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Experimental and Theoretical Study of the Influence of Pressure on SCWO

M. D. Bermejo, I. Bielsa, and M. J. Cocero
High Pressure Process Research Group, Dept. of Chemical Engineering and Environmental Technology,
University of Valladolid, Prado de la Magdalena s/n 47011 Valladolid, Spain

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It is well known that pressure is an important parameter in the SCWO process, because it produces changes in the phase behavior and thermodynamics properties of the system. The influence of pressure on the oxidation efficiency of feeds containing isopropyl alcohol as fuel and acetic acid as waste was studied in an autothermal adiabatic transpiring wall reactor at pilot-plant scale, at pressures from 13 to 25 Mpa, and temperatures from 600 to 750°C. It was found that reaction temperature decreased between 40 and 100°C, when pressure was lowered, and, subsequently TOC removal decreased. At higher-temperatures, the decreasing of TOC removal due to pressure difference was reduced. The process was simulated at different pressures using a mathematical model previously developed for the reactor. The Anderko-Pitzer EoS, especially developed for aqueous systems at high-temperatures and pressures, was used to have accurate values of the heat capacities of the reaction mixture. It was found that having into account only the effect of pressure in the thermodynamical properties and in the concentration of the reagents, the experimental results could not be explained. Thus, the influence of the pressure in the reaction rate equation had to be considered. Results were qualitatively reproduced considering the reaction rate constant variable with pressure, using a constant volume of activation of -1400 *cm*^{3}*/mol.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3958–3966, 2006
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Introduction

Supercritical water oxidation (SCWO) is a very powerful technology for the destruction of wastes. It consists of a homogeneous oxidation in aqueous medium at temperatures and pressures above the critical point of water (374 °C, 22.1 MPa). Pressure plays an important role because it has a remarkable influence on the phase behavior, and on the thermodynamics properties. In the models of the SCWO process the properties of the reaction mixture are frequently approximated to the properties of pure water. Nevertheless, when considering a thermally self-sufficient pilot plant or industrial installation, the reacting mixture contains high-fuel and oxidant concentrations, and especially when using air as an oxidant the water content can be as low as 60 mol %. In these conditions approximating the properties of the mixture to the properties of pure water is inaccurate, and it is convenient to use an EoS able to calculate the thermodynamics properties of the whole mixture, such as density, heat capacity or heat of reaction. Conventional cubic EoS are not very accurate in this region, although Peng and Robinson EoS with the translate volume correction[1] is able to calculate densities of the system water-air, and to reproduce the behavior of real SCWO reactors[2] in an acceptable way. However, for more precise calculations and especially if salts are present in the system, more detailed EoS are necessary. For modeling high-temperature and supercritical aqueous systems,

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Correspondence concerning this article should be addressed to M. J. Cocero at mjcocero@iq.uva.es.

Anderko and Pitzer[3] developed a comprehensive EoS, able to represent LV and SL equilibria, as well as volumetric properties of aqueous systems at temperatures higher than 573 K, and pressures up to 500 MPa within the experimental uncertainty. A number of articles applying this EoS to high-temperature high-pressure aqueous systems are found in literature.[4-8]

There are a great number of studies about oxidation kinetics in supercritical water, but the influence on pressure in the oxidation rate is still not clear. Some works pointed that oxidation efficiency increases when density, that is pressure.[9-12] Others[13] concluded that high-pressure is detrimental for the oxidation rate, and there are authors that pointed that pressure has no effect on SCWO rate.[14]

Li et al.[15] pointed that pressure influence in SCWO was very small compared to that of temperature and it could be neglected. However, if it is necessary to take it into account, the rate constant can be considered as a function of the pressure, as shown in Eq. 1

$$RT(\partial \ln k/\partial P)_T = -\Delta V^\circ + (1 - a - b)R \cdot T \cdot k_T \qquad (1)$$

Where k is the rate constant, ΔV° is the volume of activation; R is the gas constant, T is the temperature in K, a and b are the reaction orders of organic and oxidant, respectively, P is the pressure, and k_T is the isothermal compressibility of the mixture. This second term of Eq. 1 can be neglected when $a = 1$, and $b = 0$ (first-reaction order with respect to the organic), that are the conditions considered in this work, according to the generalized model proposed by Li et al[15]. Thus, the equation considered is as shown in Eq. 2

$$(\partial \ln k/\partial P)_T = -\Delta V^\circ/RT \qquad (2)$$

Typical values for the volume of activation in liquid reactions are between 30-(-50) cm^3/mol, but in supercritical fluids, especially in the surroundings of the critical point, the volume of activation reaches values higher than −1,000 cm^3/mol, that decrease when going away from the critical point.[16,17] Strictly, volume of activation is variable with pressure and temperature, but for smaller intervals it can be assumed constant.[18]

Some authors[10,12] have explained the influence of pressure considering that water concentration plays a role in the oxidation mechanism, and introducing the concentration of water in the kinetic expression of Eq. 3

$$r = k \cdot \mathrm{Fuel}^a \cdot \mathrm{O}_2^b \cdot \mathrm{H_2O}^c \qquad (3)$$

Recently Henrikson et al.[19,20] have reinterpreted former data of phenol SCWO, and together with new experimental data, an inhibition and acceleration effect of the concentration of water in the SCWO, independent of the pressure effect, has been found. At low-water concentrations (ca. 1–7 M) SCWO reaction is inhibited, although at higher-concentrations is accelerated. Plausible explanations to this phenomenon are that at low-water densities the rate controlling process is limited diffusion, or a decrease in polarity as the reactants form the transition state.

