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Supercritical Water Oxidation (SCWO) for the Removal of N - Containing Heterocyclic Hydrocarbon Wastes; Part II: System Kinetics

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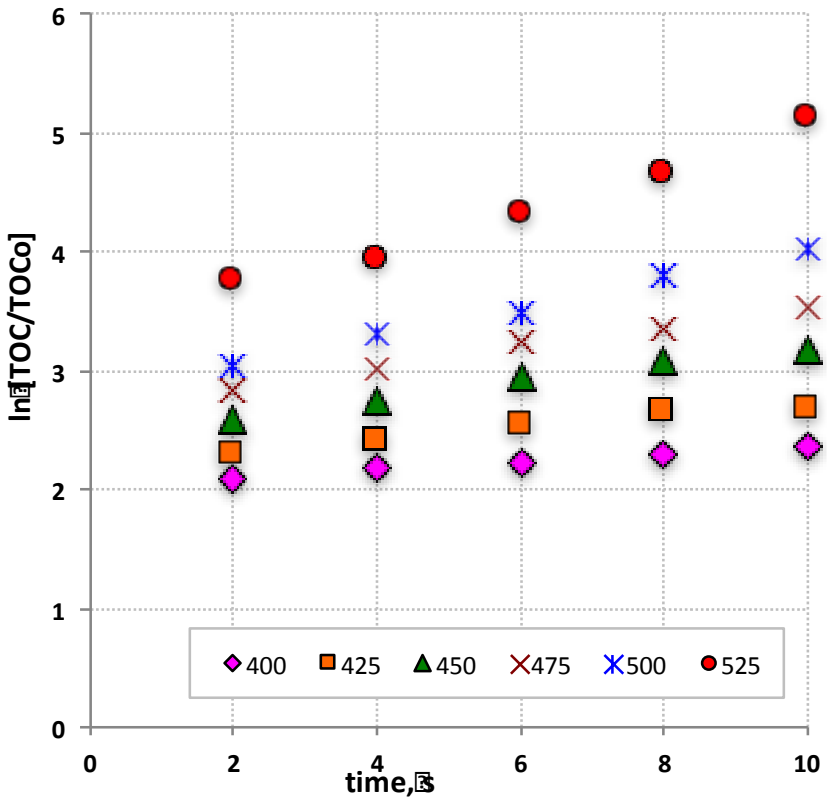
Graphical Abstract

Highlight Graph



Application of the *pseudo first order approximation* kinetic model to System II (IPA + DBU) at several temperatures. C_0 = 5 mM, *nSR* = 1.0, IPA_0/DBU_0 = 1.0.

Highlights

- SCWO kinetics of DBU and NH_4^+ feedstock was studied using IPA and IPA-free systems.
- *Pseudo First order and global power law* models, described all systems under study.
- IPA-free systems had variable O_2 dependence and lower *k* values, than IPA systems.

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- Adding IPA to NH_4^+ feedstock enhanced removal to larger extent than residual NH_4^+.

Abstract

This work investigated supercritical water oxidation (SCWO) of DBU $(C_9H_{16}N_2)^{++}$ 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 – 10mM 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.

Keywords

Hazardous waste, SCWO, kinetics, co-oxidation, IPA, Ammonia

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

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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[1] Digest of Waste and Resource statistics [1] have shown that in 2014-2015, 8m tonnes of hazardous waste were treated by incineration and 7m tonnes were sent to landfill, as shown in Figure 1.

Figure 1

[1] Department of Environment, Food & Rural Affairs

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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.

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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 model and found the latter to better fit their data. On the other hand, Shimoda *et al.* [11] investigated the SCWO kinetics at 25MPa, 530°C and $[NH_3]_0$ = 2.9-3.0mm/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.

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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, 35w%) 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 12m plug-flow SS316 reactor of 1/16" diameter (0.6mm ID) and 3.07mL volume. Oxidant and organics were separately pumped and pre-heated, then mixed in a cross-

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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:

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, $[DBU]_0$=5mM & $[IPA]_0/[DBU]_0$=1.*

[*] *T=400°C, nSR=1, & $[IPA]_0/[DBU]_0$=1.*

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

[$] *T=400°C, nSR=1, $[DBU]_0$=5mM.*

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Table 2: Experimental conditions of SCWO of ammonia at 25 MPa in System III (IPA-free) and System IV (with IPA).

Variable	**Range**
Temperature (°C)[+]	400, 450, 500, 550
Initial Ammonium concentration (mM)	10
Oxidant ratio (n SR)	0.8, 1.0, 1.25, 1.5
Initial IPA concentration (mM)	1.0, 5.0, 10.0, 15, 20, 30, 40
$[IPA]_0/[NH_4^+]_0$	0.1, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0
Residence time (s)	2, 4, 6, 8, 10

[+] *nSR=1,* $[NH_4^+]_0$*=10mM &* $[IPA]_0/[NH_4^+]_0$*=1.*

[*] *T=450°C, nSR=1, &* $[IPA]_0/[NH_4^+]_0$*=1.*

[++] *T=450°C,* $[NH_4^+]_0$*=10mM, &* $[IPA]_0/[NH_4^+]_0$*=1.*

[$] *T=450°C, nSR=1,* $[NH_4^+]_0$*=10mM.*

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 [18], thus will be summarised below. The *pseudo first order* approximation is given by Eq. (1) and (2):

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

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

Where k_0 (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:

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

The power b is evaluated from Eq. (4) and (5):

$$ln\left([TOC]/_{[TOC]_0}\right) = k[O_{2,0}]^b t \quad (4)$$

Plotting ln ($[TOC]/[TOC]_0$) versus t for a series of reactions at different initial oxygen concentrations $[O_{2,0}]$ gives the slope values of $k[O_{2,0}]^b$. According to the rule of natural logarithms:

$$ln\left(k[O_{2,0}]^b\right) = lnk + b\, ln[O_{2,0}] \quad (5)$$

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Therefore, plotting $\ln(k[O_{2,0}]^b)$ versus $\ln[O_{2,0}]$ facilitates evaluating b as the slope.

