

Investigation of the Destruction of Concentrated N-Containing Hydrocarbons by Supercritical Water Oxidation (SCWO)

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This paper presents a preliminary investigation of the supercritical water oxidation (SCWO) of dimethyl formamide (DMF) under the thermodynamically sensitive conditions of 380 – 450°C and 25 MPa using 10mM DMF (equivalent to 60mM ambient concentration). Oxidant ratio was varied from 0.28 to 1.6 times the stoichiometric value (SR), and the initial organic concentration ranged from 5mM to 30mM under reaction conditions. Residence times ranged from 0.8 to 8s. Results were presented in terms of the % Yield of key intermediates (namely trimethyl- (TMA), dimethyl- (DMA), methyl-amine (MA), and ammonia) and products (CO, CO₂ and N₂O) as function of the investigated variable. At 25 MPa there was no product formation at 380°C then began to increase at $T \geq 400^\circ\text{C}$. Initial concentration had more prominent effect on ammonia production than the amines. Oxidant ratio was more effective in the range below the stoichiometric ratio (SR), while it was not advantageous for the values much above 1.1SR.

In terms of the reaction pathway, TMA seemed to be the first intermediate, followed by DMA then MA. Ammonia followed subsequently. Hydrolysis seemed to take place in the absence of oxygen. These intermediates help identifying the reaction pathway and the sequence of bond breakage. Nitrates were not detected as temperatures were too low for nitrate production. This preliminary study aims to lend insight for detailed investigation of the system kinetics, which is underway.

INTRODUCTION

N-containing hydrocarbons are of great interest due to their abundance in a diverse range of wastes on the one hand and the difficulties associated with breaking down nitrogenous intermediates (due to their recalcitrant nature) on the other hand. Several aspects of SCWO of N-hydrocarbon were reported in literature. Lee *et al* [1] investigated the decomposition of 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* [2] obtained complete degradation of 7 wt% NH₃ at 780°C in a cooling wall reactor, while Aymonier *et al* [3] obtained complete oxidation of fenuron at 540°C and 25 MPa obtaining 99.99% COD removal. Benjamin and Savage [4] reported SCW reactions of amines and amides, reporting reaction pathways and constants. In this work, DMF is selected for investigation as an aliphatic amide which has not been investigated and represents a good starting point for N-chemistry. The study targets the thermodynamically sensitive region of 380-450°C at 25 MPa and 10mM organic concentration (supercritical), thus generating much

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intermediate compounds. Following these compounds we have attempted a hypothetical reaction pathway on the way to understanding the reaction mechanism in the light of the current system conditions.

MATERIALS AND METHODS

This work was conducted at Oshimalab, at the University of Tokyo (Japan) as part of on-going collaboration between the two authors in the UK and Japan, respectively.

SCWO of DMF (C_3H_7NO) was conducted in a 2.59-mL plug flow reactor made of 1/16" ss316 Swagelok pipes [3.3m length and 1mm ID], using hydrogen peroxide as oxidant. The organic and oxidant were pumped through *Jasco PU-980* HPLC pumps, preheated in 0.6m and 6m coils respectively, before meeting at a cross-union and entering the reactor. The preheating coils and reactor were situated in a fluidised heated sand bath where temperature was monitored by thermocouple. The reactor exit was immediately cooled in a heat exchanger, de-pressurised via an automated *Jasco* back pressure regulator before the two phases were separated in a gas/liquid separator. The gas was analysed by on-line GC-TCD, while the liquid samples were collected and analysed by GC-FID (for DMF and key liquid products), Ion chromatography for NH_3 and TOC for organic carbon content. Figure 1 shows the apparatus:

