

Process Design for Organic Reactions in Near-critical and Supercritical Water

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Water, under high-temperature and high-pressure conditions, becomes a tuneable solvent - Supercritical Water (SCW), which is now opening the door to completely new opportunities in chemistry. Here we report the process design to carry out cleaner organic reactions where SCW is used as an alternative and friendlier solvent. A multipurpose, continuous flow system has been designed for organic reactions in SCW. The configuration of the reactor was designed in order to perform either non-catalysed or homogeneously catalysed organic reactions in SCW.

INTRODUCTION

Water is abundant, inexpensive, non-flammable and non-toxic, but its use as a solvent is limited by its high polarity and the consequent poor solubility of organic molecules. As water approaches its critical point ($T_c = 374^\circ\text{C}$, $P_c = 221$ bar), its properties are very different from those at ambient conditions and vary significantly with temperature and pressure near the critical point. Thus the key advantage of using SCW is the opportunity to vary the properties of the reaction medium over a wide range solely by changing the pressure and temperature, and thus optimize the reaction without changing the solvent. For example, the static dielectric constant (ϵ) of water decreases from 78.5 at ambient conditions to 5.9 at 673.2 K, 300 bar. At a constant pressure of 250 bar, the ion product of water (K_w) first increases with temperature until K_w reaches a maximum (10^{-11}) at 523.2 K, then decreases to 10^{-19} at 673.2 K and 10^{-22} at 773.2 K. As a result, it is possible to tune the environment to favour either free radical or ionic mechanisms. In addition, many non-polar organic substances and gases are highly soluble in SCW so that restrictions in mass transfer due to phase boundaries are removed. Moreover, water can act as a reactive component as well as a catalyst in some reactions.

Supercritical water oxidation^[1] is already used commercially. Chemical syntheses such as hydrolysis^[2], hydration^[3], dehydration^[4] and partial oxidation^[5] can also be carried out in SCW. In this paper, a multipurpose, continuous flow system is presented, in which either non-catalysed or homogeneously catalysed organic reactions in SCW can be performed.

EQUIPMENT SETUP

Figure 1 is a multipurpose, continuous flow system for non-catalysed or homogeneously catalysed reactions.

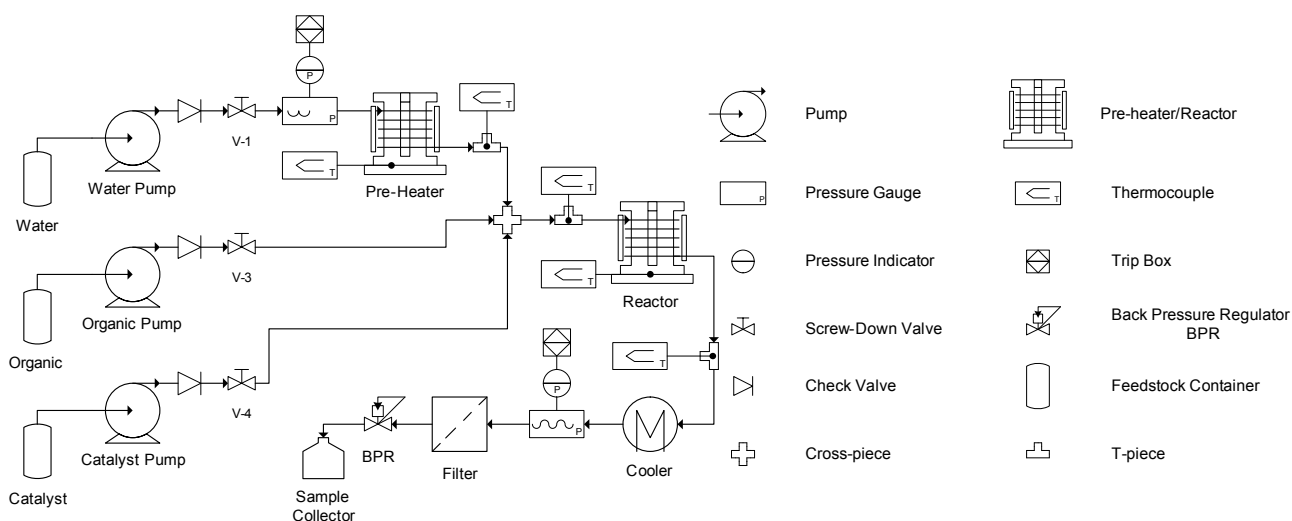


Figure 1: Diagram of a typical SCW continuous flow reactor.

Since the reactions occur at high temperature, it is important to ensure the stability of the products. Thus, the characteristics of the rig are: 1) fast heating; 2) short residence time; and 3) fast quenching.

The equipment consists of a serial reactor with the following features: 1) 1/16 inch Hastelloy™ tubing coiled around an aluminum block; 2) a cartridge heater and a band heater to supply heat; and 3) a justable reactor length.

