

SUPERCRITICAL WATER OXIDATION (SCWO) FOR HAZARDOUS WASTE DESTRUCTION: ENHANCED REMOVAL OF DIMETHYL FORMAMIDE BY USING ISOPROPYL ALCOHOL (IPA)

*Bushra Al-Duri**, Iain Kings and Faihan Alsoqyani

School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UNITED KINGDOM. Email: B.Al-Duri@bham.ac.uk, FAX: +44 (0) 121 – 414 5324

ABSTRACT

This work is about supercritical water oxidation (SCWO) for the removal of hazardous hydrocarbons in wastewater, otherwise treated by incineration. It has been found that the addition of alcohol improves the hydrocarbon conversion; shifting the reaction towards final benign products. The compound under investigation is N, N Dimethylformamide (DMF) undergoing SCWO in the presence of isopropyl alcohol (IPA). Experimental investigations were carried out in a laboratory scale, continuous plug flow reactor, testing a range of temperatures (673 – 800K) at 25MPa, initial organic concentrations (1 – 20mM in reactor conditions), relative oxidant ratios (0.8 – 2 x SR), and alcohol/organic ratios (0.5 – 2.0). Results were expressed in terms of %TOC conversion; N species yield in liquid and gas, in addition to gas products.

It was found that the addition of IPA increases the TOC conversion, in addition to affecting the nitrogen speciation, especially towards production of N₂ gas as opposed to ammonium production. Kinetic investigations were conducted via *pseudo first order approximation* and *global rate approximation*. They showed that IPA addition reduced the activation energy of reaction due to the co-fuel effect of IPA.

INTRODUCTION

Nitrogen containing hydrocarbons constitute a class of hazardous wastewaters found in a broad range of effluents including petrochemical, pharmaceutical and medical wastes. The removal of such compounds from wastes have proved challenging compared to other hydrocarbons, due to the complexity of N-chemistry and the recalcitrant nature of ammonium (NH₄⁺), an intermediate that resists treatment even at high temperatures.

SCWO is the next generation of waste treatment techniques, which offers important advantages over the prevailing approach, namely incineration. The latter is highly energy intensive (>1300 K); produces deadly dioxins and NO_x compounds; and generates ashes, which have landfill usage implication. Furthermore, incineration becomes inefficient at organic concentrations < 40% (w/w). SCWO takes place at lower temperatures (673 – 800K); yields virtually no toxic emissions; produces minor quantities of solid products <3% and achieves > 99.9% TOC removal within very short reaction time (seconds to minutes). However, the removal of NH₄⁺ intermediates has proved to require oxidation at remarkably high temperatures [1], the use of catalysts [2], and/or the addition of some environmentally challenging compounds like nitric acid.

To further investigate SCWO of such class of hydrocarbons, DMF has been selected. DMF is an aliphatic amide, which is frequently used, as solvent in acrylic fibres and plastics

* Corresponding author

industries, therefore is likely to be present in a wide range of chemical effluents. Its destruction is an appropriate start to investigate more complex heterocyclic and aromatic structures like quinoline and DBU, typically found in pharmaceutical compounds [3].

MATERIALS AND METHODS

N, N-Dimethylformamide (C_3H_7NO) (99% pure) was investigated as an organic compound, while IPA (C_3H_7OH) (99% by weight) was the added alcohol, and hydrogen peroxide (35wt-% aqueous solution) was the oxygen source. All were supplied by Sigma-Aldrich. Figure 1 shows the experimental apparatus designed and constructed at the University of Birmingham (UK):