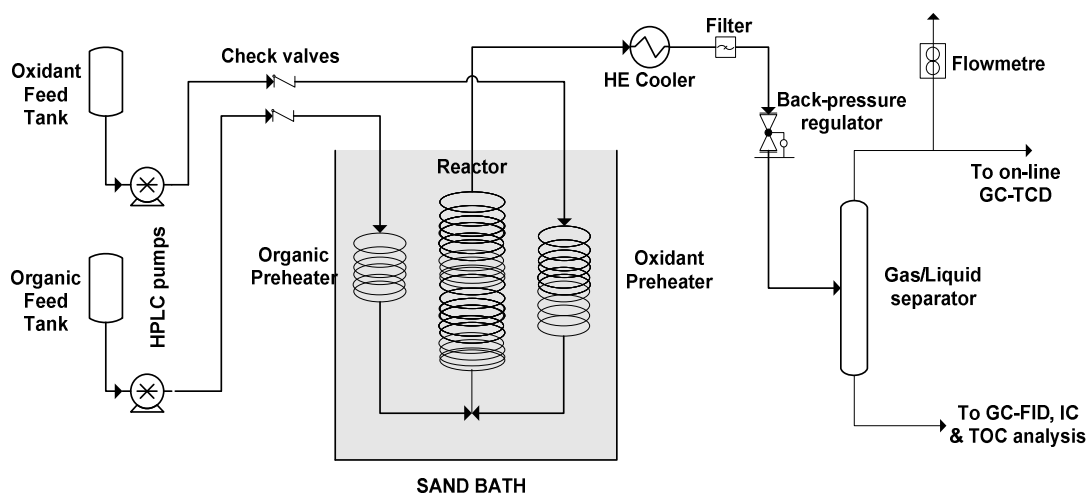


Figure 1 Conceptual diagram of the continuous SCWO Unit.

RESULTS

The Chemistry of Water: In SCW ($T > 375\text{ }^{\circ}\text{C}$, $\rho = 0.1 - 0.4\text{ mg/L}$) the H – bond network is underdeveloped with every H^+ ion is surrounded by a reduced number of water molecules. The H^+ ion with enhanced activity reacts with O atoms in the hydrocarbon to form intermediates with positive charge, which ultimately breaks into product. Also, H^+ ions interact with the N atoms in a series of acid/base reactions. Figure 2 illustrates the idea, which is applied to DMF:

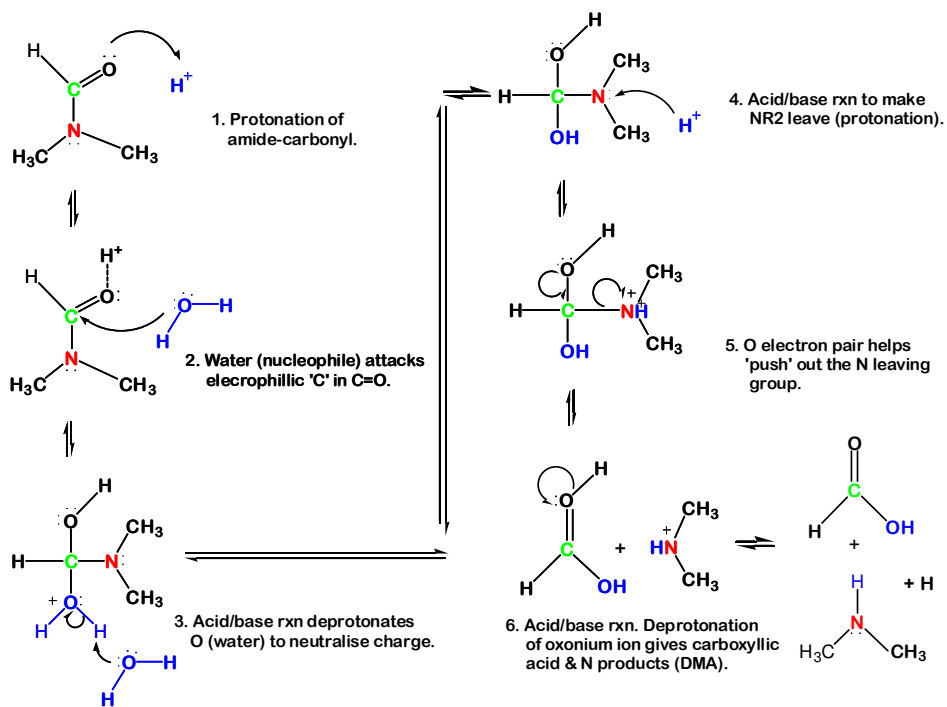


Figure 2 Proposed reaction pathway for the hydrothermal degradation of DMF.

