

Separations Using Superheated Water

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ABSTRACT

Superheated water is liquid water under pressure between 100°C and its critical temperature of 374°C. The rationale for using superheated water is explained. An overview of the work on its use for separation processes is given. The work that has been carried out is mostly of laboratory scale, although some pilot studies and small industrial processes are described.

INTRODUCTION

It is useful to define superheated water as liquid water under pressure between 100°C and 374°C to distinguish it from cold or hot water below 100°C and supercritical water above 374°C. It has the advantages of many other green solvents, being cheap and readily available, non-toxic and easily disposed of. The pressures required are much lower than for most supercritical fluids, being tens rather than hundreds of bars, making superheated water processes cheaper than supercritical fluid processes. The advantage of superheated water is that it is much less polar than water at ambient temperature and therefore more compatible with organic molecules.

The use of superheated water is not new. It has been used in the food industry for cooking a little above 100°C and the final extractions of instant coffee are sometimes up to 120°C. Recrystallizations in water contained in sealed tubes above 100°C have been carried out for 100 years or more. Superheated water has also been used for waste treatment by the so-called wet-air oxidation process [1]. Chemical reactions have also been carried out in superheated water and this work has been thoroughly reviewed recently [2-4].

However, in recent years there has been a renewed interest in superheated water as a replacement for organic solvents in separations and related processes. Over 100 research papers on this subject have been published in the last 5 years. Much of this work has been restricted to the range of 100°C to 300°C. At these lower temperatures water is not highly compressible, and the pressure of the medium does not have much effect, as long as it is high enough to maintain the water in the liquid phase. This work on superheated water has been reviewed [5] and the manipulation of water properties with temperature to achieve process ends has been made the subject of a patent [6]. Most of the work that has been described is on a laboratory scale and some of it is directed towards analysis. However, some larger-scale processes are under consideration, mainly for environmental reasons.

POLARITY OF SUPERHEATED WATER, THE SOLUBILITY OF ORGANIC COMPOUNDS IN IT AND ITS USE FOR PROCESSES

Water changes dramatically when its temperature rises, because of the breakdown in its hydrogen-bonded structure with temperature. The high degree of association in the liquid causes its relative permittivity (more commonly called its dielectric constant) to be very high at around 80 under ambient conditions. But as the temperature rises the hydrogen bonding breaks up and the dielectric constant falls, as shown in Figure 1. By 205°C its dielectric constant has fallen so that it is equal to that for methanol (i.e. 33) at ambient temperature. Thus, between 100°C and 200°C superheated water is behaving like a water-methanol mixture.

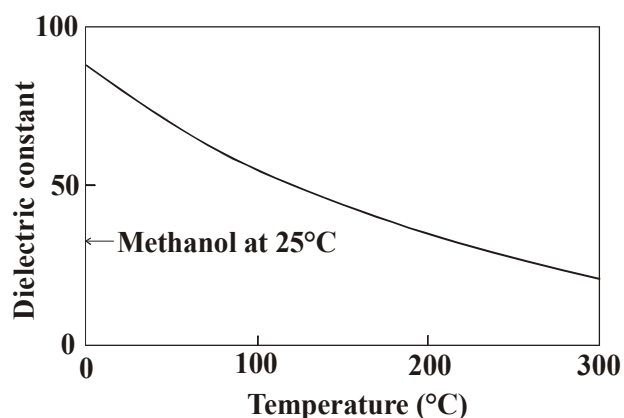


Figure 1: The dielectric constant (relative permittivity) of liquid water as a function of temperature at its vapour pressure.

