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Thermal abatement of nitrogen-containing hydrocarbons by non-catalytic supercritical water oxidation (SCWO)

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Abstract This work investigated the destruction of N-containing hydrocarbons namely DBU (1,8-diazobicyclo[5.4.0]undec-7-ene) and DMF (dimethyl formamide) by supercritical water oxidation (SCWO), using hydrogen peroxide as oxidant. Reactions were conducted under temperatures of (400–650 °C), pressures of (50–250 bars), oxidant stoichiometric ratio SR (0.9–12), initial concentrations of organics (0.1–8.4 mM) and residence time τ (6–17 s). Reactions took place in a plug flow continuous reactor and the results were presented in terms of the % removal (of TOC and the organic compound), C-fraction and N-fraction; all plotted as function of the above system conditions. Also, GC-MS analysis for DMF was conducted. Percent removal increased with temperature and complete organic- and >90% TOC removal, was obtained at 500 and 600 °C for DMF and DBU respectively. Conversion increased with the oxidant SR, residence time and initial organic concentration. Pressure affected conversion in the sub- and near-critical conditions but not in the supercritical region, yet an initial value of 150 bar was required to start the reaction. Pseudo first order-, integral power rate law-, and power law models successfully described the kinetic data; and the reaction constants for each model and energy of activation were evaluated.

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Introduction

The chemical and petroleum industries generate several million tons of wastewater annually; containing a wide variety of phenolic derivatives, polynuclear aromatics and heterocyclics [1], which even at very low concentrations are seriously hazardous [2].

Supercritical water oxidation (SCWO) is a highly promising technology, conducted at temperatures and pressures above the critical values for water (374 °C and 220 bars), when the density, dielectric constant and ionic product of water drop down, so SCW acts as a non-polar solvent of high diffusivity and complete miscibility with organic compounds and even gases (like O_2), providing an ideal reaction medium with excellent transport properties [3–5]. It is the special properties of water that provide one-phase reaction systems (unobtainable otherwise) and render water a superior reaction medium for such systems. Such properties also affect the reaction pathway and therefore product distribution. In SCWO, hydrocarbons are completely mineralised to much simpler compounds like CO_2 and H_2O or biodegradable intermediates. SCWO process competes with the already existing technique of incineration especially for low-concentration waste streams (1–40 wt% organics) where incineration becomes extremely energy intensive whereas SCWO has relatively lower operating temperatures of (380–650 °C) and leads to the favourable formation of molecular nitrogen over the toxic NO_x. It is a clean technology and can operate as a totally enclosed treatment facility used for “in process” recycling and reuse of process water [6].

Extensive investigations on SCWO of phenol took place [7, 8]. As for N-containing organic compounds, SCWO of pyridine was investigated [1, 9] in terms of reaction kinetics and catalytic activity respectively. Chen et al. [10]

investigated the COD removal efficiency by SCWO of phenol, aniline and nitrobenzene. However, the presence of heteroatoms like N, S, P and halogens in hydrocarbons greatly influence the physical properties and behaviour of SCW. It is therefore important to understand the role of heteroatoms in the reaction mechanisms in order to prevent the formation of unwanted by-products and maximise process efficiencies.

Experimental

Apparatus and procedure

The SCWO apparatus (Fig. 1) is a continuous system, with a plug flow Hastelloy C-276 coiled reactor of 11.18-mL volume. The oxidant (H_2O_2) and organic solutions (delivered by separate Gilson HPLC pumps) were preheated in Hastelloy C-276 coils, and then mixed at the reactor entrance in mixing T-piece. All were placed in a temperature-controlled furnace. The reactor exit stream was cooled, and then depressurised to atmospheric pressure by an expansion valve before passing through a gas-liquid separator, where the separated streams were taken for analysis, respectively.

Experimental conditions

Tables 1 and 2 show a summary of the experimental conditions studied in the present work.

