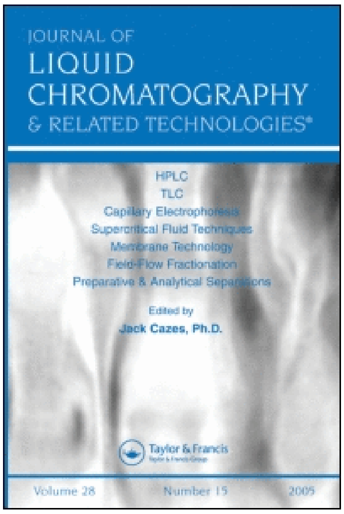

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Alicja Zawadzka[a]; Ewa Gromadzinska[b]
[a] Faculty of Process and Environmental Engineering, Technical University of Lodz, Lodz, Poland [b] Laboratory of Environmental Testing, Institute of Textile Materials Engineering, Lodz, Poland

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Analysis of Supercritical Thermohydrolysis of Aniline-Water Solution using Capillary Electrophoresis and HPLC: a Comparison

Alicja Zawadzka
Faculty of Process and Environmental Engineering, Technical University of Lodz, Lodz, Poland

Ewa Gromadzinska
Laboratory of Environmental Testing, Institute of Textile Materials Engineering, Lodz, Poland

Abstract: In this paper, an application of capillary electrophoresis and high-performance liquid chromatography for aniline thermohydrolysis in an environment of supercritical water is presented.

Keywords: Supercritical thermohydrolysis, HPLC, Aniline solution

INTRODUCTION

Supercritical water hydrolysis is a new technique of decomposing various organic compounds, based on supercritical water properties (critical temperature $T_{cr} = 374.3°C$ and critical pressure $P_{cr} = 22.1\,MPa$).

Under these circumstances, in an oxidant-free environment, many toxic organic substances undergo decomposition to simpler compounds, presenting fewer problems in further utilisation. It is possibly due to the process of hydrolysis, based on inserting a water molecule into the molecule of the compound undergoing degradation.[1,2]

Address correspondence to Alicja Zawadzka, Faculty of Process and Environmental Engineering, Technical University of Lodz, Wolczanska 175, 90-924 Lodz, Poland. E-mail: zawadzka@wipos.p.lodz.pl

Thermohydrolysis in the environment of supercritical water is analogous to the pyrolysis process.[3] Above that point, water changes its parameters; for instance, water solvation mode changes from ionic to non-ionic. Due to polarity loss, typical ionic compounds, e.g., salts, become practically insoluble, but typical organic non-polar compounds, e.g., benzene and n-heptane, become soluble. Supercritical water is unlimitedly mixable with gases, e.g., with oxygen. Due to such interesting supercritical water qualities, studies have been started on water utilisation as a medium for waste and organic toxic contaminant oxidation.[4] This process is oxygen free. Supercritical water prevents undesirable condensation and polymerization processes, which lead to production of coke breeze and high-molecular carbon compounds. The method belongs to the new, rapidly developing solvothermal sciences. Its main advantage is elimination of the problems of corrosion accompanying the supercritical water oxidation; products of this reaction are far less aggressive to the reactor wall than the products of supercritical water oxidation.[5,6]

It appears that "supercritical thermohydrolysis" can be an effective and safe method for hydrothermal utilisation of dangerous organic compounds in the future. However, the mechanism and kinetics of the hydrolysis reaction in the supercritical water should be identified. Presently, research on the thermohydrolysis process concentrates on the recognition of the process run for given chemical compounds and on the investigation of the transformation mechanism and determination of the reaction kinetics.[7–9]

The thermohydrolysis process in the environment of supercritical water has been investigated for aniline. The processes were carried out in a tubular flow reactor. Conversion ratios of these compounds were investigated to estimate the efficiency of the thermohydrolysis method as a new method of organic waste elimination.

Aniline has been chosen because it is present in dye industry wastewaters, and it is non-degradable biologically.

