

# HYDROLYSIS KINETICS FOR 2-CHLOROPYRIDINE IN SUPERCRITICAL WATER

*Carmen M. Barrera, Dolors Salvatierra and Francesc Giralt. Grup de Fenomens de Transport, Departament d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Catalunya, Spain.*

## Introduction

Pesticides (especially herbicides, fungicides and insecticides) are substances used to protect crops. Such products act preventing, destroying, repelling, or mitigating weeds, insects, rodents, fungi, bacteria or other organisms, and owe their effect to a specific active chemical group.

The extensive use of pesticides in agriculture generates a large amount of waste products such as plastic containers and wastewaters. Plastic containers can be recycled after being washed, but the generated wastewaters containing contaminant organic mixtures resistant to conventional biological treatment cannot be discharged to the environment. It is necessary an alternative treatment for the destruction of organic compounds taking into account the low concentrations of these residual waters.

Many researchers have demonstrated that Supercritical water oxidation (SCWO) is an appropriate process to treat residual waters with low nonbiodegradable organic compound concentration (<10% w/w).(1,2) Supercritical water is an excellent reaction medium for the oxidation of various waste streams, especially aqueous wastes too dilute for an efficient incineration. Above its critical point ( $T=374^{\circ}\text{C}$  and  $P=22.1\text{ MPa}$ ), the properties of water change so that it acts as a non-polar solvent. Many organic compounds and light gases (e.g. oxygen) are highly soluble in supercritical water. The low viscosity of supercritical water gives a high diffusivity to the reactants and hence a rapid and complete reaction. At 450 to 700°C, roughly half the temperature of conventional incineration, the organics are readily (0.1 to 100 s) and efficiently (99.9 to at least 99.99%) oxidized, mainly into carbon dioxide, water and nitrogen. These attributes make SCWO attractive for treatment of organic wastes, in particular high water content wastes such as the obtained from recycling process of pesticide containers.(3,4)

Additionally, it has been observed that hydrolysis is significant in the preheating section of the feed to a SCWO reactor.(5) This fact suggests the need of a better understanding of the hydrolysis kinetics prior the study and optimization of the SCWO processes. If degradation can take place before oxidation, less oxidant or shorter residence time will be needed to assure high degradation conversions in the SCWO process.

Hydrolysis is a chemical reaction in which a bond cleavage is affected by water or by acid or base produced from a reaction of water with salts. Individual water molecules may participate in elementary reaction steps as reactants or products. Examples reported in the literature include hydrolysis, hydration, hydrogen exchange, and free-radical oxidation chemistry.(6) Hydrolysis of organic compounds in high temperature water (HTW) has been pursued for different purposes, with one being destruction of organic wastes.

Experimental studies have demonstrated that many organic compounds, both small and polymeric, are hydrolyzed to various degrees in HTW, depending of their reactivity. Fully hydrocarbon compounds are generally resistant to hydrolysis in "pure" HTW or HTW without catalysts added. Compounds that are particularly susceptible to hydrolysis in HTW are those containing a saturated carbon atom attached to a heteroatom-containing functional group (6) but there are many compounds with a lack of information about its reactivity under such conditions and its kinetic data.

2-Chloropyridine (2-CP) is a common chloropyridine isomer obtained during the development process of chlorpyrifos,(7) a widely used pesticide,(8,9) and its presence in

wastewaters makes it a good candidate to be studied for treatment by hydrothermal processes. In addition, the carbon-nitrogen bond of 2-CP makes it a good product to be used as a model compound for a broader class of nitrogenous organic compounds. Then, the objective of the work was to characterize kinetics at temperatures from 450 to 575°C for the 2-CP hydrolysis using isothermal batch experiments to optimize the process design to treat those compounds by SCWO.

### **Experimental methodology**

Reaction rate constants for the acid hydrolysis of 2-CP were determined in the range between 400 and 575°C, at 280 bar and reaction times from 5 to 30 min, in a batch system.

The experimental setup, described in previous works,(10) contains a Hastelloy C-276 reactor with an internal volume of approximately 30 mL. Four ports designed to accept high pressure equipment fittings allow for temperature and pressure measurements as well as inlet and outlet connections. A pressure relief valve controls the system's internal pressure. A type K thermocouple measures the internal temperature into the reactor, this value is controlled by a temperature control system with a microprocessor controller, a transformer, a relay and four strip heaters clamped around the reactor and surrounded by insulation to heat the reaction chamber. The introduction of the sample containing the organic compound into the reactor system is made through a six-way valve.