In 1992, Hong[21] patented a method for oxidizing materials in water at supercritical temperatures and subcritical pressures known as "supercritical temperature water oxidation" that afterwards was called "semicritical water oxidation".[22] According to Hong[21], feeds with organic and inorganic pollutants were completely and rapidly oxidized without using catalysts at supercritical temperatures (500–800°C), and pressures between 2.5 and 22 MPa. To follow the destruction efficiency, the concentration of CO in the reactor effluent was monitored. It was observed that destruction efficiency increased when temperature was elevated, but it decreased when pressure was reduced. He pointed that when the pressure decreased, density also does, reducing the residence time in the reactor, but conversion remains constant down to a pressure of 17.2 MPa, and then decreased. This fact was attributed to a change in the reaction mechanism.

Hong considered that the lower-pressure limit should be selected depending on the pollutant to treat, and the concentration of inorganic salts should be taken into account because the solubility of salts decreases at lower-pressures, and this can favor the liquid-solid separation in the effluent.

Operation at pressures below the critical pressure of water may involve some benefits. The lower solubility of salts at subcritical pressures in water enhances the fluid-solid separation. Corrosion is also reduced because the solubility of the oxide protecting layer of the metal is lower when decreasing the pressure, and is the dissolution of this layer the limiting corrosion factor in water at high-temperatures.[23] Reactor vessels for "semicritical-water oxidation" are lighter than for SCWO process, because as the operation pressure is reduced, the thickness of the wall is also reduced, being the amount of material for building the reactor lower, and, consequently, decreasing the prices. Nevertheless, the volumes of the vessel for the same residence time are increased because of to the lower density of the mixture. The operation costs (pumping, heating and air compressing) could be also reduced in "semicritical-water oxidation".

The objective of this work is to study the influence of pressure in the TOC removal in a transpiring wall reactor at pilot-plant scale, and to determine the influence of the different parameters with pressure in order to minimize this influence.

For doing so, experimental results of the influence of pressure in the behavior of an adiabatic SCWO transpiring wall reactor at pilot-plant scale are shown. Isopropyl alcohol (IPA) has been chosen as a model fuel and acetic acid as a model pollutant. The IPA is a substance commonly used as a fuel in SCWO, because of economical and safety reasons. A number of articles using IPA as a reagent and as a fuel can be found in literature,[24-28] but the influence of pressure in the SCWO of IPA has not been formerly studied. Acetic acid has been chosen as a waste model because of the difficulty of its destruction. It is a refractory compound in the SCWO. This is the reason why a number of articles about the SCWO of acetic acid can be found in literature.[26-31] Li et al.[15] kinetic model considers acetic acid as an intermediate oxidation product. The influence of pressure in the SCWO of acetic acid has been considered in the following articles:

- Savage and Smith[32] found a dependence of second-order in water concentration when investigating the acetic acid oxidation at temperatures between 380 and 440°C, and the water density ranged from 6.7 to 25 M.
- Meyer et al[33] performed isothermal kinetic measurements of the SCWO of acetic acid at 550 °C over the range 160 to 263

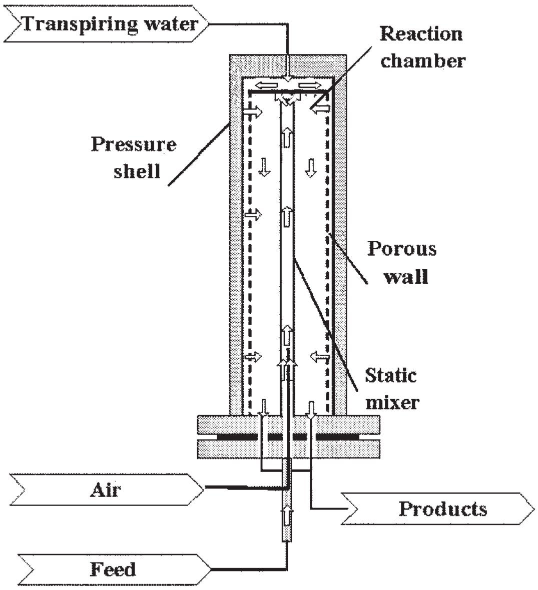

Figure 1. Scheme of the flows inside the reactor.

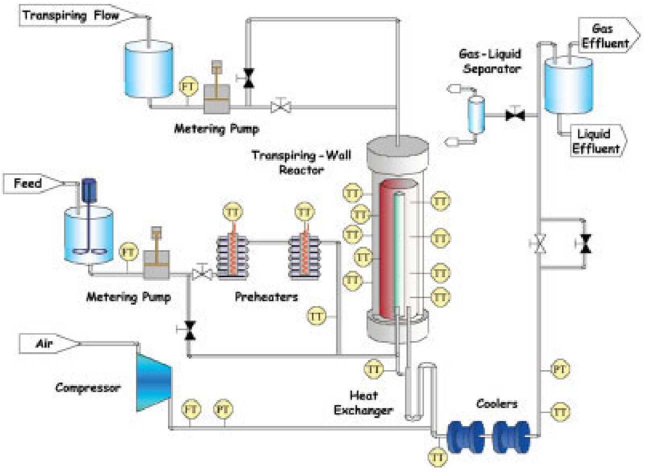

Figure 2. Flow diagram of the SCWO pilot plant of the UVa.

