An alternative method of oxidizing aqueous waste in supercritical water: oxygen supply by means of electrolysis

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Abstract

Nearcritical and supercritical water \( (T_c = 647 \, \text{K}, \, P_c = 22.1 \, \text{MPa}) \) is an excellent solvent for many organic compounds. Furthermore it has outstanding properties as a reaction medium because of the complete solubility of reactants, such as oxygen and hydrocarbons. To avoid the high technical demand for the supply of oxygen by compressing air, a new apparatus was developed, which produces oxygen under high pressure by means of electrolysis. For alkaline water electrolysis, an electrolysis cell was constructed working within a pressure range of 22–25 MPa and a temperature up to 623 K. Factors determining the destruction rate are, beside pressure and temperature, the electrical conductivity and the voltage used in the cell. The electrolysis cell was linked to a continuous high pressure extraction apparatus. Different aqueous waste streams (soil extracts, wool scouring wastewater, bilge water) were fed into the system and the destruction yield was studied as a function of these parameters. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since 1989, within the scope of ‘Treatment of Contaminated Soils’ by Deutsche Forschungsgemeinschaft, SFB 188, this research group has been working with hydrocarbon contaminated soil. Our aim was the remediation of hydrocarbon polluted sites with high pressure semi-batch extraction using carbon dioxide and water [1–4]. Like other research groups, we found water to be the most efficient extraction agent [2,4]. Later on, an apparatus was developed, which allowed co-current flow of small soil particles for continuous high pressure and high temperature extraction with supercritical water [3,5]. The experiments were very successful and led to clean soil, but also to a hydrocarbon loaded aqueous effluent stream. In order to provide a closed and efficient solvent cycle the water needed to be cleaned.

Supercritical water oxidation (SCWO) is preferentially used for aqueous waste streams with too low an organic content for traditional thermal treatment or too high or diverse an organic load for biological waste water treatment. There is
increasing interest in both chemical and physical process technology, using high pressure and high temperature, not only in scientific but also in industrial fields [6,7]. SCWO is an efficient treatment of polycyclic aromatic hydrocarbons or other pollutants, such as polychlorinated biphenyls, herbicides or even chemical weapons [8]. Substances like synthetic air or hydrogen peroxide are added to increase the destruction rate with simultaneously lowered reactor temperature, compared to processes with no oxidant. Several research groups have focussed on developing pilot plants for continuously working facilities [9], studying pathways and reaction mechanisms of several pollutants and substances [10,11] or different concepts of reactors [12,13]. All these researchers work with temperatures clearly above the critical temperature of water and with oxygen fed inline by compressing from ambient conditions. From our point of view there was an urgent need to look for an alternative, avoiding the use of an air compressing system but using the high pressure and high temperature of the extract directly after the extraction process. Furthermore it is in our interest to supply a system able to both deal with particle containing aqueous waste streams and provide an opportunity to destroy the organic load without stressing municipal waste water treatment facilities.

Electrolytic production of oxygen inside the system is promising [14] and saves both energy used to compress air and the cost of hydrogen peroxide. There are some examples of high pressure electrolysis in space technology, i.e. oxygen is used for life preservation systems and hydrogen as a fuel [15]. Other research groups have worked with ceramic electrolytes, which provide a partition of product areas [16,17]. A review of decomposition of water by electrolysis can be found in Wendt et al. [18].

2. Experimental

The apparatus consisted of a membrane pump, a pressure check valve, and an electrically heated tubular system with different tube sizes. Two different devices were used for heating the fluid and feeding it into the electrolysis cell. The pressure was held constant with a pressure control system with a pneumatically operated check valve, to provide continuous operating conditions. After passing the heated parts and the electrolysis cell, the fluid is cooled down. All piping systems were made of stainless steel 1.4404, with connecting Swagelok fittings made of 1.4401. The soil analyses yielded no or extremely low halogen content, so no corrosion or corrosion-caused failure of the material is expected or detected so far. Results shown in Figs. 2–4 were obtained using a preheating system with a 1/8-in outer diameter high pressure tube with an inner volume of 38 ml. Other results were obtained with preheating piping of 1/4-in and an inner volume of 66 ml, which is described in detail elsewhere [5]. The temperature in the preheating system was measured by NiCrNi-thermocouples and recorded. Using the 38-ml preheating reactor both upstream and downstream, the temperature of the cell was measured, in comparison to using the other system where only upstream data were taken. Pump valves were used in two ball configuration so fibrous load and small particles could not cause failure of the whole experiment.