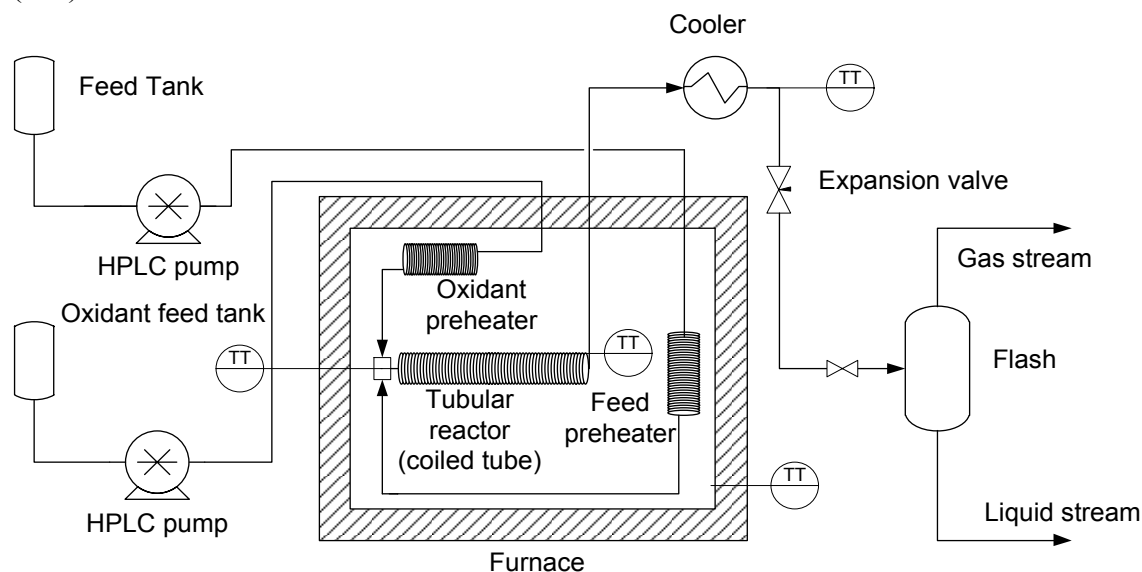


Figure 1: Laboratory scale SCWO rig.

Experiments were conducted in a 1/16" tubular reactor made of SS316 stainless steel, with 0.6mm ID and 12.53m long. The organic solution (DMF and IPA) and oxidant (H_2O_2) were pumped via HPLC pumps (Jasco PU-2086+) through 1/16" pipe preheaters (6 m long each), to a mixing cross before entering the reactor. The preheaters and the reactor were all placed inside an electric temperature-controlled furnace, where temperature was monitored and recorded (at the reactor inlet and outlet). The reactor effluent was cooled in a heat exchanger and de-pressurized via a manual GO55 back - pressure regulator, before the two phases were finally separated in a gas/liquid separator. Gas and liquid samples were collected for analysis using GC-TCD and TOC methods, respectively.

Experimental Conditions: Table 1 shows the range of experimental conditions investigated:

Table 1: Range of experimental conditions, all conducted at 25 MPa pressure.

Variable	Range
Temperature (K)	673 – 800*
Initial DMF concentration (mM)	1- 20 ⁺
Oxidant ratio (n SR)	0.8 – 2.0 [§]
IPA concentration (mM)	1 – 20 [£]
IPA / DMF ratio	0.1 – 2.0 [§]

* $C_{DMF}=10mM$, $C_{IPA}=10m$, $SR=1$; ⁺ $T=673$ K, $SR=1$, IPA/DMF ratio = 1.0; [§] $T=673$ K, $C_{DMF}=10mM$, $C_{IPA}=10m$, [£] $T=673$ K, $SR=1$, $C_{DMF}=10mM$; [§] $T=673$ K, $SR=1$.

RESULTS AND DISCUSSION

The Effect of Temperature: As expected the temperature has a positive effect in enhancing the SCWO of DMF.

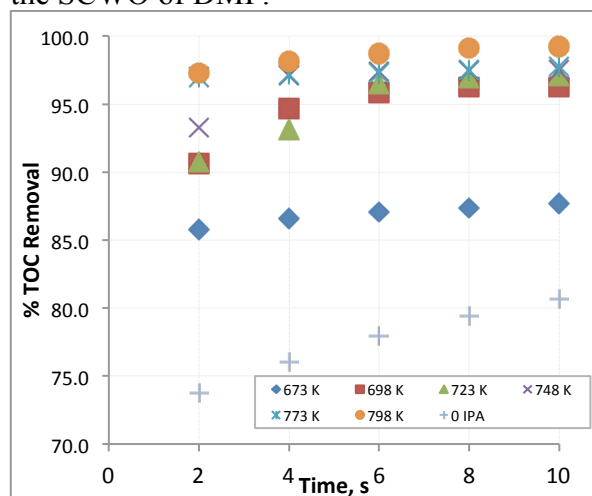


Figure 2: SCWO of 10 mM DMF using 1IPA/DMF ratio; 25 MPa; 1SR oxidant; at six temperatures.

