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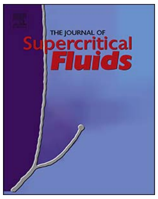

Supercritical water oxidation (SCWO) for the removal of nitrogen containing heterocyclic waste hydrocarbons. Part II: System kinetics

Bushra Al-Duri*, Faihan Alsoqyani

School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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ABSTRACT

This work investigated supercritical water oxidation (SCWO) of DBU ($C_9H_{16}N_2$)[1] in the absence and presence of isopropyl alcohol (IPA) as co-fuel. SCWO was studied in a plug-flow reactor under different temperatures (400–525 °C), initial DBU concentrations (1–10 mM at reactor conditions), oxidant ratios (0.8–2), and $[IPA]_0/[DBU]_0$ ratios (0.5–4). *Pseudo First Order* and the *Global Power Law* models expressed the kinetics, and the rate constants were evaluated. Furthermore, SCWO of aqueous ammonia (NH_4^+) as feedstock was studied at several temperatures (400–500 °C), oxidant ratios (0.8–2.0) and $[IPA]_0/[NH_4^+]_0$ ratios; and the same kinetic models were applied. Results showed that IPA addition increased the reaction rate constant k, affected oxidant utilisation, and greatly enhanced NH_4^+ removal% towards gaseous nitrogen. The influence of IPA addition was more pronounced on N-speciation than it was on TOC% removal, for all current system conditions.

1. Introduction

In many industries the sludge remaining after treatment of wastewater accounts for much of the generated hazardous waste. If sent to landfill, not only would it damage the land but would also release hazardous chemicals into air, water and soil. Thus the greatest concern with disposal of hazardous waste is landfill (or injection wells). The ideal disposal method is the destruction and conversion of hazardous waste to a non-hazardous form. Conversion to environmentally safe substances can be very expensive for some types of hazardous wastes and technically impossible for others, creating the need for alternative disposal methods of the unrecyclable wastes.

Supercritical water oxidation (SCWO) is an advanced hydrothermal technology for the complete destruction of hazardous waste, otherwise disposed by incineration and landfill. The 2016 edition of DEFRA[2] Digest of Waste and Resource statistics [1] have shown that in 2014–2015, 8 m tonnes of hazardous waste were treated by incineration and 7 m tonnes were sent to landfill, as shown in Fig. 1.

Fig. 1 Description of reaction kinetics of SCWO is an essential prerequisite for proper design. Work on SCWO kinetics covered various systems like C_1 fuels [2], CH_3 and CHO-substituted phenols [3], cutting fuel waste [4], continuous SCWO of coal [5] and municipal sewage sludge (MSS) [6]. These studies mostly investigated SCWO variables namely temperature, oxidant ratio, organics concentrations and reaction times. Also, reaction pathways were suggested and rate expressions namely *pseudo-first order* and *global power law* kinetics were proposed [2,3,5,6].

N-containing hydrocarbons have also been studied. Crain et al. [7] described the SCWO kinetics of pyridine (using high-pressure oxygen) by the *global power law*. Lee *et al.* [8] investigated the decomposition kinetics and nitrogen speciation of *p*-nitroaniline (pNA) at supercritical water conditions in the absence/presence of oxygen. Significant decomposition occurred without oxygen. The formation of oxygen, carbon monoxide, carbon dioxide, and nitrogen indicated that the nitro group in the decomposed pNA drove oxidation in the absence of oxygen. They applied the *pseudo first order* model with respect to pNA. Zhou et al. [9] conducted SCWO of ethylene di-amine tetra acetic acid (Cu(II)-EDTA) in a tubular reactor, testing a range of system conditions and found ammonia to be the most recalcitrant. Furthermore, they simulated the reaction kinetics by CFD and compared the TOC, CO and CO_2 profiles to experimental data.

Focusing on the destruction of ammonia as the rate-determining step, the role of alcohol as co-oxidant was investigated. Webley et al. [10] experimentally determined the SCWO kinetics of ammonia and ammonia-methanol mixture in a plug flow and packed bed reactors. They found the Inconel reactor wall to have a catalytic effect. Controversially, ammonia and methanol oxidation mechanisms seemed to be independent. Also, they applied the *global power law* and a catalytic

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* Corresponding author.
E-mail address: B.Al-Duri@bham.ac.uk (B. Al-Duri).

[1] (1,8-Diazabicyclo[5.4.0]undec-7-ene)

[2] Department of Environment, Food & Rural Affairs

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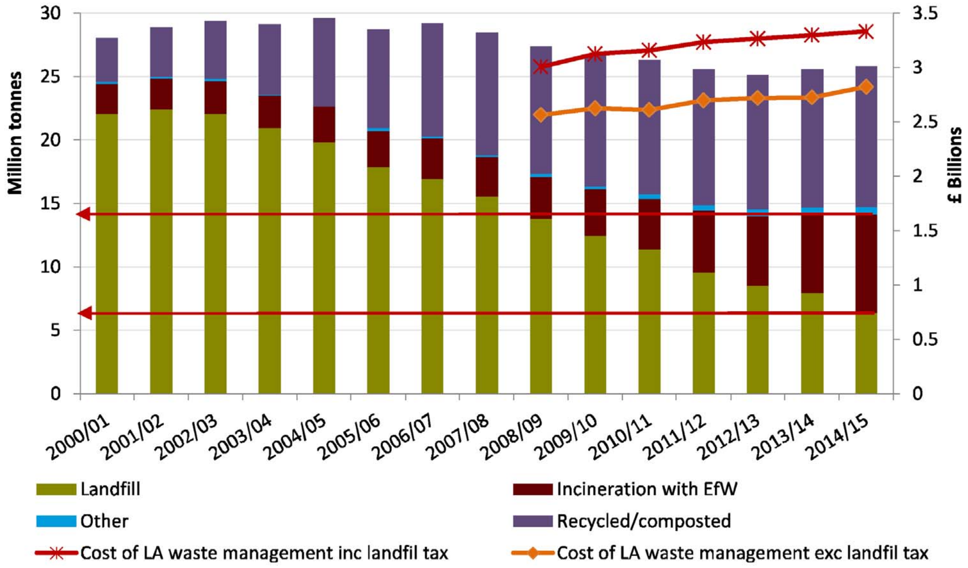

