SUPERCRITICAL WATER: A REACTIVE ENVIRONMENT FOR SELECTIVE CATALYTIC OXIDATION

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INTRODUCTION

Supercritical water (scH_2O) is a solvent possessing unusual properties which has potential for exploitation as a clean solvent for a variety of synthetic chemistries [1-4].

As temperature rises towards the critical point (T_c = 374 °C, P_c = 22.1 MPa, ρ_c = 0.317 g cm^{-3}),[5] the physical and chemical properties of the fluid change. There is a wide range of temperature over which superheated water (i.e. compressed liquid above its boiling point) is sufficiently different from "normal" water for it to be of use for organic reactions, for which water at <100°C is unsuitable.

The dielectric constant, ε (which describes the shielding effect of a fluid between two electrostatic charges) falls [6]; at a pressure of 200 bar its value decreases from 80 at room temperature (25 °C) to 36 (200 °C), 21 (300°C), 14 (350 °C), 6 (Tc, 374°C), 2 (400 °C). [7]. This enhances the miscibility of water and organic species (which have low ε values) so that by the critical point, water is completely miscible with organic chemicals. Above the critical point, scH_2O is also miscible with gases, thus overcoming mass transfer limitations for reactions such as liquid phase oxidation. This single phase environment has been exploited for both total [8] and partial [9] oxidations. Simultaneously, hydrogen bonding between molecules breaks down, and also self dissociation of water increases such that high temperature water (both sub- and super-critical) has enhanced acid and base characteristics. The ionic product, $\log_{10}Kw$, increases from a value of -14 at room temperature to a maximum value of about –11 at around 250 °C and 250 bar (at which point approximately 30 times the concentration of H_3O^+ and OH^- are present compared to "normal" water) and then decreases sharply at the critical point[10]. The sharp decrease at T_c is a result of the definition of Kw in terms of concentration of ions per litre – below T_c a

higher concentration of ions is contained within the superheated liquid phase than will be present in the single, expanded supercritical fluid phase.

These properties allow the water to act as both solvent and catalyst for acid- and base-catalysed reactions at near and supercritical temperatures without adding further acid or base.[11]. The properties are summarised in Table 1.

Although ε for ncH_2O or scH_2O may be similar to those of conventional solvents, other properties of scH_2O; acidity, basicity, and of course the temperature may be vastly different. scH_2O also has the ability to hydrolyse and to dehydrate. (Hydrolysis of metal salts occurs at temperatures above ca. 250^oC, and it is believed that the metal hydroxides formed are dehydrated to their oxides due to the acidity of the water). Hence it should not be expected that chemistry can simply be transferred from conventional solvent to nc/scH_2O; the mechanism and reaction products may be quite different. Hence we have been screening several different types of reaction to ascertain which are possible under near critical and scH_2O conditions, and which reactions give greater or lesser yields. Reactions have been studied in batch in superheated and near-critical water, in the temperature range $200-350^oC$ and with reaction times in the range 10 minutes – 2 hours. This paper provides a comparison between experiments conducted both in batch and continuously describing a range of organic transformations[12-15], including examples of heterocyclic [13] and controlled catalytic partial oxidation of aromatic substrates[15] conducted in near-critical and supercritical water conditions.

Batch Reactions

Table 2 lists a series of previously reported reactions conducted in batch mode. Entries 1-3 [12] show that, for the reduction of nitrobenzene (C) using hydrogen generated by the reduction of water by zinc, both greater residence time and higher temperature lead to greater conversion to aniline (A). At short residence times, the coupled product azobenzene (B) is also produced in low yield this is reduced as the reaction proceeds.

Entry 4 [13] involves preparation of quinolines by reduction of a nitro group followed by a cyclisation reaction of the amine with the group ortho to.

Again metallic zinc is used to react with water as the source of H_2. At short residence time (12 mins, 4), the yield of cyclised products is 85% with a 93% selectivity to quinoline (E) And 7% of tetrahydroquinoline (F)

Entry 5 is an example of a clean reaction of 2(o-nitrophenol)ethanol, giving 2,3-dihydroindole in high yield. No byproducts were detected.

Entries 6-10 [14] detail the hydrolysis of methyl, 1,3,5 trimethylbenzoate (J) to the acid, which can also undergo decarboxylation to produce1,3,5 trimethylbenzene (L).