4. Results and Discussion

4.1 Pseudo-First Order Approximation

Figures 2 shows the application of *pseudo-first order approximation* to System I:

Figure 2

IPA addition showed some influence on TOC % removal at various temperatures. In effect, this agrees with the experimental results of Part I [16], which showed that IPA addition had a minor influence on TOC % removal. Figure 3 shows the analysis of data to evaluate k_0 and E_a.

Figure 3

This gave Eq. (6) and (7) for systems I (DBU) and II (DBU + IPA), respectively:

$$ln\left(\frac{[TOC]}{[TOC]_0}\right) = 1.79x10^2 exp\left(\frac{-46703}{8.31T}\right)t \quad (6)$$

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$$ln\left(\frac{[TOC]}{[TOC]_0}\right) = 8.50x10^2 exp\left(\frac{-56638}{8.31T}\right)t \quad (7)$$

Table 3 – Reaction rate constants for SCWO of DBU in systems I and II, at various temperatures with $[DBU]_0$ = 5mM, P = 25 MPa, nSR = 1, $[IPA]_0/[DBU]_0 = 1$.

	System I		System II	
Temperature, °C	k, s^{-1}	Ln k	k, s^{-1}	Ln k
400	0.051	-2.976	0.0331	-3.408
425	0.0516	-2.964	0.0505	-2.986
450	0.0697	-2.663	0.0742	-2.601
475	0.0839	-2.478	0.0872	-2.439
500	0.1229	-2.096	0.1212	-2.110
525	0.1864	-1.680	0.174	-1.749

Table 3 displays the reaction rate constant k at the investigated system temperatures, which showed expected increase with temperature. Based on TOC removal, IPA addition did not have much influence on the reaction rate constant. Compared to SCWO of pure IPA at 400°C, Abeillera *et al.* [19] obtained k values of 0.0395 and 0.0068 s^{-1} in a two-step

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pseudo-first order reaction kinetic model in excess oxygen at 25 MPa. The present work is consistent with the fast step where k = 0.0331 s^{-1} for system II at 400°C. Overall, IPA addition increased E_A and k_0 by 20% and threefold respectively. The increased number of species and free radicals, and the diversity of intermediate species are bound to increase the collision frequency and interactions within the system. As a cyclic amidine DBU might have affinity for interaction with alcohols [20] in reactions like kinetic resolution, which would increase the favourability of degrading DBU in the presence of IPA. However, nitrogen data and analyses are also required for further understanding of N behaviour in the presence and absence of alcohol.

4.2 The Global Power Model

Figures 4 and 5 show the application of Eq. (4) to systems I, and II respectively:

Figure 4

Figure 5

Subsequently, Eq. (5) was applied and the result is shown in Figure 6 and Eq. (8a), (8b) and (9):

Figure 6

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$$-\frac{d[TOC]}{dt} = 1.79x10^2 exp\left(-46703/_{8.31T}\right)[TOC][O_2]^{0.097} \quad [O_{2,0}] \leq 1SR \qquad (8a)$$

$$-\frac{d[TOC]}{dt} = 1.79x10^2 exp\left(-46703/_{8.31T}\right)[TOC][O_2]^{0.299} \quad [O_{2,0}] > 1SR \qquad (8b)$$

$$-\frac{d[TOC]}{dt} = 8.50x10^2 exp\left(-56638/_{8.31T}\right)[TOC][O_2]^{0.534} \quad (9)$$

Results demonstrate a varied dependence on $[O_{2,0}]$ between the oxidant-deficient and oxidant-rich conditions. At low oxidant dosages, fewer free radicals (HO• and HO_2•) would be released, and thermal degradation is suggested to dominate the reaction, forming nitro groups that drive SCWO [9] more than the oxidant free radicals. This could obscure the influence of oxygen, giving rise to an almost *zero* order. However, more detailed pathway investigations are required to confirm the hypothesis. For *nSR > 1.0* the value of *b* is within the range of other works [15]. On the other hand, Eq.9 shows strong dependence of system II on the oxygen concentration, also supported by experimental work [16]. Also, the reaction rate constant increased by almost fourfold, proving the positive influence of IPA. Coexistence of IPA and DBU does enhance SCWO of both species due to the formation of extra free radicals [16] propagating a chain reaction, enhanced by the nitro groups formed due to DBU-IPA interaction [8].

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4.3 Effect of IPA on N Destruction and Speciation in DBU

In order to gain an insight into removal of aqueous ammonia (NH_4^+), this work investigated (i) intermediate ammonia released during SCWO of DBU, and (ii) ammonia as feedstock.

For residual ammonia (intermediate of SCWO of DBU) previous experimental work showed that IPA addition did increase N destruction [16]. For both systems I and II, total liquid nitrogen (TN) and NH_4^+ yield % increased with temperature due to increased thermal degradation. At 400°C, IPA addition caused about 33% and 23% reduction in TN and NH_4^+ yield %, indicating further oxidation to gas. On the other hand increasing *nSR* did not appreciably affect the TN and NH_4^+ profiles, which was attributed to the relatively low temperature of 400°C. However IPA addition (at *nSR = 0.8*) remarkably reduced TN and NH_4^+ yield % by 31 and 37% respectively, and the trend continued through the *nSR* range. This strongly suggests the reaction shift towards gaseous N, which would be predominantly N_2. No NO_x would be expected.

4.4 Influence of IPA on NH_4^+ SCWO Using Ammonia as Feedstock

In order to focus on ammonia as a particular recalcitrant the influence of IPA on the destruction of NH_4^+ as feedstock was investigated. The effects of temperature and oxidant ratio were investigated. Due to safety and analytical issues, the effect of initial NH_4^+ concentration was not investigated. It is worth mentioning that at the current operation

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conditions total nitrogen (TN) mostly consisted of NH_4^+ with negligibly low concentrations of NO_3^- and NO_2^- therefore data samples for TN were analysed for all residence times (2 – 10*s*), while for NH_4^+ only samples at *t = 6 s* were analysed.