EXPERIMENTAL

Equipment

Tests have been carried out in the equipment shown schematically in Figure 1. The equipment consists of: a high pressure tube reactor made of acid-resisting steel SS 316, 6.0 m length and internal diameter of 2.2 mm (2), electrical furnace with a paddle fan expediting the heat exchange and temperature regulation system (4, 8, 9) which served as thermostat (7), an HPLC type high pressure piston pump for feeding the solutions of tested compounds, as well as to change the speed of reacting substance flow (1), a heat exchanger "pipe in pipe" type serving as a condenser and enabling cooling of the

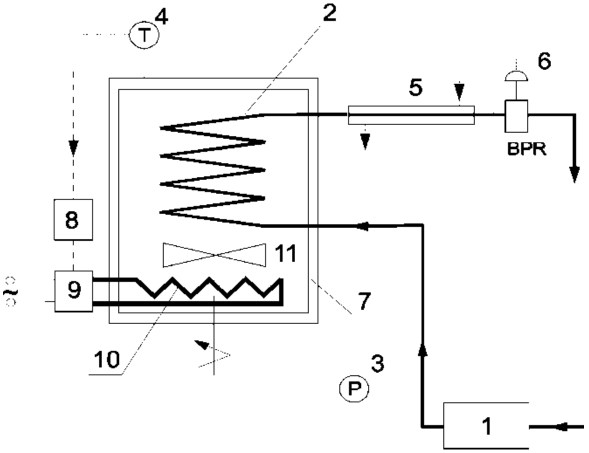

Figure 1. Schematics of the equipment for supercritical thermohydrolysis research (description in the text).

reaction mixture which leaves the reactor (5), pressure measurement (3), the pressure regulator enabling maintenance of a definite pressure in the system (6).

Experimental Methodology

Experiments have been carried out in the following manner. Solutions of the aniline, with concentrations of 0.25, 0.125, 0.063, 0.032, and 0.016 g/dm^3 have been prepared and de-aerated in the ultrasonic bath. Such solutions were fed to the tubular reactor by the HPLC high-pressure pump. Flow rates used were 2.5, 5.0, 7.5, and 10.0 cm^3/min. Pressure used was 25 MPa. Experiments have been carried out at temperatures of 20, 100, 200, 250, 300, 350, 375, 400, 450, 500, and 600°C for 20 minutes beyond the time when the temperature in the reactor reached a steady state. Five samples of reactor outflow liquid have been collected at one-minute intervals.

Analytical Methods

Concentrations of the substrates and aniline, after thermohydrolysis, have been determined by means of capillary electrophoresis (CE) and HPLC.[10]

Capillary Electrophoresis

Capillary electrophoresis is a highly efficient analytical technique for the separation and detection of the components of complicated mixtures and solutions.[11,12] This technique enables a very precise qualitative and quantitative analysis. Thanks to its advantages, i.e., short analysis time, high efficiency of the separation (10^5-10^6 theoretical plates), low consumption of reagents, and simplicity of apparatus design, CE is competitive with other separation techniques. In many applications, CE is competitive with ion chromatography. Being primarily implemented for macromolecule separation, CE is presently implemented for the determination of many classes of organic, as well as inorganic, compounds.[13]

The separation of aniline was carried out using the capillary electrophoresis analyser, Crystal 100 (Thermo Separation Products, San Jose, California, USA) and Spectra SYSTEM® UV 3000 detector (an equivalent of a DAD detector) with a positive power supply. The applied voltage was 10 kV. A deuterium lamp was used for indirect UV detection at 214 nm. The separation was carried out with a 90 cm × 75 μm I.D. fused-silica capillary (Thermo, USA). The capillary was conditioned prior to its first use by rinsing with 1 M NaOH (15 min), 0.1 M NaOH (15 min), followed by deionised water (15 min) and, finally, with buffer solution, for 15 minutes. Between each electrophoretic separation, the capillary was rinsed with the electrolyte solution for 2 minutes. All experiments were conducted at a constant temperature of 25°C (automatic temperature control). The samples were introduced into the capillary by the vacuum injection mode: injection time 5 s. The electrophoretic spectra were evaluated using the ChromQuest software system.

The working electrolyte consisted of 10 mM imidazole (Sigma, St. Louis, MO, USA) as the ultraviolet visualisation agent, 5 mM α-hydroxyisobutyric acid (HIBA, Sigma) as the complexing agent, $pH = 3.0$. The stability of the prepared electrolyte is 3 months.

The standard of aniline was generated from commercial product (Sigma). The working standard concentrations ranged from 0.5 mg/dm^3 to 10 mg/dm^3.

