

Supercritical water oxidation (SCWO) for the removal of N – containing heterocyclic hydrocarbon wastes. Part I

Al-Duri, B.; Alsoqyiani, F.; Kings, I.

DOI:

[10.1016/j.supflu.2016.05.002](https://doi.org/10.1016/j.supflu.2016.05.002)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Al-Duri, B, Alsoqyiani, F & Kings, I 2016, 'Supercritical water oxidation (SCWO) for the removal of N – containing heterocyclic hydrocarbon wastes. Part I: process enhancement by addition of isopropyl alcohol', *Journal of Supercritical Fluids*, vol. 116, pp. 155-163. <https://doi.org/10.1016/j.supflu.2016.05.002>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked 20/6/2016

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Title: Supercritical water oxidation (SCWO) for the Removal of N – Containing Heterocyclic Hydrocarbon Wastes. Part I: Process Enhancement by Addition of Isopropyl Alcohol

Author: B. Al-Duri F. Alsoqyiani I. Kings



PII: S0896-8446(16)30103-6
DOI: <http://dx.doi.org/doi:10.1016/j.supflu.2016.05.002>
Reference: SUPFLU 3627

To appear in: *J. of Supercritical Fluids*

Received date: 9-3-2016
Revised date: 5-5-2016
Accepted date: 6-5-2016

Please cite this article as: B.Al-Duri, F.Alsoqyiani, I.Kings, Supercritical water oxidation (SCWO) for the Removal of N – Containing Heterocyclic Hydrocarbon Wastes.Part I: Process Enhancement by Addition of Isopropyl Alcohol, The Journal of Supercritical Fluids <http://dx.doi.org/10.1016/j.supflu.2016.05.002>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Supercritical water oxidation (SCWO) for the Removal of N - Containing Heterocyclic Hydrocarbon Wastes. Part I: Process Enhancement by Addition of Isopropyl Alcohol

B. Al-Duri^{1*}, F. Alsoqyiani¹ and I. Kings¹

¹School of Chemical Engineering, University of Birmingham,
Edgbaston, Birmingham B15 2TT, United Kingdom. Email: B.Al-
Duri@Bham.ac.uk

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

* Corresponding Author

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.

Graphical Abstract

Concentration profiles (mg L^{-1}) for N-compounds released during SCWO of DBU, as function of oxidant ratio (nSR). Reactions were conducted at $T = 400$, $C_{\text{O,DBU}} = 5 \text{ mM}$; with and without IPA as co-fuel. This graph illustrates that IPA addition as co-fuel reduced aqueous ammonia and total nitrogen in the liquid phase indicating that it was converted to gaseous nitrogen.

Highlights

- 1,8-Diazobicyclo[5.4.0]undec-7-ene conversion was mainly influenced by temperature.
- Oxidant ratio greatly influenced N- and C-species distribution in product stream.
- Alcohol addition enhanced DBU destruction, TOC removal % and N products yield %.
- Alcohol addition shifted N species towards gaseous nitrogen.

Keywords

Supercritical water oxidation, free radicals, N-containing hydrocarbons, isopropyl alcohol, co-fuel, hazardous waste

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 22.1MPa, 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 CO₂ and N₂, 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 electricity [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 were 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. 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 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. Figure 1 shows the structural formula of DBU:

Fig. 1

Isopropyl alcohol (C₃H₇OH) 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 (H₂O₂) is a strong oxidizer with a boiling point of 150 °C when it decomposes to water and oxygen. It was purchased in a 35wt% aqueous solution with density of 1130 kg m⁻³ (at 20°C).

All compounds were purchased at Sigma Aldrich Chemicals.

2.2 Apparatus

The apparatus consists of a continuous system shown in Figure 2. All pipes were SS316, 1/16" OD and 0.6mm ID unless stated otherwise. The oxidant and organics streams were separately pumped via Jasco PU-980 HPLC pumps into 6-m coiled pipe preheaters, before mixing at the reactor entrance. The reactor is made of 12 m length 3.07mL 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.

Fig 2

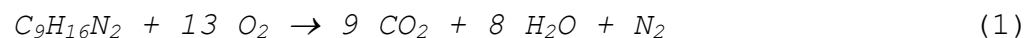
2.3 Experimental conditions

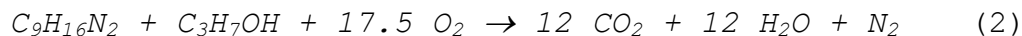
Table 1 displays the current experimental conditions; all reactions took place at constant pressure (25 MPa). The default system conditions were: $T = 400\text{ }^{\circ}\text{C}$, $n\text{SR} = 1$, IPA/DBU molar ratio = 1.0, and $C_0 = 5\text{ mM DBU}$.

Table 1 - Range of the experimental conditions in this work

Variable	Experimental Values
Temperature, $^{\circ}\text{C}$	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,

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 equations (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.

3. Results and Discussion

3.1 Proposed SCWO pathway for DBU

Previous work [18] identified several intermediate compounds during SCWO of DBU. Figures 3 and 4 show the GCMS chart and the identified compounds, respectively:

Fig 3

Fig 4

SCWO is initiated and propagated by the free radicals $\text{HO}\cdot$ and $\text{HO}_2\cdot$ produced by the oxidant decomposition in water:



Such free radicals initiate the reaction as proposed in Figure 5:

Fig 5

The $\text{HO}\cdot$ radical causes the scission of C-N by hydroxylation and breaking DBU into caprolactam, toluene and 1-acetyl piperdine, which further break down into smaller products down to

CO₂, H₂O, N₂ and possibly N₂O. Equations (4 - 7) suggest that the presence and abundance of HO• radical is of prime importance to initiate and propagate SCWO. Oxygen and water are good sources of free radicals under SC conditions, which is one of the main reasons of the vigour of the SCWO reaction. Addition of some organics (like alcohols) also enhances the oxidation process. Zhong *et al.* [19] showed that SCWO of IPA generates free radicals like HO•, HO₂•, [CH₃COHCH₃]•, •CH₃, and [CH₃CHOHCH₂O₂]•. By virtue of the extra free radicals generated (sec. 3.3), and the exothermic nature of IPA oxidation, the process is further propagated from within, reducing the need for extra heat sources.

3.2 Effects of the system conditions

3.2.1 Temperature:

Figures 6 and 7 show the effect of temperature on TOC removal %, N compound concentrations and N yield % in product stream.

Fig 6

As expected, Figure 6 shows that TOC removal % increased with increasing the reaction temperature. An increase from 400°C to 525°C resulted in 17% increase in TOC removal. C was mainly converted to CO₂. The case was different for N compounds. At t =

6 s Figure 7 shows that NO_3^- yield % decreased with temperature, while NO_2^- was at very low a concentrations throughout. This is an excellent indication that NO_3 salts are not likely to form in the reactor. On the other hand, aqueous ammonia NH_4^+ yield % increased, indicating further degradation of DBU at higher temperatures. Further degradation of ammonia (as a recalcitrant compound) would require additional measures such as catalyst or alcohol addition, or higher temperatures. Total nitrogen TN yield % also increased temperature increase, signifying that upon SCWO under the investigated temperature range, N was mostly converted to aqueous ammonia, which remained in the liquid stream alongside small yields of NO_3^- . The gas phase composition for the current work was not analysed.

Fig 7

3.2.2 Oxidant Ratio ($n\text{SR}$):

Besides temperature effect on reaction kinetics, the oxidant is the main factor to influence the reaction pathway and final products. Furthermore, ΔH_r of SCWO plays the key role in the process energy efficiency, energy integration and control of the temperature profile along the reactor. However, the present system is isothermal thus ΔH_r has no detectable influence on the reaction enhancement because the temperature profile along the

reactor was assumed constant.

