Biomass, Fig. 11 PERC process for the hydrothermal liquefaction of biomass (According to [50])

pyrolysis – and has a calorific value of 30–35 MJ/kg [68]. The pour point is about 80 °C and at room temperature the oil is solid. The average molecular weight is stated to be 300–400 g/mol [69, 78].

Compared to flash pyrolysis, the process has a higher degree of flexibility in the feed, since the water content and the particle size are hardly relevant due to the preceding conditioning to a pumpable slurry.

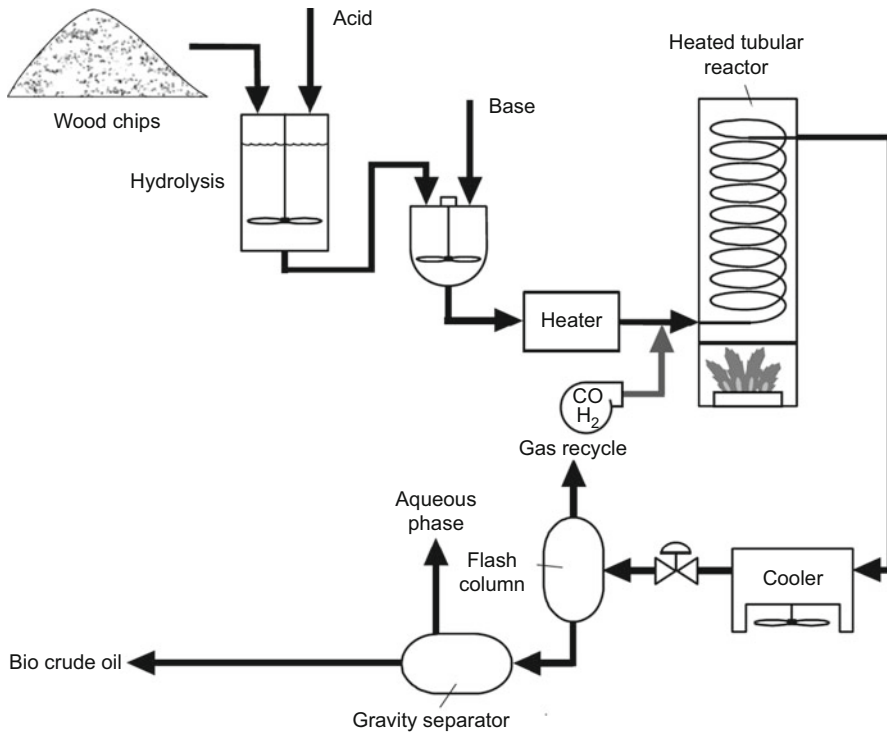
In the Netherlands, a pilot plant with a throughput of 100 kg/h of wet biomass was installed and operated for 3 weeks in permanent operation with waste from onion processing. In this case, 600 kg of HTU oil with a calorific value of 27 MJ/kg was produced [79].

In the thermally optimized process, a portion of the hot process water is recycled, heated to 350 °C, and mixed with the cold feed. The

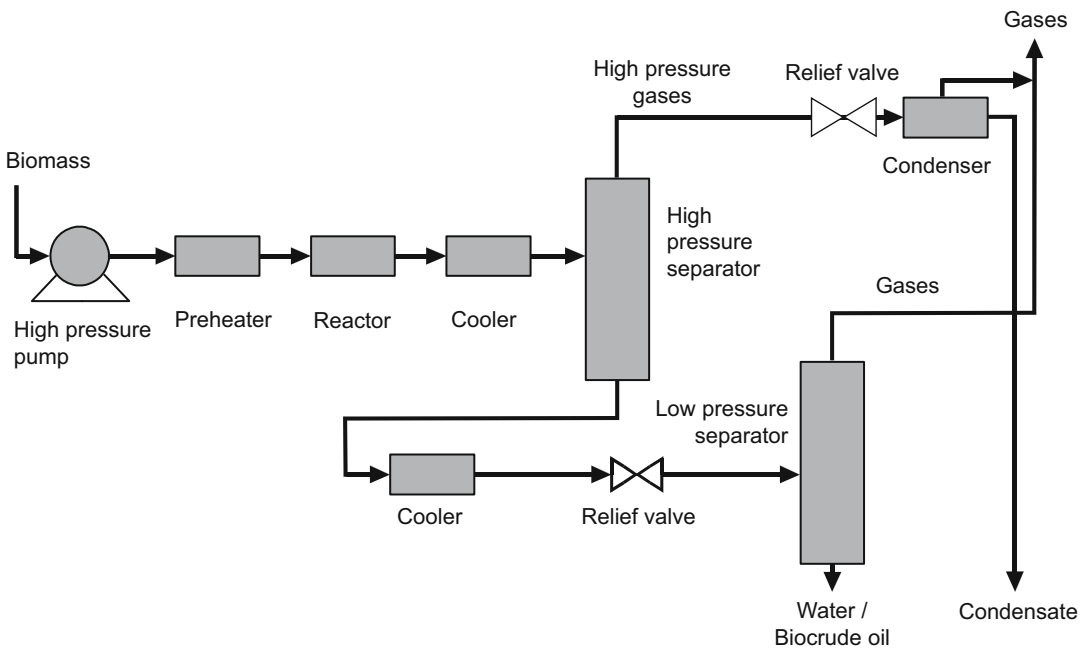
resulting mixing temperature of 230 °C leads to a well flowable mixture. This stream is further heated to the reaction temperature of 330 °C. Then it is passed into the reactor. Afterward the product stream is cooled to 260 °C; this allows separation of the oil and water phase under pressure [78]. However, an installation according to this process scheme has not yet been implemented.

Typical mass balances of the HTU process are shown in Table 8. A considerable part of the original biomass is thus lost with the dissolved organic matter.

The HTU oil can be separated into a light fraction and a heavy fraction [69]. The light oil fraction can be further processed into diesel oil. The heavy fraction is a carbonaceous solid to be burnt or gasified to produce hydrogen. The ratio of light to heavy fraction is indicated by 33:16



Hydrothermal Conversion of Biomass, Fig. 12 LBL process for the hydrothermal liquefaction of biomass (According to [50])



Hydrothermal Conversion of Biomass, Fig. 13 Schematic diagram of the thermally nonintegrated HTU process for the hydrothermal liquefaction of biomass (According to [68])

[52]. The data on the oil yield in Table 8 must therefore be reduced by the proportion of the heavy fraction, since this is not a liquid oil.

CatLiq Process

This process operates at subcritical temperatures and uses both a homogeneous (K_2CO_3) and a heterogeneous catalyst (ZrO_2). The latter is used in tablet form as a fixed bed reactor. In order to obtain a pumpable feed with the highest possible dry mass fraction, the feedstock is first pretreated batchwise under mild hydrothermal conditions within an autoclave. A special feature is the recirculation of a hot stream downstream of the fixed bed reactor, which is mixed with the cold feed stream (Fig. 14, Table 9). This results in a relatively high heating rate of the feed stream (depending on the recycle ratio), and, in addition, the recycle stream contains reactive intermediates able to prevent coking. The process was investigated on the laboratory scale [64] and then demonstrated in a campaign with a throughput of 100 kg/h [54].