4.4.1 Effect of temperature

Over the considered temperature range, Figures 7 and 8 show that SCWO of *10mM* ammonium solution was enhanced by around 77%, giving nearly 90% ammonium removal in less than *2s*.

Figure 7

Figure 8

As a first approximation, SCWO of Ammonia was assumed to follow *pseudo-first order* with respect to N, and Figure 9 shows the application of Eq. (2) to systems III and IV. For the analysis it was assumed that IPA and oxidant were both in excess, and a *zero* order with respect to both respectively was assumed.

Figure 9

Eq. (10) and (11) are the rate equations for systems III (NH_4^+) and IV (NH_4^+ + IPA) respectively:

$$ln\left({[TN]}/{[TN]_0}\right) = 0.375exp\left({-22{,}245}/{8.31T}\right)t \quad (10)$$

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$$ln\left({[TN]}/{[TN]_0}\right) = 3.647exp\left({-52064}/{8.31T}\right)t \quad (11)$$

Table 4 – Reaction rate constants for SCWO of NH_4^+ in systems III and IV, at various temperatures with $[NH_4^+]_0$ = 10mM, P = 25 MPa, nSR = 1, $[IPA]_0/[NH_4^+]_0$ = 1.

	System III		System IV	
Temperature, °C	k, s^{-1}	Ln k	k, s^{-1}	Ln k
400	0.0006	-7.419	0.0068	-4.991
450	0.0013	-6.645	0.0099	-4.615
500	0.002	-6.215	0.0113	-4.483
550	0.0034	-5.684	0.0145	-4.234

Figure 9 and Table 4 show that IPA addition had a significant influence on the reaction rate constant k (in terms of E_A and k_0. IPA addition greatly enhanced the rate of NH_4^+ oxidation. This is attributed to the high heating value of IPA ($\Delta H^{\emptyset}$ = 2021 kJ/mol), and the rapid release of extra free radicals, which propagated a chain free radical reaction. Webley *et al.* [10] investigated the SCWO of ammonia, methanol and their mixture at a wide spectrum of system conditions. At

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530°C and $[NH_4^+]_0$ of 2.6mM and *nSR = 1.0*, they obtained *k* value of 0.01 s^{-1} (log *k* = -2.00). In comparison, Table 4 shows *k* values at the same temperature range to be 0.002 s^{-1} (log *k* = -2.7) and 0.0034 s^{-1} (log *k* = -2.5) at 500°C and 550°C respectively. The difference might be attributed to the lower concentrations and excessive oxidant used by Webley and co-authors [10]. However, unlike the current work methanol addition did not show significant influence on ammonia oxidation. This can be linked to (i) the lower heat of oxidation of methanol ($\Delta H^{\emptyset}$ = 729 kJ/mol), (ii) the much reduced number of free radicals in comparison to IPA, and (iii) the relatively low temperature with respect to the recalcitrant ammonia.

4.4.2 Effect of oxidant ratio

Figures 10 and 11 show that increased oxidant ratio and IPA addition both improved SCWO of ammonium solution. In Figure 11 at *t = 6 s*, raising the *nSR* ratio from *1* to *1.5* improved TN% (ammonia) removal by around 16%. On the other hand, IPA addition enhanced TN% removal by a significant 66% raising it to over 85% N removal at 450°C.

Figure 10

Figure 11

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The effect has been observed in literature [20, 14] and was attributed to the fast formation of HO• and HO_2•. The instability of the intermediate free radicals and their affinity for alcohol causes them to react much faster with alcohol than water or oxygen, producing even more free radicals and thus accelerating the conversion of both organics and ammonia:

$$H\text{-}C_3H_6OH + O_2 \rightarrow C_3H_6OH + HO_2\bullet \qquad (12)$$

The presence of alcohol in ammonia oxidation allow the occurrence of HO_2• reactions with alcohols that produce H_2O_2 during the early stages of oxidation through the hydrogen abstraction reactions [21, 22] which in turn generates more radicals:

$$C_3H_6OH + HO_2\bullet \rightarrow C_3H_6O + H_2O_2 \qquad (13)$$

$$H\text{-}C_3H_6OH + HO_2\bullet \rightarrow C_3H_6OH + H_2O_2 \qquad (14)$$

Finally, the formation of H_2O_2 during the oxidation of alcohols can increase the production of HO• radicals [23, 24].

$$R\bullet + H_2O_2 \rightarrow 2OH\bullet \qquad (15)$$

4.4.3 Effect of IPA/NH_4^+ ratio

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Figure 12 shows the effect of increasing the $[IPA]_0/[NH_4^+]_0$ ratio on % N removal, when ammonia is an intermediate of DBU oxidation and when used as feedstock respectively. It shows that 98% ammonia removal was achievable at 450°C when IPA/NH_4^+= 4. This is indeed a promising outcome in terms of solving the problem of ammonia in industrial aqueous effluents.

Figure 12

On the other hand, although N removal from DBU feedstock was improved, it did not exceed 80%. It suggests that under the experimental conditions, IPA might use much oxidant before ammonia is released. Therefore it is advisable to feed the IPA at more than one injection port in N-containing hydrocarbon systems.

5. Conclusion:

The present work showed the positive influence of adding IPA as co-fuel on the SCWO kinetics, especially on the conversion of recalcitrant ammonia to benign gaseous product (N_2). The kinetics of TOC % removal was also improved albeit to a lesser extent, while oxygen consumption was more affected.

When fresh ammonium solution was used as feedstock, dramatically improved ammonium removal was achieved to a better extent than residual ammonia, suggesting that multi-injection of alcohol along the reactor body might be the way forward. It would enhance treatment of N containing species, by 'regulating' the usage of oxidant and IPA during SCWO.