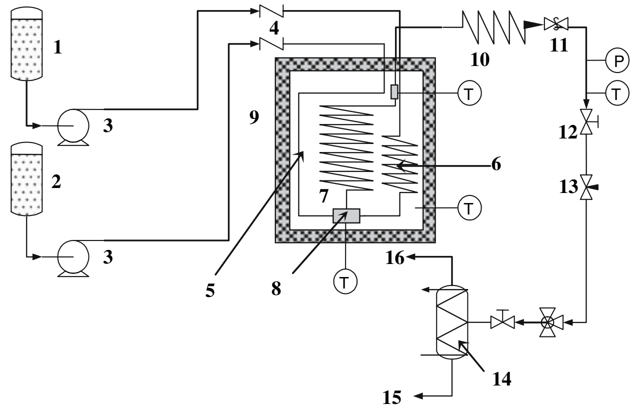


Fig. 1 SCWO apparatus with (1) oxidant feed tank, (2) organics feed tank, (3) HPLC pumps, (4) check valves, (5) organics preheating line, (6) oxidant preheating line, (7) tubular reactor, (8) T-mixing point, (9) furnace, (10) cooler, (11) expansion valve, (12) on-off valve, (13) micro metering valve, (14) gas–liquid separation condenser, (15) liquid stream, (16) gas stream

Table 1 Experimental conditions of DBU

Parameters	Range	τ (s)
Temperature	400–650 °C[a]	7
SR	0.9–12[b]	7–17
$[DBU]_o$ mM	0.1–0.9[c]	7–17
Pressure (bar)	50–250[d]	2–6

[a] $[DBU]_0 = 0.3$ mM, SR = 2, P = 250 bar

[b] T = 400, 425, 450 and 500 °C, $[DBU]_0 = 0.3$ mM

[c] T = 400, 450 and 500 °C, SR = 2 &4

[d] T = 450 °C, SR = 1.2, $[DBU]_0 = 0.3$ mM

Table 2 Experimental conditions of DMF

Parameters	Range	τ (s)
Temperature	400–650 °C[a]	7
SR	0.8–12[b]	6, 10
$[DMF]_o$ mM	0.1–8.4[c]	7–15
Pressure (bar)	50–300[d]	6

[a] $[DMF]_0 = 1$ mM, SR = 3, P = 250 bar

[b] T = 400, 500 °C, $[DMF]_0 = 1.2$ mM, P = 250 bar

[c] T = 400 °C, SR = 3, P = 250 bar

[d] T = 400, 500 °C, SR = 3.3, $[DMF]_0 = 1$ mM

Analysis

Aqueous samples were analysed for concentration by HPLC equipped with UV-detector. The gas stream composition was analysed by GC-TCD. Total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC) contents of the liquid phase and the feed streams were determined using Total organic carbon analyser with autosampler (TOC 5050A, Shimadzu Co. Japan). Measurement of ammonia, nitrate and nitrite ion (NH_4^+, NO_3^- and NO_2^-) concentration in the liquid phase was by individual Merck cell tests via the Spectroquant NOVA 60 spectrophotometer, with results reported directly in concentration units.

Results and discussion

SCWO of DBU (1,8-diazobicyclo[5.4.0]undec-7-ene) and DMF was investigated under several system conditions shown in Tables 1 and 2. Results were presented in terms of % organics-, TOC and TC removal. Also the N- and C-fractions in the organic compounds were monitored.

The effect of temperature

Temperature experiments were conducted using a temperature range of 400–650 °C keeping a constant pressure, SR,

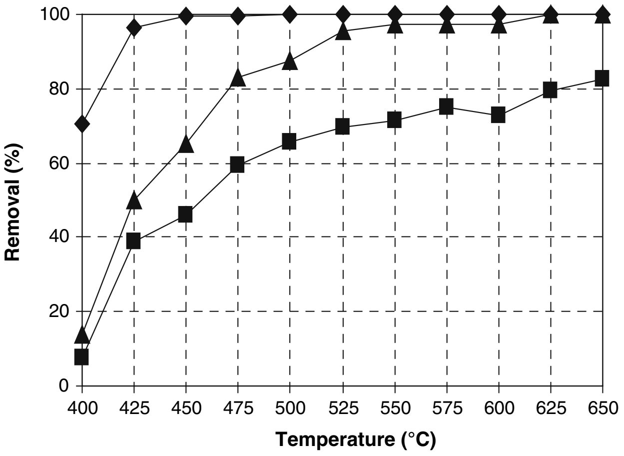


Fig. 2 Percent removal as function of temperature

C_0 and τ. Figure 2 shows that for these conditions, DBU was completely oxidised at 450 °C, however TOC approached >98% conversion only at T > 600 °C and TC conversion did not exceed 80%. The other 20% consists of intermediates that were not completely mineralised. Detailed analysis would be required to identify their nature and composition during the course of the reaction. Figure 3(a, b) give the distribution of C and N atoms in the products as function of temperature.