Figure 8 shows the TOC removal % versus time at several nSR (stoichiometric ratio) values. For all experiments, SCWO was conducted at 400°C and 25 MPa, starting with $C_0 = 10$ mM DBU at reactor conditions. TOC removal improved steadily with increasing nSR value even when 100% excess oxidant ($n = 2$) was used. It is noteworthy that increasing nSR did not exceed the temperature effect on TOC removal. Comparing Figure 8 with Figure 5 still shows the prominent effect of temperature on TOC removal. This further confirms that nSR has more effect on N compounds distribution in the product stream than TOC removal %.

Fig 8

Fig 9

Figure 9 shows N speciation as function of nSR at $t = 6$ s. Increasing the oxidant amount has a prominently positive effect on N conversion. NH_4^+ in liquid decreased by 63% upon raising nSR from 0.8 to 2.0, at the reaction temperature of 400°C, which is too low for ammonium destruction. Furthermore, TN and NH_4^+ concentrations decreased with similar trends. As TN is the total N in the liquid, this suggests that increasing the oxidant enhanced NH_4^+ oxidation to N_2 or N_2O . The lack of gaseous

nitrogen data prohibited knowing the exact distribution however, higher oxygen supply favours N_2O production as opposed to N_2 . This is to be taken into account upon deciding the optimum oxidant dosage for SCWO of nitrogenous hydrocarbons. Overall, in the destruction of N-hydrocarbons, oxygen plays a role more prominent than temperature.

3.3 The Effect of IPA

IPA was selected as co-fuel because it is easily oxidised and has a higher ΔH_r (-1908 kJ/mol) than both methanol (-650 kJ/mol) and ethanol (-1279 kJ/mol) [20], releasing more energy and free radicals [19] to further enhance the process rate and efficiency. It is pertinent to point out that in principle the increase in reaction rate is attributed to two factors: (1) the release of extra free radicals and (2) the release of extra heat (both by the SCWO of IPA). However in the current study, the excess heat is dissipated to the surroundings, hence the system is isothermal and the increased removal is entirely attributed to the formation of extra free radicals. Figure 10 shows a schematic diagram of SCWO of IPA and the main radicals produced in the reaction.

Fig 10

For all experiments other than where the effect of $[IPA_0/DBU_0]$ was being investigated, IPA to DBU molar ratio of 1 was used.

3.3.1 *Temperature:*

Results of experiments using IPA as co-fuel for SCWO of DBU are presented in terms of TOC removal % and concentrations of key N species in Figures 11 and 12 respectively. At 3 selected residence times, Figure 11 shows that TOC removal was enhanced at all residence times, showing slightly better results at lower residence times and temperatures. For instance at 400°C and 2 s, TOC removal % improved by 3.7%, while at 525°C and 10s, TOC removal % improved by <0.5%. This suggests that at longer residence times and higher temperatures, destruction of the N species predominates.

Fig 11

Figure 12 shows the influence of IPA on N speciation. Both NH_4^+ and TN yields % increased, indicating further oxidation of DBU in the presence of IPA, at the same system conditions, especially at the relatively lower temperature range of 400 to 475 °C. However, knowing that Figure 12 displays liquid N data, higher temperatures and IPA addition lead to further C oxidation but not necessarily further N oxidation. In their work on NH_3

SCWO with methanol as co-fuel, Oe et al. [21] stated that methanol addition caused further oxidation of ammonia to N_2O . However, they used a MeOH/NH_3 ratio of 5, at temperatures over 600 °C.

Fig 12

3.3.2 Oxidant ratio (nSR):

The effect of changing nSR was investigated in an IPA/DBU system undergoing SCWO at 400 °C. Figure 13 shows the TOC % removal profile versus nSR, at selected residence times for both IPA and IPA-free systems. Results show improvement in TOC removal varying between 5% to 2% improvement at 10s and 2s residence times, respectively. Also TOC removal % remained below 95 for all nSR values. This was attributed to the relatively low reactor temperature of 400 °C. Higher temperatures would show better TOC removal, as illustrated in Figure 11, where at 525 °C TOC removal reached over 99.5%. With regard to nitrogen speciation Figure 13 shows that IPA addition significantly reduced the yield % of TN and NH_4^+ in the liquid phase. At lower nSR values, NH_4^+ decreased by 37% and 26% for nSR values of 0.8 and 1.0 respectively. Similarly, TN decreased by 31% and 30% for the same nSR values respectively.

Fig 13**Fig 14**

In the light of the above, it is pertinent to say that IPA addition enhanced NH_4^+ oxidation to N_2 and N_2O , due to the extra free radical specifically $\text{HO}\cdot$, which enhanced NH_4^+ oxidation and reduced both TN and NH_4^+ in the liquid, in favour of benign gases. NO_3^- was originally produced at low yield % at the investigated system conditions, and was further reduced in IPA system. NO_2^- was also monitored; it yielded negligibly small amount and therefore is not shown in the figures.

3.3.3 [IPA₀/DBU₀] ratio:

The effect of IPA₀/DBU₀ ratio was also investigated and the results are shown in Figures 15 and 16 respectively.

Fig 15

Increasing [IPA₀/DBU₀] ratio from 0 to 4 at the studied system conditions improved TOC removal by around 7 to 12%. This implies that the dosage of IPA did not dramatically improve TOC removal. This might not be surprising since the previous

sections showed that IPA addition affected N speciation more significantly than TOC removal. This is further proven in Figure 16, where increasing $[IPA_0/DBU_0]$ ratio from 0 to 4 reduced the yields of TN, NH_4^+ and NO_3^- by 34, 49 and 47% respectively. This is a very interesting finding given that NH_4^+ is a very recalcitrant intermediate regularly found in N containing organic wastes, and NO_3^- is a source of unwanted salts.

Fig 16

4. Conclusions

From the current work it can be concluded that the destruction of N-containing hydrocarbons occurs by virtue of the vigorous free radical mechanism when $HO\cdot$ and $HO_2\cdot$ are responsible for the scission of the C-N bonds, followed by a series of C-C and C-N scissions. Temperature and oxidant ratios were found to be the primary factors, which influenced the SCWO process. While temperature was the main factor that enhanced the overall oxidation the oxidant amount had the main influence on the products distribution, specifically on N products. Addition of IPA was found to enhance DBU destruction as a whole under the wide range of investigated system conditions. Specifically it had a highly favourable effect on the conversion of the recalcitrant intermediate NH_4^+ to gaseous nitrogen, a finding that is highly advantageous in SCWO applications to nitrogenous

waste destruction.

5. References

[1] A. Loppinet-Serani, C. Aymonier, and F. Cansell, Current and Foreseeable Applications of Supercritical Water for Energy and the Environment, *Chem. Sus. Chem.*, 1 (2008) 486-503.

[2] Defra. Digest of waste and resource statistics-2015 edn. Available in: <http://www.gov.uk/government/collections/waste-and-recycling-statistics>.

[3] M.J. Cocero, E. Alonso, M.T. Sanz, F. Fdz-Polanco, Supercritical water oxidation process under energetically self-sufficient operation, *Journal of Supercritical Fluids*, 24 (2002) 37-46.

[4] M.J. Cocero, Supercritical water oxidation (SCWO). Application to industrial wastewater treatment, *Industrial Chemistry Library*, 9 (2001) 509-526.

[5] P. Marrone, Supercritical water oxidation-current status of full-scale commercial activity for waste destruction. *J Supercrit Fluids*, 79 (2013) 283 - 288.