Experiments were all done in a pressure range of 23–25 MPa at different temperatures.

Fig. 1 shows the electrolysis cell, the body of which is a 1-in high pressure pipe. Both current and oxygen amounts are linearly dependent on cell voltage. Components of the high pressure cell were Autoclave Engineer high pressure units (No. 20F91666), two 14-mm 1-in unions made of stainless steel 1.4401, one high pressure tee-fitting, and one HIP component (No. 20-21LF6-U). The cell was used in two different configurations with volumes of 35 and 50 ml, depending on the length of the 1-in pipe. The spark plug was modified by re-tapping the thread and adding a cone for sealing. The spark head was given a thread to give the rods stability. All used rods had a plain, smooth surface, which did not change significantly during the experiments. Two different anode materials were found to be durable: gold and platinum. Other anode materials were tested. Inconel 600 exhibited severe corrosion and caused breakdown. Stainless steel and welding rod anodes...
showed surface corrosion and rust. The graphite electrode seemed to be dissolved by the fluid and was found to be thinner after the experiment. Besides the two noble metals, titanium was without corrosion but colored blue afterwards, wherefore it was not used anymore.

Different voltages were applied to the system by a voltage source. At the beginning KOH solution inside the suspension enabled transportation of the electric charge. Initial conductivity and pH of the feed stream was adjusted by adding 0.1-mol/l KOH solution before the experiment and measured only under ambient conditions. Effluent conductivity, i.e. effluent pH, was not examined.

The cell was heated by pre-heating the tubular reactor: the cell itself was not heated separately. We found ohmic heating inside the cell of \(15 \text{ K}\) (Fig. 2) using a voltage of 30 V and a conductivity of 1.6 mS/cm.

This rise in temperature is caused by the given voltage and becomes constant after some time. The effect of increasing temperature must be kept in consideration when choosing the reactor temperature and the temperature in the pre-heater.

3. Results and discussion

The grade of destruction was calculated with Eq. (1):

\[
E = (c_0 - c)/c_0
\]

where \(E\) is yield of destruction, \(c_0\) is load of hydrocarbons or total organic carbon (TOC) in water before the experiment and \(c\) is load of hydrocarbons or TOC in water after the experiment.

Hydraulic residence time calculations were done under the presumption that the feed stream has the density of water.

\[
\tau = V/V'_p
\]

with

\[
V'_p = (V_a \rho_a)/\rho_p
\]

where \(V\) is volume of reactor, \(V'_a\) is volumetric feed stream under ambient conditions, \(\rho_a\) is feed density under ambient conditions and \(\rho_p\) is feed density under experimental conditions.

The yield of destruction was determined by IR-spectroscopy after method DIN 38 409 H18. Reference was the characteristic peak of the asymmetric valence oscillation of the methyl group at
Fig. 3. Current flow and dissolved amount of oxygen as a function of cell voltage; $P = 23.2$ MPa, $T = 290$ K, $\kappa = 4.33$ mS/cm, $V'_0 = 3.1$ l.h.

2930 cm$^{-1}$. Total organic carbon (TOC) was determined with Dohrmann TOC-analyzer. Quantitative description of bilge water and wool scouring water were done with gas chromatography/flame ionization detection-analyses using an HP 5890A chromatograph. Used columns were a deactivated fused silica pre-column $2$ m $\times$ $0.53$ mm and a $12$-m BPX-5, $0.32$ mm $\times$ $1$ $\mu$m, in ‘on-column’ mode. Heating rate was $20$ K per minute up to $583$ K.