Figure 3(a) shows that as temperature increased, more C-fraction (CF) was converted to CO_2 yet inorganic carbon (IC) remained around 20% conversion throughout. As for N-fraction (NF), N_2 gas was produced as T exceeded 550 °C, however, NH_4^+ did remain in solution (60%) even at 650 °C. NO_2^- and NO_3^- concentrations were insignificant. The persistence of the recalcitrant ammonia suggests the need for catalyst to achieve high conversion. This agrees with previous works [11]. In any case NO_x formation was not detected.

The effect of pressure

In SCW systems, the fluid density is highly sensitive to pressure changes; especially in the near-critical region, therefore experiments were conducted in the pressure range of 50–250 bars. Temperature was kept at 450 °C in order to monitor the pressure effect in isolation. Figure 4 shows the results for DBU presented in the form of removal percent of DBU, total organic carbon (TOC) and total carbon (TC).

Figure 4 shows that at 450 °C, % removal is sensitive to the system pressure and therefore water density at the low-pressure zone ($P < 220$). In this region, water density is around 0.01–0.08 g/mL. With methylamine, other researchers [12] indicated that at low-density region ($\rho < 0.28$ g/mL), conversion was sensitive to density,

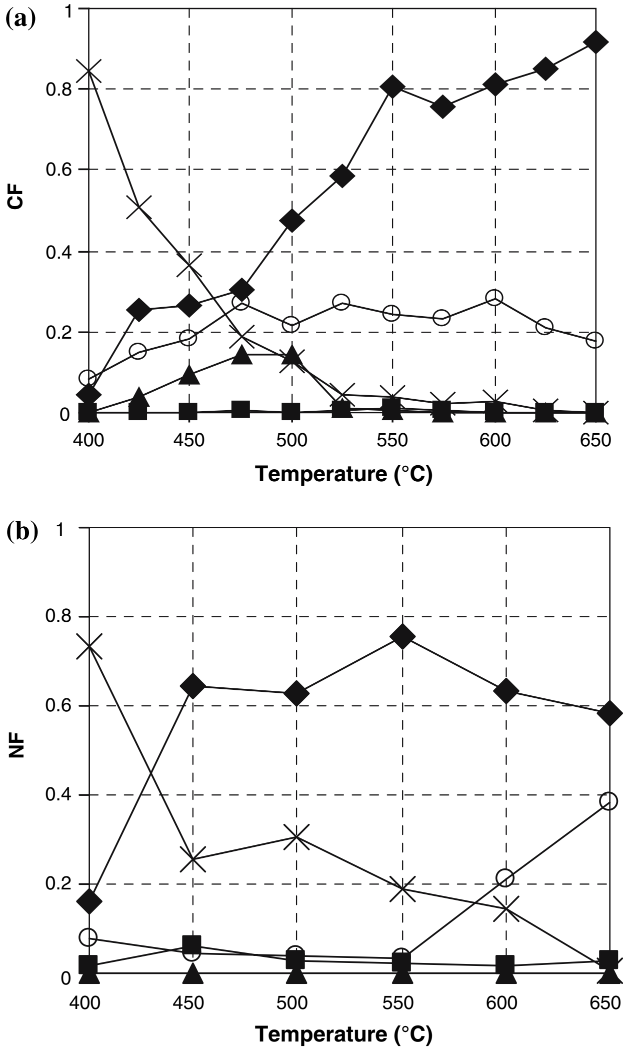


Fig. 3 (**a**) C-distribution as CO_2 (◆), CH_4 (■), CO (▲), IC (○), OC (×). (**b**) N-distribution as NH_4^+ (◆), NO_3^- (■), NO_2 (▲), N_2 (○), N in liquid (×)