Fig. 1. Local authority (LA) collected waste management in England between 2000/01 and2014/15 (courtesy of Digest of Waste and Resource Statistics – 2016 Edition).

model and found the latter to better fit their data. On the other hand, Shimoda *et al.* [11] investigated the SCWO kinetics at 25 MPa, 530 °C and $[NH_3]_0$ = 2.9-3.0 mm/L. Ammonia conversion increased with initial methanol concentration, but decreased after methanol ran out. Theoretically they described the system by the elementary rate model, and explained their findings by chain free radical reaction where reactants shared radicals, propagating the conversion process. Oe et al. [12] confirmed that methanol addition greatly enhanced the reaction rate, and that the oxidant ratio influenced the production of N_2O. Using isopropyl alcohol (IPA) as co-fuel Cabeza et al. [13] found that IPA/NH_3 molar ratio influenced the ammonia removal while the oxygen ratio did not have significant influence. Al-Duri *et al.* [14] investigated SCWO of di-methyl formamide (DMF) in the presence and absence of IPA, and found that the IPA/DMF ratio, oxidant ratio and reaction time all enhanced SCWO. They described the system kinetics by the *pseudo-first order* and the *global power law* in terms of TOC. Wang et al. [15] achieved 99.7% TOC removal for SCWO of cotton dyeing effluents by SCWO in a tubular reactor, and recommended high temperature and oxidant ratio for good ammonia nitrogen (NH_3–N).

This work investigates the kinetics of SCWO of DBU and NH_3 in the presence and absence of isopropyl alcohol (IPA), applying the *pseudo first order* and the *global power law* rate expressions to the experimental data [16].

2. Experimental section

2.1. Materials and methods

Chemicals used were DBU, $C_9H_{16}N_2$ (Sigma-Aldrich, UK, > 99%) as targeted organic compound; IPA, C_3H_7OH (Sigma-Aldrich, UK, 99%) as a co-fuel and aqueous hydrogen peroxide (Sigma-Aldrich, UK, 35 w%) as a source of oxygen. Aqueous ammonia, NH_4^+ (Sigma-Aldrich, UK, > 99%) was used as feedstock for destruction study, as the recalcitrant intermediate. Distilled water was used during all solution preparations.

2.2. Apparatus

The experimental apparatus designed and constructed at the University of Birmingham (UK), was detailed in previous work [16]. It comprises a 12 m plug-flow SS316 reactor of 1/16” diameter (0.6 mm ID) and 3.07 mL volume. Oxidant and organics were separately pumped and pre-heated, then mixed in a cross-junction at the reactor entrance. The preheater and reactor were placed in a furnace, where input and output temperatures were monitored by thermocouples. The reactor exit stream was cooled and de-pressurised before the two phases were separated in a gas/liquid separator. When used, IPA was premixed with DBU or NH_4^+ as required, before pumping the solution.

2.3. Experimental programme

Tables 1 and 2 show the experimental programme for SCWO of DBU and ammonia, respectively:

3. Theoretical background

The generalised reaction rate expression combined with Arrhenius law and the plug flow reactor performance was applied to the experimental data in order to evaluate the rate constants. Detailed kinetics analysis are given elsewhere [17,18], thus will be summarised below. The *pseudo first order* approximation is given by Eq. (1) and (2):

$$-\frac{d[TOC]}{dt} = k_0 exp\left(-{}^{E_a}\!/_{RT}\right)[TOC] \tag{1}$$

$$ln\left({}^{[TOC]}\!/_{[TOC]_0}\right) = k_0 exp\left(-{}^{E_a}\!/_{RT}\right)t \tag{2}$$

Where k_o (s^{-1}) is Arrhenius constant, E_a is the energy of activation ($J\,mol^{-1}$). The *pseudo first order* expression is extended to the *global power law model* expression when oxygen is not in excess:

$$-\frac{d[TOC]}{dt} = k_0 exp\left(-{}^{E_a}\!/_{RT}\right)[TOC][O_2]^b \tag{3}$$

Table 1
Experimental conditions of SCWO of DBU at 25 MPa in System I (IPA-free) and System II (with IPA).

Variable	Range
Temperature (°C)$^+$	400, 425, 450, 475, 500, 525
Initial DBU concentration (mM)*	1.0, 2.5, 5.0, 7.5, 10.0
Oxidant ratio (n SR)$^{++}$	0.8, 1.0, 1.25, 1.5, 2.0
Initial IPA concentration (mM)$^\$$	0.5, 2.5, 5.0, 7.5, 10.0, 15, 20
$[IPA]_0/[DBU]_0$	0.1, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0
Residence time (s)	2, 4, 6, 8, 10

$^+$nSR = 1, $[DBU]_0$ = 5 mM & $[IPA]_0/[DBU]_0$ = 1.
*T = 400 °C, nSR = 1, & $[IPA]_0/[DBU]_0$ = 1.
$^{++}$T = 400 °C, $[DBU]_0$ = 5 mM, & $[IPA]_0/[DBU]_0$ = 1.
$^\$$T = 400 °C, nSR = 1, $[DBU]_0$ = 5 mM.