The conversion of DMA was believed to occur by the abstraction of an H from C-H and N-H bonds by OH radicals [5] in a competitive fashion. This implies that while DMF decomposes (by hydrolysis) in the absence of oxygen, decomposition of amines would require an oxidant (as results show in the coming sections). Hence acid/base reaction and radical formation both take place to an extent that is dictated by the water chemistry at the investigated system conditions.

Effects of System Conditions: The current study was conducted at 25 MPa, testing the conditions displayed in Table 1:

Temperature (T), °C	Initial organic (C ₀), mM	Oxidant x Stoichiometric ratio
380, 400, 425, 450	10	1 x SR
400	5, 10, 20, 30	1 x SR
400	10	(0.345, 0.865, 1, 1.6) x SR

Results were expressed in terms of the % Yield of the products, defined by Eq. (1) and (2). Key components in the liquid and gas products were selected and monitored:

$$\% \text{Yield}_i = \frac{\text{C molar flow in } i \text{ (mmol / min)}}{\text{TOC}_0 \text{ (mmol / min) x no. of C moles in product}} \quad (1) \quad \text{for C - containing products}$$

$$\% \text{Yield}_i = \frac{\text{N molar flow in } i \text{ (mmol / min)}}{\text{N}_0 \text{ (mmol / min) x no. of N moles in product}} \quad (2) \quad \text{for N - containing products}$$

The effect of temperature: For the investigated experimental range Figure 3 shows that TMA and DMA increased as the temperature exceeded T_c then decreased again as sharp release of MA was observed indicating further degradation towards simpler products. This can be explained by the change balance between the ion and free radical mechanisms as water changed temperature.

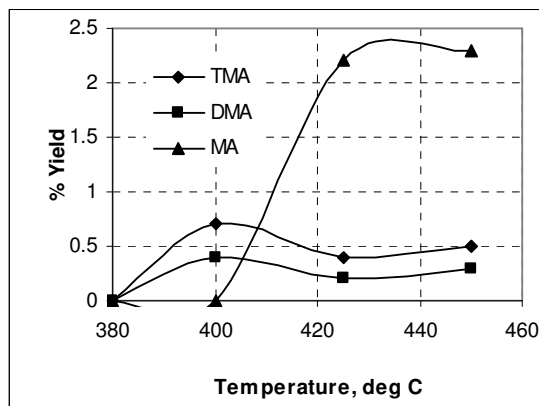


Figure 3: Effect of temperature on the % Yield of TMA, DMA and MA at $\tau = 4$ seconds.

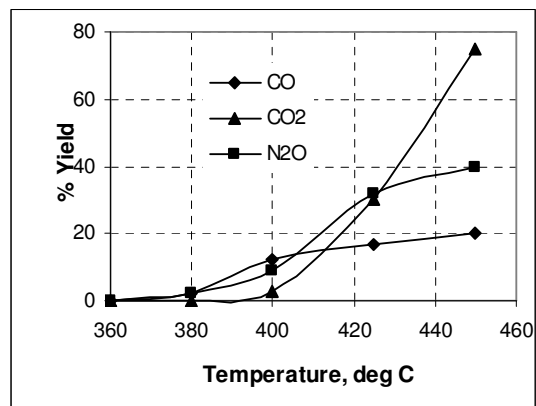


Figure 4: Effect of temperature on the % Yield of CO, CO₂ and N₂O at $\tau = 4$ seconds.

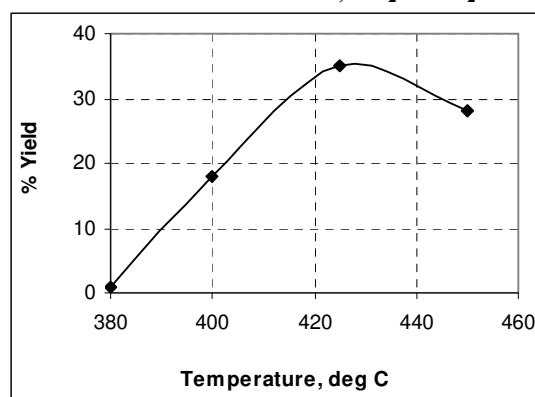


Figure 5: Effect of temperature on the % Yield of ammonia, at $\tau = 4$ seconds.