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bar that indicated that pressure or density affects very slightly the rate of acetic acid oxidation.

- Yu and Savage[34] found no pressure or water density effect in the heterogeneous catalytic SCWO of acetic acid using MnO_2.

Experimental Device

All the experimental results presented in this work were obtained working with the SCWO pilot plant of the University of Valladolid (UVa). Since 2003, the plant is working with a transpiring wall reactor that consists of a stainless steel high-pressure shell with a volume of 10 L. It contains a reaction chamber limited by a sintered porous alloy 600 wall through which clean water circulates. The feed and the air are introduced into the reactor through its lower part, and they are fed through the static mixer up to the upper part of the reaction chamber; the reagents flow down mixing with the clean water that enters the reactor through the transpiring wall, and decontaminated water leaves the reactor through its lower part. The flows inside the reactor are shown in Figure 1.

The upper section and the lower section of the reaction chamber are nontranspiring, being porous only in the central section of the reactor. A static mixer with an internal diameter of 9 mm filled with alloy 625 particles of different sizes is used. The temperature profile inside the reactor is used for monitoring its behavior. Temperature is measured at eight positions inside the reaction chamber, at two different radii (A, B) and four different lengths (1,2,3,4). The positions of the thermocouples are indicated in Table 1. The temperature profile inside the reactor is used for monitoring its behavior. More details about the experimental setup can be found in Bermejo et al[36], under the label "reactor design 3". The pilot plant has a treatment capacity of 40 kg/h of feed (water+fuel+waste), which is preheated electrically before being introduced in the reactor. It uses air as an oxidant. Air is supplied by a four-staged-compressor; air is preheated in a heat exchanger using the effluent of the reactor as hot fluid. Transpiring flow is introduced in the reactor without preheating. The inlet temperatures of feed stream and air stream after preheating are measured, while the inlet transpiring flow temperature is assumed to be 25°C. The flow diagram of the pilot plant is shown in Figure 2.

Table 1. Positions of the Temperature Measurements Inside the Reactor

	Length (mm)			
Radius (mm)	1	2	3	4
A (r = 13 mm)	55	355	755	1355
B (r = 33 mm)	55	455	855	1325

Feeds of the reactor are prepared using net water and different concentrations of isopropyl alcohol (Technical isopropyl alcohol, 99%$_{ww}$, supplied by COFARCAS (Spain)) and acetic acid (Glacial acetic acid E-260 99%$_{ww}$, supplied by COFARCAS (Spain)). As transpiring flow net water without organics is used.

Temperatures were measured with thermocouples type K with an accuracy of 1% of the measurement. Pressure is measured using a ceramic membrane pressure transmitter TPR-18 supplied by Desin Instruments (Spain) able to measure in the pressure range from 0–400 bar with a precision of 0.2%. Air flow was measured with a Coriolis gas-flow meter with a precision of 0.2%. Liquid flow rates are determined by measuring the decrease of feed volume with time. Feed solutions were prepared volumetrically, measuring water volume with a precision of 1 L and IPA/HAc volumes with a precision of 1 mL, resulting in an experimental error of 5% of % of mass, that is, 8% ±0.4% IPA.

Concentrations of total organic carbon of the effluents are determined using an off-line Shimadzu TOC Analyzer with a precision of 0.1 ppm in a concentration range 0–1,000 ppm, and with a precision of 1 ppm for TOC concentrations higher than 1,000 ppm. TOC concentration of the feed is not measured, but calculated from the composition. TOC removal is defined as the mass of organic carbon eliminated divided by the organic carbon introduced in the reactor. For correcting the dilution effect of the transpiring water, it is calculated as shown in Eq. 4

Table 2. Experimental Data of TOC Removal Variation with Pressure Changes

Experiment 1: 8%$_{ww}$IPA, F_{Ft} = 10.1 ± 0.0 kg/h, T_{Feed} = 327 ± 4°C Feed = 26 ± 1 kg/h,
Air exc = 11 ± 2% mol, T_{air} = 302 ± 7°C

N.	P (MPa)	TOC$_{rem.}$ (%)	TOC$_{ef}$ (ppm)	T$_R$ (°C)	URT(s)
1.1	17.7 ± 0.1	98.4	544.7	658 ± 5	13
1.2	17.9 ± 0.5	98.5	532.6	661.6	13
1.3	20.7 ± 0.1	99.2	286.5	651 ± 21	14
1.4	20.8 ± 0.1	99.0	350.9	662 ± 17	14
1.5	24.6 ± 1.0	99.7	103.4	688 ± 19	19
1.6	25.3 ± 0.7	99.8	68.47	703 ± 10	19

Experiment 2: 8%$_{ww}$IPA, F_{Ft} = 11.5 ± 0.4 kg/h, T_{Feed} = 341 ± 9°C Feed = 2 ± 1 kg/h,
Air exc = 24 ± 4% mol, T_{air} = 286 ± 4°C