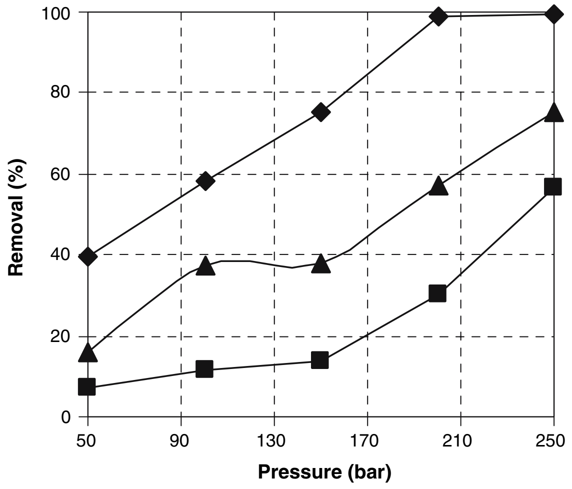


Fig. 4 Percent removal as function of pressure: DBU (◆) TOC (▲) TC (■)

which agrees with the current results. They attributed their results to the presence of two competing reaction (pyrolysis and hydrolysis), where the former is dominant at lower densities. Also, a minimum pressure of 200 bar was necessary for complete destruction of the cyclic DBU. For DMF results showed that a minimum of 150 bars were required to destruct the aliphatic compound. However, at the selected pressure range ($P \leq 200$, T = 450 °C), water is in a vapour phase and the density is very low (0.016–0.08) g/mL, which greatly hinders hydrothermal conversion, as a monophasic system could not be confirmed. A positive dependence on system pressure was also mentioned with regard to phenol oxidation at 550 °C [13, 14] and N-containing compounds like aniline [15].

Koo et al. [14] addressed the issue using phenol in a batch reactor at 400 °C and 860% excess oxygen. They increased the pressure by raising the water density first, then by keeping the density constant and raising adding helium to raise the pressure. They found that increasing water density, not increasing pressure, induced the increase in the reaction rate. In studying SCW degradation of formaldehyde at 400 °C, Osada et al. [16] reached similar conclusions.

Oxidant stoichiometric ratio

The effect of oxidant stoichiometric ratio on the distribution C- and N-fractions (CF and NF respectively) in the SCWO products for DBU was studied at 450 and 500 °C at 250 bars and 5 s residence time.

Figure 5 shows that at 450 °C, increasing the oxidant SR slowly affected C-distribution towards reducing OC and increasing CO_2, while it noticeably shifted favourably towards CO_2 at 500 °C. These findings were consistent with literature studying phenol [13, 14], aniline [15], benzene and acetic acid [17]. However, it hardly affected N-distribution as shown in Fig. 6 where in the N case, NH_4^+ remained high throughout. At longer residence time (9 s) results further improved for C-distribution, while NH_4^+ still persisted. With the current data little could be concluded with regard to the abatement of nitrogen. Increasing temperature, SR, pressure and residence time did not succeed in removing ammonia (NH_4^+).