- [6] D.S. Lee, K.S. Park, Y.W. Nam, Adsorption of p-nitroaniline from aqueous solutions onto activated carbon fiber prepared from cotton stalk, *J. Hazard Mater.*, 56 (1997) 247-256.
- [7] M. Dolores Bermejo, F. Fdez-Polanco, M.J. Cocero, Effect of the Transpiring Wall on the Behavior of a Supercritical Water Oxidation Reactor: Modeling and Experimental Results, *Ind. Eng. Chem. Res.*, 45 No. 10 (2006) 3438-3446.
- [8] C. Aymonier, P. Beslin, C. Jolival, F. Cansell, Hydrothermal oxidation of a nitrogen-containing compound: the fenuron, *J. Supercrit. Fluids*, 17 (2000) 45-54.
- [9] K.M. Benjamin, P.E. Savage, Supercritical water oxidation of methylamine, *Ind. Eng. Chem. Res.*, 44 (2005) 5318-5324.
- [10] L.P.D. Pinto, L. Freitas dos Santos, R.C.D. Santos, B. Al-Duri, Kinetics of quinoline in a continuous supercritical water oxidation plug-flow reactor- part 2", *J. Chem. Tech. Biotechnol.*, 81 No. 6 (2006) 919 - 926.
- [11] L.P.D. Pinto, L. Freitas dos Santos, R.C.D. Santos, B. Al-Duri, "Supercritical Water Oxidation of Quinoline in a Continuous Plug-flow Reactor: Effect of Key Operating Parameters- Part 1", *J. Chem. Tech. Biotechnol.*, 81 No. 6 (2006) 912 - 918.

[12] B. Al-Duri, Y. Oshima, Investigation of the Destruction of Concentrated N- Containing Hydrocarbons by Supercritical Water oxidation (SCWO), issf2009. Available at:

<http://www.isasf.net/fileadmin/files/Docs/Arcachon/oraux/c29-CO152%20Al-Duri-ISSF2009-Bordeaux.pdf>

[13] I. Kings, Supercritical Water Oxidation as a technology for the treatment of model and industrial wastewaters: Reaction kinetics and reactor configurations, PhD Thesis, The University of Birmingham, 2013.

[14] M.B. Garcia-Jarana, I. Kings, J. Sanchez-Oneto, J.R. Portela, B. Al-Duri, Supercritical water oxidation of nitrogen compound with multi-injection of oxygen", *J. Supercrit. Fluids*, 80 (2013) 23-29.

[15] B. Al-Duri, F. Alsoqyani, and I. Kings, "Supercritical water oxidation for the destruction of hazardous waste: better than incineration", available at:

<http://rsta.royalsocietypublishing.org>, *Phil. Trans. R. Soc.* A373: 20150013.

- [16] P. Cabeza, B. Al-Duri, M.D. Bermejo, M.J. Cocero, Experimental results of the co-oxidation of ammonia and isopropanol in supercritical water in a tubular reactor, *Chem. Eng. Res. Des.*, 92 (2014) 2568-2574.
- [17] B. Al-Duri, L. Pinto, N.H. Ashraf-Ball, R.C.D. Santos, Thermal abatement of nitrogen-containing hydrocarbons by non - catalytic supercritical water oxidation (SCWO), *J. Mater. Sci.*, 43 No. 4 (2008) 1421 - 1428.
- [18] O.O. Osibo, Removal of Nitrogen Containing Hydrocarbons from Wastewater by Catalytic and Non-Catalytic Hydrothermal Oxidation, in Sub- and Supercritical Conditions, PhD thesis, The University of Birmingham, 2011.
- [19] C. Zhong, G.W. Wang, F.J. Yun, S. Yang, H.Z. Chen, Y.J. Xu, Reaction pathways in the supercritical water oxidation of typical alcohols, *J. Fuel Chem. & Technol.*, 42 No. 3 (2014) 343 - 349.
- [20] J. Abelleira; J. Sánchez-Oneto; J.R. Portela; E.J. Martínez de la Ossa, Kinetics of supercritical water oxidation of isopropanol as an auxiliary fuel and co-fuel, *Fuel*, 111 (2013) 574 - 583.

[21] T. Oe, H. Suzugaki, I. Naruse, A.T. Quitain, H. Daimon, K. Fujie, Role of methanol in supercritical water oxidation of ammonia, *Ind. Eng. Chem. Res.*, 46 (2007) 3566 – 3573.

List of Figure Captions:

Figure 1 - Structural formula of DBU.

Figure 2 - Schematic diagram of the SCWO apparatus.

Figure 3a - GCMS analysis chart of DBU.

Figure 3b - Compounds detected by GCMS during SCWO of DBU.

Figure 4 - Proposed reaction pathway of the SCWO of DBU.

Figure 5 - %TOC removal of DBU versus time at various temperatures, using $nSR = 1$, $C_o = 5$ mM.

Figure 6 - Concentrations of N-species released from SCWO of DBU versus temperature, at $t = 6$ s.

Figure 7 - Yield % of NH_4^+ , NO_3^- , NO_2^- and N_2 versus temperature at $t = 6$ s.

Figure 8 - %TOC removal of DBU versus time at various nSR values, at $T = 400$ °C, $C_o = 5$ mM.

Figure 9 - Concentrations of N-species released from SCWO of DBU versus nSR , at $t = 6$ s.

Figure 10 - Mechanism of SCWO of IPA.

Figure 11 - Comparative plot of %TOC removal of DBU with and without IPA, versus temperature, at selected residence times, with $nSR = 1$, $C_o = 5$ mM.

Figure 12 - Comparative plot of yield % of N-species released from SCWO of DBU versus temperature, with and without IPA, at $t = 6$ s, with and without IPA. $nSR = 1$, $C_o = 5$ mM.

Figure 13 - Comparative plot of %TOC removal of DBU with and

without IPA, versus nSR at selected residence times at 400 C, $C_o = 5$ mM.

Figure 14 - Comparative plot of yield % of N-species released from SCWO of DBU versus temperature, with and without IPA, at $t = 6s$, with and without IPA. $nSR = 1$, $C_o = 5$ mM.

Figure 15 - The effect of $[IPA_o/DBU_o]$ ratio on TOC removal % for several residence times, at 400°C, $nSR=1$, and $C_o = 5$ mM DBU.

Figure 16 - The effect of $[IPA_o/DBU_o]$ ratio on yield % of N species at $t = 6s$, 400°C, $nSR=1$, and $C_o = 5$ mM DBU.

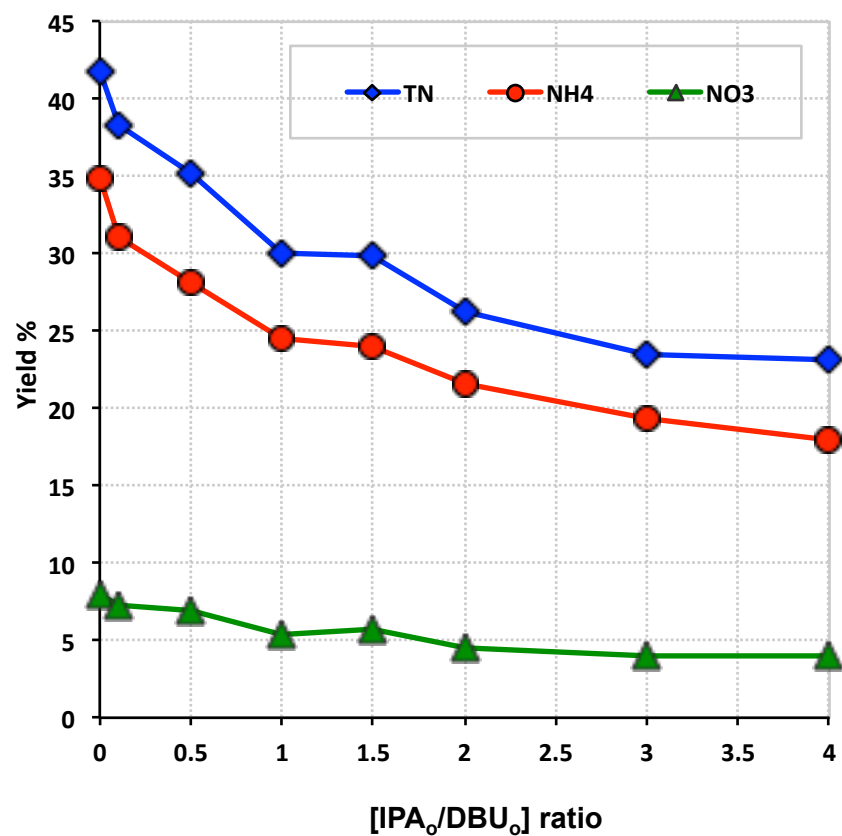


Figure 16 – The effect of [IPA₀/DBU₀] ratio on yield % of N species at $t = 6s$, 400°C , $nSR=1$, and $C_0 = 5 \text{ mM DBU}$.

