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## Analysis of supercritical thermohydrolysis of DNSDS water solution using HPLC

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### ABSTRACT

One of the negative effects of the continuous development of civilization which is observed in recent decades is an increase in the number and variety of pollutants released into the environment. These substances have ecotoxic properties and pose a serious threat to humans and proper functioning of the ecosystem. Their presence in the environment forces the development of new technologies for their disposal. Currently, a huge interest in supercritical fluids as the media for conducting various chemical processes is observed. In a supercritical state, particularly interesting properties, has water which changes radically its solvation properties from ionic to non-ionic type and is a very good solvent for non-polar organic compounds. Accordingly, new methods of using water as a medium for oxidation of waste and toxic organic impurities are searched. One of the latest and very promising method to destroy organic contaminants, using the properties of water which exceeded the critical point, (critical temperature  $T_{cr} = 374$  °C and critical pressure  $P_{cr} = 22.1$  MPa) is thermohydrolysis in supercritical water. In this paper an application high-performance liquid chromatography for 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNSDS) thermohydrolysis in environment of supercritical water is presented.

**Keywords:** thermohydrolysis, supercritical water, HPLC

## **1. 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) [1]. In such conditions, in the oxidant-free environment, many toxic organic substances undergo decomposition to simpler compounds, presenting fewer problems in further utilisation. It is possible due to the process of hydrolysis, based on inserting a water molecule into the molecule of the compound undergoing degradation [2].

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 (eg. salts) become practically insoluble, but typical organic nonpolar compounds (eg. benzene, n-heptane) become soluble. Supercritical water is unlimitedly mixable with gases, eg. with oxygen [4-6]. Due to the such interesting supercritical water qualities studies 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 coke breeze and high-molecular carbon compound production. 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 the supercritical water oxidation [5-7].

It looks as the “supercritical thermohydrolysis” can be an effective and safe method for hydrothermal utilisation of the dangerous organic compounds in the future [8-10]. However, the mechanism and kinetics of the hydrolysis reaction in the supercritical water should be identified. The research on 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 [11].

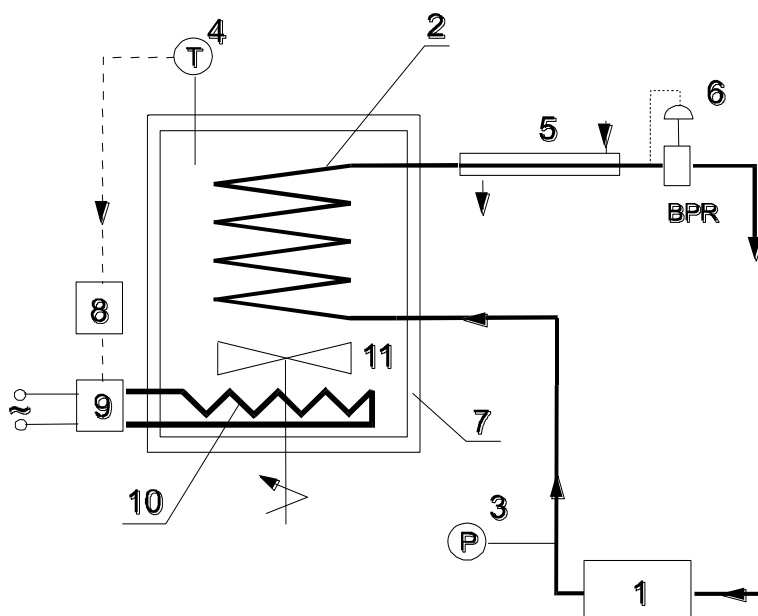
Thermohydrolysis process in the environment of supercritical water has been investigated for DNSDS. The processes were carried out in the tube flow reactor. Conversion ratio of these compounds was investigated to estimate the efficiency of thermohydrolysis method as a new method of organic waste elimination. DNSDS was chosen because it is present in dye industry wastewaters, and it is non-degradable biologically.

## **2. MATERIALS AND METHODS**

The research presents that, experiments were carried out on model wastewater containing different concentrations of 4,4'-dinitrostilbene-2,2'-disulfonic acid. It is a valuable intermediate used in the synthesis of stilbene dyes (replacing the carcinogenic benzidine dyes) and optical brighteners.

