

# Supercritical CO<sub>2</sub>: a twenty-first century solvent for the chemical industry

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Half a glass of water may be described as half full or half empty, but if the water is in a supercritical state we have to agree that the glass is filled with something that is neither a gas nor a liquid. Steam and boiling water when in equilibrium are two different phases that are clearly separated by a phase boundary, but if the temperature and pressure are raised, after a point the phase boundary disappears and water becomes a supercritical fluid (SCF). While by appropriate changes in temperature and pressure the supercritical phase for many other substances could also be reached, from the point of view of applications, supercritical carbon dioxide (scCO<sub>2</sub>) is of special interest. The main impetus for the wide-scale application of scCO<sub>2</sub> and other SCFs comes from the desire to develop environment-friendly chemical processes<sup>1-3</sup>. The environmental impact of a chemical process can be measured by its E-factor (amount of waste per unit mass of desired product). The E-factor has an inverse relationship with its environment-friendliness and includes solvent loss in the process<sup>4</sup>. Many industrial solvents are not only

hazardous (toxic, flammable, etc.), but their full recovery and recycling often are not easy, or economically viable. An appropriate example is the pharmaceutical industry where approximately only about 1% (w/v) product comes out of the solvent used, with about 50% solvent recovery in the whole process<sup>5</sup>. Furthermore even a non-hazardous hydrocarbon solvent in the long run is converted to CO<sub>2</sub> and adds to the carbon cycle. Therefore, from the point of view of the overall environment-friendliness, replacement of common organic solvent is an important objective. Although the main motivation for the wide-scale application of scCO<sub>2</sub> in recent times originated from environmental considerations, studies on scCO<sub>2</sub> have also led to many important scientific findings<sup>6-8</sup>. In this review we present some of the recent scientific and technological advances associated with the use of SCF in the industry. The focus is mainly on the chemical aspects and the underlying principles of SCF-based technologies, but technologies other than chemical are also mentioned.

**Keywords:** Carbon dioxide, E-factor, industrial application, supercritical fluids, water.

HISTORICALLY it was probably Baron Charles Cagniard de la Tour, who in 1822 first defined a supercritical fluid (SCF) as a state of matter where the liquid and vapour phases are indistinguishable<sup>9</sup>. The first technological application of SCF, however, had to wait for almost 150 years when in 1970, Kurt Zosel of Max Plank Institut Fur Kohlenforschung, used supercritical carbon dioxide (scCO<sub>2</sub>) to extract caffeine from coffee beans and raisin from hops<sup>10</sup>. This was followed by many other applications. The approximate current distributions of SCF-based technologies in different industrial sectors<sup>11</sup> are shown in Figure 1. The applications are wide, from oxidation of hazardous waste using supercritical water (scH<sub>2</sub>O) to the cleaning of ancient photographs by SCF<sup>12-14</sup>.

Here we present an overview of the industrial use of SCF in general and scCO<sub>2</sub> in particular. Given the large number of patents and publications (more than 5000 patents in the US patent database and ~15,000 papers in the web of science database), this review is necessarily highly

selective. The main emphasis is on SCF-based, commercially proven technologies that either exist, or are expected to emerge in the near future. As the long-term survival of the petrochemical industry critically depends on its ability to develop greener and sustainable processes, our focus is mainly on this sector. We begin this review by highlighting the underlying principles that make the innovative use of SCF possible.

## Physico-chemical properties of SCF

From Gibbs' phase rule it follows that once the supercritical state is reached (points  $T_c$ ,  $P_c$  in Figure 2), the pressure and temperature of the single phase (the supercritical state) can be increased simultaneously or

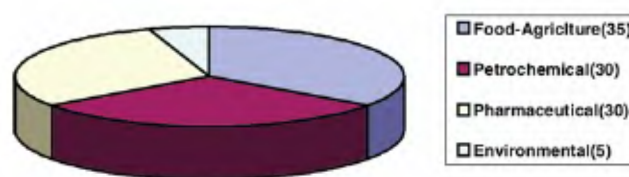
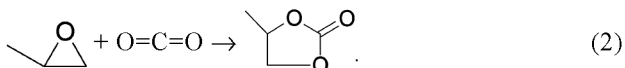
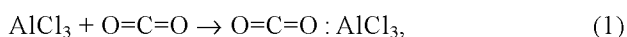


Figure 1. Industrial application of supercritical fluids.

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individually without effecting a phase change. The  $T_c$  and  $P_c$  of  $\text{CO}_2$  (30.95°C and 72.8 atm) can be easily attained in commercially available pressure reactors. In contrast, water requires far more drastic conditions, 374°C and 218.3 atm. The best applications of SCFs are usually found in the range  $1 < T/T_c > 1.1$  and  $1 < P/P_c < 2$ . Among other considerations, it is the relatively mild conditions for  $\text{scCO}_2$  that have made it emerge as the most intensely investigated SCF.