Initially, the reactor was filled up with purified water until an approximate pressure of 280 bar. The temperature control system was turned on and the temperature was fixed. The working temperatures chosen were 400, 450, 475, 500, 525, 550 and 575°C. When the reaction system reached the desired temperature and pressure conditions, 100 µL of the organic compound solution were loaded into the sample loop using a zero-volume syringe on the six way valve in the load position. The six way valve was then switched to the inject position and approximately 0,5 g of water were pumped to push the organic compound into the reactor chamber. Once into the reactor, the sample was mixed with the hot water. At this moment the timer was set to zero. The reaction times chosen were within the range of 5 to 30 min. At the desired residence time, the exit valve was opened and the sample collected in an ampoule after cooling down through the ice bath. Nitrogen was used to displace the sample out of the exit pipe to the collection vessel. Finally, samples were stored in clear glass vials to be analyzed. The same process was repeated for each reaction time and for each temperature studied.

Every sample was analyzed three times by gas chromatography (GC) and every series of experiment for each temperature was repeated at least twice, in order to guarantee repeatability of the results. Sample concentrations were determined by GC using a HP 6890 gas chromatograph with a flame ionization detector (FID). The capillary column used was a HP-5 Trace Analysis (5% PHMeSiloxane) by Hewlett Packard with helium as carrier gas and nitrogen as gas makeup.

### **Results**

First, pure organic hydrolysis experiments were conducted. The obtained results showed no relevant degradation after residence times up to 30 min.

Considering that real samples will contain acid present into the solutions, the study of the kinetics of the acid catalyzed hydrolysis was considered more interesting and convenient.

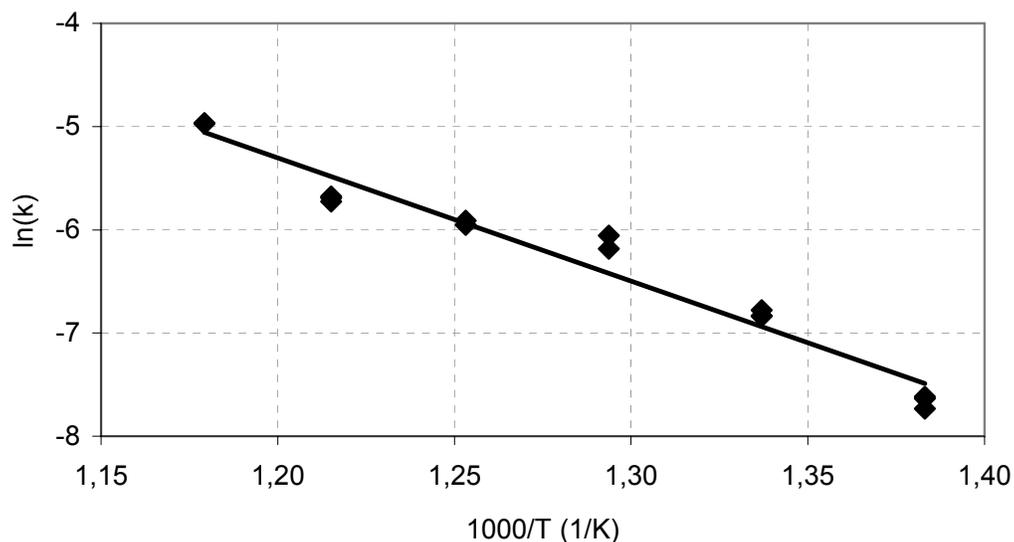
The results show that the degradation percentage increased with the residence time, confirming the first order behavior for each working temperature. Additionally, the rate constant increases as working temperature increases.

The conversion results obtained are detailed in Table 1.

T (°C)	% Conversion
400	59.71
450	20.61
475	42.47
500	71.60
525	85.20
550	88.87
575	95.63

**Table 1:** Average conversion values obtained for each temperature after 10 minutes of reaction time

From the representation of  $\ln C/C_0$  vs time for each temperature set of experiments we can conclude that the 2-CP hydrolysis follows a typical Arrhenius-type expression for the whole working temperature range as can be observed in Figure 1.



**Figure 1:** Arrhenius plot with an assumed first order rate constant for the 2CP hydrolysis in acid media at 280 bar from 450 to 575°C

The kinetic parameters  $E_a$  and  $\ln A$  have been determined for this reaction. The follow up of the generation and degradation of some secondary signals of the gas chromatogram allow us to propose some reactions paths for the acid catalyzed hydrolysis of 2-chloropyridine in supercritical water.

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