Solutions of the DNSDS with concentrations 0.25, 0.125, 0.063, 0.032, 0.016 g/dm<sup>3</sup> have been prepared and deaerated in the ultrasonic bath. Such solutions were pumped into the tube reactor by the HPLC high-pressure pump. Schematically the set-up for testing the process of the thermohydrolysis in supercritical conditions is shown on Figure 1. The equipment consisted of: 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 rationalising

the heat exchange and temperature regulation system (4, 8, 9) which was controlled by thermostat (7), 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), heat exchanger “pipe in pipe” type serving as a condenser and enabling to cool reaction mixture which leaves the reactor (5), pressure measurement (3), the pressure regulator enable to keep a definite pressure in the system (6).



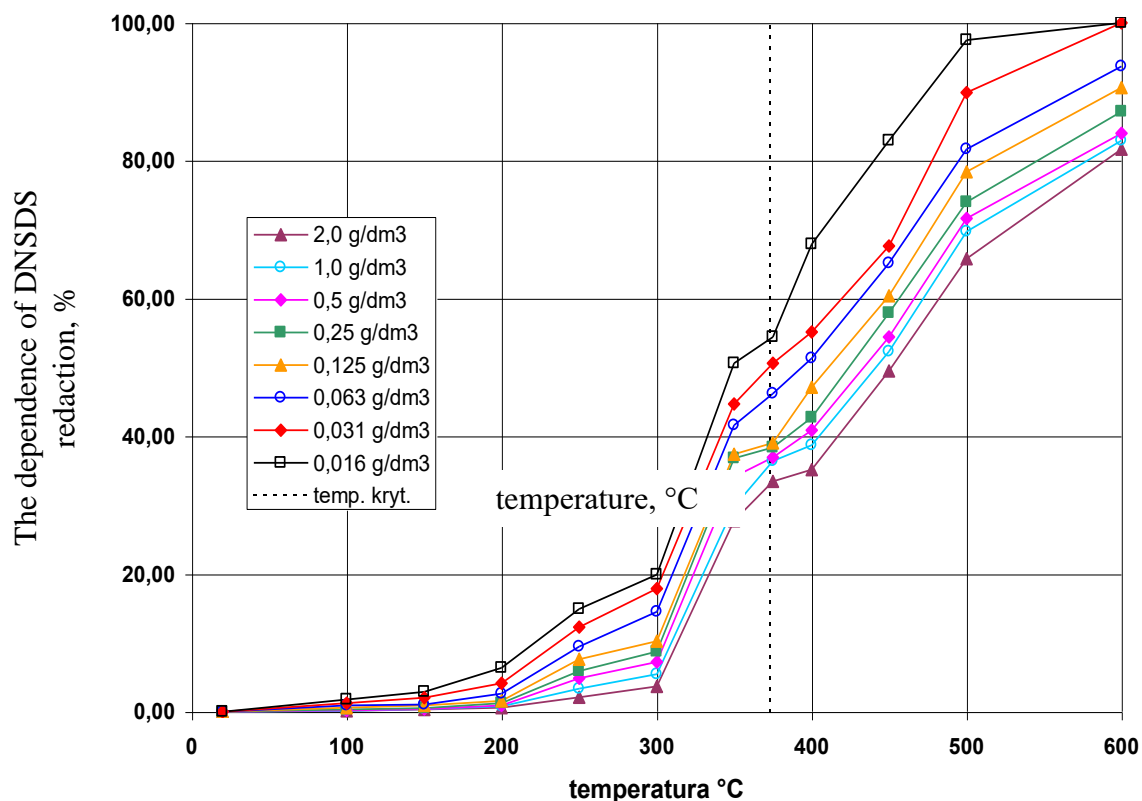
**Figure 1.** Schematics of the equipment for supercritical thermohydrolysis research.

Flow rate was used  $2.5 \text{ cm}^3/\text{min}$  and pressure was 25 MPa. Experiments were carried out in temperature: 20, 100, 200, 250, 300, 350, 375, 400, 450, 500 and 600 °C after 20 minutes the temperature in the reactor reached the steady state. 5 samples of reactor outflow liquid were collected with the 1 minute intervals.