N.	P (MPa)	TOC$_{rem.}$ (%)	TOC$_{ef}$ (ppm)	T$_R$ (°C)	URT(s)
2.1	18.4 ± 0.1	95.7	1420	617 ± 3	9
2.2	18.5 ± 0.4	95.4	1493	617 ± 3	8
2.3	20.8 ± 0.1	96.3	1190	624 ± 2	11
2.4	20.9 ± 0.1	96.3	1203	623 ± 3	11
2.5	21.0 ± 0.1	96.4	1193	638 ± 7	11
2.6	21.0 ± 0.3	96.5	1174	633 ± 2	11
2.7	22.7 ± 0.3	97.6	781.7	651 ± 3	12
2.8	22.8 ± 0.1	96.8	1026	630 ± 4	12
2.9	22.8 ± 0.1	97.7	730.6	651 ± 4	12
2.10	22.8 ± 0.1	97.3	886.4	633 ± 6	12
2.11	22.9 ± 0.1	98.1	627.4	646 ± 4	12
2.12	24.9 ± 0.1	99.0	333.4	660 ± 3	14
2.13	24.9 ± 0.1	98.8	387.9	660 ± 3	14
2.14	24.9 ± 0.1	98.7	429.8	659 ± 3	14
2.15	25.0 ± 0.4	99.2	252	695 ± 30	15

Experiment 3: 8.5%$_{ww}$IPA, F_{Ft} = 14.0 ± 0.4 kg/h, T_{Feed} = 343 ± 6°C, Feed = 24 ± 0.4 kg/h,
Air exc = 14 ± 2% mol, T_{air} = 293 ± 5°C

N.	P (MPa)	TOC$_{rem.}$ (%)	TOC$_{ef}$ (ppm)	T$_R$ (°C)	URT(s)
3.1	18.3 ± 0.2	98.1	610.4	659 ± 1	10
3.2	18.5 ± 0.1	98.1	616.7	660 ± 2	10
3.3	18.5 ± 0.1	98.3	561	661 ± 3	10
3.4	20.8 ± 0.2	99.3	226.9	687 ± 3	11
3.5	20.8 ± 0.1	99.2	256.7	685 ± 53	11
3.6	22.8 ± 0.1	99.8	52.32	713 ± 4	12
3.7	22.9 ± 0.1	99.9	42.89	716 ± 3	12
3.8	25.3 ± 0.1	99.8	61.57	710 ± 6	14
3.9	25.3 ± 0.1	99.9	43.91	720 ± 10	14

Experiment 4: 8.5%$_{ww}$IPA, F_{Ft} = 14.2 ± 0.3 kg/h, T_{Feed} = 323 ± 10°C. Feed = 25 ± 1 kg/h,
Air exc = 4 ± 2% mol

N.	P (MPa)	TOC$_{rem.}$ (%)	TOC$_{ef}$ (ppm)	T$_R$ (°C)	URT(s)
4.1	18.0 ± 0.2	98.6	476.5	682 ± 4	9
4.2	18.1 ± 0.3	98.8	384.8	676 ± 12	9
4.3	20.7 ± 0.1	99.6	122.4	694 ± 9	11
4.4	20.7 ± 0.1	99.5	170.7	688 ± 13	11
4.5	25.4 ± 0.1	99.4	181.8	705 ± 5	14

Experiment 5: 9%$_{ww}$IPA, F_{Ft} = 15.2 ± 0.5 kg/h, T_{Feed} = 332 ± 15°C, Feed = 24 ± 1 kg/h,
Air exc = 8 ± 7% mol, T_{air} = 290 ± 10°C

N.	P (MPa)	TOC$_{rem.}$ (%)	TOC$_{ef}$ (ppm)	T$_R$ (°C)	URT(s)
5.1	13.2 ± 0.9	93.9	2047	589 ± 9	13
5.2	13.8 ± 1.5	93.9	2032	600 ± 18	14
5.3	15.7 ± 0.1	95.7	1447	631 ± 14	15
5.4	16.3 ± 1.1	96.0	1351	639 ± 9	15
5.5	18.2 ± 0.4	97.2	944	662 ± 10	15
5.6	19.0 ± 1.3	98.0	672.3	670 ± 9	15
5.7	20.8 ± 0.3	98.3	571.1	682 ± 10	15
5.8	21.7 ± 1.1	98.6	457	690 ± 12	16
5.9	22.8 ± 0.4	99.7	92.5	715 ± 12	16
5.10	22.8 ± 0.6	99.4	202.8	712 ± 13	16
5.11	24.5 ± 0.5	99.9	23.2	732 ± 15	16
5.12	24.8 ± 0.2	99.9	24.8	737 ± 3	16

Table 2. (Continued)

Experiment 6: 8%$_{ww}$IPA/1%$_{ww}$HAc, F_{Ft} = 17.4 ± 0.5 kg/h, T_{Feed} = 332 ± 6°C. Feed = 25 ± 1 kg/h,
Air exc = 2 ± 4% mol, T_{air} = 291 ± 3°C