The basic physical properties that are of critical importance in the innovative use of SCF are density, viscosity and diffusion. A comparison of these properties<sup>15</sup> for typical gases, liquids and SCFs is given in Table 1. The potential ability of  $\text{CO}_2$  to interact with Lewis acids (eq. (1)) and Lewis bases (eq. (2)), is also of importance in many applications, where it acts as a solvent and/or a reactant.



Low viscosity, high solute diffusibility, and almost no surface tension impart high penetrating capability to SCFs. This makes them suitable for applications such as microencapsulation, impregnation, etc.<sup>7</sup>. Due to low viscosity SCFs generally have good mass and heat transport properties and are therefore attractive potential solvents for chemical reactions. However, for applications as a solvent, solubility of the reactants in a given SCF is obviously an important consideration. Although small non-polar molecules are generally soluble in  $\text{scCO}_2$ , many other substances are not. However, using a co-solvent such as methanol and by varying the pressure and temperature, the composition, density and solubility properties of dilute binary mixtures may be tailored to some extent.

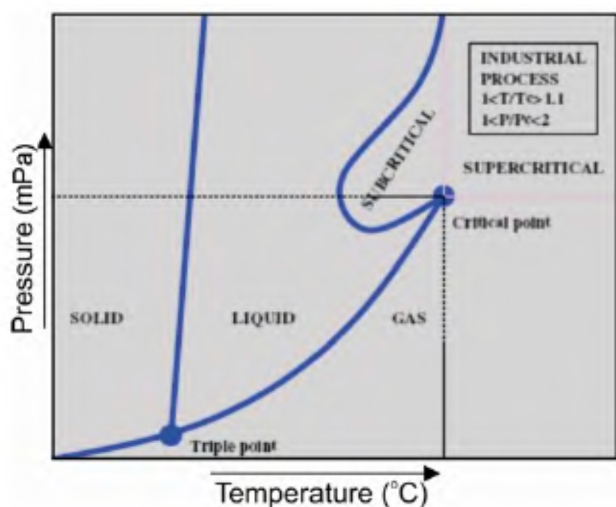


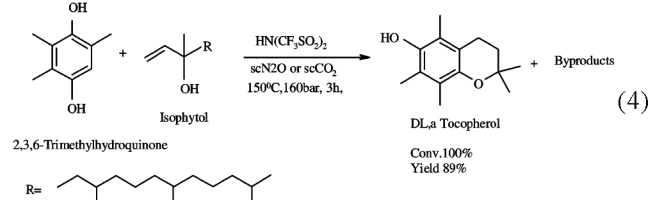
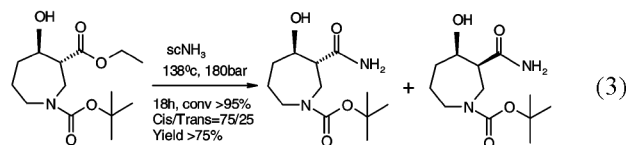
Figure 2. Phase diagram of a typical compressible fluid.

## Chemical industry and SCF

As mentioned earlier, the interest in exploring the use of SCFs in chemical reactions arises mainly from a desire to replace volatile organic chemicals (VOCs) with SCFs. For obvious reasons, reactions that are normally carried out in the liquid phase using organic solvents have received more attention than those where no such solvents are needed, e.g. heterogeneous catalytic reactions. Among many reactions that have been studied, noteworthy are the use of SCF in reactions such as polymerization, oxidation, metathesis, alkylation, hydrogenation, hydroformylation, etc. (Scheme 1). The use of SCFs in some these reactions has already been implemented on an industrial scale, while the scientific and technological viabilities are being actively explored for the others.