Concentrations of the substrates and aniline after thermohydrolysis were determined by HPLC. An LC 250 type liquid chromatograph with a 235C type DAD detector with spectral sweep from 195 to 360 nm was used for the analyses. Chromatographic column had 250 mm length and 4.6 mm internal diameter with Altech C18 column packing (octadecyl phase) and  $5\mu\text{m}$  particle size. Mixture of methanol: aqueous buffer pH 7.0 (80:20v/v). The eluent flow rate through the column was  $1 \text{ cm}^3/\text{min}^{-1}$ , at the pressure of about 10 MPa. The analyses were performed in the isocratic system. Chromatograms of samples coming from the investigations of thermohydrolysis in supercritical water of aniline were recorded at wavelength  $\lambda = 280 \text{ nm}$ . The standard of aniline was generated z commercial product (Sigma). The working standard concentrations ranged from  $60 \text{ mg}/\text{dm}^3$  to  $300 \text{ mg}/\text{dm}^3$ .

### 3. RESULT AND DISCUSSION

Figure 2 shows the dependence of reduction degree of the tested acid solutions in a function of operating temperature of the reactor for the set flow rate of  $2.5\text{cm}^3/\text{min}$  and a different initial concentration.

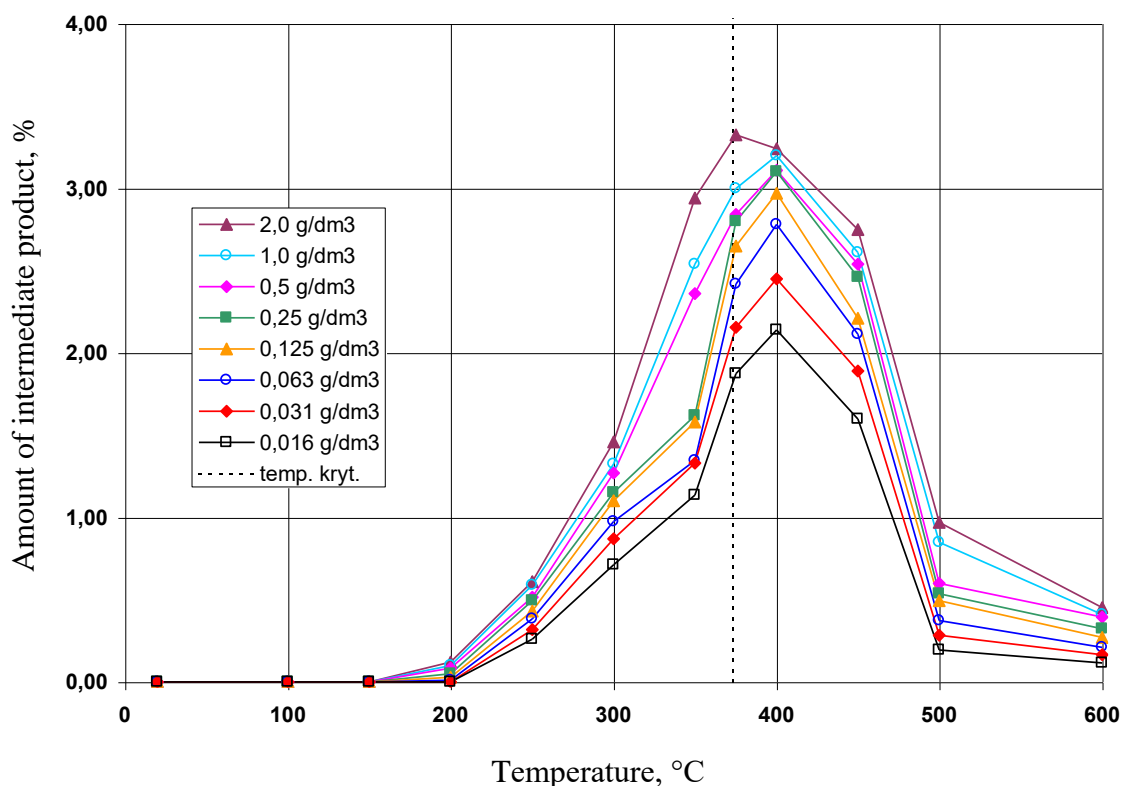


**Figure 2.** The reduction of DNSDS in a temperature.

Volumetric flow rate of fluid through the reactor was  $2.5\text{ cm}^3/\text{min}$  and pressure 25 MPa.