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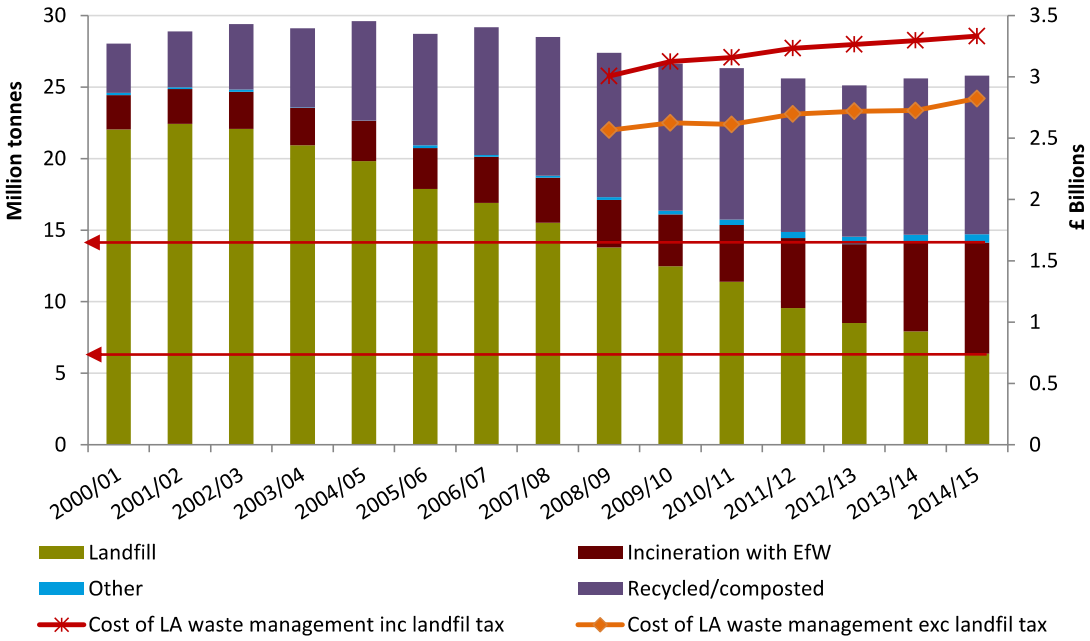

Figure 1 – Local authority (LA) collected waste management in England between 2000/01 and 2014/15 (courtesy of Digest of Waste and Resource Statistics – 2016 Edition).

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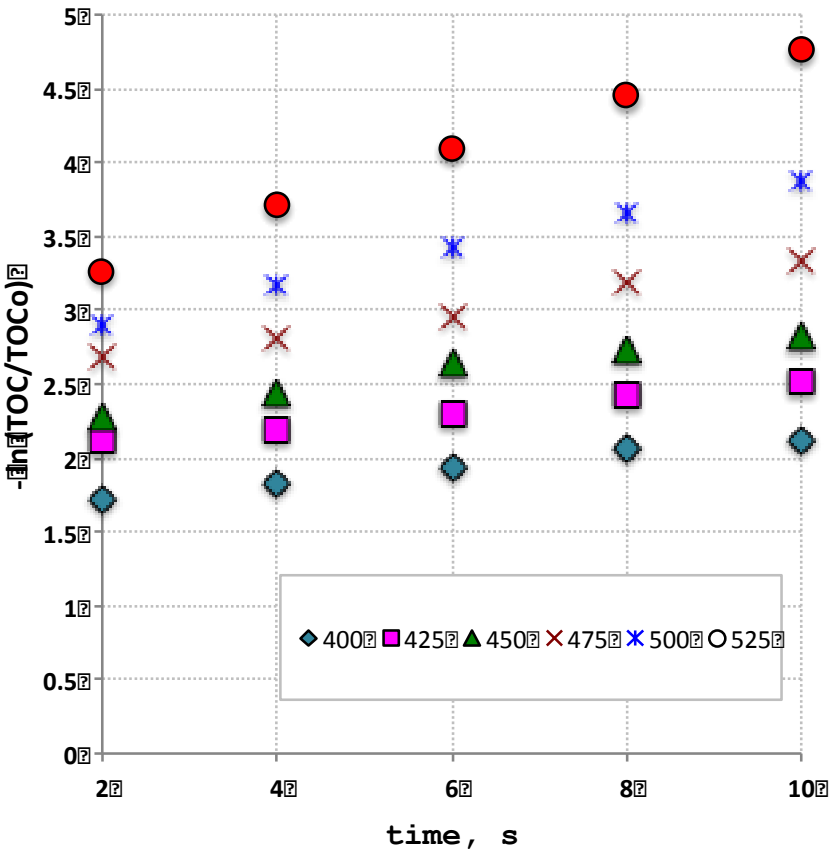

Figure 2 - Semi logarithmic plot of [TOC/TOC$_o$] versus time for System I, at several temperatures (°C), C_0 = 5mM, *nSR* = 1.0.