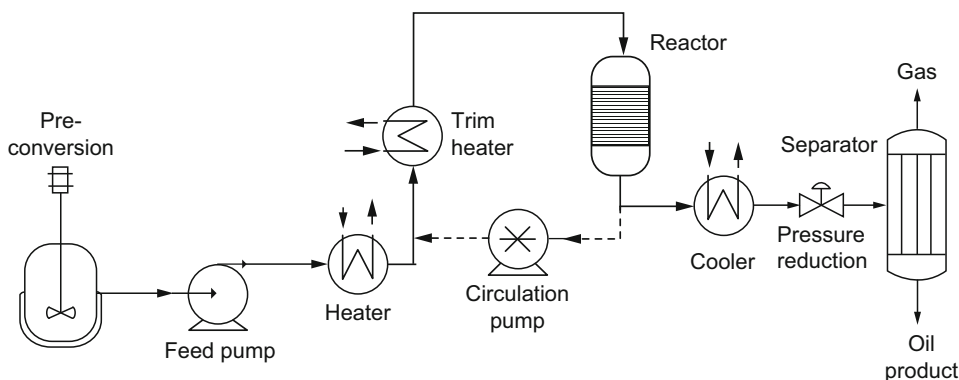
Hydrofaction Process

On the basis of the CatLiq process, an improved liquefaction process was developed. For this purpose, the ZrO_2 catalyst was no longer used [59]. The recirculation of a hot stream was also replaced by a rapid heating of the feed stream by means of induction heating systems.

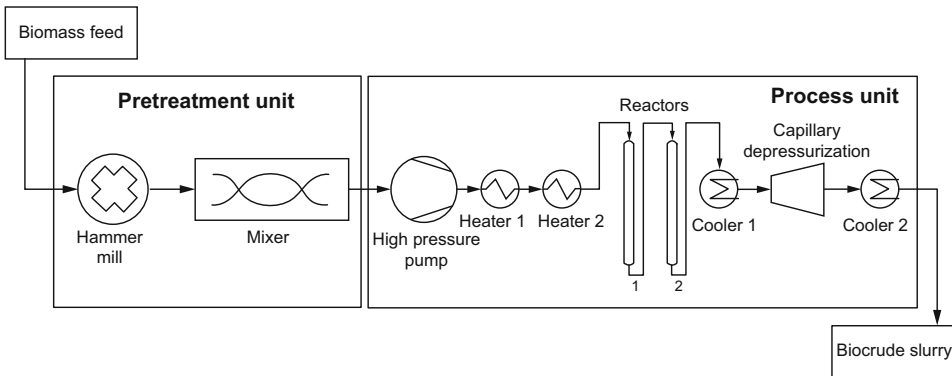
At the same time, the process temperature was raised to supercritical temperatures [77]. The Hydrofaction process was realized and tested in a pilot plant with a throughput of approx. 20 kg/h (Fig. 15, Table 9).

A central aspect of the Hydrofaction process is the conditioning of the feed since high feed concentrations are necessary due to economic reasons. Since the pumpability decreases with the feed concentration, especially with woody biomass, a special conditioning procedure was developed. For this purpose, the wood is first crushed to a mean particle size of about 0.5 mm in a hammer mill. This wood flour is mixed with process water, the homogeneous catalyst K_2CO_3 , and tall oil or HTL oil to form a slurry. A typical mixture contains 18.7% wood flour, 2% K_2CO_3 , 19.1% recycled HTL oil, and 60.2% recycled process water [76]. This mixture gives a dry matter content of 37.8%, since the HTL oil is also determined as a dry mass. This conditioning is based on the PERC method, but additionally involves a recycling of process water. It is assumed that the organic matter dissolved in the process water has a beneficial effect on the liquefaction.

After pressure letdown, an emulsion of HTL oil and water, as well as partially dissolved or suspended solid particles, is present. The HTL oil is separated from the water phase and the solids by centrifugation. The suspended fraction in the water phase is removed in a further centrifugation step [76].



Hydrothermal Conversion of Biomass, Fig. 14 CatLiq process (According to [75])



Hydrothermal Conversion of Biomass, Fig. 15 Hydrofaction process (the comminution of the biomass and the pulping of the feed mixture are performed offline, Biocrude = HTL oil, according to [76])

Hydrothermal Conversion of Biomass,

Fig. 16 Distillation curve of an HTL oil from the Hydrofaction process (Aspen wood) compared to that of crude oil of the Brent quality (According to [84]; triangles: HTL oil from the LBL process [50])

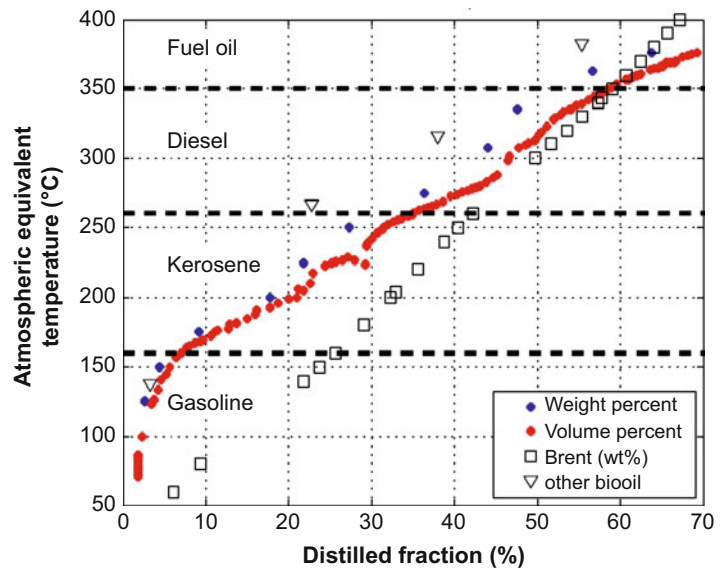


Figure 16 shows a distillation curve of the HTL oil together with that of petroleum (“Brent” type). The HTL oil contains hardly any volatile substances. This is presumably related to the drying step of the oil prior to distillation. A part of the volatile compounds will also go away with the gas while depressurizing the product stream. The kerosene content of the HTL oil, on the other hand, is higher than that of petroleum and the diesel shares are comparable. This also means that the proportion of heavy fuel oil in HTL oil is somewhat higher.