All solutions and standards were prepared with deionized water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Before use, all solutions were filtered through a 45 μm membrane filter (Millipore) and degassed by ultrasonication.

HPLC

An LC 250 type liquid chromatograph with a 235C type DAD detector, with spectral sweep from 195 to 360 nm (Perkin-Elmer, USA) was used for the analyses. The chromatographic column was 250 mm length and 4.6 mm internal diameter with Altech C_{18} column packing (octadecyl phase) and 5 μm particle size. Mobile phase:a mixture of methanol:aqueous buffer, pH 7.0 (80:20 v/v). The eluent flow rate through the column was 1 $cm^3 min^{-1,}$ at a pressure of about 10 MPa. The analyses were performed isocratically.

Chromatograms of samples coming from the investigations of thermohydrolysis in supercritical water of aniline were recorded at a wavelength of

$\lambda = 280$ nm. The standard of aniline was a commercial product (Sigma). The working standard concentrations ranged from 60 mg/dm^3 to 300 mg/dm^3.

Validation of the Method

The reason for analytical method validation is to check whether this method, in a specific application, follows the requirements for use of the results.[14,15]

It was assumed that the validated method for determination of sodium and potassium hydroxides should conform to the following requirements:

a) Total uncertainty calculated according to PN-EN 482:2002 below 30%.[16]

b) Standard uncertainty according to the GUM Guide below 10%.[17]

c) Correlation coefficient, r, of the calibration curve, used for the calculations, should not be less than 0.99.

Validation conditions were assumed according to the recommendation of Dobecki, Gromiec, and Więcek, and parameters characterizing the analytical method were based on Guide to the Expression of Uncertainty in Measurement and Polish standard PN-EN 482:2002.[16,18]

RESULTS

The CE separation system was optimised by the instrumental parameters (length of the capillary, voltage, injection time, temperature). Figure 2 shows a representative electropherogram of aniline after thermohydrolysis.

The HPLC separation system was optimised by the instrumental parameters. Figure 3 shows a representative chromatogram of aniline after thermohydrolysis.

Repeatability experiments of migration times and peak areas were performed for 3.75 mg/dm^3 (CE) and for 60 mg/dm^3 (HPLC) standard solutions. For ten consecutive standard solution injections, good migration times and peak surfaces were obtained (see Table 1).

Linearity

CE calibration curves for aniline were prepared at various concentrations (0.5, 1, 2, 5, and 10 mg/dm^3) on the basis of the commercial product. For aniline, the linear dependence of the peak surface and concentration was observed within the tested range.

HPLC calibration curves for aniline were prepared at various concentrations (60, 120, 180, 230, and 300, mg/dm^3) on the basis of commercial

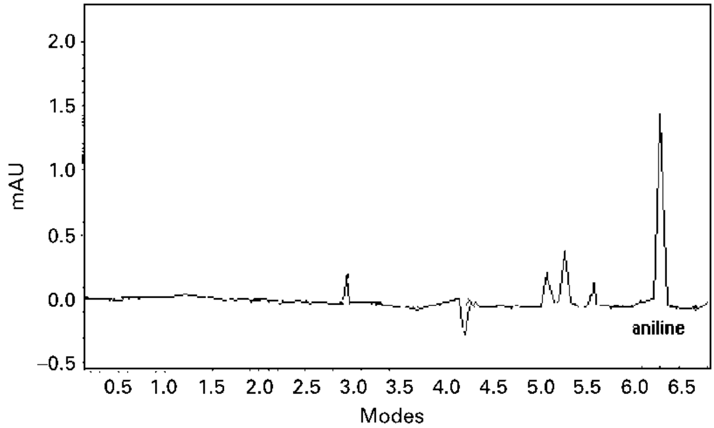

Figure 2. Determination of aniline in the reaction matrix by CE.

product. For aniline, the linear dependence of the peak surface and concentration was observed within the tested range.

The calibration data for both methods are presented in Table 2.

Thermohydrolysis Process Analysis

For CE separations, the thermohydrolysed samples were diluted with deionised water. A comparison of CE and HPLC aniline analysis in samples, after thermohydrolysis, is shown in Table 3.