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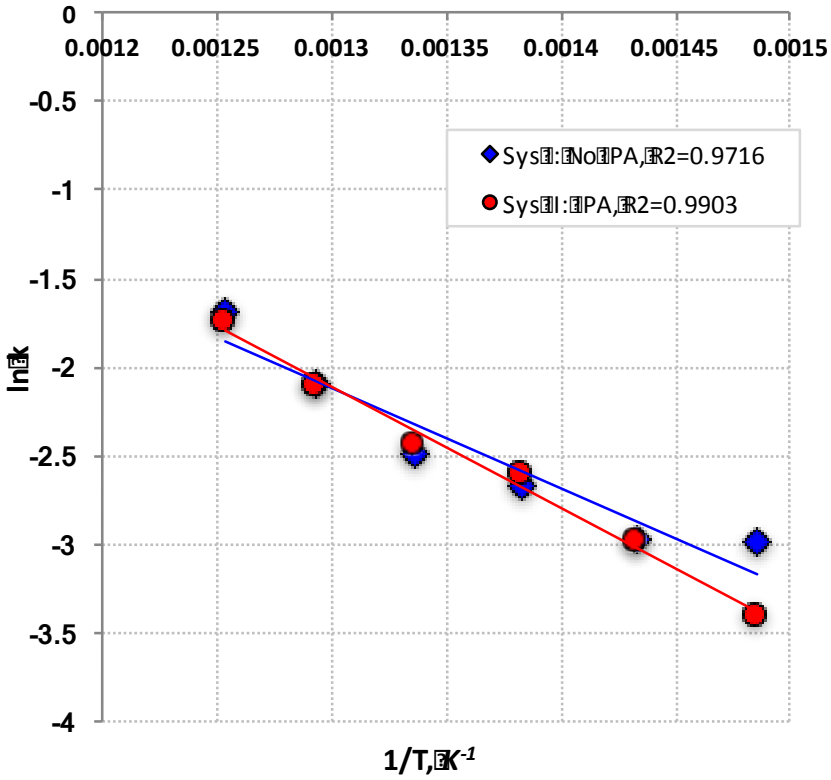

Figure 3 – Pseudo-First Order model analysis for systems I and II.

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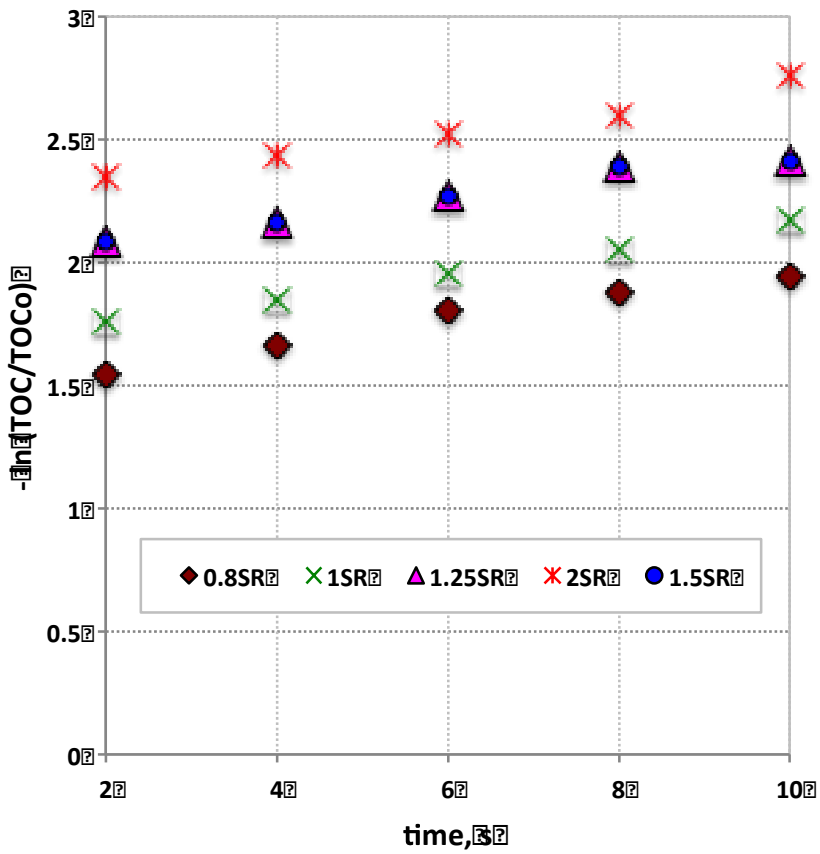

Figure 4 - Semi logarithmic plot of TOC conversion versus time in System I, at several oxidant ratios (*nSR*), C_0 = 5mM, T = 400°C.

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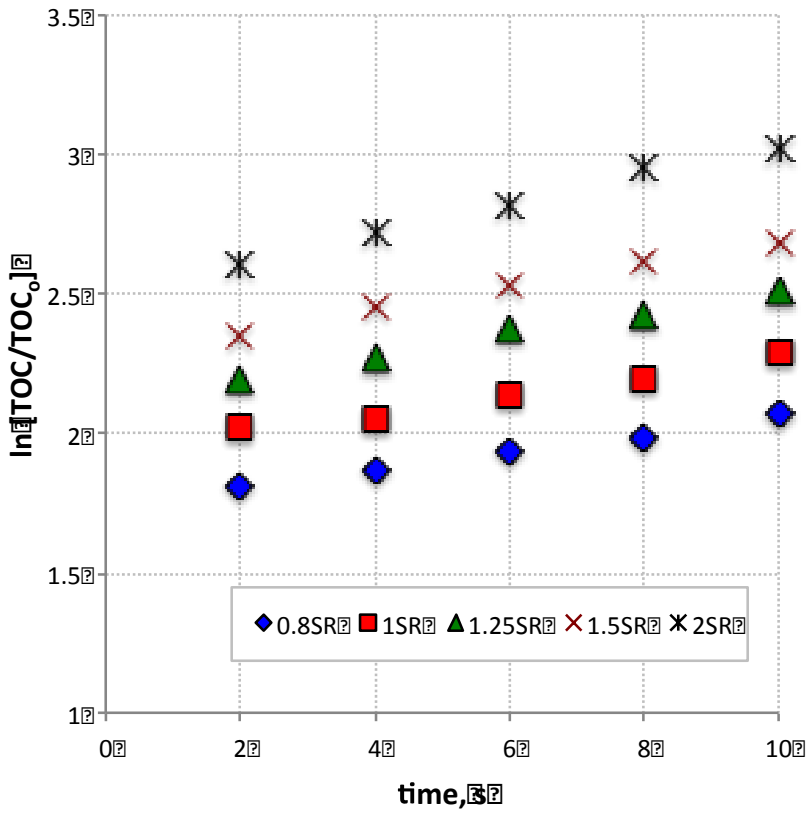

Figure 5 - Semi logarithmic plot of TOC conversion versus time in System II, at several oxidant ratios (*nSR*), C_0 = 5mM, T = 400°C.