N.	P (MPa)	$TOC_{rem.}$ (%)	TOC_{ef} (ppm)	T_R (°C)	URT(s)
6.1	18.3 ± 0.1	99.5	144.5	740 ± 6	9
6.2	18.3 ± 0.1	99.5	152.8	741 ± 6	9
6.3	20.8 ± 0.0	99.7	102.5	753 ± 9	10
6.4	20.8 ± 0.1	99.8	62.2	757 ± 6	10
6.5	22.6 ± 0.2	99.9	34.0	778 ± 7	12
6.6	22.7 ± 0.3	99.9	37.3	779 ± 3	12
6.7	24.6 ± 0.1	99.9	38.2	775 ± 8	12
6.8	24.6 ± 0.1	99.8	48.8	769 ± 9	12

Experiment 7: 7.5%$_{ww}$IPA/2%$_{ww}$HAc. F_{Ft} = 15.3 ± 0.3 kg/h, T_{Feed} = 331 ± 7°C, Feed = 22 ± 2 kg/h,
Air exc = 31 ± 12% mol, T_{air} = 291 ± 5°C

N.	P (MPa)	$TOC_{rem.}$ (%)	TOC_{ef} (ppm)	T_R (°C)	URT(s)
7.1	15.7 ± 0.3	99.0	331.1	696 ± 5	10
7.2	16.3 ± 1.2	98.9	335.5	699 ± 7	10
7.3	18.2 ± 0.7	99.7	104.6	710 ± 2	12
7.4	18.4 ± 0.2	99.6	127.4	713 ± 6	12
7.5	20.5 ± 0.7	99.7	81.9	724 ± 2	13
7.6	21.0 ± 0.6	99.7	84.9	727 ± 7	14
7.7	22.8 ± 0.4	99.8	46.3	731 ± 4	15
7.8	22.8 ± 0.4	99.8	46.4	727 ± 9	15
7.9	22.9 ± 4.1	99.9	22.6	728 ± 26	13
7.10	24.0 ± 3.1	100.0	13.8	735 ± 24	15

$$TOC\ rem = \frac{Feed \cdot TOC_0 - (Feed + F_{FT}) \cdot TOC_{ef}}{Feed \cdot TOC_0} \tag{4}$$

where feed is the feed flow in kg/h, F_{FT} is the transpiring flow in kg/h, TOC_0 is the TOC concentration in the feed, TOC_{ef} is the TOC concentration in the effluent.

To evaluate how flooding affects the behavior of the reactor, two parameters have been defined.[29] Useful length (UL) in the reactor is defined as the length of the reactor at supercritical conditions. The reactor has a total length of 1,470 mm, but a part of this length is at subcritical temperature ($T<374$°C). In this part in subcritical conditions the reaction is much slower than in the supercritical part, so this part is not a "Useful Length" for TOC oxidation. It is calculated by interpolating between the temperatures measured at known lengths. The fraction of useful length (%UL), is the fraction of reactor at a temperature higher than 374°C. Useful residence time (URT) is defined as the time that the reagents are in the UL of the reactor. It is calculated as the relation of the *useful volume of the reactor* (it is the volume of reactor considering the UL) by the product of the mass flow and the density. The density is calculated at the mean temperature in the supercritical area using the same PR EoS with the translate volume correction, as a function of temperature, composition, and the operational pressure.

Experimental Results

An experimental study of the influence of pressure on the SCWO destruction efficiency of feeds containing isopropyl alcohol (IPA), and IPA/Acetic Acid (HAc), in a pressure interval from 13 to 25 MPa was carried out. The pressure interval has been selected in order to keep the inlet feed, the transpiring water and the effluent of the reactor under liquid conditions in order to keep salt dissolved. The experimental data obtained are listed in Table 2. Seven different series of data are presented, using different IPA concentrations or IPA/acetic acid (HAc) concentration ratios. For each experiment, the reactor was started-up, and once the reaction is initiated the selected feed is charged, and when pseudo-stationary state is reached, samples are taken. Then, the pressure is reduced, and when reactor is stabilized samples are taken. As working at pilot plant scale, small variations in factors sometimes without control, such as the initial temperature of the reactor, the exact fuel concentration of the feed or other factors, sometimes caused variations in operational results. Thus, in order to exclusively study the effect on pressure variations, only samples taken in identical conditions, that is, in the same experiment, are compared.

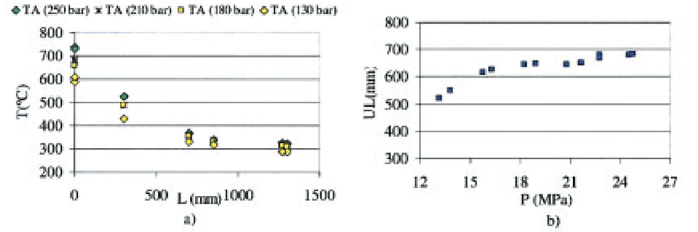
In all the cases, TOC removal decreases when the operating pressure decreases. Additionally a decrease in reaction temperatures when pressure is reduced is always observed. Despite of the decreasing of pressure, when temperature is high enough, the negative effect on pressure effect on TOC removal is attenuated. Thus, the influence of temperature on TOC removal is more important than that of pressure.

