Supercritical Water Oxidation - Waste Destruction and Synthesis

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The recycling and disposal of halogenated compounds such as polymers (polyvinylchloride), flame retardants (tetrabromobisphenol A) and chlorocarbons (γ -hexachlorocyclohexane, hexachlorobenzene) lead to the formation of byproducts and residues, which cannot be passed on to the environment. Prior to this background the oxidation of halogenated compounds in supercritical water (*Supercritical Water Oxidation*) is of special interest. First results are shown that a complete oxidation without formation of hazardous products can be achieved. Under supercritical water conditions hydrolysis, pyrolysis or oxidation of organic compounds are different from classical gas phase reactions. First experiments have shown, that in presence of supercritical water the concentration of intermediates assumes relatively high values.

1. INTRODUCTION

High pressures not only influence the physical and chemical properties of substances and substances mixtures, but also their chemical reactions. In a large number of large-scale processes in the chemical industry e.g. ammonia synthesis, oxo synthesis and ethylene polymerization, pressure is one of the decisive process variables.

Pressure influences both, the thermodynamics as well as the kinetics of a chemical reaction. In this context it is necessary to make a difference between reactions in the gas phase and those in the liquid phase.

Supercritical fluids like water are of special interest, if the density should be continuously changed from gas-like densities to high liquid-like ones. Water is one fluid that is capable to dissolve inorganic and organic substances. Therefore a large number of chemical reactions, synthesis as well as waste destruction, can be studied in water under supercritical conditions.

2. WASTE DESTRUCTION

Waste include problematic substances which, for ecological reasons, cannot be passed on to the environment but have to be supplied to a specific and proper disposal process. As a rule, these substances are disposed of by incineration. However, as the waste materials contain halogen and nitrogen compounds, their disposal is connected with considerable problems. Thus, in the elimination of chlorine containing organic waste, we must reckon with the formation of chlorine and dioxines, whereas nitrous oxides may also be produced on the destruction of waste materials containing nitrogen.

At all events, present legal regulations demand that any hazard to the environment be completely excluded where the destruction of waste materials is concerned. The supercritical water oxidation or hydrothermal oxidation process is a new environmentally friendly technology for waste treatment e.g.

- chlorocarbons
- polymers
- polymer additives

2.1. THE SUPERCRITICAL WATER OXIDATION (SCWO)

Above the critical point of water its properties are very different to those of normal liquid water or atmospheric steam. The following properties of supercritical water are of special interest:

- Complete miscibility with organic compounds
- Complete miscibility with air or oxygen
- Complete miscibility with gaseous reaction products
- Low solubility of inorganic compounds

From this it can already be seen that all reaction partners which are involved in an oxidation process are completely miscible with supercritical water.

The supercritical water oxidation process (SCWO) is described in figure 1.

Fig. 1. SCWO - Process

Waste characterized by the following elements i.e. carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur and chlorine would be oxidized in the presence of oxygen and water at temperatures above 374 °C and pressures above 221 bar in a batch-reactor to the following reaction products: water, carbon dioxide, nitrogen, phosphorus acid, sulphuric acid and chlorine acid.

Figure 2 shows the construction of the apparatus for examining hydrolysis and oxidation reactions in sub- and supercritical water. The reaction vessels are made of a high-strength and corrosion-resistant CrNiMo-steel. The available interior volume reaches from 0.2 to 2 liters. The autoclaves can be used for temperatures up to 500 °C and pressures up to 1000 bar. At the top the reaction vessel is sealed with a conical tightening piston. A rotary permanent magnet unit is supported on axial and radial bearings in a pressure tight housing screwed onto the autoclave lid. An outer unit of the same magnetic material is driven mechanically. The inner magnet unit is connected with the stirrer. The piston is perforated and communicates with the manometer or pressure transducer, the safety valve and the expansion valve. Via the expansion valve the autoclave is connected with the sample removal apparatus. Through another opening thermocouples can be introduced.