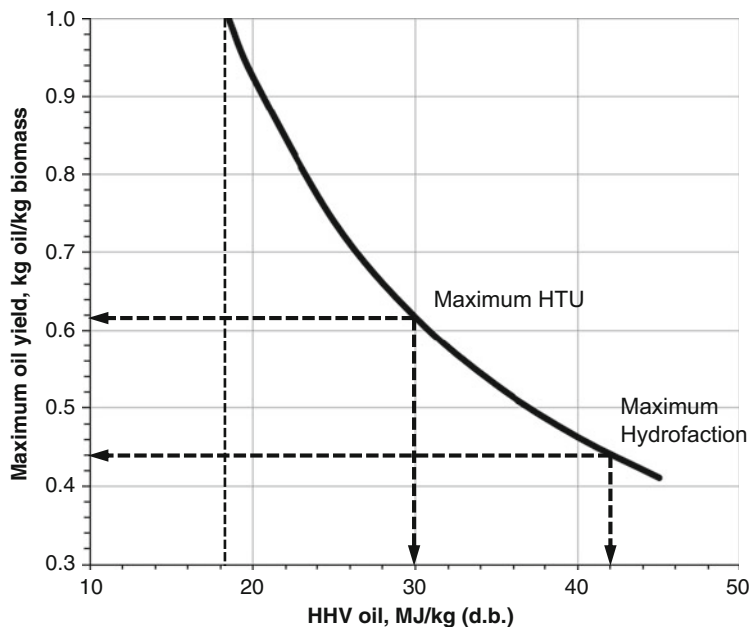
In a loss-free HTL process, the oil yield (Y_{oil} in kg of oil per kg of biomass) and the higher heating value of the oil (HHV_{oil}) are linked to the HHV of the biomass (HHV_{BM}) and the reaction enthalpy ($\Delta H_{R, 298}$) via an energy balance (Eq. 7):

$$Y_{oil} HHV_{oil} = HHV_{BM} + \Delta H_{R, 298} \quad (7)$$

The reaction enthalpy of HTL should be lower than that of HTC. If a thermoneutral reaction ($\Delta H_{R, 298} = 0$) is assumed for simplicity, a maximum oil yield is obtained as a function of the

Hydrothermal Conversion of Biomass,

Fig. 17 Maximum achievable oil yields for the Hydrofaction and the HTU process as a function of the higher heating value of the HTL oils



calorific value of the oil and of the biomass. Assuming a higher heating value of 18.5 MJ/kg (dry) for the biomass, the resulting dependence is shown in Fig. 17 for the Hydrofaction and the HTU processes. The former produces oils with a calorific value of up to 42 MJ/kg. As a result, the maximum achievable oil yield is limited to approx. 44% of the biomass (dry mass). The oil of the HTU process has a lower calorific value. This results in a higher maximum oil yield of up to 62%.

Comparison of these limits with the effective oil yields (Table 9) shows that the Hydrofaction process is already close to the maximum. In the HTU process, higher yields would be possible by reducing the loss of organic matter in the process water (Table 8).

Energy Balance

To date, no data from any of the discussed HTL processes have been obtained from a trouble-free, stationary operation, which enables the establishment of a closed energy balance. At present, only calculated energy balances for the HTU process exist. These are given here as an example for a hypothetical plant with a throughput of 130,000 t/a dry mass [78].

For the calculation of the process efficiency, as defined for HTC in Table 5, the heating value of the HTU oil (33.3 MJ/kg), multiplied by the oil yield (0.41 kg oil/kg biomass), is set in relation to the heating value of the biomass (17.5 MJ/kg (daf)) including the external heat input (1.3 MW). This results in a process efficiency of about 75%.

Heat losses of the heating medium due to temperature differences in the heat exchangers are not considered. Furthermore, a large proportion of the organic matter dissolved in the process water can be converted into biogas in a downstream biogas plant, which can be used to cover some of the externally supplied heat. However, if it is taken into account that the yield of light HTU oil is less than or equal to 0.3 kg/kg (Table 9), the process efficiency of such a stand-alone HTU plant (i.e., no valorization of dissolved organic matter in a biogas plant) would be at most 50%.

Hydrothermal Gasification (HTG)

The gasification of woody biomass in near- and supercritical water was first investigated at the Massachusetts Institute of Technology (MIT) in the USA in the 1970s. However, the gas yield was

low, although different catalysts had already been tested [85]. It was important to note that the wood did not form any tars or coke at the critical point of water. Approximately at the same time, a catalytic hydrothermal gasification process for wet biomass was developed. The so-called TEES (Thermochemical Environmental Energy System) process runs at 350°C and 20 MPa and produces a methane-rich gas using a catalyst [86]. In the 1990s, a high-temperature hydrothermal process was developed to produce hydrogen from wet biomass. In 2002, VERENA, the world's largest pilot plant for hydrothermal gasification, went into operation with a throughput of up to 100 kg/h at a maximum temperature of 700 °C and a maximum pressure of 35 MPa in Germany [87]. In Japan, a similar process was investigated to produce hydrogen in the presence of activated carbon as a catalyst [88]. A high-temperature process was also used to produce hydrogen in the Netherlands. Furthermore, it was shown that methanol can be produced with the H₂/CO₂ mixture from the hydrothermal gasification in a subsequent catalytic high-pressure process [89, 90]. In Switzerland, a catalytic process was developed above the critical point of water to produce a methane-rich gas from wet biomass and recover the nutrient salts as a concentrate [91]. From the 2000s onward, aqueous phase reforming (APR) was developed in the USA, a catalytic process to produce hydrogen from carbohydrates at temperatures below 250 °C, from which kerosene-like fuels can then be produced via further reaction steps. Several groups are also working in China on the hydrothermal gasification of coal and biomass to hydrogen [92].

From this development, three technology pathways of hydrothermal gasification can be identified, which are discussed further below:

- Production of a hydrogen-rich gas at high temperatures (>500 °C) without heterogeneous catalysts, with homogeneous catalysts, or with activated carbon as a catalyst
- Production of a hydrogen-rich gas at low temperatures (<270 °C) from carbohydrates by means of a heterogeneous catalyst

- Production of a methane-rich gas at medium temperatures (350–450 °C) with a heterogeneous catalyst

Main Influencing Parameters

The main influencing parameters for hydrothermal gasification are discussed below.