Because of the greater solubility of some organic compounds in superheated water, this medium can be considered for the extraction and other processes, to replace conventional organic solvents. As would be expected, reactions of the compounds being processed may also occur, by hydrolysis, oxidation, etc. In some cases these reactions are to be avoided as far as possible by choice of conditions, such as temperature. In others, they are desirable and

Table 1: The solubility of chloranthonil in water [8] over a range of temperature

T / K	x_2
323	5.41×10^{-8}
373	1.89×10^{-6}
423	6.43×10^{-5}
473	1.58×10^{-3}

form part of the process for example by degrading and destroying the extract or by producing desired products. It might be imagined that superheated water processes were costly in energy terms. However, this is not the case because water stays as a liquid and the latent heat of evaporation is not required. As an example, we compare superheated water extraction with steam distillation. A greater mass of superheated water may be needed for a given mass of material to be extracted. However, only 505 kJ kg^{-1} is required to heat liquid water from 30°C to 150°C , compared with 2550 kJ kg^{-1} required to convert water at 30°C to steam at 100°C . Moreover, it is relatively easy to recycle the heat in a superheated water process by passing the water leaving the extraction cell through a heat exchanger to heat the water flowing to the cell. More than 80% of the energy can be realistically recovered in this way, as will be shown below.

EXTRACTIONS AND RELATED PROCESSES ON A LABORATORY SCALE

A simple example of an extraction apparatus for work on a small scale is shown schematically in Figure 2, which was designed for plant material extraction. The system is readily adapted for related work, the main consideration being the pressure required at the temperature to be studied. Water is deoxygenated, by sparging with helium for half an hour. It is then pumped at around 1 mL per minute into the extraction cell in an oven at the required temperature, through a long tube, which acts as a heat exchanger to bring the water up to temperature. On

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reasons, one being the polarity change. The other is that a compound with low solubility at ambient temperature will have a high positive enthalpy of solution, and thus a large increase in solubility with temperature as shown in Table 1 for the pesticide chloranthonil. A large number of solubility and phase behaviour measurements have been made.

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exiting from the oven, the water stream is cooled using a coil of tubing in air and passes through a narrow tube into a collection vial. The narrow tube acts as a restrictor to maintain the pressure in the system above the vapour pressure, typically at 50 bar. Minor refinements are not shown here. Other studies, referred to below use very similar experimental systems. For kinetic experiments, to

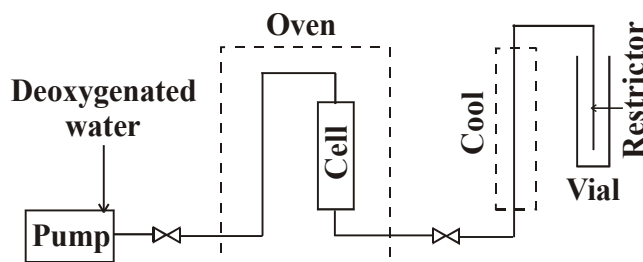


Figure 2: Schematic diagram of a small laboratory system for superheated water extraction.

study extraction rates, the vial is replaced at known intervals. The extract is then back-extracted into a solvent, such as pentane, and then analysed and quantified by gas chromatography, for example. For studies on liquid extraction, the cell is filled with packing material and the oil pumped through a tube so that it enters 20 mm above the bottom of the cell.

Studies made on a laboratory scale have been numerous and include extractions of pollutants, biomass, polymers and liquids. Studies of the extraction of pollutants from soils, sediments, sludges, coal and other matrices have been carried out extensively on a laboratory scale. In some cases degradation of the extracted compounds occurs during the process to benign waste or useful products. For example chlorinated compounds are converted into hydrocarbons and explosives become small molecules. In other studies, a degradation step, such as supercritical water oxidation, has been added in-line to destroy the extracted compounds. These laboratory studies have been aimed at developing both analytical procedures and clean-up processes. In some studies superheated water extraction has been directly coupled to analytical methods.

The first biomass studied with respect to superheated water reaction was rosemary (*Rosmarinus officinalis*) and this showed that the oxygenated compounds were preferentially extracted compared with the terpene hydrocarbons [6]. In essential oils, the valuable components, which give the flavour and fragrance of the essential oil, are the oxygenated compounds, whereas the monoterpenes are the less valuable components. A more detailed study of the extraction of rosemary [9] was subsequently carried out. Figure 3 shows results obtained at 150°C for the extraction of rosemary with liquid water, presented in the form of