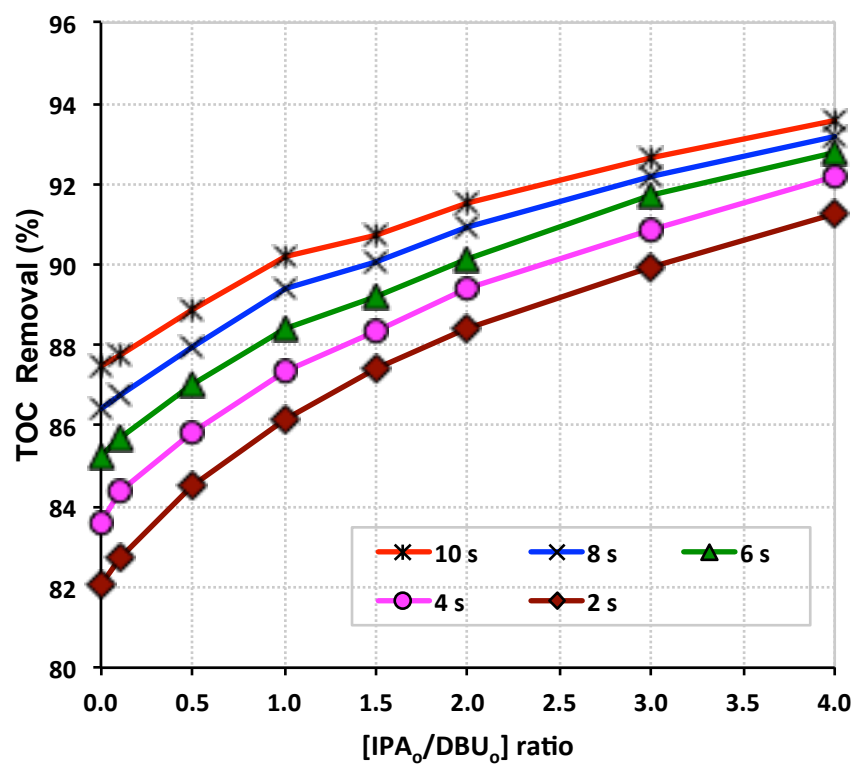


Figure 15 – The effect of [IPA₀/DBU₀] ratio on TOC removal % for several residence times, at 400°C, $nSR=1$, and $C_o = 5$ mM DBU.

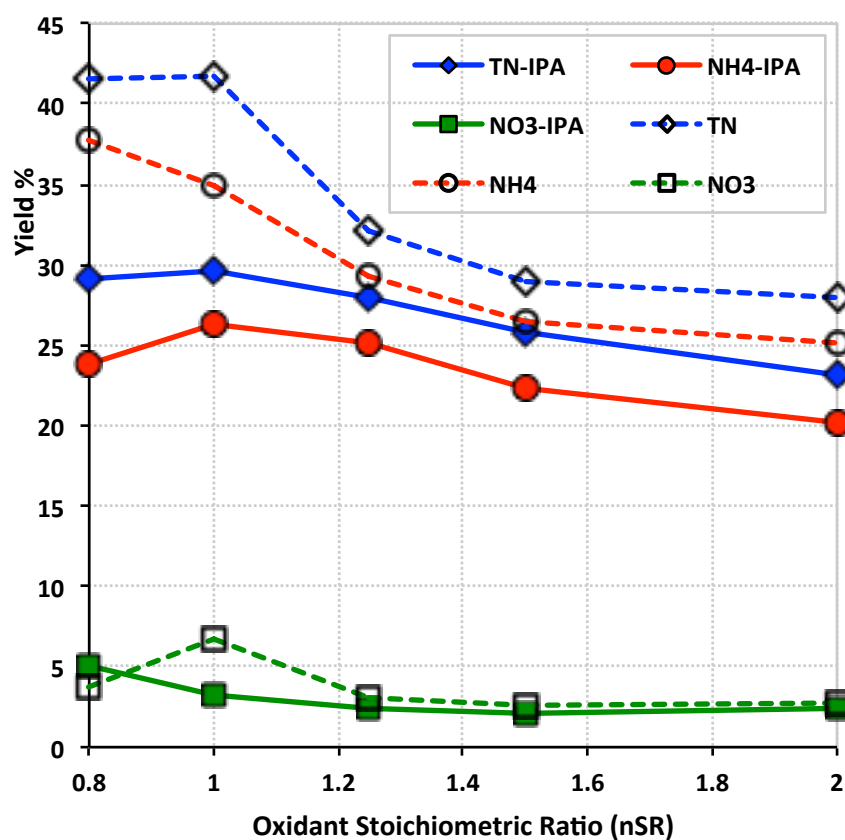


Figure 14 - Comparative plot of yield % of N-species released from SCWO of DBU versus temperature, with and without IPA, at $t = 6s$, with and without IPA. $nSR = 1$, $C_o = 5$ mM.

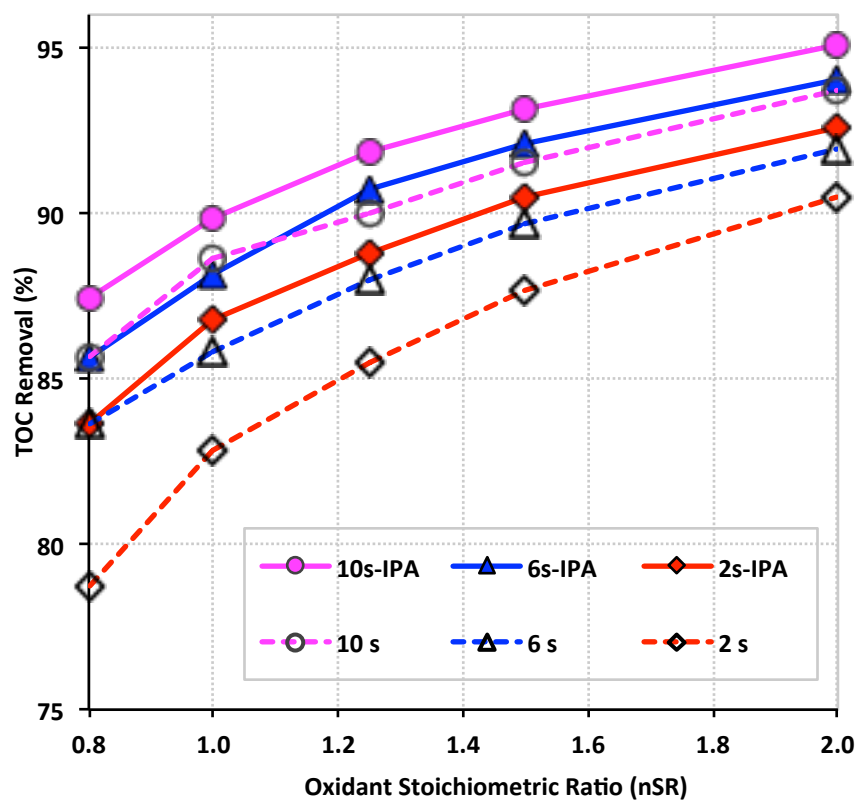


Figure 13 - Comparative plot of %TOC removal of DBU with and without IPA, versus nSR at selected residence times at 400°C, $C_0 = 5$ mM.