Dry Matter Content in the Feed

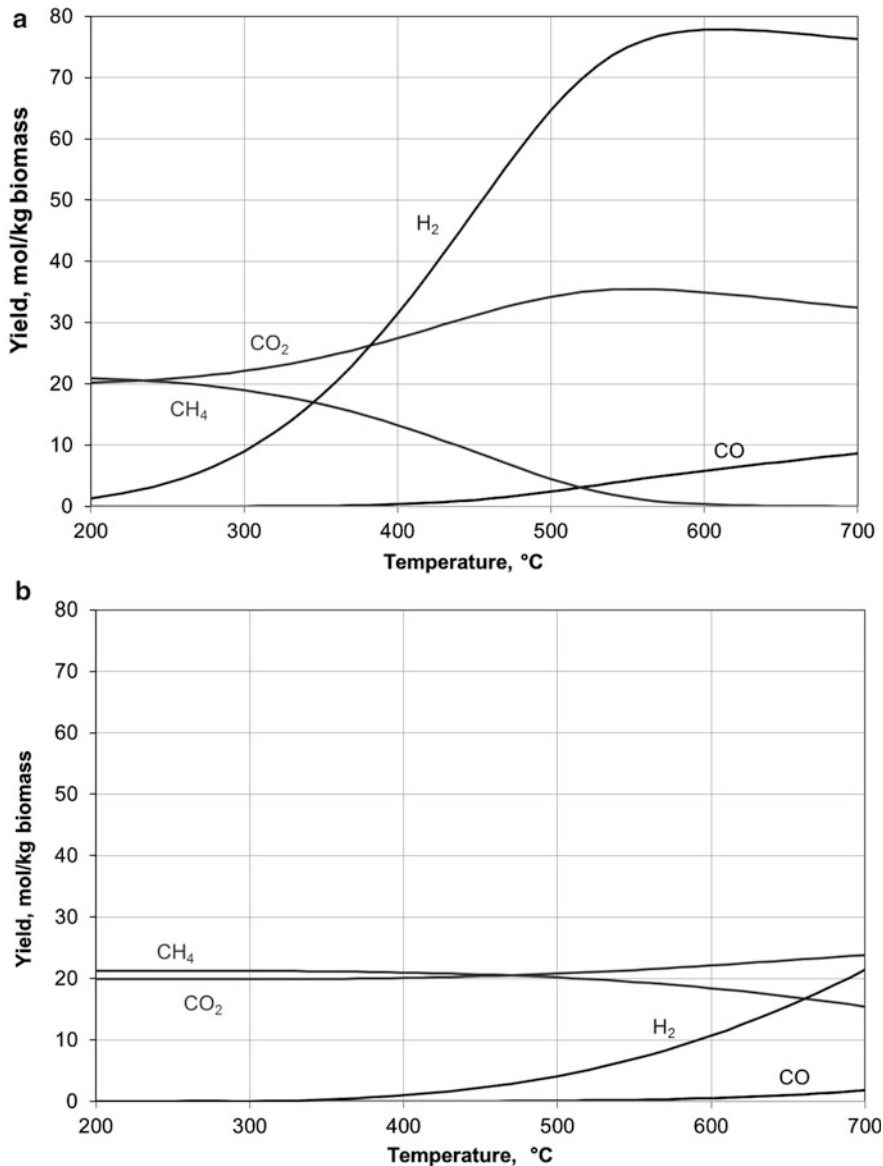
As with HTC and HTL, this parameter also influences the exploitation of the high-pressure system in HTG (i.e., m³ gas per hour and per unit of money invested), since the gas production rate is proportional to the biomass supplied. An organic dry matter content of approx. 10% is regarded as the lower limit for an economically and energetically viable operation (section “Processes and Installations” of section “Hydrothermal Gasification”).

Also during HTG the increased formation of tars and coke at high feed concentrations has to be expected. Although the gasification conditions (high temperatures and/or catalysts) can usually cope with the high feed concentrations, there may be considerable tar and coke formation in the preheaters [93]. Here, too, the strategies discussed for HTL are effective: rapid heating to supercritical conditions or partial recirculation of a hot stream. Often an alkali salt (e.g., K₂CO₃, KHCO₃) is also added to suppress coke formation during heating [94].

The dry mass fraction affects the gas composition. The higher the ratio of water to dry mass, the more hydrogen and the less methane is formed. This is consistent with thermodynamic equilibrium calculations.

Temperature

The temperature has a great influence on the gas yield and the reaction kinetics. For HTG, there is no temperature window for optimum gas yield. The gas composition is largely determined by the thermodynamic equilibrium, which can be approximately achieved with catalysts and/or high temperatures. Figure 18 shows the calculated gas composition in thermodynamic equilibrium for a mixture of 20% wood and 80% water at 0.1 and 30 MPa.



Hydrothermal Conversion of Biomass, Fig. 18 Calculated gas yields in thermodynamic equilibrium for a mixture of 20% wood ($\text{CH}_{1.50}\text{O}_{0.67}$) and 80%

water (H_2O) at a pressure of 0.1 MPa (a) and 30 MPa (b) (the formation of solid carbon was not taken into account)

Under hydrothermal conditions, methane and carbon dioxide are the only thermodynamically stable carbonaceous products up to approx. 550 °C. Only at higher temperatures will carbon monoxide be formed as a stable product. The hydrogen content increases continuously from about 350 °C. At ambient pressure in a steam

atmosphere, methane is significantly less stable and hydrogen dominates the gas composition at around 400 °C.

Without catalysts, the kinetics of hydrothermal gasification of biomass are relatively slow. A slurry of 10% spruce wood was converted to 21% to gas only after 92 min at 409 °C [12]. At a

temperature of 550 °C, cornstarch was gasified to 41% after 2 min. At 700 °C and 2 min, the conversion increased to 92% [95]. Starting from about 250 °C, the low molecular weight hydrolysis products formed can be gasified with a suitable catalyst. The continuous gasification of these components prevents accumulation of aldehydes and acids in the reaction medium; this suppresses the formation of tars and coke. For example, a slurry with 30% of spruce wood could be completely gasified at 403 °C in a batch reactor in the presence of a skeletal nickel catalyst [12].

The temperature dependence of the conversion to gases generally follows Arrhenius' law. If only well-gasifiable components are present, the increase in the temperature leads asymptotically to a complete conversion to gases. However, if poorly gasifiable (refractory) substances are present (e.g., acetic acid) or if these are formed in parallel reactions, the conversion with increasing temperature will asymptotically go toward a value <1 (Fig. 19a).

Residence Time

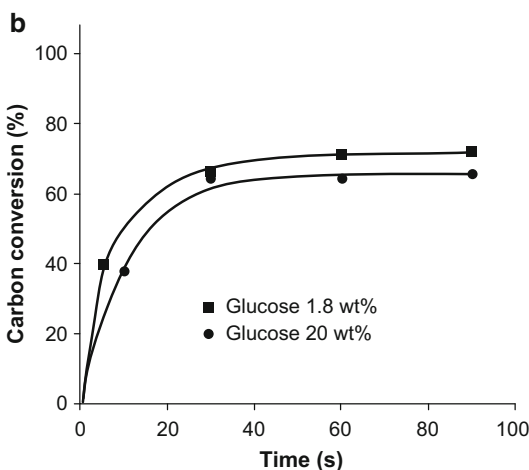
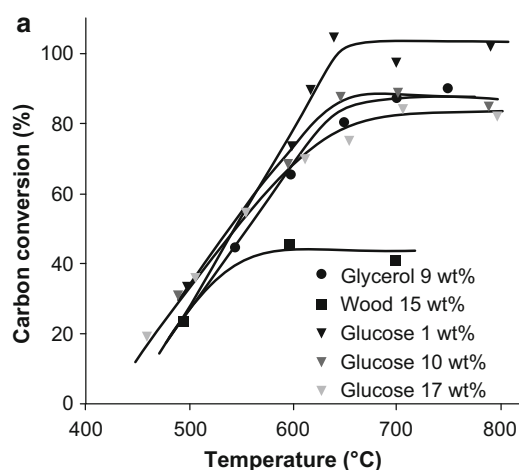
The dependency of the carbon conversion X_C on the residence time τ can often be approximated with a first-order kinetic approach (Eq. 8). Here, k denotes the first-order reaction rate constant (in 1/s):

$$X_C(\tau) = X_\infty(1 - e^{-k\tau}) \quad (8)$$

If all components are readily gasifiable, the conversion approaches the value 1 with increasing residence time (i.e., $X_\infty = 1$). If the gasification does not proceed quickly enough, the low molecular weight products can react in parallel to tars and coke, which gasify only very slowly. This leads to a flattening of the conversion versus residence time curve before a complete conversion can be achieved (Fig. 19b; $X_\infty < 1$). The formation of acetic acid as a hydrothermally refractory molecule also leads to this effect.