Longer residence times and higher temperatures favourdecarboxylation to (L). Increasing the basicity of the solution by adding 2% KOH gives powerfully nucleophilic alkaline ncH$_2$O, which results in selective hydrolysis to the acid with greater yield.

Table 1   Comparison of batch reactions in near critical water

Entry	Substrate	RT/min	Temp/^{o}C	Conversion%	Yield %	Selectivity%	Notes
1	C	6	250	22	20	A90 + B10	
2	C	150	250	90	90	A90	
3	C	120	300	>95	>95	A100	
4	D	12	250	85		E93 + F7	100-150 bar
5	G	120	250	91		H100	
6	J	30	250	21	K20		
7	J	120	250	73	K53+L20		
8	J	30	300	100	L89		
9	J	30	250	60	K57		+ 2%KOH
10	J	30	300	100	K90		+ 2%KOH

Scheme 1

Homogeneously Catalysed Continuous Reactions

Use of a homogeneous catalyst requires that the catalyst remains solvated in both "normal" and scH$_2$O. In "normal" water, MnBr$_2$ exists as an ionic species, as separately solvated ions, which would be expected to be insoluble in scH$_2$O. In acetic acid, MnBr$_2$ exists as an ion-paired entity [16]. It has been shown that there is a strong structural similarity of metal/bromide coordination compounds in the active oxidation solvents (acetic acid and scH$_2$O) which does not exist in the much less active H$_2$O at lower temperatures. This is thought to be due to the very different properties of scH$_2$O (especially the dielectric constant), which results in the MnBr$_2$ being solvated in a similar way in scH$_2$O compared to in Acetic acid, thus leading to successful catalysis. A conventional acetic acid/MnBr$_2$

mixture is poisoned by water; the presence of H_2O lowers the catalytic activity of $MnBr_2$ in the conventional process for oxidation of p-Xylene (pX) to Terephthalic Acid (TA) in CH_3COOH. [17].

At temperatures above ca. 300°C, many organic molecules undergo thermal decomposition [18] and the amount of conversion is dependent on the residence time at high temperature. Reaction times at around T_c are orders of magnitude lower than at conventional process conditions, and by use of a continuous flow reactor the residence time at high temperature can be short enough for thermal decomposition to be avoided[6].   Use of continuous reactors also allows for the fine tuning of process conditions, which can be varied independently; pressure, temperature, flow rates, residence time - thus allowing control of reaction conditions leading to high selectivity and yields.

These properties make scH_2O a suitable medium for oxidation chemistry. Conventionally, many oxidations are often performed at temperatures of 150-200°C, requiring a stable organic solvent.   Acetic acid is a common solvent used, but still suffers from some oxidation itself.   Use of water removes this temperature constraint since H_2O has the important advantage over conventional solvents that it cannot be oxidised.
Process economic advantages gained include more efficient heat recovery form the exothermic reaction due to the elevated temperature[19].

At the University of Nottingham, technology for continuous, catalytic, selective partial oxidation is being developed, at temperatures around the critical point, which is around 150-300°C lower than temperatures utilised for destructive total oxidation of wastes at temperatures of 550-700°C. scH_2O acts as a solvent for $O_2,$ organic substrates and catalyst, overcoming mass transfer limitations inherent in liquid phase processes.

Table 2   Comparison of best reported results for pX-TA oxidation

Entry	Mode	RT min	Temp °C	O₂: organic	MnBr₂ Catalyst Concentration	Yield %	Selectivity%
Clarke [20]	Batch, 3ml	10	314	36:1	[Mn^{2+}]1000ppm [Br$^-$]	70	90 TA 10 tolualdehyde
Clarke [20]	Batch, 3ml	10	308	36:1	No catalyst	44	75 TA 25 tolualdehyde
Holliday [21]	Batch, 10ml	40	333	4:1		64 TA	14 p-toluic acid 3 p-tolualdehyde
Dunn [22]	Batch 1.54ml	60	300			41-57	
Dunn [23]	Batch 1.54ml	7.5	380	4:1		42-72	
Hamley [15]	Continuous	0.3	400	3.6:1	[Br$^-$] 1640ppm	95	95 TA 5 benzoic acid
[24] Mid Century	Continuous	40	200	3:1		98	95

These results indicate, that for the oxidation of methyl aromatic compounds, a high temperature and short residence time process is optimal.