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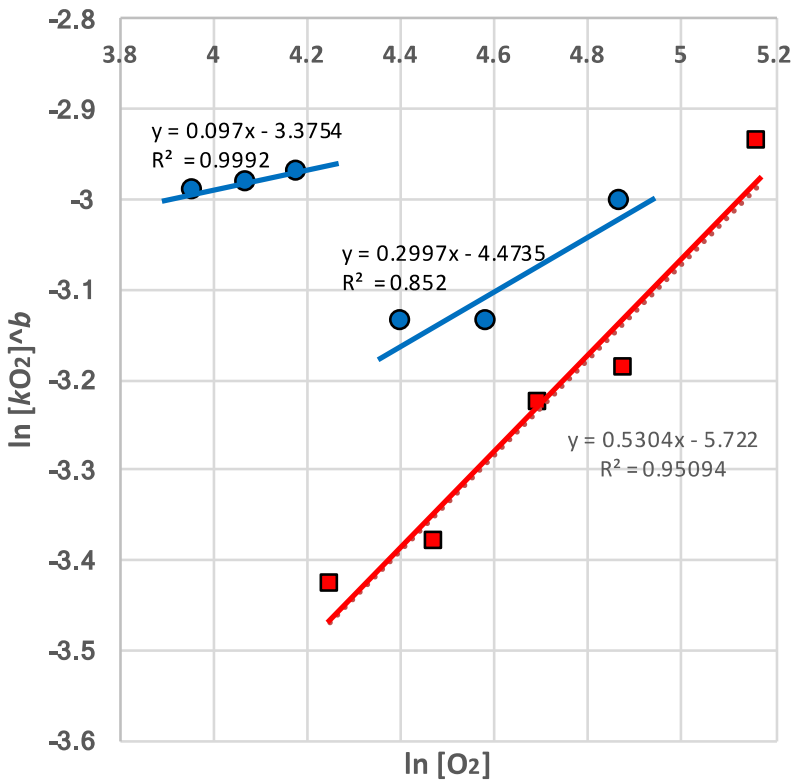

Figure 6 – Logarithmic plot of reaction rate constant ln $[kO_2]^b$ versus oxygen concentration ln$[O_2]$.

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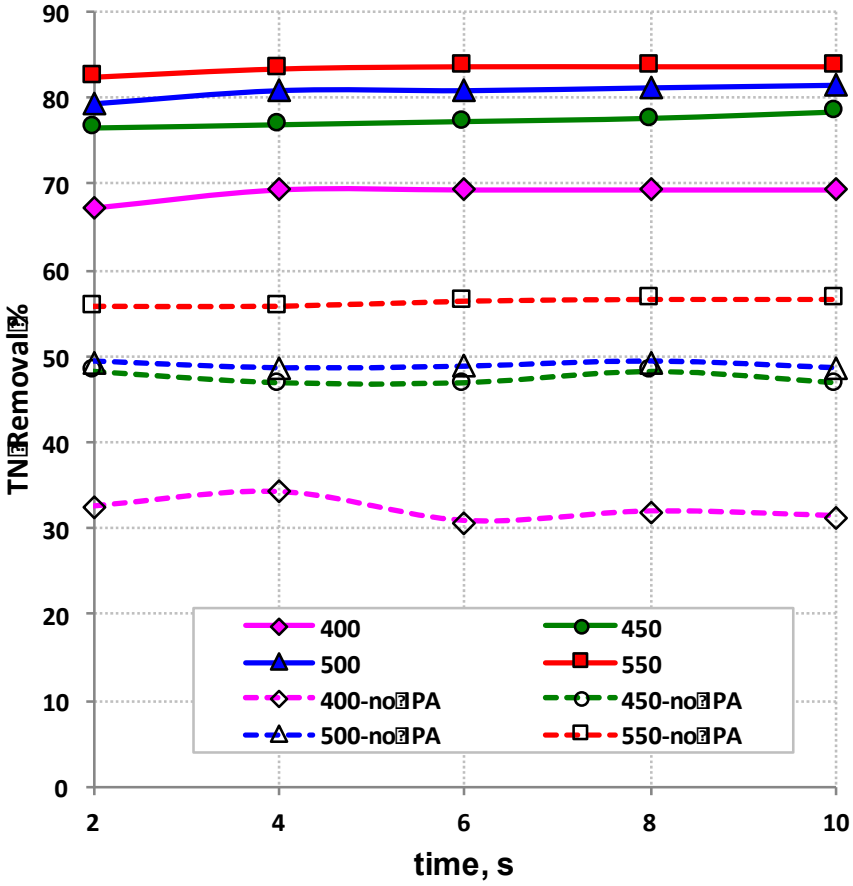

Figure 7 – SCWO of ammonia (C_0 = *10mM*) as function of time, at several temperatures in Systems III & IV using nSR = 1.