Pressure and Fluid Density

For HTG, the pressure has virtually no effect on conversion. However, it affects the gas composition. Overall, higher pressures favor gas compositions with a lower number of moles (i.e., less hydrogen and more methane). Since higher pressures also mean a higher water partial pressure, higher pressures shift the equilibrium of the water-gas shift reaction to the side of carbon dioxide and hydrogen. A higher fluid density also increases the solubility of salts and other substances, which may be undesirable for their separation from the supercritical medium.



Hydrothermal Conversion of Biomass, Fig. 19 Dependence of carbon conversion to gases on the temperature at a residence time of 1 min (a) and on

the residence time at a temperature of 600 °C (b) in the absence of a catalyst (According to [96])

Particle Size

Since for the gasification the biomass has to be liquefied first, the particle size plays an important role for the kinetics of the liquefaction. Particles that are not completely liquefied to low molecular weight fragments as well as coked particles can only be gasified at very high temperatures.

pH Value of the Feed

The pH value of the feed affects the reaction path taken by the hydrothermal transformation of the biomass. Acidic conditions promote dehydration and carbonization. Basic conditions favor the liquefaction to oils. However, the pH value may vary greatly during liquefaction; e.g., the formation of carboxylic acids decreases the pH value and ammonia released from proteins raises the pH value.

If the feed stream is brought to high, supercritical temperatures quickly enough, acidic feed streams can also be gasified well. However, in the case of processes with a gasification temperature below about 500 °C, the homogeneous side reactions (tar and coke formation) must be given greater attention during the heating phase. Here an adjustment of the feed's pH value can be worthwhile.

Additives/Catalysts

The addition of additives or homogeneous and heterogeneous catalysts is central in HTG in order to obtain the highest possible gas yield. However, the biomass often already contains enough alkalis to produce the desired effect.

Reactor Design and Mixing Behavior

Since hydrothermal gasification is always preceded by liquefaction, the statements made there are also valid for HTG. The liquefaction is already taking place in the preheater where, depending on the conditions and the type of biomass, some of the organics are already gasified. A mixture of water, liquefied, oil-like biomass, and gas thus enters the gasification reactor. In addition, there is usually a solid or partially liquid phase of salts and other minerals. Thus, the reactor should be designed to cope with this heterogeneous mixture.

A turbulent flow is particularly important for the heat transfer since the gasification reactors are generally heated externally. If sedimentation zones are present in the reactor, it must be ensured that the precipitates (salts, minerals, coke) are removed continuously or at least periodically.

In the case of catalytic reactors, fixed bed reactors are generally used. In this case, the design is more complex, since in particular the mass transfer to the mostly porous catalyst substrate must be taken into account. Diffusion processes in the catalyst grain must also be taken into account. For this purpose, the design rules of heterogeneous gas or liquid phase reactors with the corresponding physical property data at hydrothermal conditions can be used. Even fluidized bed reactors have been designed and tested with supercritical water using the current correlations [97].

Most HTG processes run in supercritical water. This is completely miscible with gases such as carbon dioxide, methane, and hydrogen; with regard to water and product gases, a homogeneous single-phase system is present. The oil components of the liquefied biomass and the salts also influence the phase behavior. Presumably, a heavy tar phase can be formed which is insoluble even in supercritical water and precipitates [93]. So far, the phase behavior of such a complex mixture has not yet been investigated experimentally. However, a few indications are available from optical observations of the processes during the liquefaction and gasification of wood [98, 99].

The scale-up of results from continuous laboratory reactors to pilot plants is more reliable than that of small batch reactors to continuous laboratory equipment. The main reason is the different heating and mixing behavior of batch and continuous reactors and their influence on the complex reaction network of liquefaction and gasification.

Heating Rate

The heating rate also influences the gasification via the liquefaction. If poorly gasifiable components (e.g., heavy tars, coke) are formed due to a slow heating rate, the gasification conversion decreases. In the case of a continuous plant,

therefore care must be taken to ensure that the temperature window of maximum tar and coke formation is crossed as quickly as possible.

Catalysis

At the lower temperatures at which methane is preferred as a stable product, catalysts are required to obtain high gasification rates. However, catalysts are used not only to increase the rate of reaction (activity) but also to obtain a desired product distribution (selectivity). Since the catalyst does not affect the chemical equilibrium, a catalyst can only be used in HTG under conditions enabling the desired thermodynamically stable products to be formed. Conversely, a catalyst can also be used under thermodynamically unfavorable conditions if the aim is not to reach the chemical equilibrium, as is the case with HTL.

The gas yields shown in Fig. 18 in chemical equilibrium always correspond to a 100% conversion of the biomass. In practice, it is hardly possible to obtain a complete conversion to gases and a gas composition close to the equilibrium at temperatures far below 600 °C without a catalyst. This has the following reasons:

- Reactive intermediates (e.g., furfurals) can react to secondary coke, which, although thermodynamically unstable, shows a very small reactivity for the gasification.
- Methane can be formed by the decarboxylation of acetic acid, the decarbonylation of acetaldehyde (“primary” methane), or the hydrogenation of CO and/or CO₂ (“secondary” methane). Since the hydrogenation of the carbon oxides is very slow, the methane concentration will always be below equilibrium at the lower temperatures without catalyst.
- Conversely, methane is both thermodynamically stable and kinetically largely inert under the conditions of hydrothermal gasification. If primary methane is formed at relatively low temperatures, it does not react to the carbon oxides even at higher temperatures (“steam reforming”). As a result, in the case of biomass generating a high proportion of primary methane at low temperatures, the

methane concentration can be above the chemical equilibrium at higher temperatures without a catalyst.

However, even without the conscious use of a catalyst, certain reactions can be catalytically accelerated by the following:

- The reactor walls, especially when using nickel base alloys
- Alkali salts, which are present in the biomass and function as homogeneous catalysts, especially for the water-gas shift reaction
- Corrosion products (transition metals such as Ni, Fe, Cr or alloyed precious metals such as Pd, Ru) from the reactor or upstream apparatus

The general understanding of how catalysts achieve a complete conversion of the biomass assumes that the catalyst is capable of rapidly converting the reactive intermediates from the hydrolysis of the biomass (furfurals, phenols) to CO, CO₂, H₂, and CH₄. This is already the case starting from about 250 °C [12]. As a result, the intermediates do not react further to tars and coke. The low molecular weight intermediates adsorb on the catalyst surface and are cleaved to form C_xH_yO_z fragments. For example, on a ruthenium catalyst these fragments often have $x = 1$ and $z = 0$ or 1 [100]. A good catalyst can break C-C bonds and open aromatic rings as well as cleave water into O, H, and OH radicals. These radicals react on the catalyst surface with the adsorbed C_xH_yO_z fragments of the intermediates; this leads to the release of CO, CO₂, CH₄, and H₂. Thus, the product gases are formed simultaneously.

There is an important difference between the various catalysts with regard to their ability to release methane. For the formation of CH₄ on the catalyst surface, specially arranged centers of reactive metal atoms are necessary, which are very pronounced in the case of ruthenium and are not present in the case of platinum [101].

For this reason, hydrogen is primarily formed on platinum catalysts, whereas methane is the main product on ruthenium catalysts [1, 102, 103].