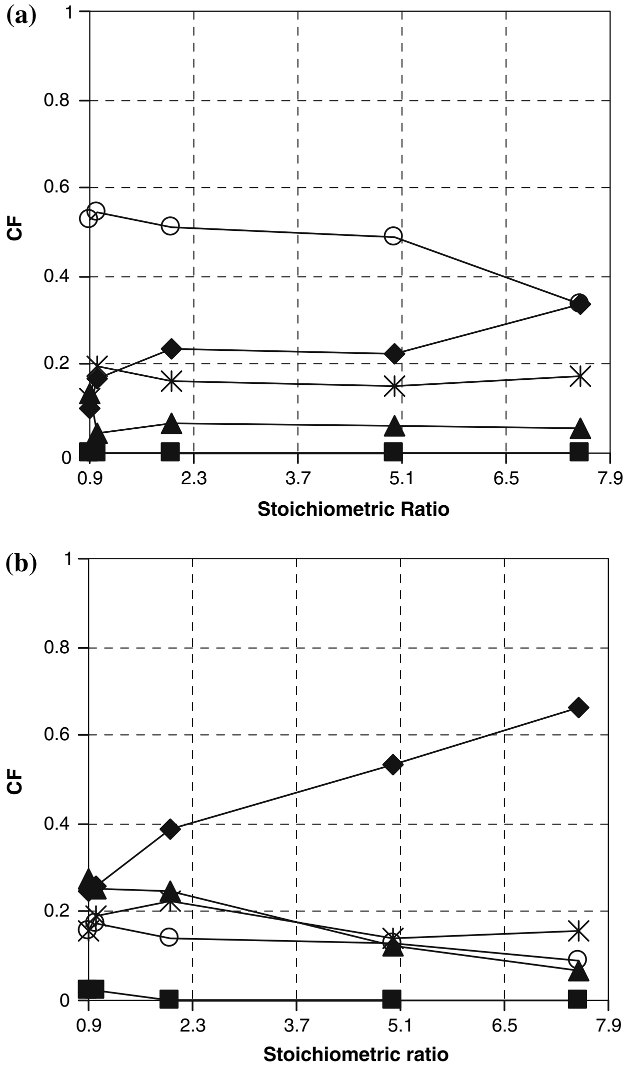


Fig. 5 C-distribution as function of SR at **(a)** 450°: CO_2 (◆), CH_4 (■), CO (▲), IC (×), OC (○). **(b)** C-distribution in DBU removal as function of SR at 500 °C: CO_2 (◆), CH_4 (■), CO (▲), IC (×), OC (○)

Kinetics investigation

Supercritical oxidation in the tubular reactor was described by the Global rate equation (Eq. 1 below) using regression analysis of data to evaluate the constants *a, b* and *c*. In Eqs. 1–7 $[C_A]$, $[O_2]$ and $[H_2O]$ are the concentrations of organics, oxygen and water respectively (mM), $[C_{A0}]$ is the initial organic concentration, X_A is the conversion, k is the reaction constant, E_A (kJ/mol) is the energy of activation, A ($M^{-1}\ s^{-1}$) is the Arrhenius constant, T (K) is the temperature, R (kJ/mol K) is the Universal Gas constant and τ (s) is the residence time.

$$(-r_A) = \frac{d[C_A]}{dt} = k[C_A]^a[O_2]^b\ [H_2O]^c \qquad (1)$$

$$k = A\ \exp\left(\frac{-E_A}{RT}\right) \qquad (2)$$

$$\frac{d[C_A]}{dt} = A\ \exp\left(\frac{-E_A}{RT}\right)[C_A]^a[O_2]^b \qquad (3)$$

The reaction constant k is related to the activation energy E_A and the Arrhenius constant A by Eq. 2. As water was abundant, $c = 0$ (Eq. 3). k was evaluated by assuming

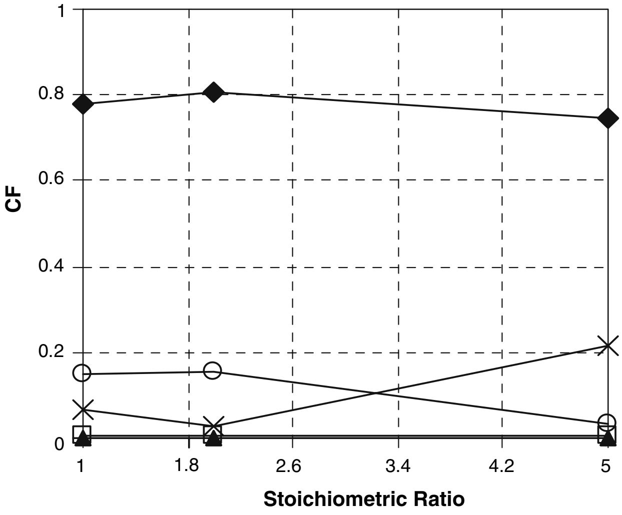


Fig. 6 N-distribution in DBU removal as function of SR: NH_4^+ (◆), NO_3^- (■), NO_2^- (▲), N_2 (×), N in liquid (○)

pseudo-first order reaction with excess oxidant ($b = 0$ in Eq. 3), and plotting $\ln[C_A/C_{A0}]$ against residence time τ as shown in Fig. 7 where k is the slope. Repeating it for all temperatures, the obtained k values were plotted against *1/T* to obtain E_A and A as shown in Fig. 8.

Figure 7 suggests the presence of an induction time of 3.6 and 1.5 s before reactions started at temperatures of 400 and 450 °C respectively, which indicated the time required for the formation of free radicals. This was reported in previous literature [18] and was related to the quality of feed mixing. Meyer et al. [11] suggested that the length of induction time might be a function of other experimentally controlled parameters such as the initial organic concentration. Nonetheless, the presence of an induction time is indicative of a complex reaction mechanism and may interfere with the modelling of rate equation.