Fig. 2. SCWO-Autoclave

2.1.1. HALOCARBONS

The disposal of highly chlorinated compounds such as γ -hexachlorocyclohexane (γ -HCH) is a very pressing problem at the moment. Hexachlorocyclohexane can be decomposed very well in supercritical water.

Hydrolysis experiments were carried out in the subcritical and supercritical ranges. It was found that a maximum of 50 % of the organically bonded chlorine is converted to chloride at temperatures up to 300°C. Under subcritical conditions no breakdown of the hydrocarbon structure occurs. From approx. 350°C close to the critical point of water, the conversion rate increases to 97 % (see figure 3).

A decomposition of the hydrocarbon structure occurs in the supercritical range. Hydrogen, carbon dioxide and methane are produced as gaseous reaction products.

By the addition of an oxidizing agent, a complete breakdown to carbon dioxide, water and chloride is possible. The conversion ratio arises up to 99 %. A formation of chlorine and dioxines as in thermal decomposition was not observed.

Fig.3. Hydrolysis and oxidation of γ -HCH

2.1.2. POLYMERS

It is only possible to obtain a breakdown to the initial materials in those polymers which had been synthesized via polycondensation or polyaddition, i. e. polyamides, polyesters, polycarbonates or polyurethanes. By a specific attack of the water molecule at the chemical bond of the initial components, it is possible to recover the original materials, e.g. diol and dicarbonic acid from a polyester or diamine and diol from a polyurethane. In alkaline hydrolysis of polyurethanes at subcritical conditions the isocyanate function is lost as decarboxylation occurs.

Radically manufactured polymers such as polyvinylchloride (PVC) can also be decomposed via alkaline hydrolysis, although only in the supercritical range. Investigations on the breakdown of polyvinylchloride at 150°C have shown that less than 1 % of the organically bonded chlorine can be split off the polymer chain.

When alkaline hydrolysis is carried out in the supercritical range, e.g. at 500°C, we find over 93 % of the organically bonded chlorine in the aqueous phase (see figure 4). In this process the principal polymer chain is also decomposed. The main products are hydrogen and carbon dioxide, with methane and C₂-hydrocarbons occurring as secondary products. Under supercritical water oxidation conditions a complete breakdown can be achieved with chlorine-conversion up to 99 %.

Fig. 4. Hydrolysis and oxidation of PVC

2.1.3. POLYMER ADDITIVES

Additives like flame retardants could also be converted into environmental acceptable reaction products in supercritical water. First results have shown that compounds like tetrabromobisphenol A break down in supercritical water to form carbon dioxide, hydrogen and bromide. At temperatures above 500°C more than 90 % of the organic bonded bromine was converted into bromide.

By adding oxygen complete breakdown to carbon dioxide and water is possible. Under supercritical water oxidation conditions more than 99 % of the organic bonded bromine was found in the aqueous phase. A formation of bromine and dioxines as in thermal decomposition was not observed.

With these results we are able to adapt the SCWO-process together with industrial partners to printed circuit boards. Our strategy consists in the oxidation of organic components to recover process energy, the recovery of inert components e.g. metals and glass fibers and the recovery of bromine.

The process itself can be described by the following steps:

- Grinding of printed circuit boards
- Separation of the metallic fraction from reinforced resin
- Supercritical water oxidation
- Separation of water from gas and residues
- Neutralization of the water phase
- Separation of solid residues.

2.1.4. NITRO AROMATICS

In connection with the purification of water from cleaning contaminated soil investigations were carried out as to whether it is possible to decompose nitroaromatics like dinitrotoluene (DNT) and trinitrotoluene (TNT) in subcritical and supercritical water.

When alkaline hydrolysis is carried out at 150 °C and 5 bar, an oily, highly viscous emulsion is obtained. The basic aromatic structure is not destroyed in doing this. Only a splitting off and conversion of the nitro groups occurs. As a gaseous product we principally find nitrogen occurring., in addition to traces of nitrous oxides and dinitrogen oxide. Nitrite and ammonium occur as ionogenic compounds and no formation of nitrate is observed. Furthermore, the liquid phase contains a complex mixture of nitrotoluenes and aminotoluenes.