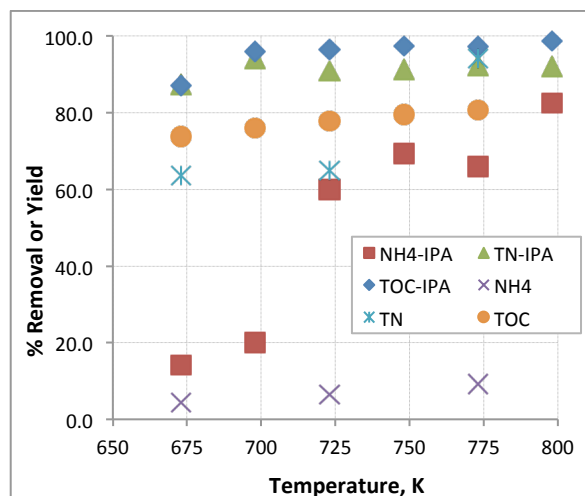


Figure 3: Effect of temperature on TOC removal, total N removal and ammonia yield, at t = 6s.

Compared to IPA free system, Figure 2 shows that addition of IPA improved %TOC removal by 16%, at the same conditions. As a general profile, the effect of temperature is more pronounced at shorter residence times, proving that most of the process takes place at the ‘front end’ of the reactor: over 85% TOC destruction takes place at t = 2s. This increases rapidly as the temperature increases by 25 K between 673 and 698 after which, it continues to improve but to less extent. This is attributed to the dramatic change in thermodynamic properties in this temperature range, leading to highly improved TOC removal. Figure 3 shows the %TOC removal, total N removal and % ammonia yield. The increase in ammonia yield with temperature is a sign of further destruction of other intermediates (tri-methylamine, and di-methylamine) to ammonia. Total N here represents that in the liquid phase; we therefore assume that total N removal is conversion towards N₂ gas therefore increased removal is highly favourable. Adding IPA has led to positive outcome for all species.

The Effect of Oxidant: Figures 4 and 5 show the effect of increasing the oxidant on %TOC and N removal, and % ammonia yield. Increasing the oxidant ratio has certainly improved the % TOC removal. Clearly, oxygen is the source of OH• free radicals that start the reaction. Due to the co-oxidation of alcohol with the organic, adding more oxidant continued to allow further improvement even to double the stoichiometric ratio, unlike IPA free system when oxidation did not improve beyond 1.2SR. Figure 5 shows improvement in total N removal but not much in ammonia yield. Addition of oxidant does not directly ‘shift the ammonia’. The latter needs significantly higher temperatures.

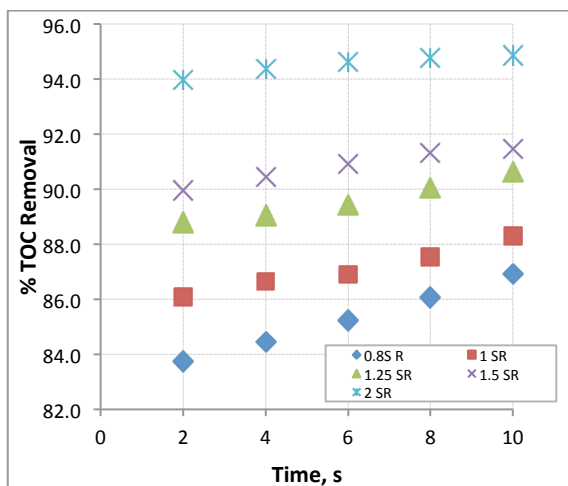


Figure 4: Effect of oxidant ratio on SCWO of 10mM DMF at 673 K, 1 IPA/DMF ratio.