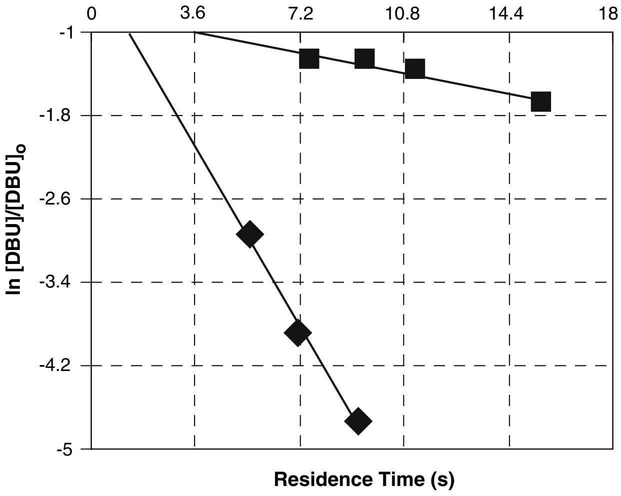


Fig. 7 Normalised decay profile for DBU oxidation at 400 °C (■) and 450 °C (◆)

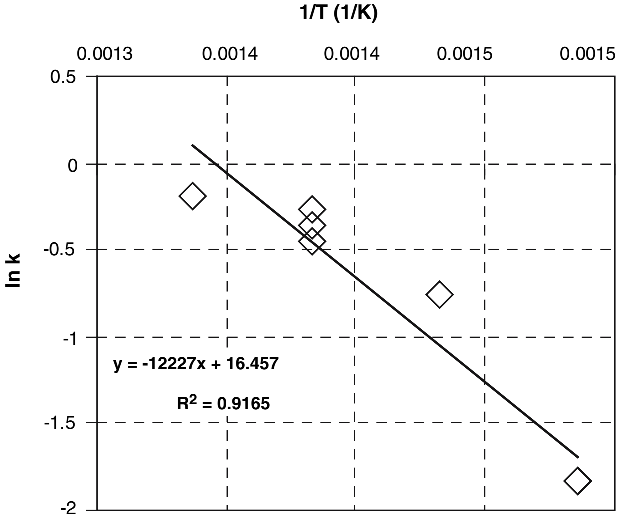


Fig. 8 Arrhenius plot for DBU

As the reaction took place in a plug flow reactor, Eq. 1 was placed in the performance equation of the Plug Flow reactor (Eq. 4) assuming complete oxidation reaction (Eq. 5). The substitution is given in Eq. 7, which was integrated to give Eq. 8. Table 3 shows the kinetic parameters as evaluated by Matlab Power Law:

$$\frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{4}$$

$$C_9H_{16}N_2 + 13O_2 \rightarrow 9CO_2 + 8H_2O + N_2 \tag{5}$$

$$C_A = C_{A0}(1 - X_A) \tag{6}$$

$$\frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{k[C_{A0}(1 - X_A)]^a[O_2 - 10.75C_{A0}X_A]^b} \tag{7}$$

$$X_A = 1 - \left(1 - (1 - a)A\exp\left(\frac{E_A}{RT}\right)\tau[C_{A0}]^{a-1}[O_{20}]^b\right)^{1/(1-a)} \tag{8}$$

This model did not take the induction time into account and was based on complete oxidation hence a more accurate description of the kinetics would be

Table 3 Kinetic parameters of current systems

	DBU	DMF
a	0.9 ± 0.1	1.3 ± 0.1
b	0.4 ± 0.1	0.4 ± 0.1
A	$6.3 \times 10^{10 \pm 3}(M^{-0.3}\ s^{-1})$	$1.4 \times 10^{9 \pm 2}(M^{-0.1}\ s^{-1})$
E_a	145 ± 45 kJ mol^{-1}	107.5 ± 20 kJ mol^{-1}