In summary, the following statements on the catalysis for HTG can be made:

- Heterogeneous catalysts active for HTG consist of one of the metals Ru, Rh, Pt, and Ni on a hydrothermal stable support material (e.g., activated carbon, α -Al₂O₃, ZrO₂, TiO₂). Nickel is also active as a skeletal catalyst (Raney nickel), but sinters rapidly under hydrothermal conditions. Supported nickel catalysts require a high Ni loading (>40% by weight) for sufficient HTG activity. Metal oxides such as RuO₂ are also suitable as starting materials; these are reduced to the metals under HTG conditions.
- For the production of methane, catalysts with 2–8% ruthenium on activated carbon have proven useful. In the production of hydrogen by the APR (aqueous phase reforming) method, platinum-rhenium catalysts on ZrO₂ are applied [60].
- Sulfur components from the biomass form irreversible bonds with the catalytic metal and poison the metal catalysts. Sulfur must therefore be eliminated to a large extent before the catalytic HTG reactor. Other inorganic components can also damage the catalyst by precipitation and blocking the catalyst surface or the pores of the support material [1].

Product Properties and Use

Properties of HTG Gases

The gases from the HTG mainly consist of CO₂, H₂, CH₄, CO, C₂H₆, and C₃H₈ and, in some cases, also small amounts of higher alkanes/alkenes. The formation of small amounts of N₂ can also occur. Typical gas compositions from the non-catalytic HTG at high temperatures (>500 °C) are shown in Table 10. Under these conditions, H₂ is usually the main component. Since real substrates often contain larger amounts of salts that catalyze the water-gas shift reaction, the gases contain relatively small amounts of CO. They are therefore not typical synthesis gases. Due to the good solubility of HCl, SO₂, NH₃, and NO_x, these remain to a large extent in the aqueous phase, depending on the pH of the process water, and react to the corresponding salts or acids. The HTG gases are therefore virtually free of such impurities. Since the separation of the gases from the water is preceded by condensation (usually under pressure), most of the higher-boiling organic residual components which have not reacted in the reactor are also precipitated. The HTG gases are therefore free of tars and solid particles.

The specific heating value of the HTG gases depends primarily on the ratio of methane to hydrogen. It is in the range of approx. 10–13 MJ/m³ for the high-temperature HTG and between 17 and

Hydrothermal Conversion of Biomass, Table 10 Gas compositions (dry) from the HTG of corn silage, pyrolygneous acid, and glycerol in the pilot plant VERENA [104, 105]

	Corn silage	Pyrolog. acid	Glycerol
Temperature in °C	610	620	549
Pressure in MPa	28	27	28
Residence time in min	4	3.9	3.5
Carbon content of the feed in g/kg	39.6	37.4	259
H ₂ content in vol.-%	31.6	36.4	63
CO ₂ content in vol.-%	27.8	27.4	22
CH ₄ content in vol.-%	28.0	31.0	9
CO content in vol.-%	0.5	0.5	4
C ₂ H ₆ + content in vol.-%	9.9	3.2	2
N ₂ content in vol.-%	2.3	ns	ns

ns not specified

22 MJ/m³ for the catalytic low-temperature HTG (under standard conditions).

Use

Due to their high purity, gases from the HTG are well suited for direct thermal use in a gas engine, in a (micro) gas turbine, or in a solid oxide fuel cell.

The methane-rich gases from the catalytic low-temperature HTG can be upgraded – similar to biogas – by removal of the CO₂ to the quality required for feeding into the natural gas grid. The HTG gases can then be used in all applications similar to natural gas – and in particular also as a biofuel (biomethane).

The hydrogen-rich gases from the high-temperature HTG can be worked up to pure biohydrogen. The synthesis of methanol directly from the high pressure gas of the HTG is also possible [89].

By-Products: Salts

Wet organic wastes can contain large amounts of inorganic substances (salts, minerals). Therefore, the fate of these substances must also be taken into account when using such material streams. In addition, from the processing point of view, such inorganic constituents can lead to operational problems (e.g., corrosion, clogging, fouling). But certain inorganic ingredients (e.g., alkali ions) can suppress the unwanted coke formation.

Most of the HTG processes do not separate the salts from the process stream beforehand, but instead pass the organic-water-salt-gas mixture through the whole process. Recovery is then carried out from the process water under ambient conditions. Both in the case of the non-catalytic high-temperature HTG and the catalytic low-temperature HTG, however, an enriched salt stream could be removed directly from the process. This can be done either after the complete gasification of the organics at high temperatures or before the catalytic gasification. The latter variant results in a reduction in the sulfur load to the reactor, which affects the subsequent catalytic steps. In the separation of the salts, the phase behavior of the respective salt-water-organic mixture must be taken into account.

This phase behavior is usually very complex (section “[Thermodynamics and Phase Behavior](#)”). For example, in the PSI process (see below), a specially constructed salt separator is used, which simultaneously functions as a superheater to supercritical conditions. The feed stream is fed into the separator via a dip tube, where rapid heating is achieved by mixing with the supercritical contents. Most of the salts are precipitated and can be removed continuously as concentrated brine at the bottom of the salt separator. Depending on the salt and operating conditions, enrichment factors from the feed stream to the brine from 3 to 30 were obtained [106]. The depleted stream is fed from the salt separator into the catalytic reactor. Injection of the cold or only moderately preheated feed stream in the salt separators operated at supercritical conditions also reduces coke formation due to the high heating rate by direct contact heating.

Processes and Installations

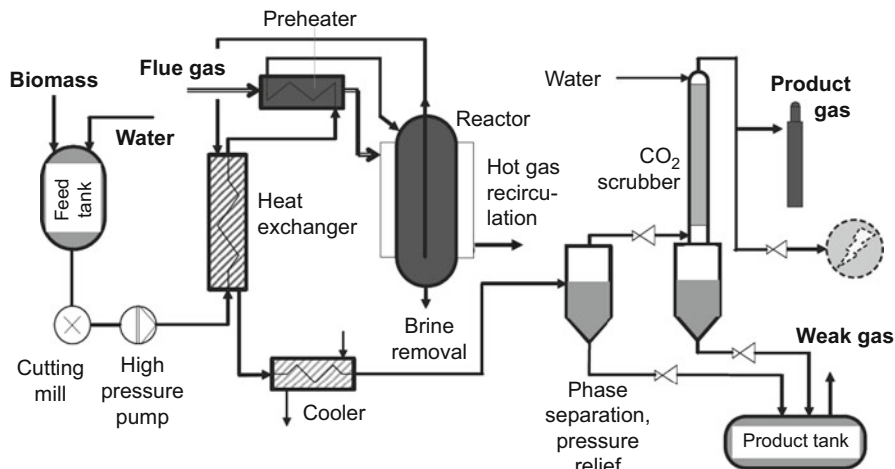
Selected HTG processes and installations are discussed below; a distinction is made between non-catalytic and catalytic processes (i.e., high- and low-temperature processes). The energy balance is also discussed.

Non-catalytic Processes

The KIT process (pilot plant VERENA) [104] is discussed as an example for this process group.