When decreasing the pressure, the temperatures in the entire reactor decrease as shown in part (a) of Figure 3. Thus, the UL in the reactor reduced (Figure 3b), and the URT is also reduced (Figure 3c) because of the reduction of the UL, and of the lower density of the mixture. This reduction in the URT affects negatively to the TOC removal, as shown in the part d of Figure 3.

Modeling and Discussion

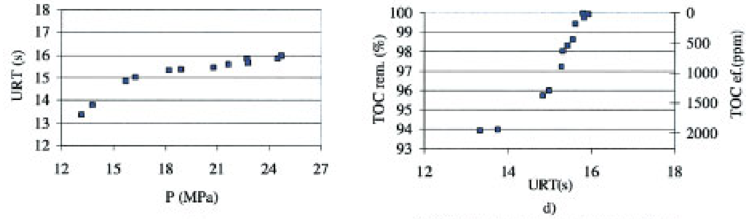
Influence of pressure in the properties of the SCWO mixture

The changes in temperature and TOC removal in the SCWO process are partially due to the change of the thermophysical properties of the reaction mixture, especially the heat capacity and the density of the mixture. The heat capacity of the mixture is



Temperature profile for different pressures in Exp. 5 (9% IPA)

Useful lenght vs. operation pressure in exp. 5 (9%IPA)



c)
Useful residence time vs. Pressure in exp.5(9%IPA)

d)
TOC removal vs. Residence time at different pressures at exp.5 (9% IPA)

Figure 3. (a) Temperature profiles vs. pressure in exp. 5 (9%IPA); (b) useful length (UL) vs. pressure in experiment 5 (9% IPA); (c) useful residence time vs. pressure in experiment 5 (9% IPA); d) TOC removal and effluent TOC vs. useful residence time at different pressures in exp. 5 (9% IPA).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

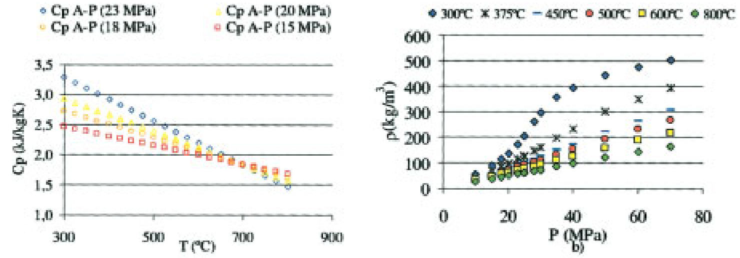
reduced when decreasing pressure down to 700°C. Thus, as the heat of reaction is almost constant with pressure, the temperature increases in the reaction mixture, favoring the reaction, and thus, the TOC removal. In Figure 4a, heat capacities of a mixture 65%$_{ww}$ water-air are shown for different pressures and temperatures, calculated using Anderko and Pitzer EoS. The density of the mixture decreases with temperature, so the concentration of the reagents is decreased influencing negatively the reaction, and so decreasing the TOC removal. In Figure 4b, densities of a mixture 65%$_{ww}$water-air are shown for different pressures and temperatures, calculated using Anderko and Pitzer EoS.

Modeling results when considering k constant with pressure

A mathematical model of the reactor was developed by Bermejo et al[26]. The model considers that the flow pattern in the reactor can be approximated as a combination of plug flow (PF), and completely stirred regions (CSTR). PF is assumed in the mixer and the lower section of the reaction chamber, and CSTR flow at the mixer exit, and the upper section of the reactor. Only steady-state calculations are performed. The kinetics assume that organic matter is transformed rapidly into acetic acid, considered as the only intermediate compound, following the kinetic pathway reported by Li et al[15], that is shown in Figure 5. The rate constants recommended by Li et al.[15] were used (Table 3). This kinetic model gives a simple and accurate description of the SCWO phenomenon for technical purposes, and have been used to reproduce SCWO experimental results obtained by our group.[26,27]

This model has been used in order to explain the experimental results. To consider the effect of pressure on the physical properties, some modifications to the model were performed:

- The heats of reaction were calculated using the Peng-Robinson EoS using the Boston-Mathias alpha functions,[28] and correlated as a function of the temperature for four pressures: 15. 18. 20 and 15 MPa. The correlations are shown in Table 4..
- The density of the mixture is calculated using the EoS of Peng-Robinson with the translated volume correction,[1] as a function of pressure, temperature and composition.
- The C_p of the mixture is calculated considering a mixture



a)
Heat capacities of a mixture 65% H2O-air calculaed with Anderko Pitzer EoS

b)
Density of mixtures 65% H2O-aire cuculated with Anderko-Pitzer EoS, at different temperatures and pressures

Figure 4. (a) Heat capacity of a mixture 65%$_{ww}$ water-air at different pressures and temperatures calculated with Anderko-Pitzer EoS and (b) densities of a mixture 65%$_{ww}$ water-air at different pressures and temperatures calculated with Anderko-Pitzer EoS.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

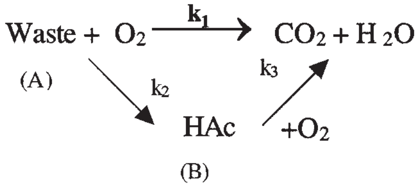


Figure 5. Kinetic model scheme.