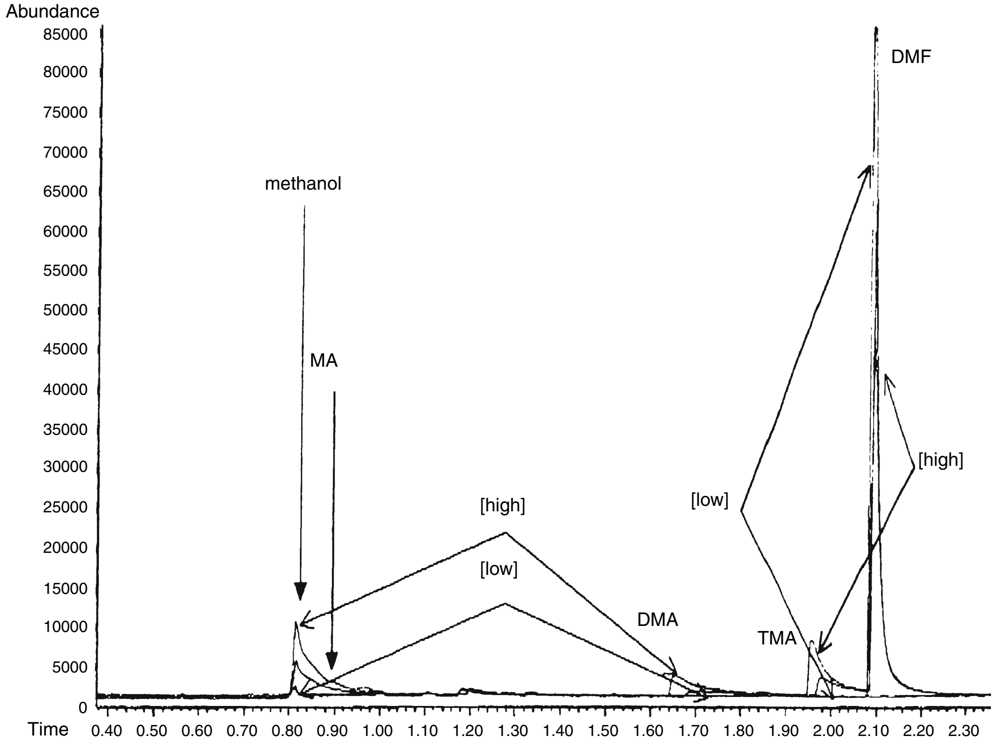
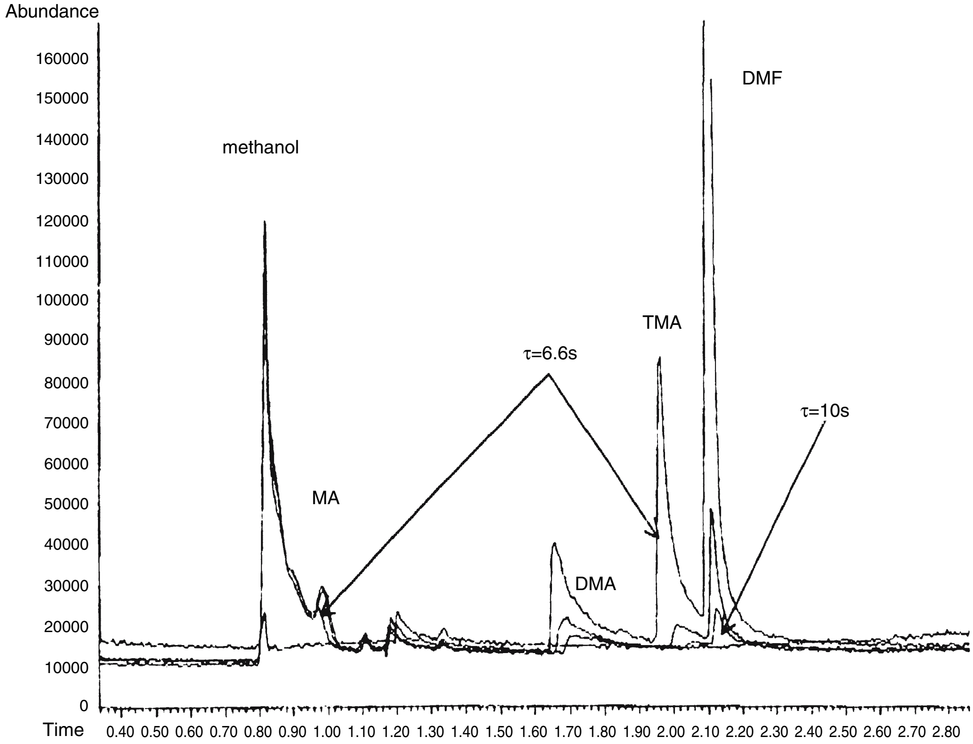


