



Supercritical water oxidation (SCWO) for the removal of N-containing heterocyclic hydrocarbon wastes. Part I: Process enhancement by addition of isopropyl alcohol



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ABSTRACT

The present work investigates the destruction of nitrogen-containing heterocyclic hydrocarbons frequently encountered in hazardous wastes by supercritical water oxidation (SCWO), with focus on the process enhancement using isopropyl alcohol (IPA) as co-fuel. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was selected for SCWO in a continuous plug flow reactor, under a range of temperatures (400–525 °C), oxidant ratios nSR (0.8–2.0) and IPA/DBU ratios (0.5–3.5). Experimental results were presented in terms of total organic carbon (TOC) removal %, and nitrogenous products yield %. Based on GC–MS analysis, a free radical reaction mechanism for SCWO of DBU was proposed. Results showed that temperature was the predominant factor to influence the rate of DBU oxidation, while oxidant ratio (nSR) significantly affected the N speciation in the exit stream. IPA addition had a significant impact on shifting recalcitrant aqueous ammonia NH_4^+ in the liquid stream to gaseous nitrogen. It also increased TOC removal % (DBU + IPA) due to the increased free radicals produced by IPA oxidation.

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1. Introduction

For 2–3 decades supercritical water oxidation (SCWO) had been investigated as a promising advanced technology for the removal of chemically stable organics found in a diverse range of wastes. Due to its thermodynamic properties above its critical point of 374 °C and 22.1 MPa, supercritical water (SCW) becomes completely miscible with all organics and gases, and a powerful medium for hydrothermal processes under supercritical conditions [1]. The SCWO process takes advantage of the unique SCW properties, where complex hydrocarbons are rapidly oxidised in SCW medium with >99% removal efficiency, producing liquid water, benign gases like CO_2 and N_2 , and minor amounts of inorganic salts (depending on the feedstock composition). Such advantages potentially place SCWO as the technology to replace incineration, with added advantages: (i) zero toxic emissions, (ii) no ash formation (landfill issues), (iii) no pre-drying of waste is required. On the treatment hierarchy scale SCWO replaces the two most undesirable approaches namely landfill and disposal (incineration with no heat recovery) [2]. Furthermore, SCWO is highly exothermic, producing enough energy to make it self-sustaining in addition to production of green electric-

ity [3]. Despite its advantages SCWO suffers some well-documented problems like corrosion, salt formation and pipe plugging [4], which has hampered commercial advancement over the 90s and 00s. However, more recently, Marrone [5] has demonstrated in a comprehensive review of the status of commercial activity of SCWO plants, that the process future had a positive outlook. Considering the existing operational challenges, more science and engineering research is required in terms of process design and reactor performance.

Nitrogen-containing hydrocarbons represent an important category of industrial waste, which has received little attention in recent years. The abundance of N-containing hydrocarbons in a diverse range of wastes, formation of recalcitrant N intermediates like aqueous ammonia (NH_4^+) and the complex nature of N chemistry make investigation of such compounds both challenging and interesting. A relatively small body of literature on SCWO of N-hydrocarbon was reported. Lee et al. [6] investigated the decomposition of *p*-nitroaniline (pNA) at 380–420 °C in the presence and absence of oxygen and concluded that the *nitro* group in pNA drove the degradation in the absence of oxygen. Bermejo et al. [7] obtained complete degradation of 7 wt.% NH_3 at 780 °C in a cooling wall reactor, while Aymonier et al. [8] obtained complete oxidation of fenuron at 540 °C and 25 MPa obtaining 99.99% COD removal. Benjamin and Savage [9] reported SCW reactions of amines and amides, reporting reaction pathways and constants.

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In their studies Pinto et al. [10] investigated continuous SCWO of quinoline following C and N species profiles under various conditions. In a follow-up study they reported SCWO kinetics assuming Arrhenius type models [11]. Detailed investigations of continuous SCWO of *N,N* dimethyl formamide (DMF) were conducted by the author [12] identifying the release of intermediates at different system conditions. Enhancement of SCWO of DMF was also investigated using multi-port oxidant injection [13,14], which showed improved TOC% conversion and N speciation upon gradual oxidant feed. Other studies confirmed the positive influence of IPA addition to SCWO of DMF, in view of process enhancement [15,16].

1,8-Diazabicyclo[5.4.0]undec-7-ene or DBU ($C_9H_{16}N_2$) is an amidine, which is an oxyacid derivative (carboxylamidine). It is used in organic synthesis as a catalyst, a complexing ligand, a non-nucleophilic base, and a curing agent for epoxy. DBU is widely used in the cephalosporin production of semi-synthetic antibiotics, and can also be used as a rust inhibitor. DBU is used in fullerene purification with trimethyl benzene; and it is also used as a catalyst for polyurethane. DBU is mainly used as a good organic alkali de-acidification agent in drug synthesis. It also exhibited its dual character (base and nucleophile) in the synthesis of aryl- & styryl-terminal acetylenes.

