Hot compressed water—a suitable and sustainable solvent and reaction medium?

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Abstract

Hot compressed water in the sub- and supercritical state exhibits exciting
physical and chemical properties, which can be varied continuously from
gas-like to liquid-like behaviour. Correspondingly, the solvent properties
can change from non-polar behaviour as present, for example, in organic
solvents to highly ionic characteristics like in salt melts. This opens up several
promising opportunities for separation processes and chemical reactions. Under
supercritical conditions, substantial amounts of gases and organic substances
can homogeneously be mixed with water, which then can be separated by
adjusting the subcritical conditions by forming additional phases. This can
beneficially be combined with chemical reactions occurring in the homogeneous
state leading to integrated processes, which are more effective and competitive.
Three approaches to the technical application of hot compressed water are
presented to show and discuss the technology, potential, technical hurdles and
future research demand in this area of research and development.

- In supercritical water oxidation (SCWO) water is used as a medium
  in which organic pollutants are completely degraded under the addition
  of oxygen, which is completely miscible with water under the process
  conditions of up to 650 °C and pressures around 25 MPa. Thus, high
  space–time yields in compact reactor designs can be realized.
- Hydrogen is produced from biomass by hydrothermal gasification. Here, in
  an excess of water, the reaction at temperatures up to 700 °C and pressures
  around 30 MPa directly leads to valuable hydrogen instead of synthetic
  gas, as in conventional gasification processes, or methane at subcritical
  conditions in water. After reaction, pressurized hydrogen is obtained and
  can easily be enriched due to the different partition coefficients of hydrogen
  and carbon dioxide between the aqueous and gas phase.
- Even homogeneous catalysis is possible in supercritical water. This
  has been demonstrated with the cobalt-catalysed cyclotrimerization of
  acetylenes to form benzene derivatives or hydroformylation to produce
  aldehydes from olefins. There, only the addition of CO is necessary, the H_2

required being formed by the equilibrium of the water–gas-shift reaction. After a homogeneous reaction in the supercritical state, the reaction mixture can be separated at subcritical conditions.

In support of the chemical and technical developments and to principally understand the experimental findings fundamental aspects have to be investigated as well. Intensive studies have been devoted to chemical kinetics including the modelling with elementary reaction steps, e.g. to separate ionic and radical reaction pathways. Depending on the reaction conditions, ionic or radical reaction pathways can be favoured or suppressed, allowing for control selectivity. Furthermore, corrosion of relevant reactor materials has been investigated.

1. Properties of HCW

Water is an ecologically safe substance widespread throughout nature. Below the critical point, the vapour pressure curve separates the liquid and vapour phase [1]. The vapour pressure curve ends at the critical point ($T_c = 373\,°C$, $p_c = 22.1$ MPa and $\rho_c = 320$ kg m^{-3}). Beyond the critical point, the density of the supercritical water (SCW) can be varied continuously from liquid-like to gas-like values without any phase transition over a wide range of conditions. This behaviour of density and the density-dependent dielectric constant as well as the ionic product of water, both relevant within this discussion, are shown in figure 1 at sub- and supercritical conditions.

Liquid water at ambient conditions ($T = 25\,°C$, $p = 0.1$ MPa) is poorly miscible with hydrocarbons and gases. In contrast, it is a good solvent for salts because of its high relative dielectric constant of 78.5 at a high density of 997 kg m^{-3}. At nearly critical temperature and pressure the relative dielectric constant is in the range of 10 [2]. This is approximately the relative dielectric constant of methylene chloride at standard conditions and it further decreases with increasing temperature. SCW is completely miscible with many organic compounds and gases and a poor solvent for salts. The complete miscibility of supercritical water and gases as well as many organic compounds makes SCW an excellent solvent for homogeneous reactions of organic compounds with gases, like the oxidation of organic compounds with oxygen and air. The absence of phase boundaries leads to a rapid and complete reaction.