Fig. 9 GC-MS: effect of C_0 at 400 °C, 250 bar, 6.6 s

Fig. 10 GC-MS: effect of τ at 400 °C, 250 bar, 8.4 mM



achieved by taking the induction time into account. Much more data would be required to improve the accuracy such as detailed description of the phase behaviour, an insight into the reaction pathway and identification of intermediates. Such work is currently underway. For reactor design and scale-up purposes, this

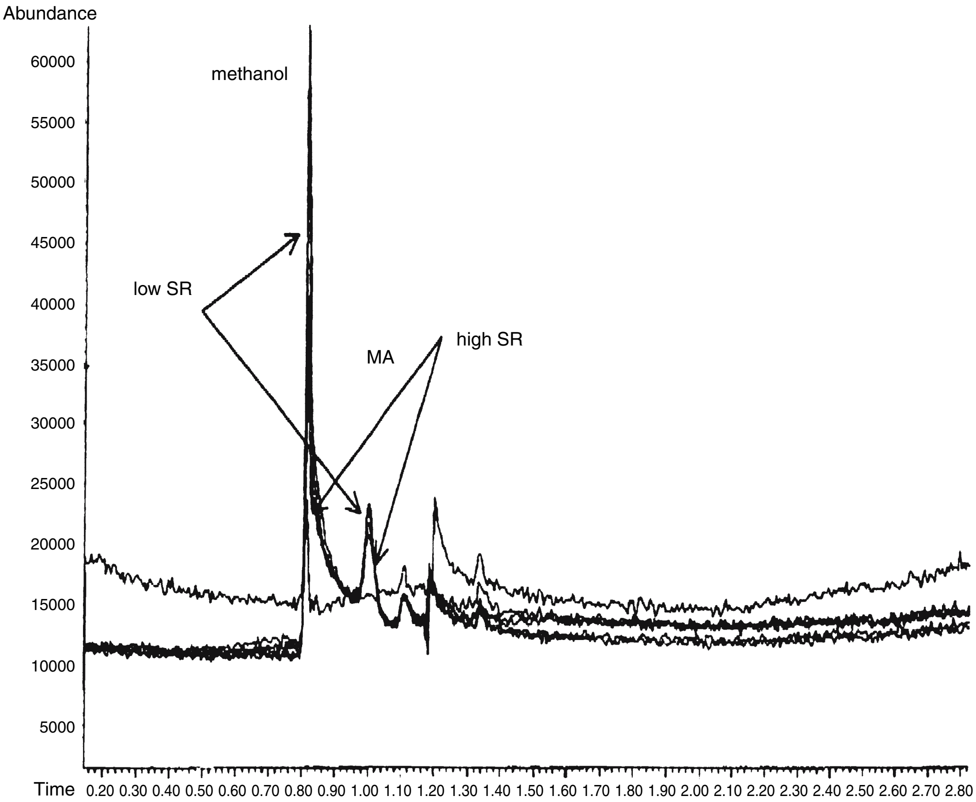


Fig. 11 CG-MS: effect of SR at 500 °C, 250 bar, 8.4 mM

model would provide a good starting point. However, more work is required with regard to the effect of heteroatoms on the system kinetics and phase behaviour or reaction mixtures. Future work also involves kinetics of two-reactant systems.

GC-MS analysis

The intermediates identified by GC-MS upon DMF oxidation were: trimethyl amine (TMA), dimethyl amine (DMA), methyl amine (MA) and methanol. Figures 9, 10 and 11 show some of these analyses at different conditions. Figure 9 shows that more DMF was converted to methanol than other intermediates for higher initial concentrations. The same trend appeared in Fig. 10 for higher residence time τ. In Fig. 11, where oxidation was at 500 °C, all DMF disappeared but more methanol appeared at lower SR.

Conclusions

N-containing hydrocarbons can be completely destructed by SCWO to much simpler benign compounds, the main driving condition being the temperature. For maximum % conversion, higher temperature, residence time and SR were required. Pressure had more important effect in the near-critical region due to the high sensitivity of water density to pressure in this region. However, the above seemed valid for the C-conversion path more than N conversion. Ammonia was a major constituent of the intermediates, and due to its recalcitrant nature, was still abundant at 650 °C (the highest experimental temperature) on the one hand, and N-distribution did not seem to alter much with system conditions on the other hand. Abatement can be improved by using catalysts. System kinetics was successfully modelled by the Power Law expression in a plug flow reactor.

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