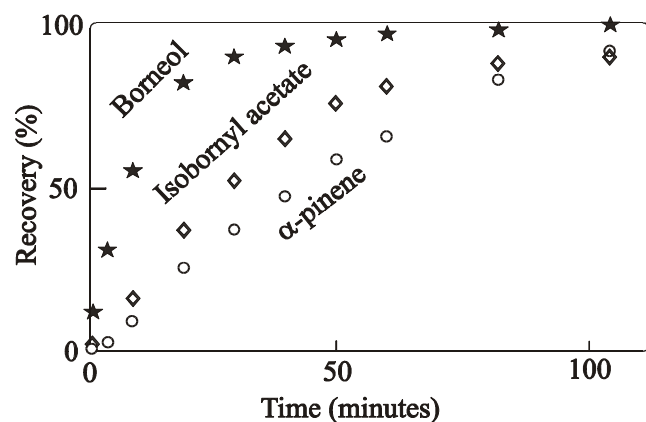


Figure 3: Recovery curves for compounds extracted from rosemary by liquid water at 150°C

the percentage of each of three representative compounds obtained after a given time compared with the amount that can be obtained after a long extraction. The monoterpene α -pinene extracts relatively slowly. The ester isobornyl acetate is extracted a little more quickly and the alcohol borneol even more quickly. Of course many other more water-soluble compounds are also extracted from plants by superheated water, such as antioxidants from rosemary [11]. Treatment of polymers by superheated water at high

temperatures can result in its decomposition/hydrolysis to monomers or lower oligomers. At lower temperatures the polymer is stable and the small amounts of monomers, initiators, low oligomers and other small compounds can be extracted from polymers with superheated water. For example, at 200°C styrene, alkylbenzene contaminants and styrene dimers were extracted from polystyrene without destroying the polymer. Although it was stable at 200°C, at 250°C polystyrene was decomposed into substituted benzenes [6]. Tyres can also be depolymerised.

Experiments on liquid extraction have been carried out on the partitioning of aromatics between gasoline and diesel and superheated water [10]. There is an increase in the partition coefficient between ambient and 200°C of a factor of 10 or greater. This behaviour could be the basis of a process for the removal of aromatics from petroleum products. Oxygenated flavour and fragrance compounds can also be extracted from essential oils by superheated water.

Finally a brief mention is made of chromatography using superheated water, which was first published in 1981 [12]. It uses silica and polymer-based mobile phases and an FID detector can also be used [6]. This is of interest both for analytical chemistry and for its use for a process, either alone or following superheated water extraction.

PILOT PLANT STUDIES

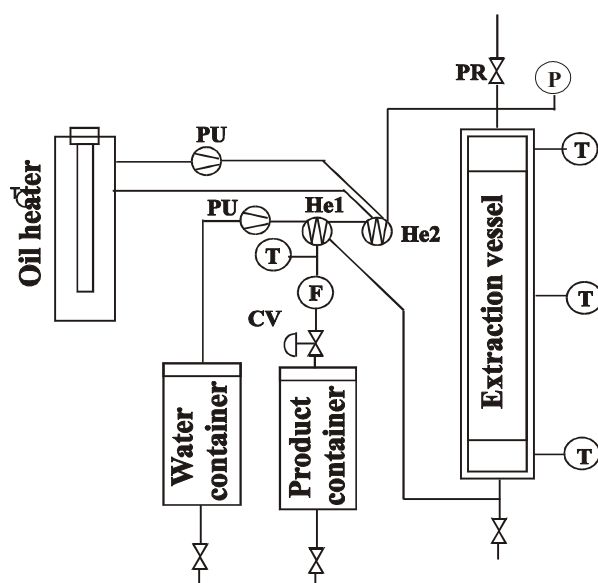


Figure 4: Schematic of a pilot plant



Figure 5: Photograph of the pilot plant

Figure 4 is a schematic diagram of a representative pilot plant located at Critical Processes Limited in the UK and Figure 5 is a photograph of it. It has an extraction cell of 32 L volume and will operate up to 200°C. The maximum water flow rate is 60 L per hour. The oil heater is 6 kW and the flow rate of oil is 120 L per hour. The oil flow rate is higher because of the lower heat capacity of oil. In the system water is pumped from a container through two heat exchangers into the cell. The first heat exchanger is heated by the product emerging from the cell, and the second by oil from a heater. The flow rate is measured and the pressure is controlled by a valve at the exit. Temperatures are measured throughout the system.