From the macroscopic point of view SCW is a 'non-polar' solvent while, from a microscopic view, water is a molecule with a strong dipole moment of 1.85 D. Water in the supercritical state is able to react with different compounds. Therefore water is both solvent and reactant in a variety of reactions.

The interest in supercritical water as a reaction medium firstly focused on degradation reactions. The reason is obvious: the rather high critical temperature seems to favourite reactions which lead to small, at high temperature, thermodynamically stable compounds.

2. Oxidation in supercritical water

The complete miscibility of organic compounds and gases with supercritical water opens the possibility to carry out an oxidation in an inert solvent. No phase boundaries occur, which avoids incomplete conversion due to incomplete mixing of the fluid.

The oxidation of harmful organic compounds contained in aqueous waste effluents, known as supercritical water oxidation (SCWO), has been worked out since the 1980s (for reviews
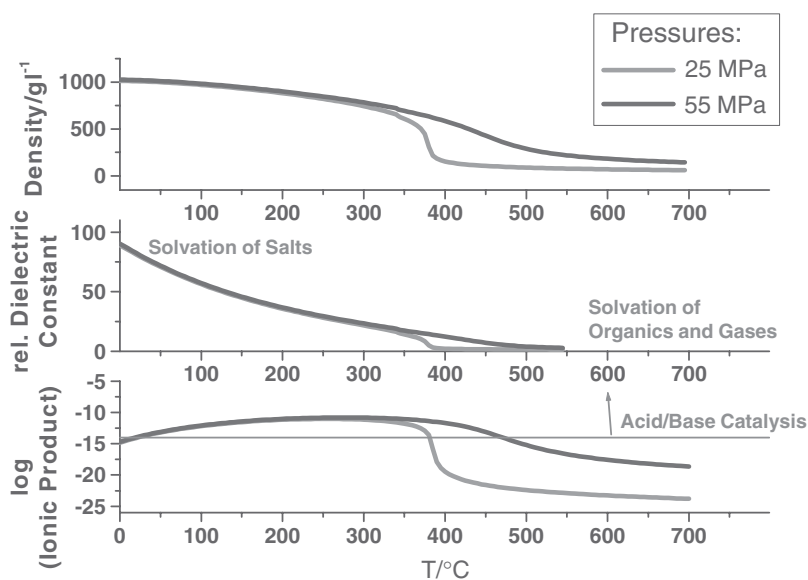
Figure 1. Selected properties of water at high temperature and high pressure (see [1], data are taken from [2]).

see [3–10, 36]). During the SCWO process, the organic compounds react completely with the oxidant—mostly airborne oxygen—forming CO_2 and H_2O. The heteroatoms chlorine, sulfur or phosphorus present in the organic wastes are transformed into the mineral acids HCl, H_2SO_4 or H_3PO_3, respectively. Organic-bonded nitrogen predominantly forms molecular N_2 and small amounts of N_2O. Undesired by-products known from incineration, like dioxins and NO_x, are usually not formed [9]. To achieve the desired conversion efficiency of about 98% (for some hazardous wastes it can be even higher), usually temperatures of 500–600 °C at pressures between 25 and 35 MPa and a reactor residence time of up to 1 min are applied.

Besides the investigation of numerous model compounds, real wastes from the chemical, pharmaceutical and food industries, from municipal sewage treatment plants, and from military and nuclear power facilities were tested in bench and pilot scale plants [6].

For dioxins the destruction efficiency was 99.999 99% [11]. Wastes investigated include radioactive sludge from the nuclear industry, brewery effluents, electronic scrap, sewage sludge, municipal sludge, naval hazardous wastes, paper mill effluents, percolate, chemical and pharmaceutical industries, polymers and rocky flats. Here usually a destruction efficiency of higher than 99% is achieved [3].

To describe the oxidation of simple compounds in supercritical water different groups created kinetic models. These models consist of elementary reactions [12–14] or lumped chemical reactions [15] in the mathematical form of ordinary differential equations.