The temperature is controlled by a thermocouple placed in the base of the aluminum block, and monitored by an Inconel™ thermocouple secured inside the T-piece at the outlet and recorded by the PicoLog™ program. The temperature is also adjustable by varying flow rates of the streams (at the mixing point).

The pressure is generated by the pumps which are computer controlled, and the system pressure is maintained by the BPR. There are two pressure-monitoring points: one before the pre-heater; the other after the cooler. Either of these readings is connected to a feedback system to ensure the pumps are tripped off in the event of overpressurization.

RESULTS AND DISCUSSION

Rapid heating is required to drive the reaction mixture rapidly into the supercritical region and thus potentially avoid side reactions. Fast heating is achieved by mixing the hot stream of SCW with the cold streams of organic and catalyst. In this continuous flow system, there is a thermocouple after the mixing point, which is connected to the cross-piece with 1/16 inch tubing, $L = 0.03$ m (Figure 2). For example, when $p = 350$ bar and $T > 350^\circ\text{C}$, $\rho < 700$ kg/m³. Then the heating time $t < 0.06$ s at a total flow rate of 5.5 ml/min.

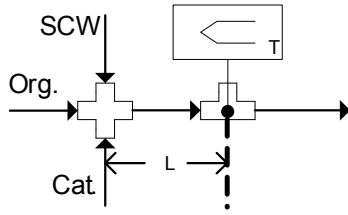


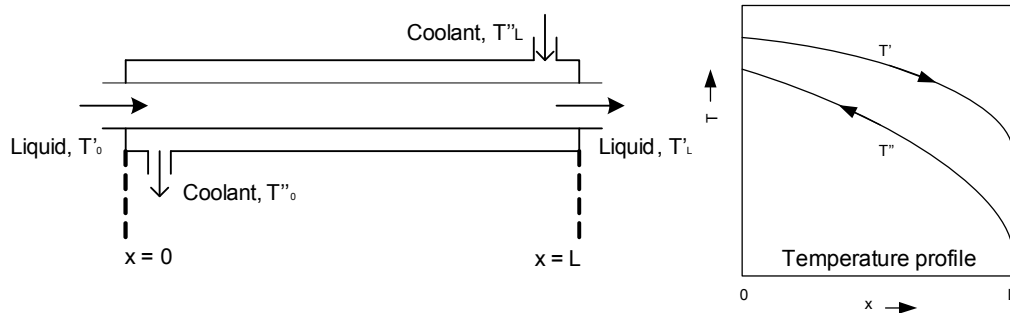
Figure 2: Scheme of the design for fast heating.

It is necessary to have a very short residence time for the organic substrates in SCW to avoid side reactions and decomposition of the products. The residence time in the reactor is estimated by using equation (1), where V (m^3) is the volume of the reactor; Q (m^3/s) is the volume flow rate of the fluid in the reactor.

$$\tau = \frac{V}{Q} \quad (1)$$

When $p = 350$ bar, $T = 400^\circ\text{C}$, and $Q = 5.5$ ml/min (ambient condition), the residence time τ of the fluid in the 1/16" tubular reactor (1.5 m in length) is 2 s.

Figure 3: Scheme of the cooling process and temperature profile in the tubular cooler.



The quenching in the heat-exchanger is a complicated isobaric cooling process (Figure 3). The residence time in the tubular cooler is estimated by using equation (2)

$$dt = \frac{dV}{Q} = \frac{\frac{\pi d^2}{4} dL}{\frac{M}{\rho_L}} \quad (2)$$

Where t (s) is the residence time in the cooler, V (m^3) is the volume of the cooler, Q (m^3/s) is the volume flow rate, d (m) is the inner diameter of the cooler, L (m) is the length of the cooler, M (kg/s) is the mass flow rate and ρ_L (kg/m^3) is the density of the fluid at L .

If the density ρ_L is assumed to be changing linearly with the cooler length L , and the state of the fluid is assumed to change from (400°C, 350 bar, 477.23 kg/m³) at the beginning of the cooler to (100°C, 350 bar, 1000 kg/m³) at the end, then:

$$\rho_L = 3485L + 477.23 \quad (3)$$

Equation (2) may then be solved with $M = 5.5 \times 10^{-3}$ kg/min, $d = 0.5715 \times 10^{-3}$ m, and $L = 0.15$ m. The calculated residence time of the fluid in the cooler is 0.31 s. However, the real L is less than 0.15 m, and thus the residence time in the cooler should be less (<0.31 s).

CONCLUSION

A multipurpose, continuous flow system has been designed for organic reactions in SCW. Temperature and pressure were effectively monitored and controlled. Alloy material was utilized to prevent corrosion. Key characteristics of this continuous flow system are fast heating, short residence time and fast quenching – these ensure the stability of the reactants, products and catalysts.

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