Pilot-scale studies have also been carried out on the superheated water extraction of polyaromatic hydrocarbons, pesticides, and polychlorinated biphenyls from soils. At 250°C almost complete soil clean-up is achieved in less than 1 hour. The plant has an 8 L cell and operates batchwise. A device has also been developed which can be hammered into soil to carry out decontamination *in situ* [6]. A pressure cell is formed when the device penetrates a clay layer. Alternatively the soil at the bottom of the device is frozen with liquid carbon dioxide. The natural organic (humic) content of the soil largely remains with these processes and it can be used for successful cultivation. Hydrocarbons are re-precipitated as the water cools, whereas some compounds, such as pesticides, are degraded to less toxic materials during the extraction process. Soil containing explosives has also been treated in the same pilot plant using static extraction. The destruction of TNT, RDX and HMX was 99.99%, 99.9% and 97.9%, respectively.

SUPERHEATED WATER PROCESSES

Process development is at an early stage and, because of commercial confidentiality little information is available for release. I therefore here can only describe the processes in which we are involved and give no details of the materials being processed. A few general points about processes can also be made. The main problems to be solved are the separation of the desired components at the end of the process from both the extracting water and from highly

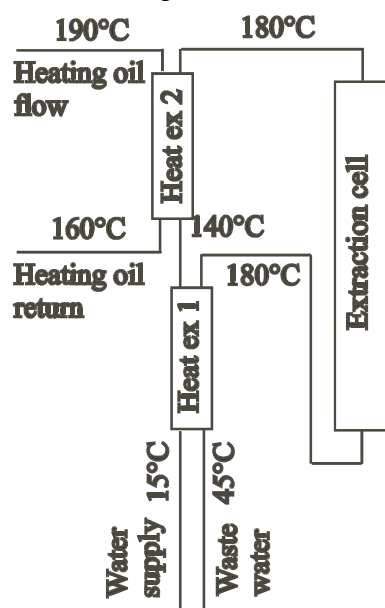


Figure 6: Heat recycling in the process plant

water-soluble material also present in the plant material and therefore water extract. The extract is often coloured brown like tea and often contains a precipitate in which the oxygenated compounds are absorbed. On the small scale these are back extracted using an organic solvent, such as pentane for analysis, but this would not be acceptable in an environmentally friendly process. One suggestion is to back extract with supercritical carbon dioxide, which is also a clean solvent. Another alternative is to do the reverse, i.e. extract the plant material first with carbon dioxide to obtain a 'concrete' or 'oleoresin', which contains heavy materials, such as plant waxes. The concrete can then be treated with superheated water, as described in the section on liquids. However, the use of supercritical carbon dioxide is probably not economically viable for most products. In some cases there is not a problem. For example, the extraction of flowers, such as rose petals, leads to a white precipitate containing the fragrance compounds. This may be a product, which can be accepted as an additive to soaps and other cosmetics.

Another situation is the production of flavour materials, which are normally obtained by hot-water infusion, such as spices. The use of superheated water seems to give a more concentrated extract and thus may be more cost-effective.

In our company we are developing a process involving the extraction of a biomass, while a clean-up process for a polymer is now in operation. The polymer plant has an extraction cell of 700 L and 82% of the heat is recycled. A schematic diagram of the plant with approximate temperatures is shown in Figure 6. At the beginning of each run the plant must of course be brought up to temperature which uses further energy.

Figures 7 and 8 are photographs of the plant both before and after cladding, which is to protect staff from escaping hot water and steam. Figure 7 shows the hopper, which is used to fill the cell and which is lifted by a fork lift truck. It also shows the vessel and the water tank, which contains deionised water used for the extraction. An important part of the process is drying the polymer after extraction, which requires a large compressor and refrigerator to remove ambient water from the air. These can be partly seen in Figure 8.



Figure 7: Process plant before cladding



Figure 8: Process plant after cladding

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