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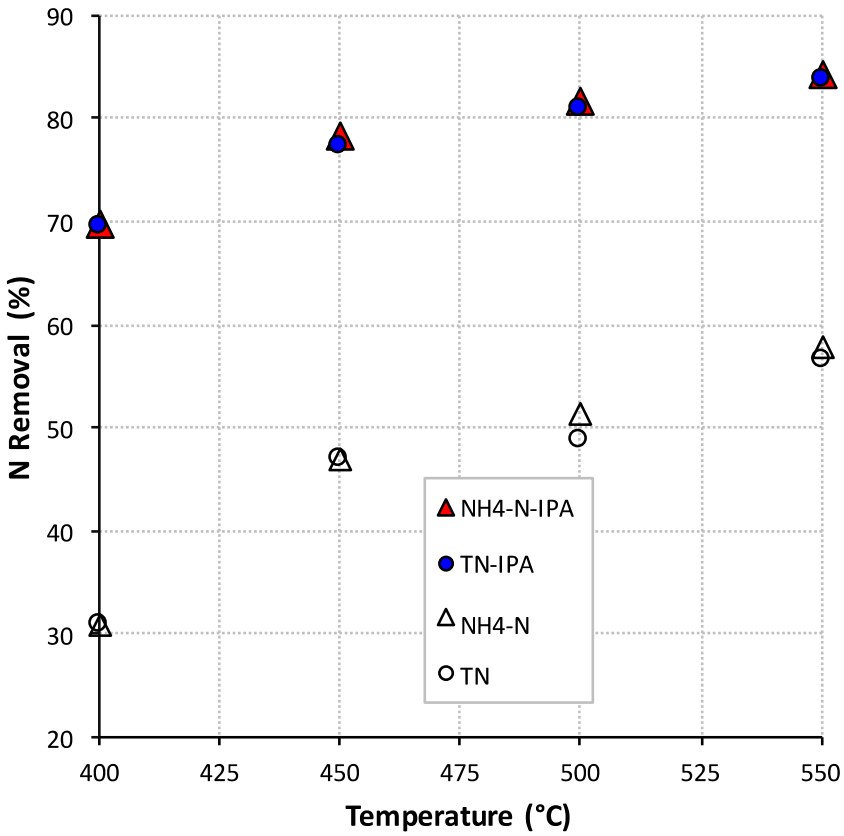

Figure 8 – SCWO of Ammonia (C_0 = *10mM*) as function of temperature at *nSR = 1.0 and t = 6s*, in Systems III & IV.

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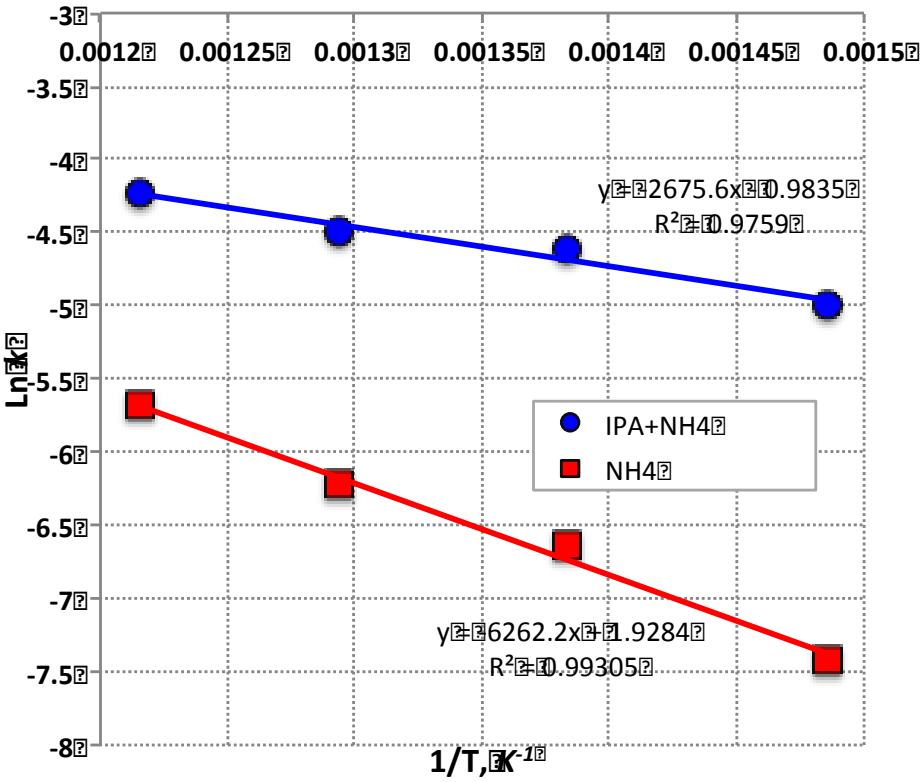

Figure 9 – *Ln k* versus *1/T* in Systems III and IV.

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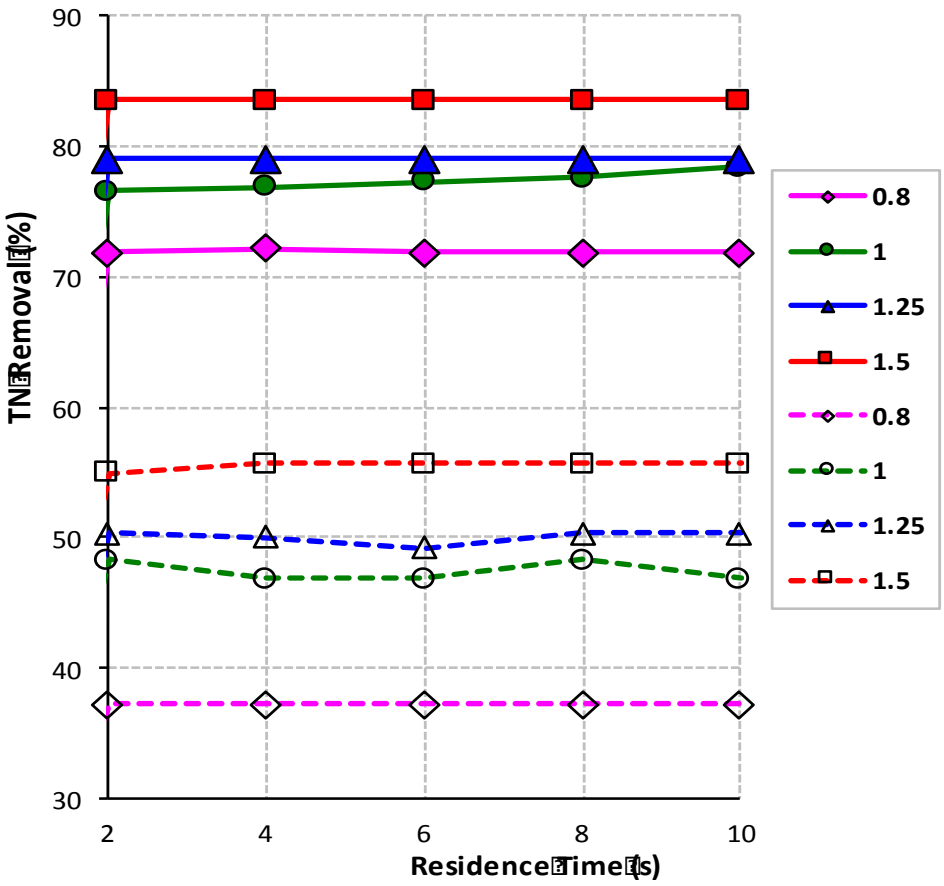

Figure 10 – SCWO of Ammonia (C_0 = *10mM*) as function of time using several *nSR* values at *450°C*, in Systems III & IV.