with a constant composition of 65%$_{ww}$ H_2O and air, using the Anderko-Pitzer EoS[3]. The ΔH of that mixture was calculated at different pressures and temperatures, and correlated as a function of temperature at four different pressures: 15, 18, 20 and 15 MPa, for a temperature interval from 300 to 800 °C

$$\Delta H(\text{kJ/kg}) = (-1.8204 \cdot 10^{-3} \cdot (T_2^2 - T_1^2) + 4.3865 \cdot (T_2 - T_1) + 6537.2);\ P = 23\ \text{MPa} \quad (5)$$

$$\Delta H(\text{kJ/kg}) = (-1.3587 \cdot 10^{-3} \cdot (T_2^2 - T_1^2) + 3.7497 \cdot (T_2 - T_1) + 6760.2);\ P = 20\ \text{MPa} \quad (6)$$

$$\Delta H(\text{kJ/kg}) = (-1.1049 \cdot 10^{-3} \cdot (T_2^2 - T_1^2) + 3.3940 \cdot (T_2 - T_1) + 6888.1);\ P = 18\ \text{MPa} \quad (7)$$

$$\Delta H(\text{kJ/kg}) = (-7.8360 \cdot 10^{-4} \cdot (T_2^2 - T_1^2) + 2.9366 \cdot (T_2 - T_1) + 7056.7);\ P = 15\ \text{MPa} \quad (8)$$

Several simulations were performed without considering variation with pressure in the rate constants, in order to check if the results could be explained exclusively by the changes in the physical and thermodynamics properties of the mixture. The results are shown in Table 5. The model predicts a behavior opposite to the experimental behavior, that is, TOC removal and reaction temperature increase when decreasing pressure. The lower C_p allows that temperature increase faster accelerating the oxidation rate.

In order to check that the behavior predicted was not a consequence of the perfect mixing zone considered in the reactor, a simulation considering only the plug flow mixer of the reactor was considered. The predictions are shown that at the beginning of the reactor the reaction rate is higher at the higher-pressure, and the conversion is higher, but when the reaction progresses the temperature increase rapidly at lower-pressures due to the lower C_p of the mixture.

Modeling results considering k variable with pressure

As the change in the thermophysical properties was not enough to justify the decrease of TOC removal and reaction temperature found experimentally, the influence of pressure in the reaction rate is considered.

Table 3. Kinetic Parameters in the Arrhenius Equation used to Simulate the IPA Oxidation

	A (s^{-1})	E_a (J/mol)
k_1 (IPA to CO_2)	$2.61 \cdot 10^5$	63800
k_2 (IPA to HAc)	$2.61 \cdot 10^5$	63800
k_3 (HAc to CO_2)	$2.55 \cdot 10^{11}$	172700

Table 4. Heats of Reaction Calculated Using the Peng-Robinson EoS Using the Boston-Mathias Alpha Functions

Reaction	P = 23 MPa	P = 20 MPa	P = 18 MPa	P = 15 MPa
IPA → CO_2	$-\Delta H_R = -9.71E - 4{\cdot}T^2 + 1.174{\cdot}T - 2133.2$	$-\Delta H_R = -9.85E - 4T^2 + 1.179T - 2128.3$	$-\Delta H_R = -9.90E - 4T2 + 1.176T - 2123.3$	$-\Delta H_R = -9.849E - 4T^2 + 1.159T - 2112.9$
HAc → CO_2	$-\Delta H_R = 0.2693T - 901.59$	$-\Delta H_R = 0.2655T - 898.49$	$-\Delta H_R = 0.2629T - 896.34$	$-\Delta H_R = 0.2599T - 893.83$
IPA → HAc	$-\Delta H_R = -0.0008T^2 + 0.6251T - 752.52$	$-\Delta H_R = -0.0008T^2 + 0.6329T - 751.75$	$-\Delta H_R = -0.0008T^2 + 0.6326T - 749.61$	$-\Delta H_R = -0.0008T^2 + 0.6168T - 742.33$

Correlated as a function of temperature for different pressures, ΔH_R (kJ/mol reagent), T(°C).

Table 5. Simulated Results for a 4% IPA Feed

P (MPa)	T_R (°C)	F_b (mol/h)	TOC (ppm)
15	552	0.03500	18.101
18	539	0.06438	33.018
20	529	0.1036	53.111
23	513	0.2292	117.540

Feed = 30 kg/h. T_{Feed} = 350°C; F_{ft} = 18 kg/h; Air = 16 kg/h; at different pressures, considering k invariable with pressure.

Henrikson et al.[19] affirms that the enhancement of TOC removal at higher-pressures is due to a water concentration effect on SCWO, and has developed a very precise reaction rate model, that is able to reproduce both inhibition and acceleration effect of water on phenol SCWO. However, this equation rate has been obtained at reaction temperatures and concentrations much lower than that used in this work, being the reaction rates 10 times lower than that proposed by Li et al.[15] So this kinetic equation is not appropriated for representing the data presented in this work.