To prove the working principle of the apparatus, experiments electrolyzing water without hydrocarbon freight were carried out. The electrolyte was a KOH solution of $\kappa_a = 4.33$ mS/cm in a temperature range of $290$–$543$ K. In principle the resulting water decomposition should follow Eqs. (4)–(6):

Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (4)
Anode: $2\text{OH}^- \rightarrow \text{H}_2\text{O} + 0.5\text{O}_2 + 2\text{e}^-$ (5)
Total: $\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$ (6)

The following results are evaluated only with respect to the produced oxygen. Hydrogen is assumed to be dissolved in the effluent. The resulting current and the dissolved amount of oxygen as a function of cell voltage is shown in Fig. 3. The two straight lines, both the produced amount of oxygen and the resulting current, are linearly dependent on cell voltage. It is shown that oxygen can be produced by electrolysis under low voltages and low electrolyte concentration. Interpolating the voltage-to-current measurements the decomposition voltage can be determined as the intercept point of the two straight lines. The ‘true’ decomposition voltage was not measured potentiometrically inside the cell during experimental work. The cell voltage can be divided into different terms of a sum Eq. (7):

$$U = U_{dv} + \eta_{\text{anode}} + |\eta_{\text{cathode}}| + I^*R_i$$

(7)

where $\eta_{\text{anode}}$ is excessive voltage anode, $\eta_{\text{cathode}}$ is excessive voltage cathode, $U_{dv}$ is decomposition voltage, $U$ is cell voltage and

$$R_i = l/((\kappa^*A_{el})$$

(8)

where $l$ is length of rod, $\kappa_a$ is ambient conductivity of electrolyte and $A_{el}$ is surface area of rod.

The static construction of electrodes and electrolyte is assumed to be constant and therefore assumed as a series of resistors. With increasing cell voltage the current is low but suddenly rises when overcoming the decomposition voltage. The decomposition voltage is dependent on temperature and pressure. The temperature dependency varies in the discussed temperature range [19,20], but with increasing temperature the dependency decreases to 0.292 mV/K [21]. There were different equations [19,21,22] that show increasing decomposition voltage with increasing pressure, for example at 623 K and 24.9 MPa the decomposition voltage of 0.23 V increases compared to ambient pressure. These equations have in common that with increasing pressure the dependency decreases. There are two competing effects affecting the change in the decomposition voltage under high pressure and high temperature. The overall change caused by changes in state conditions are so insignificant, that they are neglected in further experimental discussion.

Fundamental research experiments with water and an electrolyte were carried out measuring the resulting electric current. The electric current for different voltages of KOH solutions ($\kappa_a = 4.33$ mS/cm) are shown in Fig. 4 as a function of temperature. Residence times of the solution varied between $14$ s ($290$ K) and $18$ s ($542$ K). The conductivity of an electrolyte varies with the temperature.
The current increases with increasing temperature. This influence was more distinct with incremental voltage.

For optimizing cell operating conditions, experiments with soil extracts having different electric conductivity under ambient conditions were carried out. Aqueous soil extracts with conductivities up to 14.8 mS/cm were studied. The soil was naturally contaminated with a former paint factory and weathered over 20 years. The extract was produced by semi-batch fixed bed extraction of this soil with water under supercritical conditions, described in detail elsewhere [5]. The hydrocarbons in the water or remaining in the soil are detected as a sum. No special attention is paid to auto-oxidative decomposition or decomposition products and their stability in detail. For the soil extracts we assume the auto-oxidative processes are of minor importance, because the electrolysis temperature is equal to or less than the extraction temperature. The description of the soil contamination is given in Table 1 [3,23]. The influence of conductivity on total destruction is shown in Fig. 5.