Continuous oxidation of pX by O_2 in supercritical H_2O at ca. 400°C catalysed by MnBr$_2$ gives a selectivity for TA of greater than 90%. Significantly, the impurity 4-carboxybenzaldehyde (4CBA) is not produced. This is thought to be due to the more rapid reaction at high temperature, which facilitates oxidation to the desired product. Also, in scH$_2$O, it is believed that single phase conditions are present, thus giving enhanced mixing of substrate, oxygen and catalyst.

Compared to the existing "Mid Century" industrial process [24], the reaction has the potential for a significant increase in energy efficiency and a substantial reduction in waste, due to the higher process temperature involved (ca. 400°C vs ca. 200°C) and avoidance of the use of acetic acid solvent, around 10% of which is lost through oxidation..

The process is also applicable to a wide range of similar methylaromatic compounds, such as (1,4-dimethylbenzene (*p*-xylene), 1,3-dimethylbenzene (*m*-xylene), 1,2-dimethylbenzene (*o*-xylene), 1,3,5-trimethylbenzene (mesitylene) and 1,2,4-trimethylbenzene (pseudocumene)) under similar conditions, also using MnBr$_2$ as catalyst

No partially oxidized intermediates (i.e. toluic acid and benzaldehydes) were detected for the dimethylbenzenes and mesitylene reactions, which again, is a function of good mixing and high temperature. Aromatic acids produced by the loss of one methyl group occurred in all of these reactions i.e. 3-6% benzoic acid formed during the oxidation of the dimethylbenzenes. Part of this loss is thought to be due to thermal decarboxylation. The thermal decarboxylation process has been monitored via Raman spectroscopy[25,26].

CONCLUSION

In batch experiments, the reactions studied generally give the best yields under subcritical conditions. Increasing residence time at high temperature leads to thermal decomposition (one route being decarboxylation). Note the very different residence times utilised in batch reactions at ca. 200-300°C (6-150 minutes) and in continuous mode at or above T$_c$ (0.1-0.5 minutes). Even the fastest heating and cooling times reported (Dunn) require 5 minutes, compared to a residence time of around 10 seconds between mixing and quenching in a small continuous reactor.
The advantages of supercritical conditions; a single phase beneficial to mass transfer, faster reaction times due to temperature and mixing, and enhanced heat recovery for industrial

processes can only be accessed for molecules which are sufficiently stable to avoid thermal decomposition.

Fortunately the rapid reaction rate at high temperature in the case of pX-TA allows for conversion and quenching to occur before much decarboxylation occurs.

Batch experiments may be used to screen reactions for their potential in scH_2O, the process should include investigation of the stability of the desired product at high temperature.

ACKNOWLEDGEMENTS:

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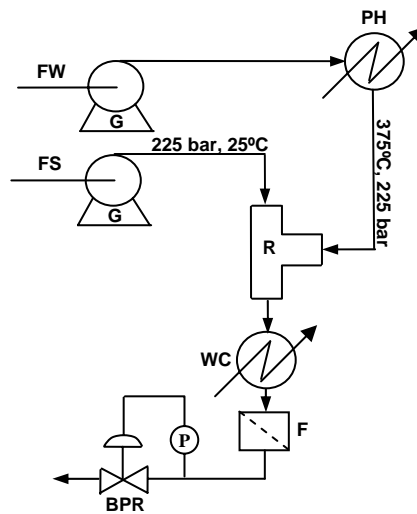[26] Y.E. Gorbaty, G.V. Bondarenko, E. Venardou, S.J. Barlow, E.G. Verdugo, M.Poliakoff.

Figure 1: *: Flow diagram of the continuous supercritical reactor system used by the Clean Technology Group. This equipment is used for various supercritical reactions including metal oxide and mixed metal oxide nano-particle production. Key: FW – water feed, FS – aqueous metal salt feed, G – Gilson HPLC Pump, PH – preheater, R – continuous reactor, WC – water cooling, F – 0.5μm Filter, BPR – Tescom back pressure regulator, P – pressure transducer.*