DBU was initially investigated by Al-Duri et al. [17] in a plug flow reactor of $\frac{1}{4}$ in outer diameter and 11 mL volume over a limited experimental range, restricted by the rig capacity. However, results were encouraging and therefore DBU has been selected as a heterocyclic N-containing compound, for more detailed studies in the current system. This work studied SCWO of DBU in a continuous $\frac{1}{16}$ in 12 m plug flow reactor, using hydrogen peroxide as oxidant and IPA as co-fuel. In the current work (Part I) it investigated the process under a range of temperatures, oxidant ratios, and IPA/DBU feed molar ratios. Based on GC-MS analysis this work proposes a SCWO pathway and describes the influence of IPA co-oxidation on the proposed pathway. Results are presented in terms of TOC removal %, and yield % of several N related products. Part II will investigate the reaction kinetics and the influence of IPA on the destruction of TOC and ammonia.

2. Material and methods

2.1. Materials

DBU is a colourless liquid at room temperature (b.p. = 83 °C) with chemical formula $C_9H_{16}N_2$, density = 1018 kg m⁻³, and mass number = 152.2 kg kmol⁻¹. Fig. 1 shows the structural formula of DBU:

Isopropyl alcohol (C_3H_7OH) is a secondary alcohol. It is a colourless liquid (IUPAC name 2-propanol) with density = 786 kg m⁻³, b.p. = 82.6 °C and mass number = 60.1 kg kmol⁻¹.

Hydrogen peroxide (H_2O_2) is a strong oxidizer with a boiling point of 150 °C when it decomposes to water and oxygen. It was purchased in a 35 wt% aqueous solution with density of 1130 kg m⁻³ (at 20 °C).

All compounds were purchased at Sigma Aldrich Chemicals.

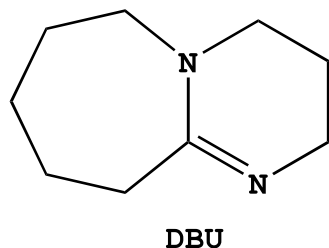


Fig. 1. Structural formula of DBU.

Table 1

Range of the experimental conditions in this work.

Variable	Experimental Values
Temperature, °C	400, 425, 450, 475, 500, 525
Oxidant ratio, SR	0.8, 1.0, 1.2, 1.5, 2.0
Residence time, s	2, 4, 6, 8, 10
Initial DBU concentration, mM	1, 2.5, 5.0, 7.5, 10
IPA/DBU molar ratio	0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0

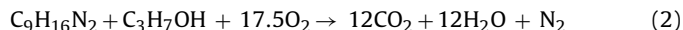
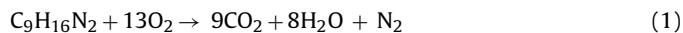
2.2. Apparatus

The apparatus consists of a continuous system shown in Fig. 2. All pipes were SS316, 1/16" OD and 0.6 mm ID unless stated otherwise. The oxidant and organics streams were separately pumped via Jasco PU-980HPLC pumps into 6-m coiled pipe preheaters, before mixing at the reactor entrance. The reactor is made of 12 m length 3.07 mL volume, coiled and situated (with the preheaters) in the furnace, where input and output temperatures were monitored by thermocouples. The reactor products were cooled in a heat exchanger, de-pressurised via a 66-PR GO back pressure regulator (GO, Inc.) before the two phases were separated in a gas/liquid separator. When used, IPA was premixed with DBU at the required concentration and amount, before pumping into the system.

2.3. Experimental conditions

Table 1 displays the current experimental conditions; all reactions took place at constant pressure (25 MPa). The default system conditions were: T = 400 °C, nSR = 1, IPA/DBU molar ratio = 1.0, and $C_o = 5$ mM DBU.

It is important to highlight that the amount of oxidant supplied in the current work was based on the stoichiometric amount required for the complete oxidation of DBU and (DBU + IPA) systems as shown below:



Oxygen was produced by decomposition of hydrogen peroxide upon heating:



The stoichiometric ratio (SR) of oxygen is defined as the quotient of the molar flowrate of oxygen delivered and the molar flowrate required for complete oxidation of the organic feed as described in Eqs. (1) and (2). The value of 'n' denotes excess ($n > 1$), stoichiometry ($n = 1$), or shortage ($n < 1$) of oxygen. Eq. (3) can easily be used to determine the concentration of oxidant solution required to supply oxygen for each run.

The reaction mixture was more than 99% water thus all calculations were based on the thermodynamic properties of pure water under the reactor conditions. It is worth mentioning that all reactions took place in an *isothermal* furnace, hence it was assumed that the thermodynamic properties of the reactants remained constant throughout the reactor. Heat produced during the reaction would dissipate through the large temperature – controlled furnace. Residence times were calculated from the reactor volume and reactants' (organics + oxidant) flow rates at the reactor entrance, and under the conditions inside the reactor at each set of system conditions.

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