Two hurdles occur for technical applications: corrosion and plugging by salts. In order to find a suitable material for such SCWO reactors, a lot of corrosion studies on different metals, alloys and ceramics have been carried out [16–23].

Investigations on the corrosion phenomena of the nickel-based alloy 625 (UNSNO6625), which is regarded as representative of other nickel-based alloys and stainless steels, in strongly oxidizing solutions of different acids (HF, HCl, HBr, H_2SO_4, HNO_3, H_3PO_4), salts (NaCl, $NaHSO_4$) and bases (NaOH, Na_2SO_4) show an interesting temperature dependence. In all cases, except in the presence of NaOH and H_3PO_4, the corrosion was strongest in the subcritical
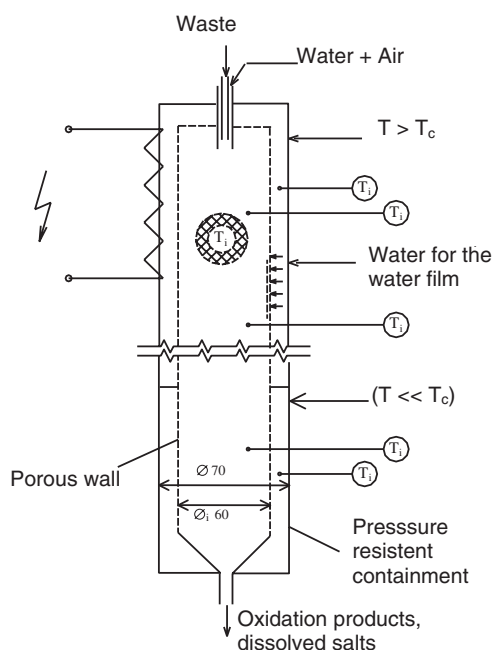
Figure 2. Transpiring wall reactor.

region. Above a certain temperature corrosion effects vanish, which is correlated to the change of water properties at the critical point. At higher temperature and lower density the dissociation of acids and the solubility of salts is decreased, which leads to an increased stability of Ni(II) oxide, forming a protective layer. On the other hand, in the case of NaOH and H_3PO_4 the corrosion was most drastic in supercritical water. This means for most reaction systems and in many SCWO plants, that corrosion occurs mainly in the preheater and less in the reactor [16]. For the preheater titanium liners have proved to be suitable except in the presence of fluoride [9, 22].

Another possibility for avoiding corrosion is a so-called transpiring wall reactor (see figure 2). Here the inner, porous wall is penetrated by water. This resulting water film on the internal surface protects the wall from corrosion. In addition the precipitation of salts on the wall is avoided [24, 25]. The lower part of the reactor has a temperature below the critical temperature. Salts are dissolved again and can be transported easily out of the reactor. This reactor design makes it possible to overcome the hurdles of SCWO.

3. Gasification in supercritical water

Energy from biomass may contribute in a major way to the growing future energy demand. Energy from biomass avoids the net increase of carbon dioxide in the atmosphere and would help to fulfil the obligations of the European Union to reduce carbon dioxide releases. Waste from, for example, the agricultural or food industries is biomass, which can be gasified to produce fuel gases. These gases can be used subsequently to produce electricity or fuel either via methanol or Fischer–Tropsch synthesis.

One the other hand, the formation of hydrogen from methanol is also interesting, mainly for the application of fuel cells in cars. Studies of methanol reforming in supercritical water

show that methanol conversions of up to 99.9% were achieved at 600 °C, 25–45 MPa and some seconds' reaction time without the addition of a catalyst. Conditioning of the reactor surface enhances the reaction rate and decreases the CO yield [26].

A large portion of the residual biomass is wet biomass containing up to 95% water. Such wastes may have high negative costs (disposal costs), which are a benefit for the gasification process. For water contents of more than 40% the thermal efficiency of a traditional steam (reforming) gasification plant decreases drastically to about 10% at 80% water content [27].