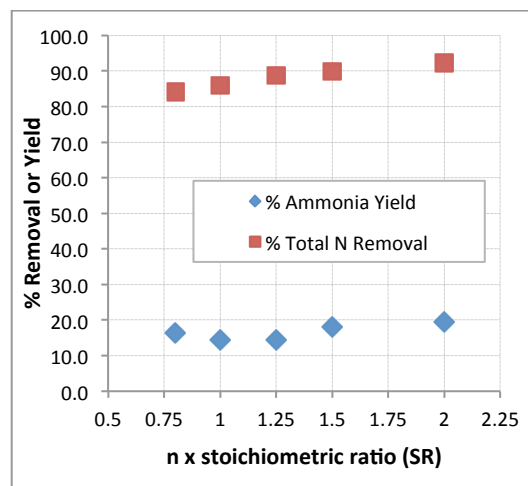


Figure 5: Effect of oxidant ratio of % yield of ammonia and % total N removal, at t = 6s.

The effect of IPA concentration: Figures 6 and 7 show the effect of increasing IPA concentration on improving the SCWO of DMF:

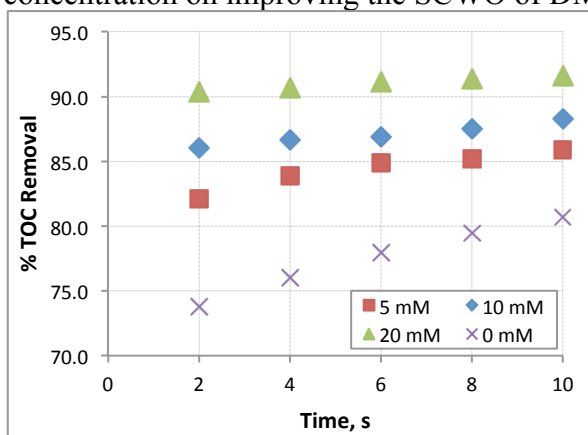


Figure 6: SCWO of 10mM DMF at 673K, 1SR adding 5, 10 and 20mM IPA.

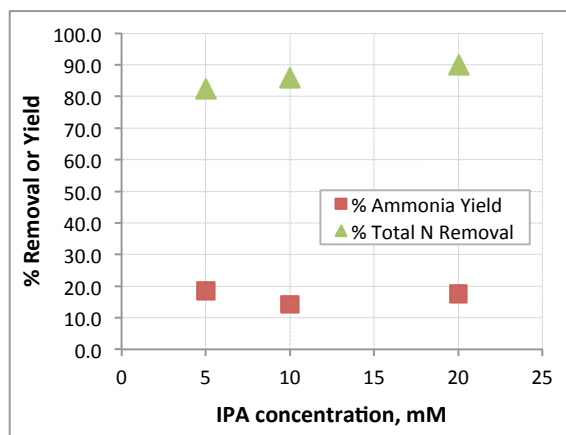


Figure 7: Effect of IPA concentration on total N removal and ammonia yield, at t = 6s.

While keeping all other operating conditions similar, IPA addition has clearly improved TOC and total N, which indicated better conversion of DMF. However, ammonia yield decreased slightly then gravitated around the same value. We can suggest that IPA addition encouraged N conversion to gas (explained by the improved % total N removal) as opposed to following the ammonia path.

Effect of DMF concentration: Figures 8 and 9 show the effect of initial DMF concentration on SCWO of DMF, while keeping a constant IPA/DMF molar ratio of 1. Figure 8 show that increasing organics concentration increases the TOC conversion by around 125%, the effect being most prominent at the lower concentration range. Figure 9 illustrates that ammonia yield increases slowly as DMF concentration increases. Interestingly IPA increase while keeping DMF constant (at 10mM), did not influence ammonia yield. This is logical since DMF is the only source of ammonia; this also supports the hypothesis that IPA has a positive influence on the ‘later stages’ of SCWO (after ammonia is produced). This is proved in another work by the authors [4], where ammonia rather than DMF is the feedstock.