Various mills (cutting mill, colloid mill) are available for the conditioning of the biomass. The solid biomass used is circulated through the mills until a sufficiently small particle size (<1 mm) is achieved for the trouble-free pumping with a hose membrane pump. The electrical power consumption of the feed pump at a throughput of 100 kg/h and a pressure of 28 MPa is about 2 kW. KHCO₃ or K₂CO₃ is generally added to the feed as a catalyst. The feed stream is then heated in a tube-in-tube heat exchanger with an area of 1.1 m² countercurrent to the product stream. In the superheater heated with the exhaust gas of a propane burner, the feed stream reaches approximately the reaction temperature.

The reactor is an elongated, vertical cylinder with an internal diameter of 110 mm and a volume



Hydrothermal Conversion of Biomass, Fig. 20 Simplified process scheme of the VERENA pilot plant (According to [107])

of 35 L. Precipitated salts and other substances can be drawn off via a bottom drain in order to prevent clogging of the subsequent heat exchanger. After the reactor, the product stream is first cooled in the heat exchanger and then in a cooler and decompressed in two stages. The second phase separator is equipped with a scrubbing column, which allows a major portion of the CO_2 in the product gas to be separated by pressurized water scrubbing at approx. 10 MPa (Fig. 20). For example, a product gas with a hydrogen content of approx. 95% can be achieved.

Typical gas compositions are shown in Table 10. The relatively high content of methane is striking for the two biomasses, which is not expected from the thermodynamic point of view at low feed concentrations and high temperatures. Presumably it is primary methane (see section “Main Influencing Parameters” of section “Hydrothermal Gasification”).

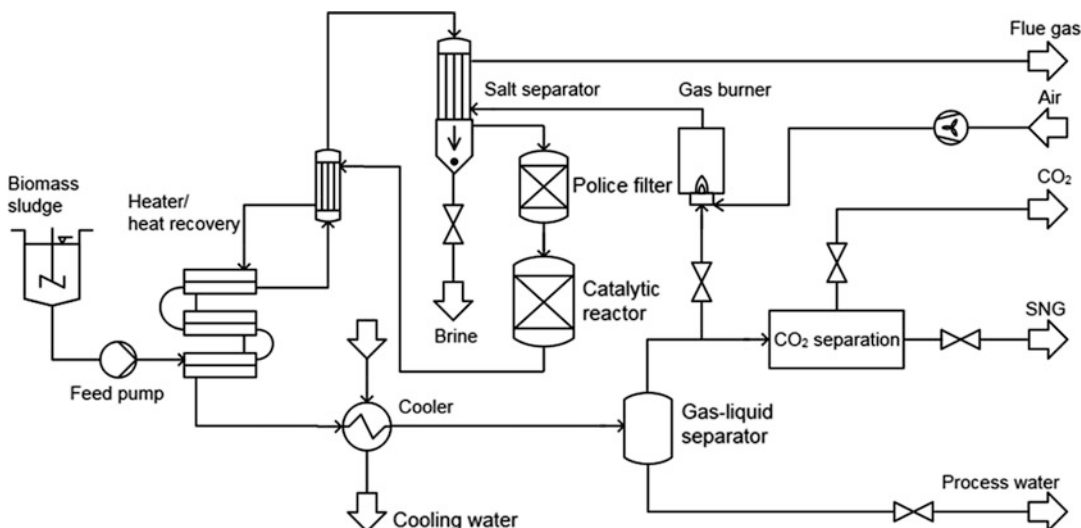
This process was implemented on pilot scale with the construction and operation of the world’s largest plant of this type with a throughput of 100 kg/h at a maximum temperature of 700 °C and a pressure of 35 MPa [104].

Catalytic Processes

Below, selected low temperature processes will be discussed.

PSI Process After the feed preparation and comminution into a pumpable slurry, the feed stream is fed through a tube-in-tube heat exchanger with a high-pressure pump at 25–30 MPa. When the biomass is completely liquefied, a tubular heat exchanger is used for further heating (Fig. 21). In the following salt separator, the temperature is increased to about 450 °C, whereby dissolved inorganic material precipitates as a salt brine to be removed from the hot biomass stream and processed further. The brine is cooled and expanded. A first adsorber, which serves as a “police filter” (protection of the subsequent catalytic reactors), follows in the main stream. In the following catalytic reactors, biomass gasification and methanation takes place in supercritical water at 400–450 °C. The used catalyst contains 2–5% ruthenium on granulated activated carbon (Table 11). Since the reaction is only slightly exothermic, the reactors need neither be heated nor cooled.

After passing through the two heat exchangers, the product mixture is cooled and, after expansion, separated into HTG gas and process water via a phase separator. A gas burner is fired with a small part of the product gas and provides the process heat required for heating the salt separator. Depending on the application, the carbon dioxide in the product gas can be separated by



Hydrothermal Conversion of Biomass, Fig. 21 Flow chart of the PSI process (SNG synthetic natural gas (HTG gas))

Hydrothermal Conversion of Biomass, Table 11 Comparison of HTG processes

	KIT	PNNL/TEES	PSI	UH	APR/ Virent
Main product	H ₂	CH ₄	CH ₄	H ₂	H ₂
Temperature in °C	600–700	350	400–450	600	200–265
Pressure in MPa	28–30	20	28–30	25	<6
Catalyst	K ₂ CO ₃ , KHCO ₃	8% Ru/C	2–5% Ru/C	Powdered activated carbon	Pt-Re/ ZrO ₂ Pt-Re/C
Reactor type	Standing cylinder	Catalytic fixed bed	Catalytic fixed bed	Tubular	Catalytic fixed bed
Largest installation in kg/h	100	10	1, 50	50	n.s.
Comments	Salt removal from the bottom of the reactor or before the reactor with a cyclone; CO ₂ removal by pressurized water scrubbing	CSTR upstream of main reactor for liquefaction; solids removal (batch); sulfur trap (adsorption)	Integrated continuous salt separator; autothermal reactor operation	Liquefaction of the feed at 180 °C, 1.2 MPa, 27 min, before pumping	

KIT Karlsruhe Institute of Technology, PNNL Pacific Northwest National Laboratory, PSI Paul Scherrer Institute, UH University of Hiroshima, APR Aqueous Phase Reforming, CSTR continuous stirred tank reactor, n.s. not specified

means of pressurized water scrubbing or other methods.

The PSI process was successfully demonstrated at a throughput of 1 kg/h during a long-term test for over 100 h with an algae suspension. An upscaling to 50 times the throughput was realized.

PNNL/TEES Process This method is similar to the PSI process. But this process is operated under subcritical conditions of 350 °C and 20 MPa (Table 11). A catalyst with 8% ruthenium on carbon is used. A special feature is the use of a continuous stirred tank as a preheater with an

average residence time of approx. 25 min. A separator for solids (salts and other minerals) as well as a sulfur adsorber is also provided. While the discontinuously operated solids separator worked well, the sulfur adsorber could not provide the desired sulfur retention [108]. A mobile HTG system on a trailer allows on-site tests with a throughput of 10 kg/h.

With the TEES process, a large number of various types of biomass and wet waste streams were gasified and the principle feasibility was demonstrated. However, an industrial plant has not yet been implemented.