This was also accompanied by increase in CO₂ yield as CO yield levelled off at higher temperatures. Similar observation is valid for ammonia as its % yield rapidly increased then decreased due to its further conversion to N₂O.

The effect of initial organic concentration: High organic concentration range of 5 – 30 mM (~ 2000 – 13000 ppm ambient) was investigated. As expected, for such high concentrations much reaction would slowly progress with appreciable intermediates namely TMA and DMA. Figure 6 shows that the TMA release decreased as the concentration increased from 5 to 30 mM, while DMA slowly increased, signalling further oxidation progress. No MA was detected. However, the % yield of ammonia rapidly decreased with concentration (Figure 7) with more release of N₂O (Figure 8) in the gas phase. The decrease in N₂O release at 30 mM was attributed to the low oxidant supply at this condition (0.28SR) due to restrictions in the pump capacity. Figure 8 also shows that CO release increased with concentration, highlighting the poor conversion to favourable gases at ‘kinetically interesting’ conditions; no

clear trend was observed for CO₂. As mentioned before the experimental conditions cover a complex area with high possibility of intermediate release. In effect, it was not possible to conduct a C-balance due to the large number of unidentified intermediates.

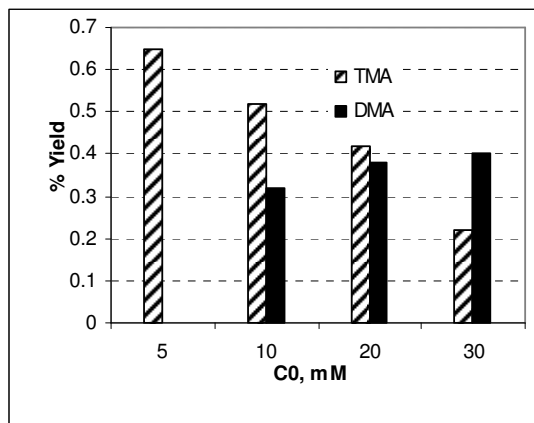


Figure 6: Effect of initial concentration on the % Yield of TMA and DMA at $\tau = 4$ seconds.

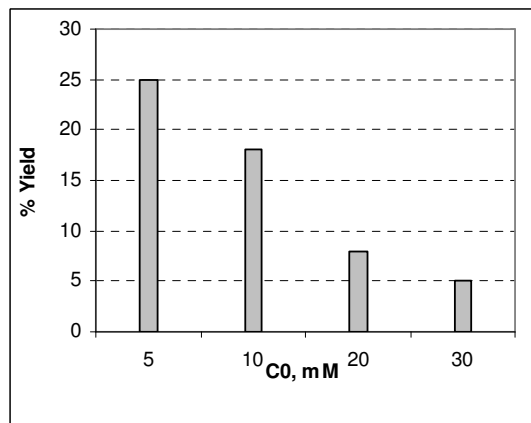


Figure 7: Effect of initial concentration on the % Yield of ammonia at $\tau = 4$ seconds.

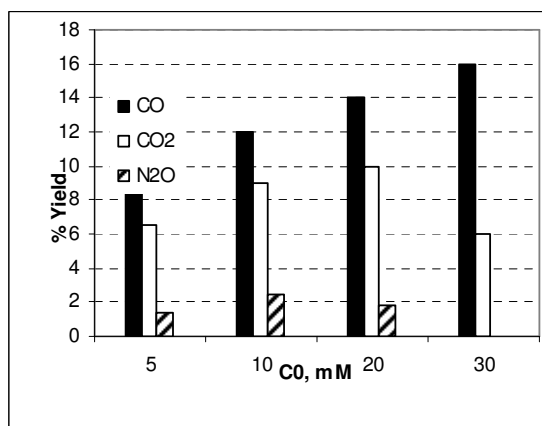


Figure 8: Effect of initial concentration on the % Yield of CO, CO₂ and N₂O at $\tau = 4$ seconds.