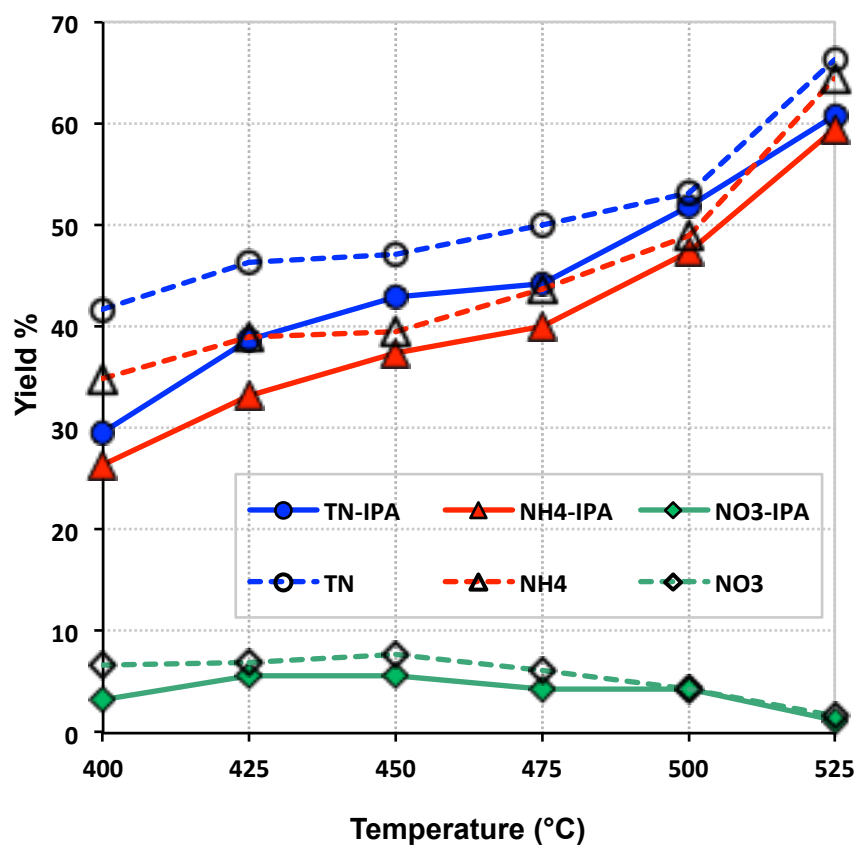


Figure 12 – Comparative plot of yield % of N-species released from SCWO of DBU versus temperature, with and without IPA, at $t = 6\text{s}$, with and without IPA. $n\text{SR} = 1$, $C_o = 5\text{ mM}$.

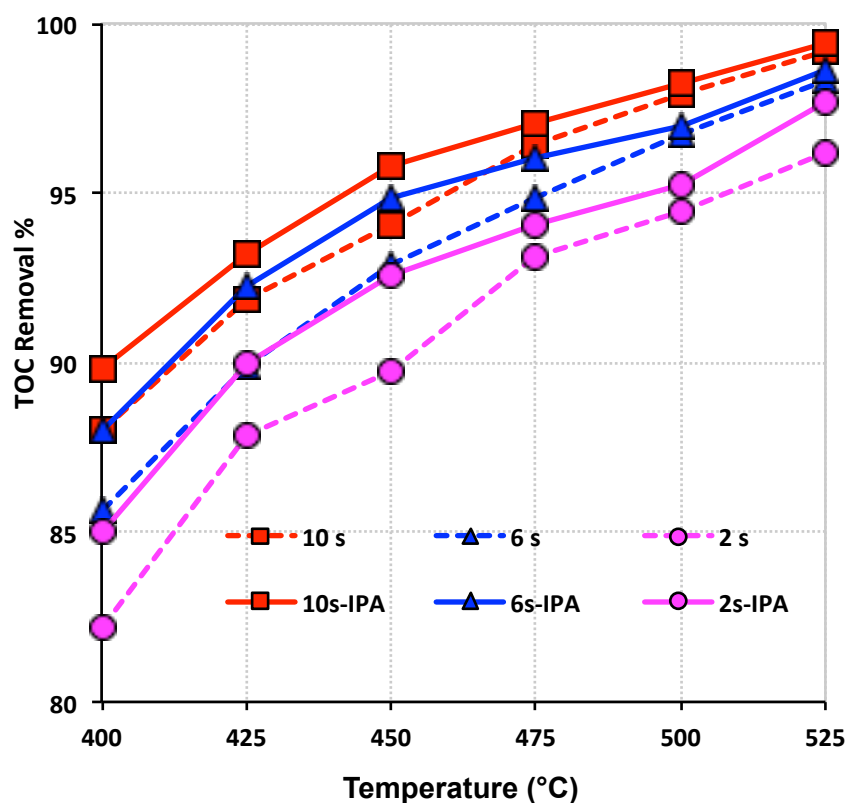


Figure 11 – Comparative plot of %TOC removal of DBU with and without IPA, versus temperature, at selected residence times, with $nSR = 1$, $C_o = 5$ mM.