When alkaline hydrolysis is carried out in supercritical water, the aromatic structure is also broken down. This can be recognized from the emissions of the gaseous reaction products methane, hydrogen, carbon dioxide and carbon monoxide. The nitrogen of the nitroaromatics is principally converted to ammonium or nitrogen. Only traces of nitrous oxides or dinitrogen oxide are found. It is also not possible to achieve a complete decomposition of the nitroaromatics at supercritical hydrolysis conditions, as the liquid phase still contains organic compounds.

By adding oxygen a complete breakdown of the nitroaromatics is possible. The liquid phase contains only ammonium. As gaseous products nitrogen, dinitrogen oxide, carbon dioxide and traces of nitrous oxides, hydrogen and carbon monoxide are identified. Approx. 83 % of the nitrogen from the nitroaromatic was converted to molecular nitrogen, 10 % to dinitrogen oxide and 7 % to ammonium. The yield of nitrous oxides was smaller than 0.01 %. The destruction efficiency was greater than 99 %.

3. SYNTHESIS

Under supercritical water conditions oxidation and pyrolysis of hydrocarbons are different from classical gas phase reactions. Thus in the oxidation of methane, the methanol concentration assumes relatively high values, while oxidation at gas phase conditions only leads to the formation of carbon dioxide.

For the oxidation of hydrocarbons the stability of the reaction products in supercritical water is of special interest.

3.1. OXIDATION OF HYDROCARBONS

The selection of the reaction conditions for the oxidation of hydrocarbons is principally determined by the following factors:

- The phase equilibrium of the system water-hydrocarbon
- The phase equilibrium of the system water-oxygen
- The ignition temperature in the water-hydrocarbon-oxygen system.

The fact must here be taken into account that the ignition temperature depends both on the pressure and on the composition of the mixture. The ignition temperature decreases as pressure rises, in the same way as it does with a rising hydrocarbon content in the supercritical mixture. If the reaction temperature is below that of the ignition temperature, we are able to investigate flameless oxidation, but if it is above the ignition temperature, flames are formed.

Hydrogen, carbon monoxide, carbon dioxide and alcohols constitute the main products in the oxidation of hydrocarbons with oxygen in supercritical water. The reaction conditions have a particularly marked influence on alcohol selectivity and the relation between the quantities of carbon dioxide and carbon monoxide.

3.2 HYDROTHERMOLYSIS OF HYDROCARBONS AND ALCOHOLS

In connection with studies on the oxidation of hydrocarbons the question presents itself as how far the decomposition of pure hydrocarbons plays a part.

Our studies have shown that hydrocarbons are still predominantly stable at higher temperatures in supercritical water than in a gas atmosphere.

The formation of the reaction products can be described by the following reactions:

- Synthesis gas reaction
- Conversion reaction
- Pyrolytic reaction

Under specific reaction conditions, the alcohol concentration assumes very high values in the oxidation of hydrocarbons. For an interpretation of the results, the question on the thermal stability of alcohols in supercritical water is of importance. Two aspects are here of interest:

- The dependence of the alcohol decomposition on temperature
- The influence of the reaction medium on the decomposition.

4. SUMMARY

The *Supercritical Water Oxidation* (SCWO) demonstrate a number of highly notable advantages. These can be summarized as follows:

- Suitable for organic waste materials containing water and waste waters containing few organic substances.
- The reaction takes place in a closed system.
- The organics are oxidized in a controlled but rapid reaction.
- A single-phase reaction system is involved.
- Air, oxygen or hydrogen peroxide can be used as oxidizing agents.
- The reaction times are shorter than those involved in wet oxidation by a magnitude of one.
- The reaction temperature is lower than that found in incineration.
- Hydrocarbons can be oxidized to partial oxidated reaction products.

- Partial oxidated reaction products are very stable in supercritical water.

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