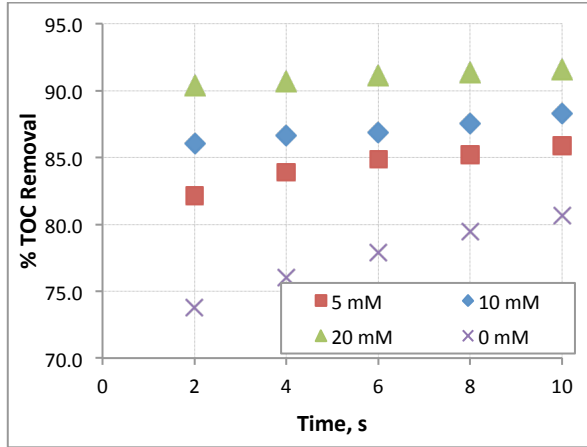


Figure 8: SCWO of DMF at 673K, 1SR and 1 IPA/DMF ratio; at five initial DMF concentrations.

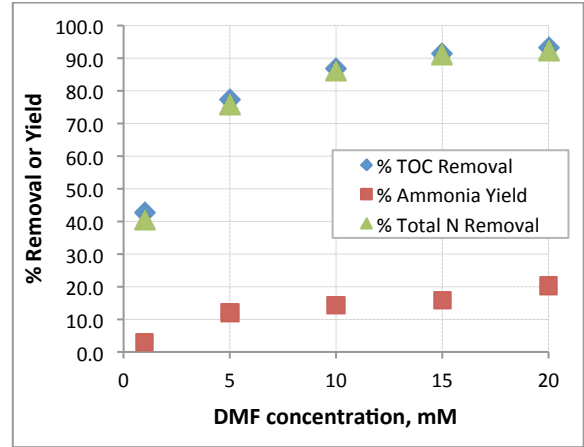


Figure 9: TOC removal, total N removal and ammonia yield as function of initial DMF concentration, at $t = 6s$.

Kinetic Analysis: Due to the system complexity, the reaction kinetics were analysed with respect to the concentration of TOC. Two approaches were adopted namely the *pseudo first order approximation* and the *integral method approximation* [5]. The *global reaction rate* is given by Eq. (1):

$$-r_{TOC} = \frac{d[TOC]}{dt} = k[TOC]^a [O_2]^b [H_2O]^c \quad (1)$$

$$k = A \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

Where k is the reaction rate constant, E_a is the activation energy ($J mol^{-1}$), $R = 8.314 J mol^{-1} K^{-1}$, T is the reaction temperature (K), a , b , and c are the reaction orders with respect to organics, oxidant and water, respectively. As water is in great excess it is safe to assume c to be *zero*. Following the *pseudo first order approximation* with respect to TOC ; the oxidant is assumed to be in excess rendering $a = 1$ and $b = 0$ and leading to Eq. (3), which was plotted as shown in figure 10 at six different temperatures:

$$k = \frac{-\ln(TOC/TOC_0)}{t} \quad (3)$$

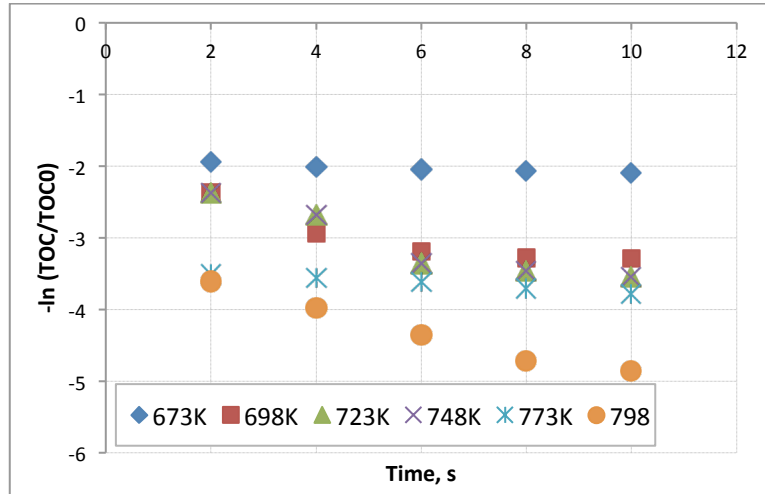


Figure 10: Semi-log plot of organics conversion versus time, at various temperatures.