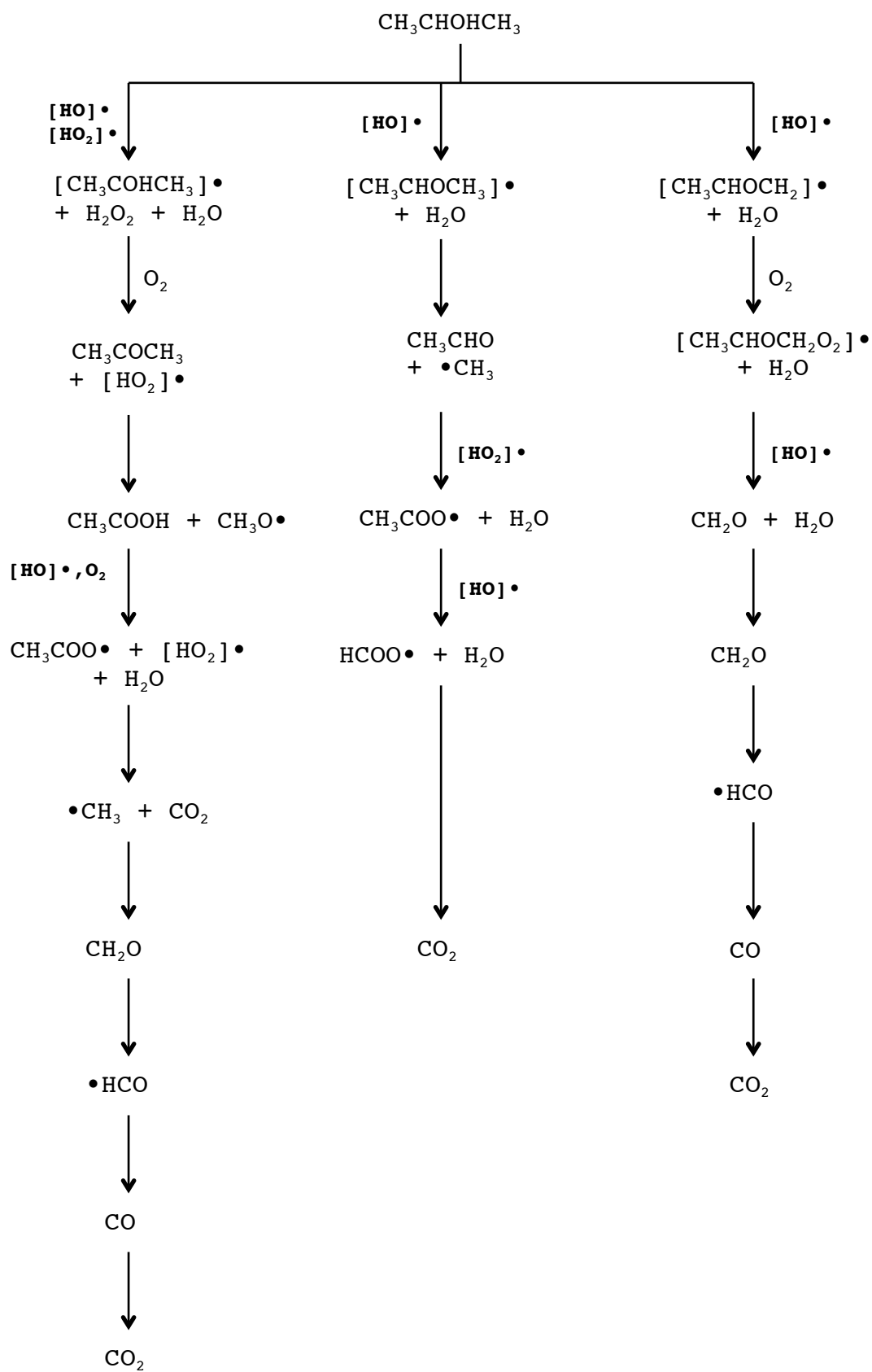


Figure 10 – Mechanism of SCWO of IPA.

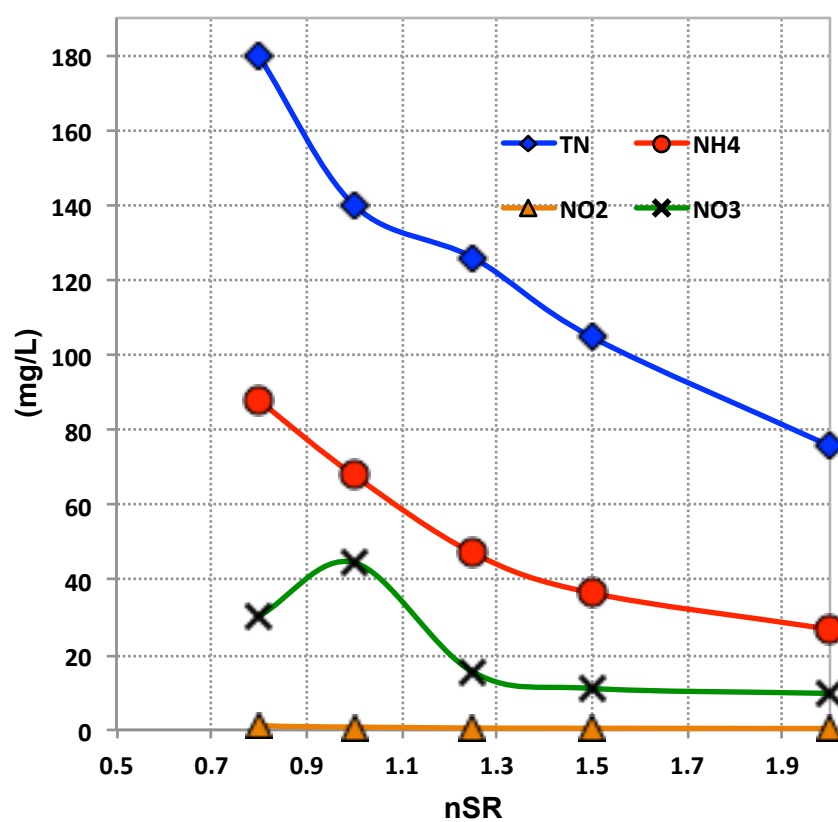


Figure 9 – Concentrations of N-species released from SCWO of DBU versus nSR, at t = 6 s.

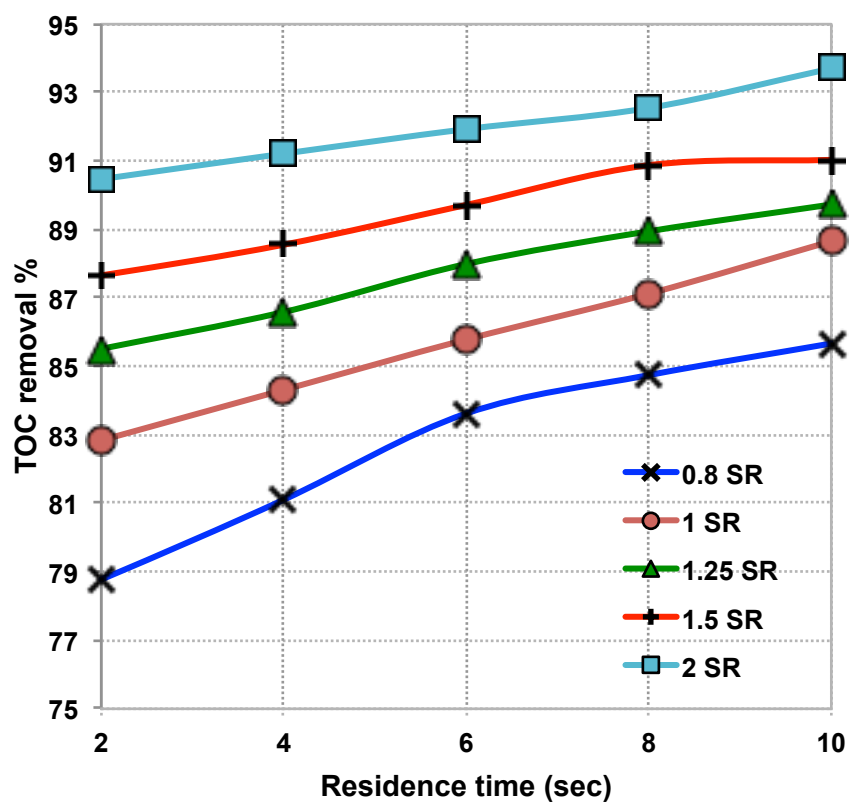


Figure 8 – %TOC removal of DBU versus time at various nSR values. $T = 400\text{ }^{\circ}\text{C}$, $C_o = 5\text{ mM}$.