A very promising alternative for wet biomass is the less investigated hydrothermal gasification (expected thermal efficiency 70% at 90% water content [27]). In principle there are three different ways to use biomass for energy production:

(1) Liquefaction: formation of liquid fuels near the critical temperature (300–400 °C) of water.
(2) Gasification to methane: at 200–400 °C in the presence of nickel and alkali salts methane is produced from wastes.
(3) Gasification to hydrogen: at 600–700 °C hydrogen is the main product of the biomass conversion in supercritical water. The presence of alkali salts often improves the hydrogen yield.

One benefit of near- and supercritical water is valid in all these conversion processes of biomass. The good solubility of organic compounds, which could be the precursor of tar, and the high reactivity of biomass in near- and supercritical water decreases the formation of char and coke and increases the yields of the desired products. Compared to traditional gasification processes for hydrogen production the following advantages of hydrothermal gasification for a wet biomass/organic waste feedstock can be expected:

- Much higher thermal efficiency.
- A hydrogen-rich gas with low CO content can be produced in one process step.
- Soot and tar formation can be suppressed.
- Heteroatoms (S, N and halogens) leave the process with the aqueous effluent, avoiding an expensive gas cleaning process.
- CO_2 can easily be separated at high pressure because of the high solubility in water.
- Hydrogen is available at high pressure.

To develop a technical process it is necessary to optimize from a chemical point of view to find, for example, the best reaction conditions and from an engineering point of view, for example, feeding, heating, etc. For a chemical optimization of the process it is important to know the chemical reaction pathways. Studies with model compounds have been used to get information about the chemical reaction pathways, which were used to interpret the results with real biomass [28]. A simplified reaction scheme comprising the most relevant key substances is shown in figure 3. Two important tasks of a chemical optimization are to maximize the yield of H_2 and to minimize the coke formation. Studies with the model compound glucose and with biomass show that fast heating up decreases coke formation. The reason might be that, at subcritical temperatures, large amounts of furfurals (see figure 3) are formed which can polymerize after passing the critical point. With rapid temperature increase less furfurals are formed, because no polymerization can occur and degradation becomes predominating. On the other hand, the addition of alkali salts decreases the amount of furfurals and coke formation.

The presence of alkali salts also improves the hydrogen yield at high temperatures by accelerating the water–gas-shift reaction [29, 33, 34]. Investigation of the gasification of pyrocatechol as a model compound for lignin shows an increase of the hydrogen content by a factor of three, corresponding to a drastic decrease of CO formation at 500 °C by adding up
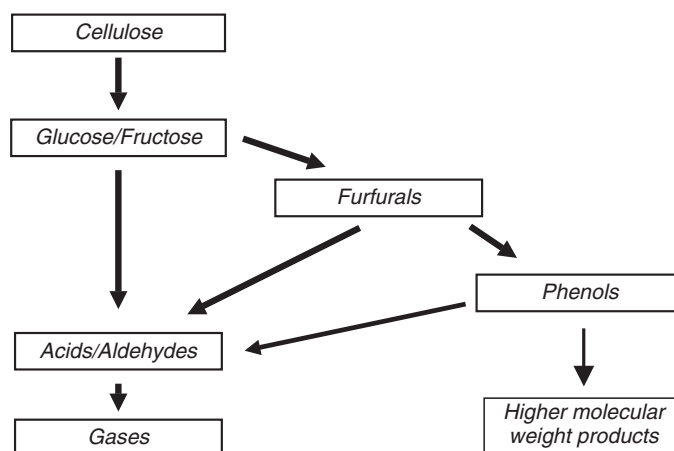
Figure 3. A simplified reaction scheme of biomass degradation.