k values were then found from the slopes of Figure 10, then plotted versus $1/T$ in Figure 11. The slope is E_a/R and the intercept is e^A . Calculations showed that for the *pseudo first order approximation*, $E_a = 63,993 \text{ J mol}^{-1} \text{ s}^{-1}$ and $A = 1.51 \times 10^8 \text{ mol l}^{-1} \text{ s}^{-1}$. It is important to point out that the ‘straight line’ in Figure 11 is an approximation of two lines: for temperatures (673–723 K), slope gives an E_a value of $117,554 \text{ J mol}^{-1}$ while it is $42,676 \text{ J mol}^{-1}$ for temperatures of 748–798. This ensures the favourability of high temperatures in SCWO. However, other factors such as the conversion extent; oxidant ratio; organic chemical and physical properties besides mechanical factors, decide the best operating temperature.

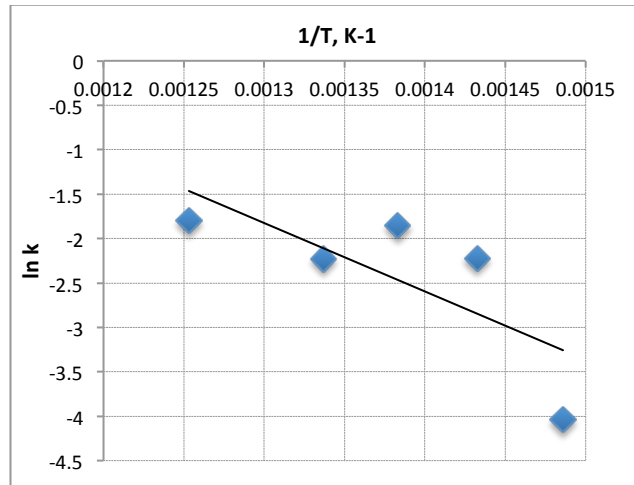


Figure 11: Semi log plot of k values at five temperatures to evaluate A and E_a values.

Based on the *pseudo first order approximation* the rate of TOC removal is described by Eq. (2):

$$\frac{d[TOC]}{dt} = 1.51 \times 10^8 \exp \left\{ - \left(\frac{63,993}{RT} \right) \right\} [TOC] \quad (2)$$

However, as experimental data clearly showed the effect of oxidant concentration on TOC conversion, the *integral method approximation* was carried out to find the value of b in

Eq. (1). This is carried out by plotting a similar graph to Figure 10, at different oxidant stoichiometric ratios (Figure 11):

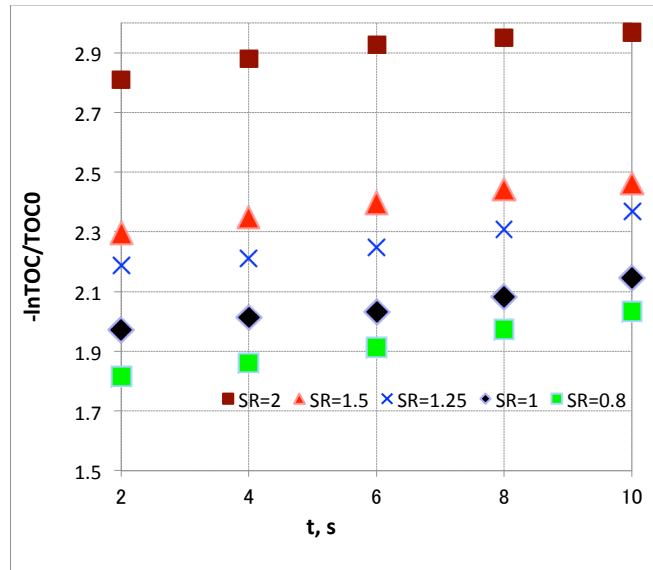


Figure 12: Semi-log plot of organics conversion versus time, at various oxidant SR.