The conductivity of electrolyte solutions under extreme conditions is assumed to be dependant on the ion mobility, on the grade of dissociation, and on the varying concentration due to changes in compressibility [24]. Some research studies show that these three effects together cause a conductivity maximum in dependence on density and temp-

Table 1

<table>
<thead>
<tr>
<th>Description of weathered soil material*</th>
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</thead>
<tbody>
<tr>
<td>Kind of contamination</td>
</tr>
<tr>
<td>Lubricating oil, diesel, oil</td>
</tr>
<tr>
<td>Age of contamination</td>
</tr>
<tr>
<td>&gt;20 years</td>
</tr>
<tr>
<td>Total amount of contamination</td>
</tr>
<tr>
<td>((&lt;d_p = 355 \mu m))</td>
</tr>
<tr>
<td>188 g hydrocarbons/kg soil</td>
</tr>
<tr>
<td>Finest particle fraction ((&lt;d_p = 63 \mu m))</td>
</tr>
<tr>
<td>99%</td>
</tr>
<tr>
<td>Average particle diameter ((d_p))</td>
</tr>
<tr>
<td>10 \mu m</td>
</tr>
<tr>
<td>pH-value</td>
</tr>
<tr>
<td>7.4–7.6</td>
</tr>
<tr>
<td>TOC ((&lt;d_p = 355 \mu m))</td>
</tr>
<tr>
<td>140 g C/kg soil material</td>
</tr>
<tr>
<td>TIC ((&lt;d_p = 355 \mu m))</td>
</tr>
<tr>
<td>&lt;34 g C/kg soil material</td>
</tr>
<tr>
<td>Humidity (air dried)</td>
</tr>
<tr>
<td>≈50 g H2O/kg soil material</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
</tr>
<tr>
<td>37 wt%</td>
</tr>
<tr>
<td>Monoaromatic hydrocarbons</td>
</tr>
<tr>
<td>34 wt%</td>
</tr>
<tr>
<td>Diaromatic hydrocarbons</td>
</tr>
<tr>
<td>16 wt%</td>
</tr>
<tr>
<td>Polyaromatic hydrocarbons</td>
</tr>
<tr>
<td>12 wt%</td>
</tr>
</tbody>
</table>

*Hydrocarbon specification after solid phase extraction.
perature [25–27]. The results of the experiments shown in Fig. 5 are taken at steady state. The decreasing yield of destruction in this experiment can be explained by the reaction being hindered by increasing ionic concentration inside the water.

The results of these first investigations imply the use of the highest possible temperature and voltage with not too high conductivity for further research.

In Fig. 6 the rate of destruction is referred to the load of hydrocarbons after heating. The yield of destruction is shown as a function of cell voltage for different temperatures, conductivities and pH-values.

As a result it is determined that higher temperatures with equal pH-value and conductivity caused higher destruction rates. The original aqueous extract without added KOH was acidic and despite a high reaction temperature destruction rates of only 20% were reached. The destruction curves show an effect of plateau and asymptotic behavior after passing the 20-V border. This can be explained by a limited amount of ions or too short a residence time.

Proving the functionality of both extraction and oxidation, the electrolysis cell (50 ml) was directly linked to the extraction reactor. Thus extraction and oxidation of the contaminated soil was studied in one step. By adding the electrolysis cell the volume of the reactor was nearly doubled and so was the residence time.

Fig. 7 shows the degree of destruction which was calculated with the organic fraction that was dissolved out of the solid phase (soil particle, 1 wt%) into the aqueous phase. It is not possible to distinguish between the destruction mechanisms.

The two anodes varied in surface area by a factor of ~0.7, because one rod was solid and the other a pipe. The surface area can cause a limitation in produced oxygen. The yielded destruction rate varied between 90 and 99%. No significant change in destruction was observed with varying conductivity of solution or anode material. Dependence on voltage was very small. Differences in destruction can be identified as fluctuations in analytic methods. It was not possible to thoroughly investigate soil in water suspensions with a soil freight greater than 1 wt% since a higher concentration led to a failure of the
pump valves. Wool scouring water is an aqueous waste stream that is loaded with organic material, liquid and solid. Raw wool is fed into a cleaning process which yields water containing fibrous substance, fat and detergents. This water has a high TOC and is a special problem for municipal waste water facilities [28]. The wool water feed was analyzed quantitatively by gas chromatography as shown in Fig. 8.