to 5 wt% KOH (5 wt% pyrocatechol, 250 bar, 1 h reaction time [30]). Experiments in tubular reactors show that at a temperature of 600 °C a complete gasification of the model compounds (glucose, pyrocatechol) used can be achieved [30]. The methane yield in these experiments was always smaller than expected because of thermodynamic calculations. The reason is that no catalyst for methane formation was added and that the reactor was 'aged' before use to avoid catalysis at a 'clean' reactor wall. Aromatic rings included in biomass as lignin are rather stable under supercritical water conditions [31, 32]. Therefore their degradation behaviour during gasification is of particular interest. Usually real biomass already contains alkali salts, so the effect of salt addition is less drastic [33, 34]. Concluding these results, the chemical optimization of biomass gasification for H_2 formation in HCW means:

(1) Catalysis of H_2 formation (if necessary by the addition of alkalis salts).
(2) No catalysis of unwanted by-products like methane.
(3) Degradation reactions have to be significantly faster than polymerization reactions, which, for example, can be achieved by rapid heating.

To optimize the process of biomass gasification from an engineering point of view a pilot plant with components that can be scaled-up is necessary. The first plant for hydrothermal biomass gasification was built at the Forschungszentrum Karlsruhe [35]. A simplified flowsheet is depicted in figure 4. Here, the feed is heated up in a heat exchanger and then in the preheater. The main reaction occurs in the reactor. After passing the heat exchanger and the cooler phase separation occurs. The solubility of CO_2 in water is very high; therefore a significant amount of CO_2 remains dissolved in the aqueous phase under pressure. A washing column can be used to further reduce the CO_2 content in the gas phase. The resulting gas is burned for security reasons. The first experiments have been very successful; feeding and heat exchange work perfectly. Here the task will be to optimize energy consumption, for example.

4. Supercritical water in chemical synthesis

In a variety of organic reactions like hydrolysis, or certain rearrangements, water (for reviews see [36–39]) is both solvent and catalyst via self-dissociation, and sometimes also a reactant. The advantage of the use of water is that the addition of acids and bases may be avoided.
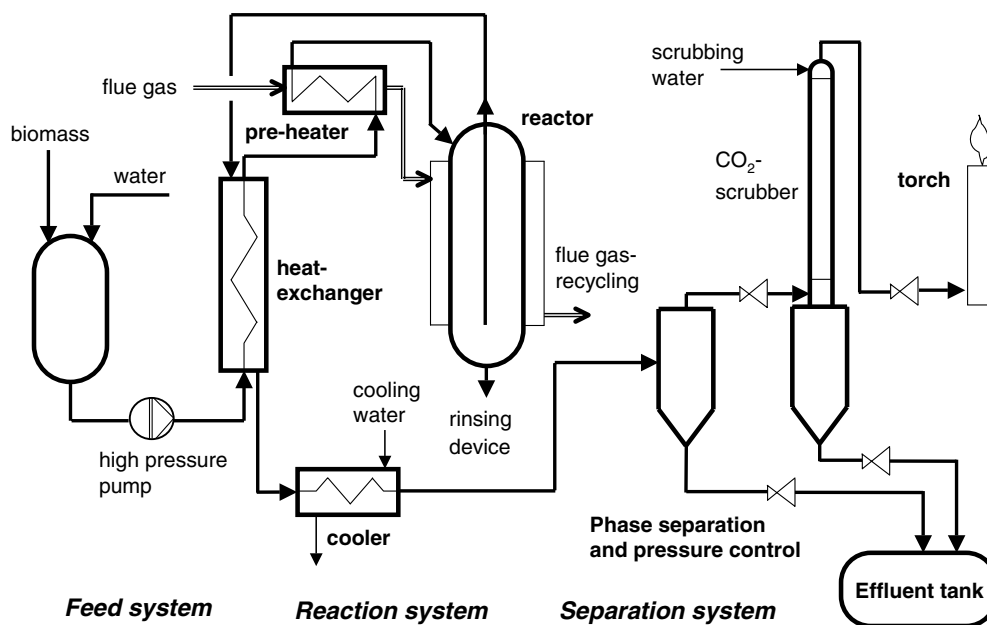
Figure 4. A simplified flowsheet of the pilot plant for hydrothermal biomass gasification.