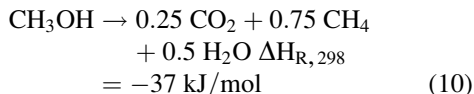
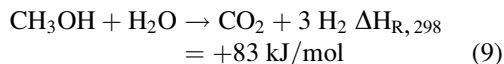
UH Process In this process (UH, University of Hiroshima), fine activated carbon powder ($d_p = 27 \mu\text{m}$) is added to the feed. The biomass is first made pumpable under mild hydrothermal conditions before it is pumped into the gasification part under high pressure. A mixture of 9% chicken litter and 5% active carbon powder resulted in a practically complete gasification of the chicken litter at 600 °C, 25 MPa and a residence time of 2 min. The activated carbon settles in the process water and can be recovered. An advantage of activated carbon is the adsorption of salts; this prevents settling and fouling in the reactor. At present, a pilot plant with a throughput of approx. 50 kg/h is operated [88].

APR/Virent Process With platinum catalysts diluted, aqueous solutions of glucose, glycerol, methanol, and ethylene glycol can be reformed at temperatures of 265 °C and pressures just above the saturation pressure to form a virtually carbon monoxide-free and hydrogen-rich gas [109] (Table 11). This gave rise to the spin-off Virent, which was refocused on the catalytic production of petrol and kerosene-like fuels on the basis of the APR (aqueous phase reforming) process, due to the lack of a market for hydrogen [110].

Energy Balance

A comparative energy balance based on reliable process data is presently not available. In order to show the expected differences, a theoretical balance for the complete gasification of methanol

with a throughput of 100 kg/h is generated on the one hand to form hydrogen according to Eq. (9) and on the other hand to form methane according to Eq. (10):



For the hydrogen path, a reaction temperature of 650 °C and for the methane path of 450 °C are assumed. For both paths, the pressure is 28 MPa. In both cases, 80% of the heat required for heating the feed stream to reaction temperature is recovered from the product stream in the process. The enthalpy streams are calculated for pure water, and heat losses are not taken into account.

The process efficiency η_{th} for the hydrogen path is calculated according to Eq. (11). $LHV(\text{H}_2)$ and $LHV(\text{MeOH})$ are the specific lower heating values of hydrogen and methanol, respectively. $\dot{m}(\text{H}_2)$ and $\dot{m}(\text{MeOH})$ are the hydrogen and methanol mass flow rates, respectively:

$$\eta_{\text{th}} = \frac{LHV(\text{H}_2) \dot{m}(\text{H}_2) - \dot{Q}_{\text{th}, H2}}{LHV(\text{MeOH}) \dot{m}(\text{MeOH})} \quad (11)$$

The external process heat input $\dot{Q}_{\text{th}, H2}$ is calculated from the effective heat demand for heating to the reaction temperature plus the heat requirement of the endothermic reaction according to Equation (12). $\dot{n}(\text{MeOH})$ is the molar flow rate of methanol and $\Delta H_{R, 298}$ the reaction enthalpy at standard conditions:

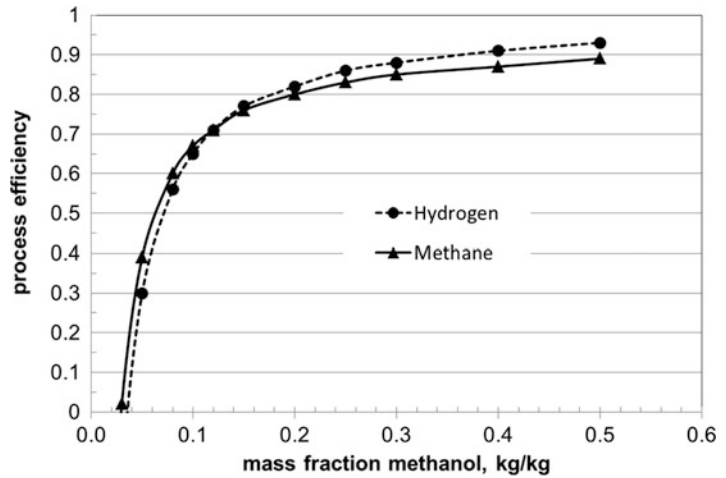
$$\begin{aligned} \dot{Q}_{\text{th}, H2} = & 0.2(h_{\text{water}}(650 \text{ °C}, 28\text{MPa}) \\ & - h_{\text{water}}(25 \text{ °C}, 28\text{MPa})) \times \dot{m}(\text{Feed}) \\ & + \dot{n}(\text{MeOH})\Delta H_{R, 298} \end{aligned} \quad (12)$$

The change in the reaction enthalpy with temperature and pressure was neglected.

For the methane path, the procedure was analogous, with the difference that the heat of reaction

Hydrothermal Conversion of Biomass,

Fig. 22 Theoretical process efficiencies for the hydrothermal gasification of methanol solutions to hydrogen or methane



does not contribute to the external process heat input \dot{Q}_{th,CH_4} , (Eq. 13). h_{water} is the specific enthalpy of pure water at the given pressure and the corresponding temperature. $\dot{m}(\text{Feed})$ is the feed mass flow rate:

$$\dot{Q}_{th,CH_4} = 0.2(h_{water}(450^\circ\text{C}, 28\text{MPa}) - h_{water}(25^\circ\text{C}, 28\text{MPa})) \times \dot{m}(\text{Feed}) \quad (13)$$

The result is shown in Fig. 22. Both paths therefore require a minimum methanol mass fraction in the feed of 3–4% to produce net energy. Up to a methanol mass fraction of 12%, the efficiency of the methane path is slightly higher than that of the hydrogen path. At higher feed concentrations, the hydrogen path has a slight advantage. At very high feed concentrations of over 30%, efficiencies of 90% and above are achievable. While this is easy to achieve with methanol and other water-soluble substances, a limit is set for solid biomass by the pumpability of the feed slurry. Depending on the biomass and pretreatment type, this limit is approx. 15–40% dry matter content.

Future Directions

Hydrothermal technologies for converting biomass into energy carriers have not yet found their way into the market. It is still regarded as

more economic viable to invest into well-known but inefficient conventional conversion technologies. A good example is sewage sludge management. Most of this waste is dried using fossil fuel energy (natural gas or crude oil), transported to cement plants, and used as “green” alternative fuel for the cement kilns. The overall environmental impact and the energy efficiency are both negative, mainly because of the drying step.

For such wastes with a high water content, hydrothermal technologies are far superior, producing transportable and storable energy carriers with high energy density. The energy densification that these processes achieve, i.e., from ca. 3 MJ/kg (mechanically dewatered sludge) to ca. 33 MJ/kg in HTC coal up to 52 MJ/kg in biomethane, is the key to a sustainable use of wet biomass. At the same time, nutrients and water may be recovered, which is a very important aspect in light of the dwindling resources of phosphorus and other elements.

All three hydrothermal technologies, i.e., HTC, HTL, and HTG, have passed the stage of successful pilot plant operations. Some smaller technical challenges remain for certain feedstocks and/or applications. But they do not seem to be unsurmountable obstacles anymore. There are still many open scientific questions, as with every new technology, which, however, are not key to a successful implementation of this technology. Hopefully, first commercial operations of these technologies will be seen in the near future,

replacing the older inefficient processes that prevent a larger usage of biomass as green and storable primary energy.

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