The analysis of curves characterizing the dependence of reduction degree of starting compounds on temperature leads to a conclusion that the degree of conversion depends on concentration. The higher the concentration of the starting compound subjected to thermohydrolysis, the lower the reduction degree of the tested compound.

Figure 3 shows the amount of intermediate substances obtained after the thermohydrolysis process of the tested acid as a function of operating temperature of the reactor for the set flow rate of  $2.5\text{ cm}^3/\text{min}$  and different initial concentrations. Their amount in the mixture exiting the reactor was estimated on the basis of chromatograms. To sum up, the peaks of all intermediates refer to the areas of the peaks of the solutions entering the reactor.



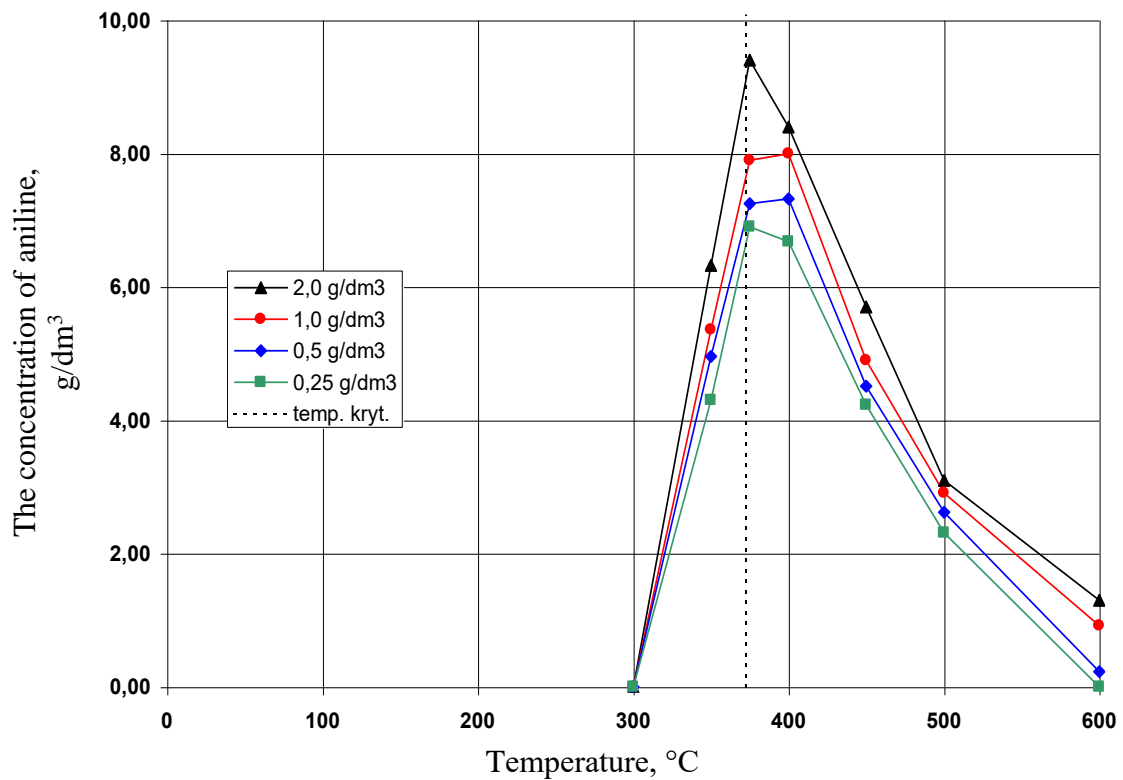
**Figure 3.** Number of intermediates formed during thermohydrolysis process of DNSDS (based on starting substrate, %). Volumetric flow rate of fluid through the reactor was 2.5 cm<sup>3</sup>/min and pressure 25 MPa.

Figure 4 shows the dependence of the concentration of aniline formed in the DNSDS thermohydrolysis process, depending on the concentration of the starting substrate at the constant flow rate of 2,5 cm<sup>3</sup>/min and pressure 25 MPa.