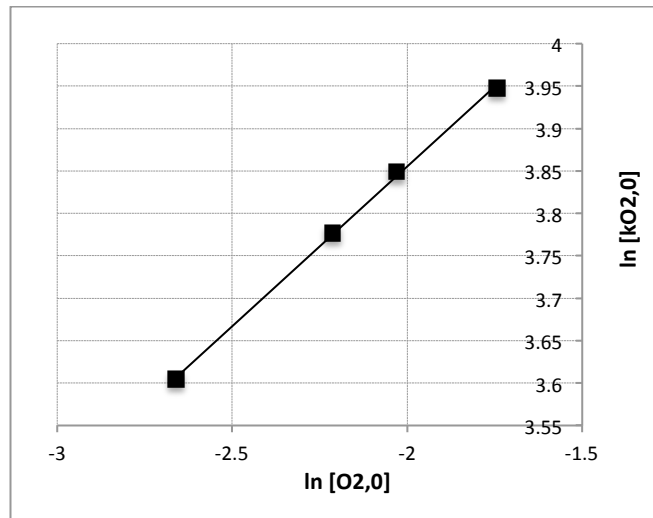


Figure 13. Logarithmic plot in order to determine b (Eq.1).

The slope of the plot in Figure (13) is b and has the value of 0.38 . Following the above analysis, k is plotted as function of $-\ln [TOC/TOC_0]$ according to Eq. (3), the solution equation for Eq.(1):

$$k = -\ln \left[\frac{TOC}{TOC_0} \right] x \frac{1}{t} x \frac{1}{O_2^b} \quad (3)$$

According to the above analysis the reaction rate expression is:

$$\frac{d[TOC]}{dt} = 4.06 \times 10^{16} \exp\left(\frac{-69364}{3.814T}\right) [TOC][O_2]^{0.38} \quad (4)$$

Previous work on the kinetics of SCWO of DMF in IPA free system showed E_a value to be 140,432 J mol⁻¹ [6] following the same analysis, and therefore using IPA has reduced the activation energy by 50%. This is a promising finding; further work is required on other aspects of the system.

CONCLUSIONS

The above preliminary investigation of SCWO of DMF in the presence of IPA has shown that adding alcohol has certainly improved the destruction of organics, represented by %TOC removal. Furthermore it has improved the % removal of total nitrogen found in the liquid phase, which implies that it has been converted to gaseous nitrogen. Ammonia is a highly recalcitrant, which needs extra measures like high extreme temperatures or catalyst. However, obtaining “more ammonia” could be a sign of further conversion of organics from the feed to intermediates. Increasing oxidant ratio led to continuing improved conversion even up to 2SR, which implies more utilisation of oxidant compared to IPA free system. This is no surprise, as oxidising additional organics requires extra oxidant; it also releases extra enthalpy. The system rate equation was also evaluated, showing reduced activation energy, compared to oxidant-free systems.

REFERENCES

- [1] M.D. Bermejo, M.J. Cocero, J. Hazardous Materials, Vol. 147 (2), **2006**, p. 965.
- [2] C. Aymonier, P. Beslin, C. Jolival, F. Cansell, J. Supercritical Fluids, Vol. 17(1), **2000**, p. 45.
- [3] B. Al-Duri, L. Pinto, N.H. Ashraf-Ball, R.C.D. Santos, J. Materials Sciences, Vol 43(4), **2008**, p. 1421.
- [4] P. Cabeza, B. Al-Duri, M.D. Bermejo, M.J. Cocero, Chem. Eng. Res. Des., *in review*.
- [5] J. Sánchez-Oneto, F. Mancini, J.R. Portela, E. Nebot, F. Cansell, E.J. Martínez de la Ossa, Chem. Eng. J. Vol. 144(3), **2008**, p. 361.
- [6] I. Kings, PhD thesis, The University of Birmingham, June **2013**, p.195.