The Limits of Quantification (LOQ) for aniline-0.2 mg/dm^3, (CE method) and 40 mg/dm^3 (HPLC method).

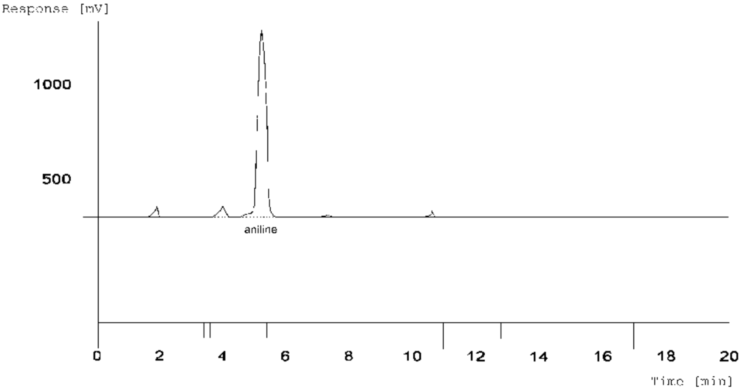

Figure 3. Determination of aniline in the reaction matrix by HPLC.

Table 1. Migration time and peak area repeatability

Method of aniline analysis	Migration time (min)	Peak area
CE	6.32 ± 0.12	9438 ± 230
HPLC	5.71 ± 0.18	985 ± 33

On the basis of analytical data contained in Table 3, the following conclusions can be drawn:

a) the HPLC method is not reliable for aniline analysis within the required concentration range. CE method seems to be adequate.

b) aniline is not thermohydrolysed in the applied process conditions.

Validation

The following data were calculated: the variation coefficient, standard expanded and overall uncertainties, standard deviation of the mean value, standard deviation of repetition, and standard deviation of the method based on the analysis of aniline in the thermohydrolysed samples. The values obtained are given in Table 4.

Overall uncertainty is significantly less than 30% which, according to Polish Standard PN-EN 482:1994, is a sufficient recommendation to apply this method for aniline analysis. The standard expanded uncertainty below 10% confirms a quantitative characteristic for the analytical method. The coefficient of variation shows that the method is characterised by good precision. The obtained values of aniline determination in the after-thermohydrolysis mixture matrix did not significantly deteriorate the parameters of the method.

CONCLUSIONS

From the examples presented above, a conclusion can be drawn that a single qualitative and quantitative analysis with the use of HPLC and capillary

Table 2. Calibration data for aniline studied

Method of aniline analysis	Linear range (mg/dm^3)	Equation of regression line	Correlation coefficient (r^2)
CE	0.5–10.0	$y = 2484.07x + 44.55$	0.9998
HPLC	60–400	$y = 218,73x - 5758$	0.9964

y = Peak area; x = concentration.

Table 3. A comparison of the aniline samples analysis results for the CE and HPLC taken after supercritical thermohydrolysis process (500°C, 25 MPa)

Concentration of aniline in test samples		
Before thermohydrolysis (g/dm^3)	CE result after thermohydrolysis (g/dm^3)	HPLC result after thermohydrolysis (g/dm^3)
0.25	0.240 ± 0.002	0.26 ± 0.02
0.125	0.123 ± 0.002	0.13 ± 0.02
0.063	0.064 ± 0.002	0.06 ± 0.02
0.032	0.031 ± 0.002	<LOQ
0.016	0.014 ± 0.002	<LOQ

Table 4. Validation results of aniline in a reaction matrix

Method of aniline analysis	CE	HPLC
Mean value (mg/l)	3.8	181.8
Standard expanded uncertainty	1.6%	1.5%
Overall uncertainty	5.2%	5.4%
Variation coefficient	2.20%	2.44%
Standard deviation of the mean value	0.09	3.99
Standard deviation of repetition	0.07	3.28
Standard deviation of the method	0.10	4.65

electrophoresis allows us to determine aniline contents in solutions. Both methods meet validation requirements; however, the CE method gives proper results at low concentrations.

In the course of thermohydrolysis, less than 13% of aniline is being degraded. Due to the determination limits, the process can be analyzed only by the CE method. The HPLC method can be used in the case of aniline concentration of approximately 40 mg/dm3, and the CE method in the case when the concentration is approximately 0.5 mg/dm3.

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