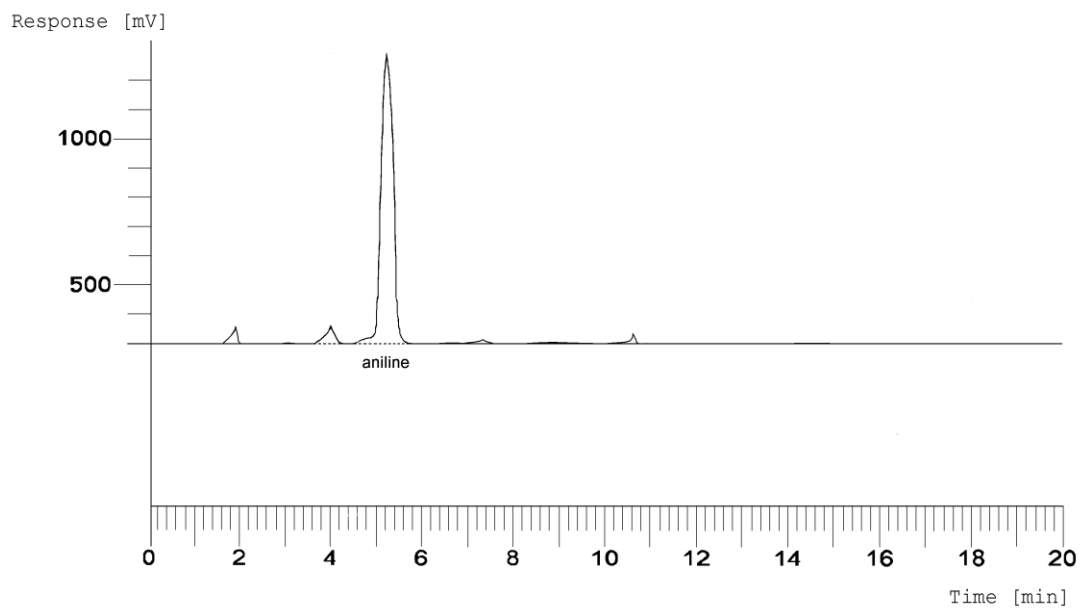
Chromatographic studies of the reaction mass after the thermohydrolysis process of DNSDS show that tested compound decomposes in different degree. A representative chromatogram of intermediate product, which was identified is shown in the Figure 5.

A repeatability of experiments of migration of the analyzed time and peak areas were performed for 60 mg/dm<sup>3</sup> (HPLC) standard solutions. For 10 consecutive standard solutions injections, good migration times and peak surfaces were obtained (Table 1)

HPLC calibration curves for aniline were prepared in various concentrations (60, 120, 180, 230, 300, mg/dm<sup>3</sup>) on the basis of commercial product. For aniline, the linear dependence of the peak surface and concentration was observed in the tested range. The calibration data for HPLC method is presented in Table 2.



**Figure 4.** The aniline concentration in the reaction mass formed during thermohydrolysis proces of DNSDS depending on the concentration and temperature. Volumetric flow rate of fluid through the reactor was 2.5 cm<sup>3</sup>/min and pressure 25 MPa.



**Figure 5.** 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
HPLC	5.71±0.18	985±33

**Table 2.** Calibration data for aniline studied.

Method of aniline analysis	Linear range (mg/dm <sup>3</sup> )	Equation of regression lines	Correlation coefficient (r <sup>2</sup> )
HPLC	60-400	y = 218.73x-5758	0.9964

### 3. CONCLUSIONS

In this paper thermohydrolysis process of DNSDS was analyzed. Solutions containing from 0.016 to 2.0 g/dm<sup>3</sup> of all tested compounds were subjected to thermohydrolysis. Studies were carried out in the temperature range from 20 to 600 °C, at a pressure of 25.0 MPa and different concentration of the starting compound. The studies led to the conclusion that destructive hydrolysis of the tested compound is a very slow and extremely complicated process. Their complexity are associated with varying degrees of their conduct, which strictly depend on the temperature of the process. Examining the effect of certain factors on the rate of thermohydrolysis it was found that the process depended on the process temperature and concentration of the starting compound.

The results of the DNSDS conversion during thermohydrolysis suggest that at a flow rate of the reaction mixture equals to 2.5 cm<sup>3</sup>/min and at a temperature of 600 °C at a concentration of 0.016 g/dm<sup>3</sup> DNSDS (pressure 25 MPa) maximum 100% conversion of the compound is reached.

In this work the amount of intermediate products obtained after the thermohydrolysis process were identified. For the tested compound, the major intermediates were identified using HPLC. In the thermohydrolysis process of 2,2'-dinitrostilbenedisulfonic acid-4,4', the major intermediate product is aniline.

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