This means that the cleaning of the effluent is much more facile and less expensive. Synthesis reactions carried out in HCW are the cleavage of N–C and O–C bonds by hydrolysis and condensation reactions forming double bonds or new C–C bonds like in the Friedel–Crafts reactions. Also rearrangements like the pinacol–pinacolone-rearrangement or the Beckmann rearrangement and Diels–Alder reactions have been studied in HCW. Most of the reactions investigated are acid-catalysed but also reactions usually performed in the presence of bases, like aldol condensation and aldol splitting, as well as the Cannizarro reaction are observed in HCW. Partial oxidations were studied, but up to now the results are not satisfactory, mainly because it is difficult to find suitable heterogeneous catalysts, which do not suffer from corrosion. Reduction by Zn or $NaHCO_3$ with palladium on carbon as catalyst are also carried out in HCW.

In organometallic reactions water is a thermally very stable solvent with macroscopic properties like an organic solvent but which may also be a reactant. Here water from a macroscopic view is a non-polar solvent and from a microscopic view a polar molecule. This opens new opportunities for unusual reactions. A special advantage of doing reactions in supercritical water, which are usually performed in organic solvents, is that the high solubility for organic substances only exists at supercritical conditions. After the reaction and cooling to ambient conditions water and organic compounds separate. No distillation or other expensive separation techniques are necessary. Organometallic reactions investigated are the Heck reaction, the cyclotrimerization of alkynes and hydroformylation.

The cyclotrimerization of alkynes is also a typical reaction via organometallic complexes, which is usually carried out in organic solvents. At 400 °C this reaction was successfully carried out in SCW, using $CpCo(\eta^4\text{-}H_2C=CH–CH=CH_2)$ and $CpCo(CO)_2$ [40, 41] as pre-catalysts. The yields and relative amounts of both benzene isomers formed are comparable to results obtained from catalysis in organic solvents [42–46].

The hydroformylation of hexene and cyclohexene in the presence of Co–carbonyl complexes in SCW has been examined, showing that hydroformylation under these conditions

is possible [40, 47]. The product distribution of hydroformylation has been investigated by varying the amount and composition of the synthesis gas and the catalyst. Hydroformylation of hexene is also observed in the absence of hydrogen, because under the reaction conditions hydrogen is formed by the water–gas-shift reaction. In these experiments about 10% of hydrogen was found in the gas phase after the reaction. In the absence of added hydrogen less hydrogenation of the aldehydes is observed, leading to higher selectivities towards aldehydes and less formation of alcohols.

5. Conclusions

The variability of the properties of HCW as a function of temperature and density makes it an 'adjustable' reaction medium for many types of reactions. In addition it can be a reactant. The degradation reactions, in particular the SCWO process, are well studied and near to technical application. The high conversion of toxic compounds also makes SCWO a very interesting alternative to incineration. Hurdles for the SCWO, like corrosion and salt deposition, are solved by means of advanced reactor design.

Hydrogen production by gasification of biomass in HCW is also a very promising reaction. The lab scale experiments show that biomass gasification is, in spite of the high temperature, a reaction which is highly determined by chemical kinetics, so it can be optimized by, for example, catalysts. That a technical application is possible was demonstrated by the pilot plant. Residual biomass can contribute via SCWG to the energy, fuel or chemical supply. Concerning technical applications there is still some work to do concerning the improvement of our fundamental knowledge and engineering.

Studies of synthesis reactions in particular benefit from the 'adjustability' of HCW. A huge variety of chemical reactions were observed and many more may be found in the future. These reactions are currently a long way from application, but HCW is a very extraordinary reaction medium opening the door to completely new opportunities in chemistry. Here a lot of studies to obtain a better understanding of this suitable reaction medium are necessary, in particular on catalysis in HCW. Here the stability of homogeneous and heterogeneous catalysts is of special importance.

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