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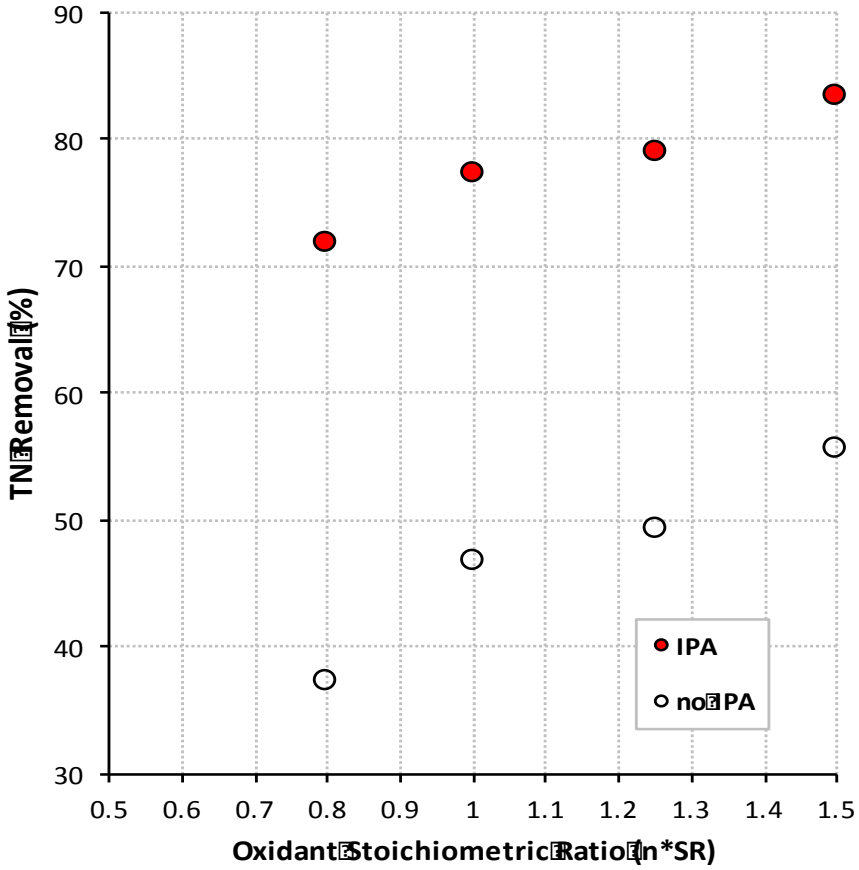

Figure 11 – SCWO of Ammonia (C_0 = *10mM*) as function of nSR at *450°C and t = 6s*, in Systems III & IV.

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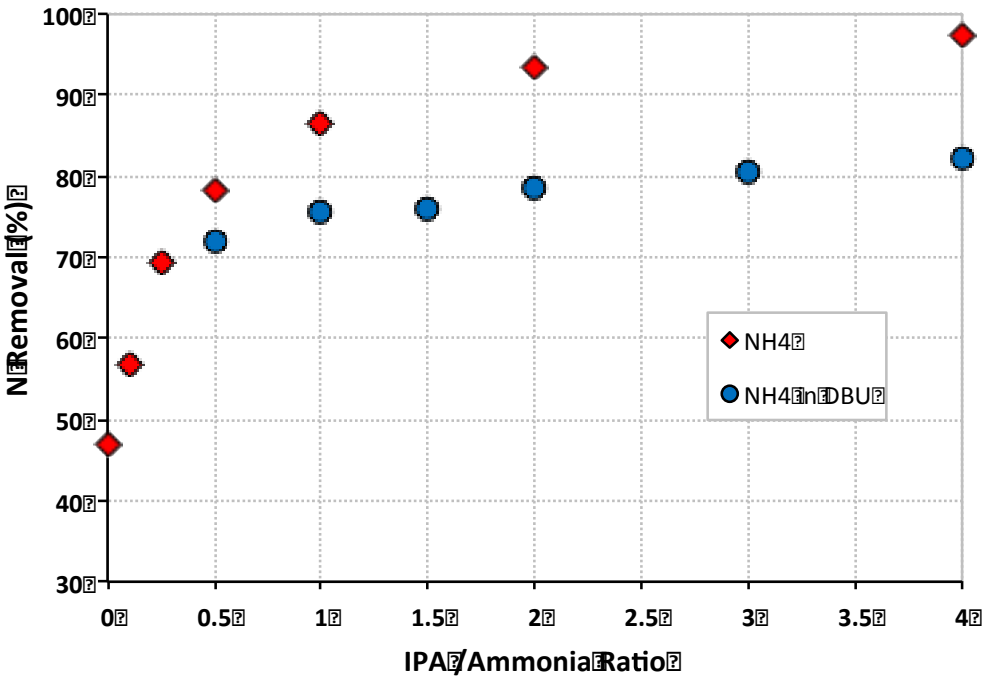

Figure 12 – Comparative plot of N removal % as function of $[IPA]_0/[NH_4^+]_0$ ratio, at t = 6s, in systems II and IV.