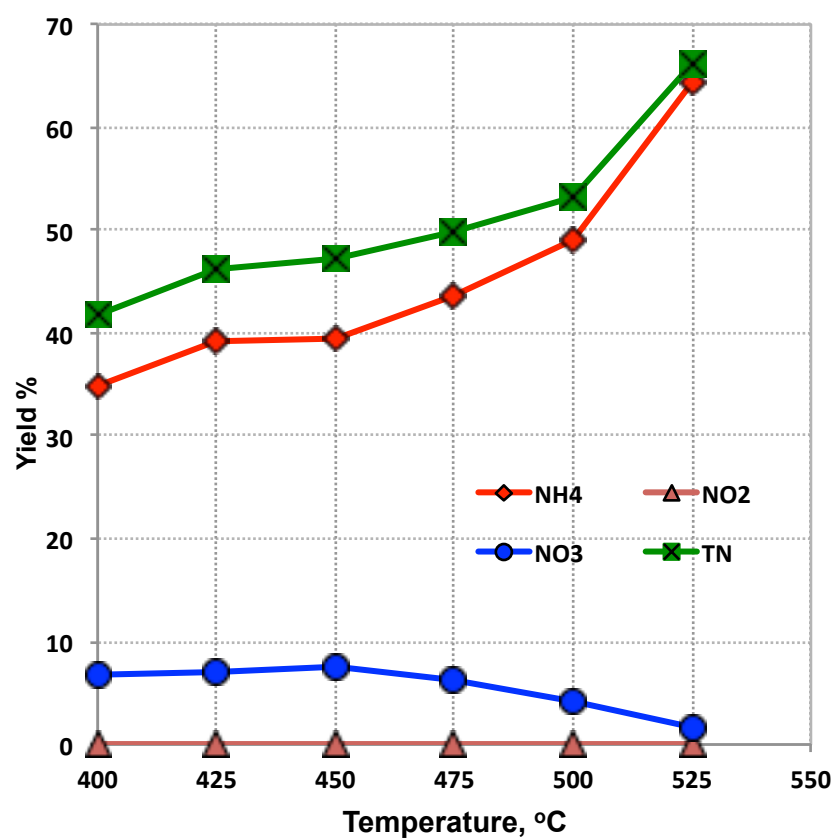


Figure 7 – Yield % of NH_4^+ , NO_3^- , NO_2^- and N_2 versus temperature, at $t = 6$ s.

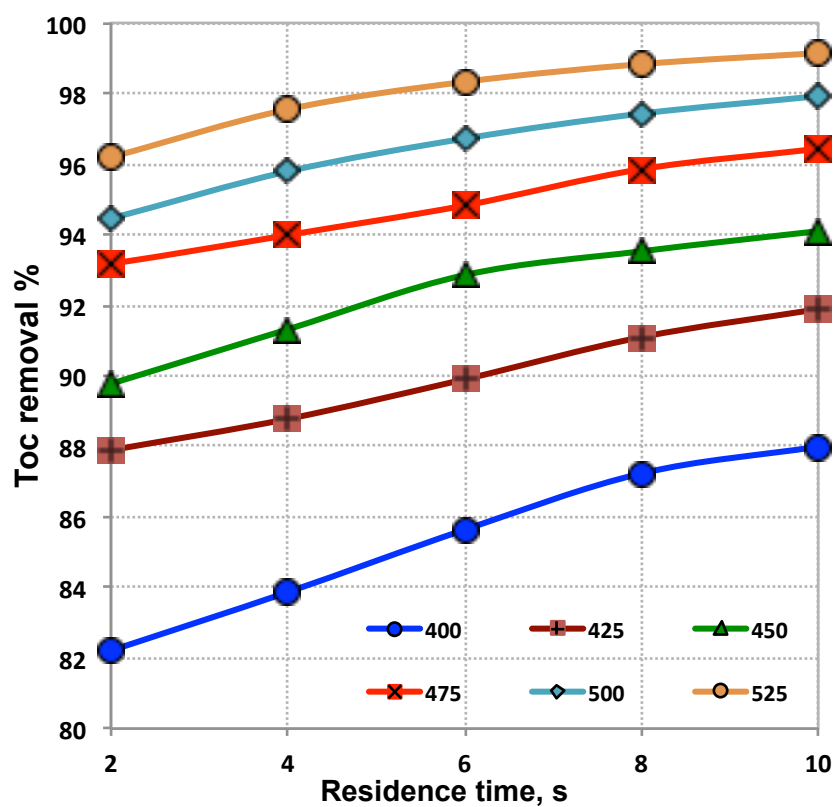


Figure 6 - %TOC removal of DBU versus time at various temperatures, using $nSR = 1$, $C_o = 5$ mM.

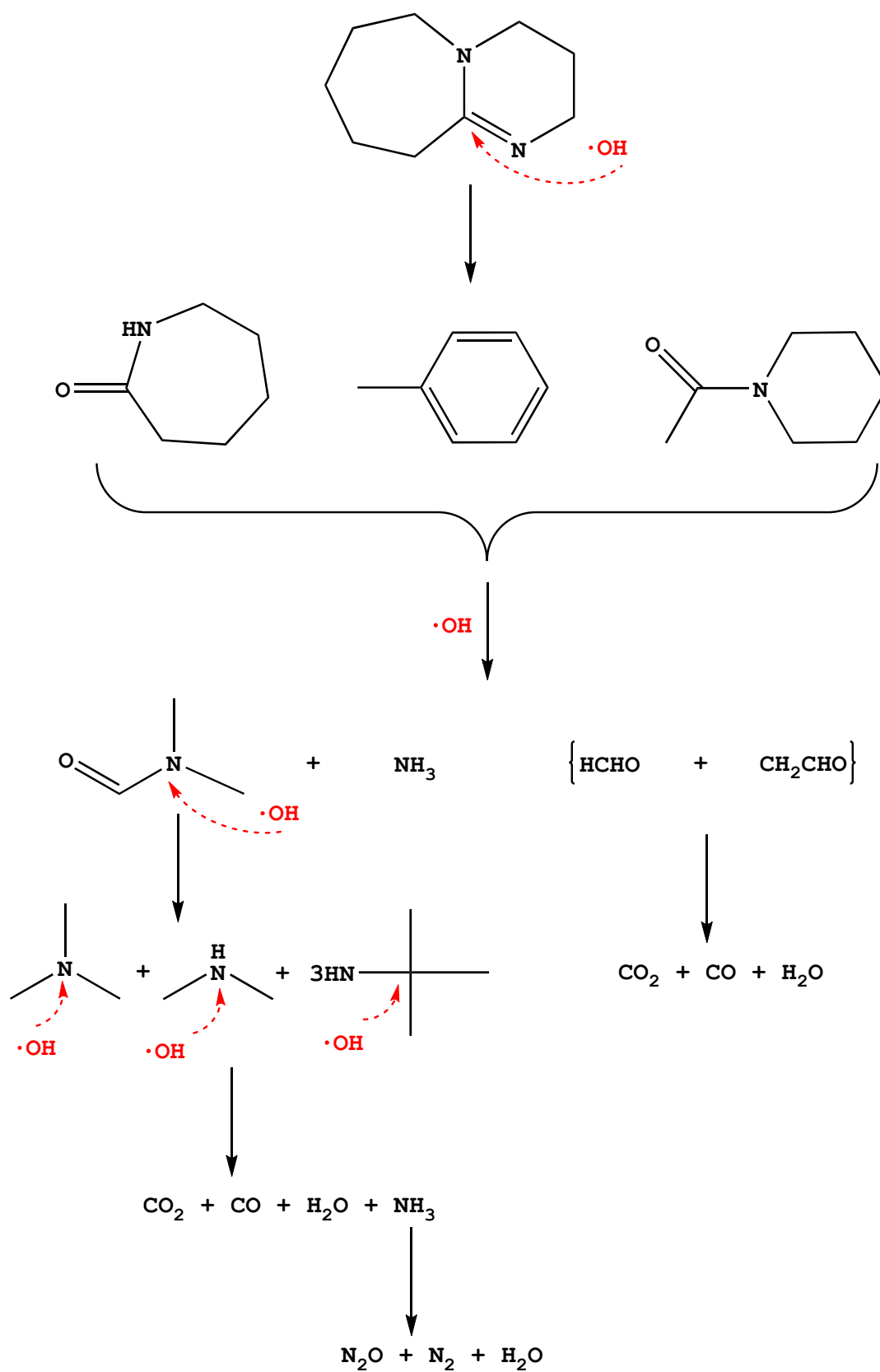


Figure 5 – Proposed reaction pathway of the SCWO of DBU.