Effect of Oxidant Ratio: The present work confirmed previous findings [2] that the amount of oxidant need not be much higher than the SR, in order to achieve effective conversion. Figures 9-12 show that at *zero* oxidant supply, none of the target intermediates were detected though DMF did decompose by about 20% (Figure 9). % Yield increased as the fraction stoichiometric ratio (xSR) increased from 0 to 1 and then levelled off. Ammonia release showed much less dependence on oxidant ratio compared to the TMA and DMA. However, it production decreased as SR exceeded 1. This was attributed to the different N chemistry on the one hand, and to further progression to gas phase on the other hand. At this point this cannot be verified as there is no further yield of N₂O, and N₂ release was not calculated for this particular work.

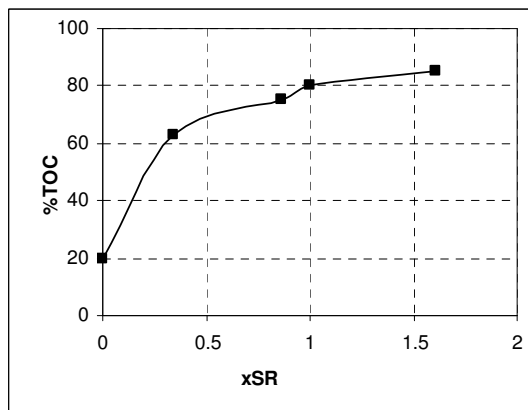


Figure 9: Effect of oxidant ratio on TOC at $\tau = 4$ seconds.

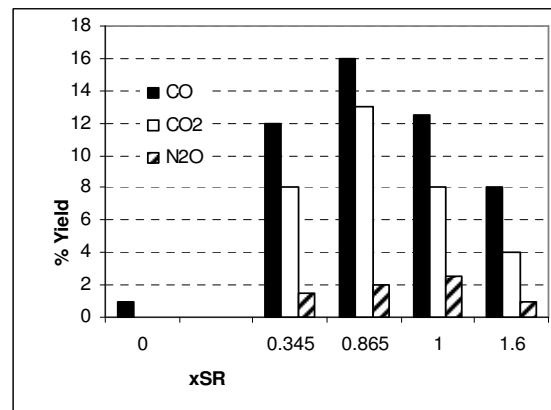


Figure 10: Effect of oxidant ratio on the % Yield of CO, CO2 and N2O at $\tau = 4$ seconds.

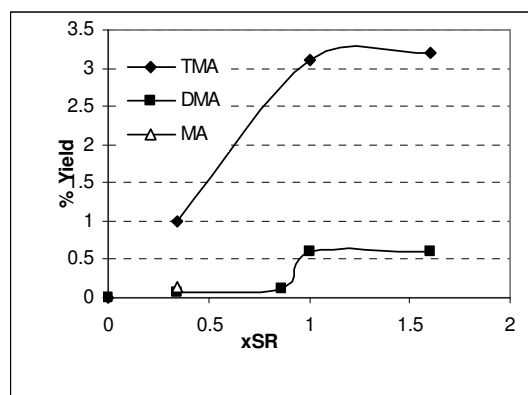


Figure 11: Effect of oxidant ratio on the % Yield of TMA, DMA & MA at $\tau = 4$ seconds.

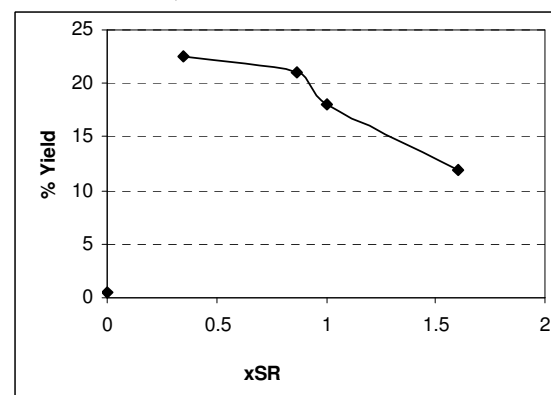


Figure 12: Effect of oxidant ratio on the % Yield of ammonia at $\tau = 4$ seconds.

CONCLUSION

SCWO of DMF was influenced by two mechanisms namely ionic and free radicals and the extent of each was determined by the system conditions. Intermediates namely TMA, DMA and MA appeared in this order, while ammonia was early to appear; indicating that it was formed by the C-N cleavage. Ammonia yield was highly influenced by the organic concentration while C-intermediates were more sensitive to the oxidant ratio (when below SR value).

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