In order to reproduce the experimental data, Eq. 1 is used taking as volume of activation –1,400 cm^3/mol, obtained for the SCWO of phenol at 380°C by Thorton and Savage[37], and taking as a reference pressure 23 MPa, applying it to the three kinetic equation rates. Although the volume of activation is not strictly constant with pressure and temperature, and is highly variable in the surroundings of the critical point, it is going to be used as an approximation to describe the phenomenon from the technical point of view. In first place, this value was used as an initial estimation for adjusting a value of reduced volume that could perfectly describe the system, but the better description was obtained with –1,400 cm^3/mol, so this value was kept. This way of modeling the system is only a technical approximation used due to the lack of kinetic equations available in our work range. We do not claim this is the most correct from the theoretical point of view.

Results of the simulation are shown in Table 6. The TOC removal increased when pressure is increased, but the simulated maximum temperature in the reactor increases when pressure is decreased, because of the lower C_p. This apparently contradicts what the experimental results show, but if the temperature profile predicted by the model at different pressures shown in Figure 6 is observed, it can be seen the point where maximum temperature is reached in the reactor is delayed when decreasing the pressure. If in the reactor a maximum in the temperature is happening between temperature measurements points 1 and 2, it cannot be registered with this reactor configuration.

Conclusions

The effect of pressure in the SCWO process was studied experimentally at pilot-plant scale using the transpiring wall reactor of the University of Valladolid. For this, feeds of 25 kg/h of IPA-water and IPA-HAc-water mixtures were oxidized at different pressures from 25 to 13 MPa using air as oxidant, with the reactor working adiabatically. It has been observed that reaction temperature decreased about 40–100 °C when pressure was lowered, and, subsequently, TOC conversions also decreased. Removals of 99.9% (TOC = 22 ppm) were reached at supercritical pressures, obtaining conversions of only 95% (TOC = 1,400 ppm) at the lowest pressures. Elevating reaction temperature can compensate the adverse effect of reducing pressure: it was observed that working at higher-reagent concentrations the reactions temperatures were higher, and the negative effect of pressure was attenuated.

Table 6. Predicted Results for the SCWO of a Feed 7.5% IPA/2% HAc for Different Pressures

P (MPa)	T max (°C)	TOC_{ef} (ppm)
23	579	0.091
20	576	17.2
18	583	66.2
15	601	127.1

Feed 25 kg/h, at different pressures.

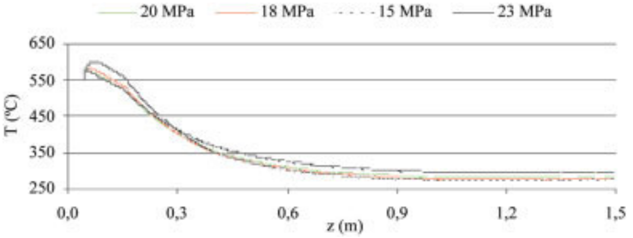


Figure 6. Temperature profile predicted for the SCWO of a feed 7.5% IPA/2% HAc for different pressures, feed=25 kg/h, at different pressures.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The effect of pressure in SCWO was also studied theoretically focusing in both themodynamic properties and kinetics. The density of the reaction mixture decreases with pressure affecting negatively the reaction, but the heat capacity is reduced with pressure, so for the same fuel concentration higher-reactions temperatures are expected for lower pressures. The kinetic effect used to be described in both ways: writing the kinetic rate constant, as a function of water concentration or considering the volume of activation, being according to literature this option less convenient for the SCWO.

The process was modeled using a previously developed mathematical modeling and considering physical properties at different pressures. Experimental results cannot be explained considering exclusively the effect of the pressure in the physical properties of the mixture. Thus, the effect of pressure in the reaction rate has to be considered. As there are not kinetic rate equation available in literature to describe the reaction rate in our working range, we decided using a constant value of volume of activation of −1,400 cm^3/mol for all the reactions as an approximate way of describing the influence of pressure in the kinetic rate constant. This approximation is able to describe TOC removals qualitatively, but apparently does not predict even qualitatively the temperature profile. The performance of the modeling could be improved if a kinetic model considering the effect of pressure were developed for high-temperature, high-reagent concentration conditions of SCWO.

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Notation

A = Arrhenius pre-exponential factor, s^{-1}
Air = air mass flow, kg/h
Cp = heat capacity, kJ/kg K
C_{IPA} = concentration of IPA, %ww
C_{HAc} = concentration of Hac, %ww
E_a = energy of activation, J/mol
$Feed$ = feed mass flow, kg/h
F_b = acetic acid flow, mol/h
F_{FT} = transpiring flow, kg/h
HAc = acetic acid
ΔH = specific enthalpy, kJ/kg
IPA = isopropyl alcohol
k = rate constant, s^{-1}
k_T = isothermal compressibility, Pa^{-1}
L = length, mm
P = pressure, MPa
R = *T*ranspiring flow relation defined by Eq. 2
T = temperature, K
T_{Feed} = inlet temperature of the feed °C
T_{FT} = temperature of the transpiring flow °C
$Tmax$ = maximum temperature in the reactor °C
T_R = reaction temperature °C
TOC *R*em = TOC removal
TOC_0 = TOC concentration in the feed, ppm C
TOC_{ef} = TOC concentration in the effluent, ppm C
TWR = transpiring wall reactor
$SCWO$ = supercritical water oxidation
UL = useful length in the reactor, m
URT = useful residence time, s
ΔV^o = volume of activation, cm^3/mol
z = position, m

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