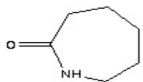
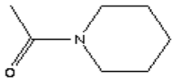
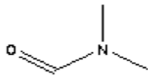
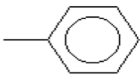
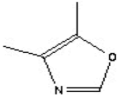
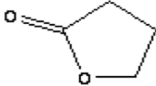

Detected Compound	Molecular Weight	Molecular Structure
Caprolactam	113	
1-Acetyl-Piperidine	127	
N,N-dimethyl-Formamide	73	
Toluene	92	
4,5, Dimethyl-Oxazole	97	
Butyrolactone	86	
Pentanenitrile	83	

Figure 4 – Compounds detected by GCMS during SCWO of DBU.

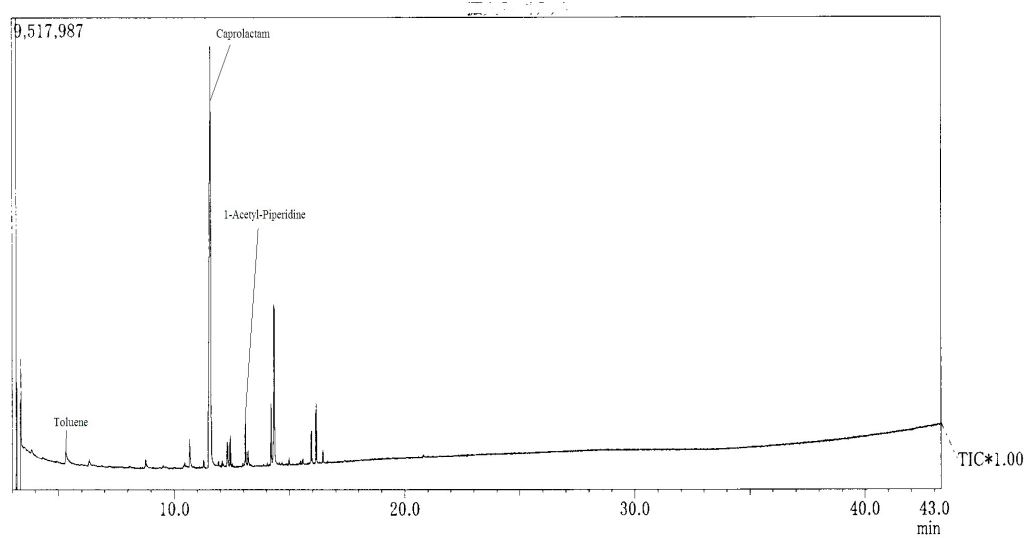


Figure 3 – GCMS analysis chart of DBU.

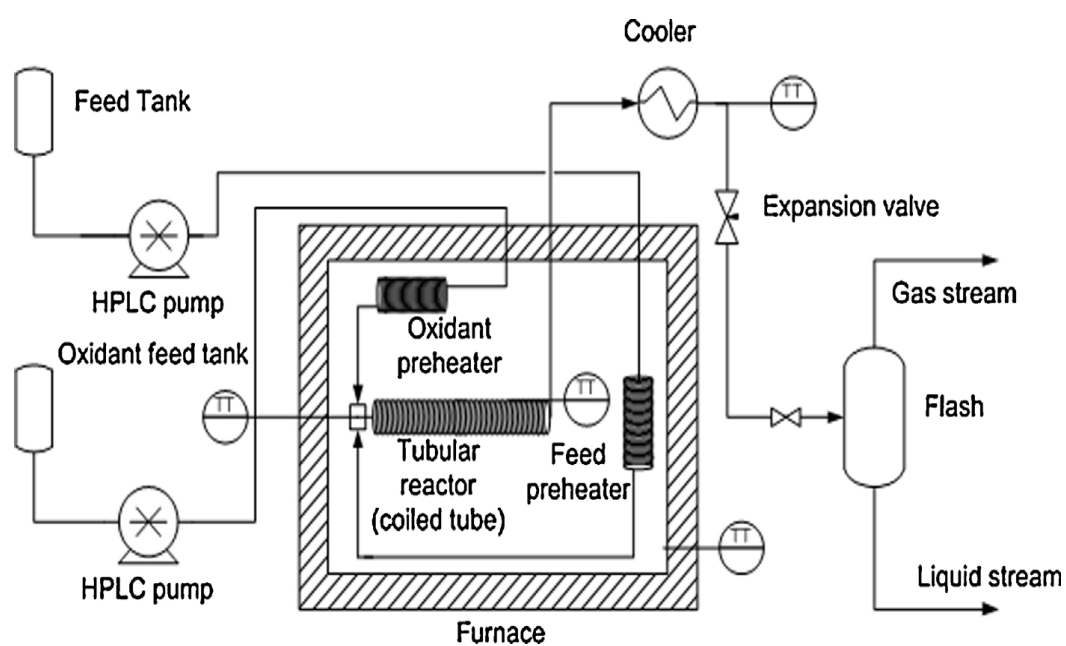


Figure 2 – Schematic diagram of the SCWO apparatus.

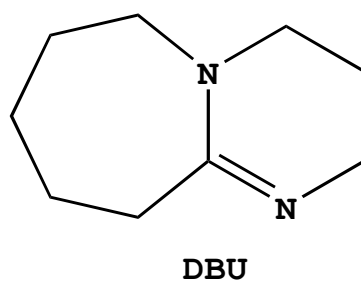
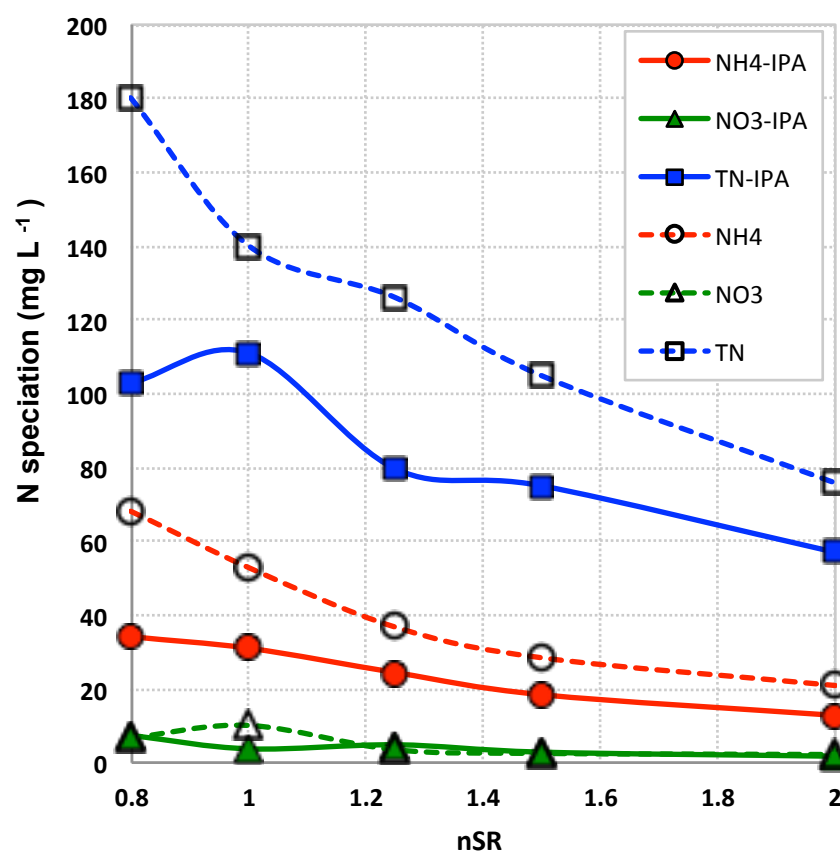


Figure 1 – Structural formula of DBU.

Graphical Abstract

Concentration profiles (mg L⁻¹) for N-compounds released during SCWO of DBU, as function of oxidant ratio (nSR). Reactions were conducted at T = 400°C, C_{o,DBU} = 5 mM; with and without IPA as co-fuel.