In Fig. 9 the rate of destruction for two different temperatures and conductivities detected by TOC analysis is shown as a function of voltage.

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**Fig. 6.** Isotherms of destruction as a function of voltage referred to the hydrocarbon freight at high pressure and temperature but no voltage; *P* = 25 MPa.

**Fig. 7.** Total destruction of soil extract as a function of voltage, coupled system extraction + electrolysis; *P* = 24.1 MPa, *T* = 613 K.
that higher temperature with higher conductivity led to lower destruction yield. One reason for this effect might be the already discussed hindrance of ions and therefore limited oxygen production. The pure wool scouring water is characterized by a pH-value \( \sim 11 \) and a conductivity of \( \kappa_a = \sim 30 \) mS/cm. The high salt load means that it is necessary to dilute the scouring water to lower conductivity, which also decreases the organic load: therefore the analysis is more susceptible to mistakes. The obtained yield of destruction is satisfactory. It is obvious that optimal operating conditions have not been found so far and are still being investigated.

Bilge water (oil in water; see chromatogram in Fig. 10) from ships, collected in the hull, at the moment is collected on board and given to local waste water treatment facilities on shore. Depending on the amount of bilge water, big reservoirs are needed for storage, and storage room is expensive on board. Storing bilge water is a cost, which could be lowered by treating the water directly, for example with high pressure electrolysis. Clean water could be recycled for drinking water. Focussing on a system which is suitable for direct installation on board, it is necessary to assume the reactor volume or the required residence time for treating bilge water for example.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8}
\caption{Gas chromatogram of wool scouring water; 1 ml dissolved in hexane, injection volume 1 \( \mu \)l.}
\end{figure}

The detected decomposition without voltage is nearly 20\%.

Destruction increased with increasing voltage. This effect was more pronounced with lower temperature and lower conductivity. It is remarkable

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig9}
\caption{Destruction of wool scouring water as a function of voltage; anode: gold; \( P = 24.1 \) MPa, \( \tau = 100 \) s.}
\end{figure}
results of these experiments are shown in Fig. 11.

Sink water can also be fed into the electrolysis cell, after draining, to avoid unnecessary consumption of drinking water. Installing such a system on board a ship would be more efficient in marine activity. We used tap water mixed with a dish washing agent to simulate sink water. In Fig. 12 experiments with sink water of different conductivities caused by adding KOH-solution are shown as a function of cell voltage. The destruction obtained is 65%. Yield increased with increasing voltage. The experiment with higher conductivity yielded higher destruction. In contrast to experiments with wool scouring water, this waste stream seemed not to be susceptible to ion hindrance and hence no limitation in oxygen production was observed.

The bilge water was not offset with KOH but diluted with water. A destruction yield of 80% was reached within one reactor run. Increasing residence time did not result in greatly increased destruction. The maximum destruction obtained was ~ 90%. Investigations concerning bilge water are still underway regarding optimal destruction conditions. The difficulties are a great diversity of oil composition depending on age and origin, therefore leading to differing destruction results.

Therefore experiments investigating total destruction as a function of residence time were conducted. Bilge water was collected after passing the reacting system and fed inline again. Residence time was calculated using Eqs. (2) and (3). The

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Fig. 10. Gas chromatogram of bilge water; 1 ml dissolved in hexane, injection volume 1 μl.

Fig. 11. Destruction of bilge water as a function of residence time, $P = 24.1$ MPa, $T = 648\ K$, $U = 30\ V$. 
Fig. 12. Destruction of sink water as a function of voltage; anode: gold; $P = 24.1$ MPa, $T = 648$ K, $t = 80$ s.

4. Conclusion

A flexible apparatus was built to produce oxygen inline under high pressure and high temperature. Different aqueous waste streams containing hydrocarbons were treated and organic load was destroyed. Even waste streams with small particles and fibrous content are compatible with this process and do not cause problems. The system so far is dimensioned for laboratory scale application and needs to be scaled up.

Acknowledgements

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References