### Pharmaceuticals and chiral intermediates

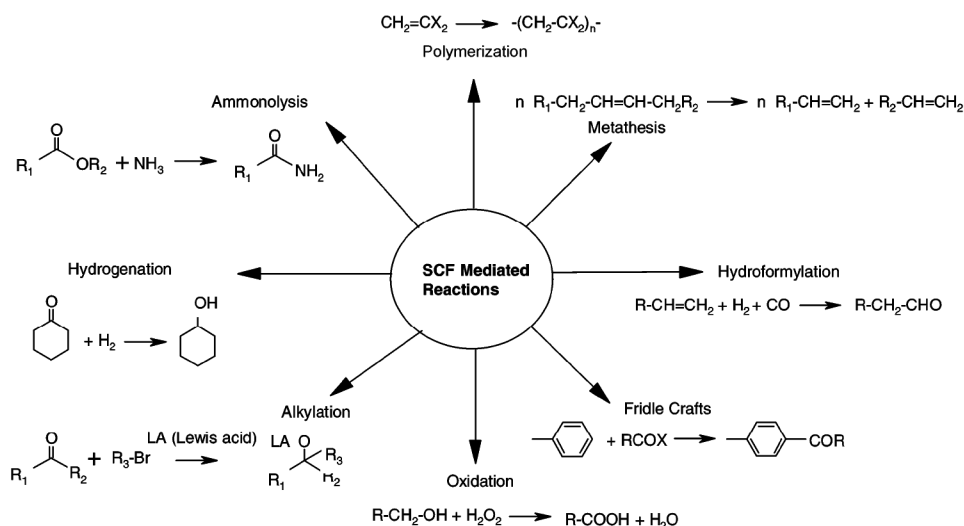
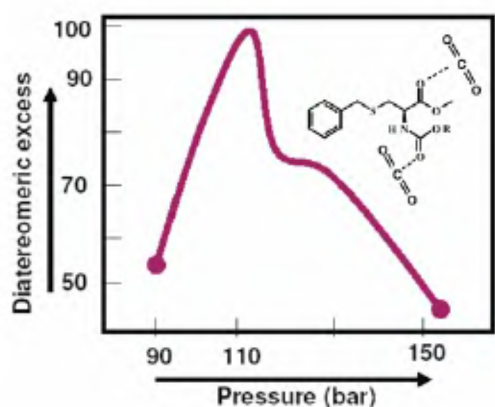
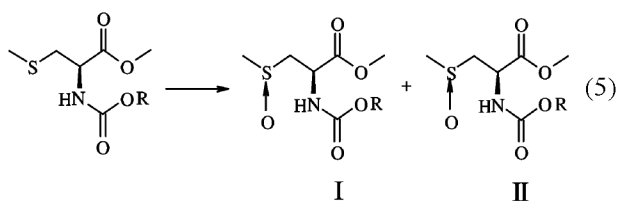
Researchers from Hoffmann-La Roche (HLR) have recently reported<sup>16</sup> the use of  $\text{scNH}_3$ ,  $\text{scN}_2\text{O}$  and  $\text{scCO}_2$  in the manufacture of pharmaceutical products and intermediates. Ammonolyses of organic esters, mesylates or other sulphonates are normally carried out in aqueous ammonia, but product isolation from aqueous solutions requires cumbersome separation processes. The use of  $\text{scNH}_3$  rather than aqueous ammonia as a reaction medium (eq. (3)) simplifies the process by eliminating the additional separation step. The HLR workers also reported the synthesis of D,L- $\alpha$ -tocopherol, a pharmaceutical intermediate, from trimethyl hydroquinone and isophytol in  $\text{scCO}_2$  (eq. (4)). Interestingly, for the same reaction  $\text{scN}_2\text{O}$  ( $T_c = 36.4^\circ\text{C}$ ,  $P_c = 72.45$  bar), rather than  $\text{scCO}_2$  can also be used with satisfactory results.



Optical purity of chiral drugs in the pharmaceutical industry is of importance. Rayner and co-workers have reported pressure-optimized diastereocontrol in the asymmetric catalytic oxidation of cysteine and methionine to the corresponding sulfoxides (eq. (5))<sup>17</sup>. A diastereomeric excess of ~95% is achieved at ~110 bar of  $\text{CO}_2$  (Figure 3). Interestingly, no such diastereoselectivity is observed in the conventional ( $\text{mCPBA}/\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ ) oxidation reaction that involves no  $\text{CO}_2$ .

**Table 1.** Comparison of some physical and transport properties of gases, liquids and SCFs

Property	Gas (ambient)	SCF ( $\geq T_c, P_c$ )	Liquid (ambient)
Density $\rho$ (kg/m <sup>3</sup> )	0.6–2	200–500	600–1600
Dynamic viscosity $\eta$ (mPa)	0.01–0.3	0.01–0.03	0.2–0.3
Kinematic viscosity $\nu (= \eta/\rho)$ (10 <sup>6</sup> m <sup>2</sup> s <sup>-1</sup> )	5–500	0.02–0.1	0.1–5
Diffusion coefficient $D$ (10 <sup>6</sup> m <sup>2</sup> s <sup>-1</sup> )	10–40	0.07	0.0002–0.002

**Scheme 1.** Few industrial chemical reactions in SCF.**Figure 3.** Effect of pressure (at 40°C) on diastereomeric excess. (Inset) Suggested interaction between CO<sub>2</sub> and the substrate.

- (1) mCPBA, CH<sub>2</sub>Cl<sub>2</sub>, -78°C = Racemic  
 (2) Amberlyst Resin = Major isomer I  
 tBuOOH, 40°C scCO<sub>2</sub>

A plausible reason for pressure-dependent diastereoselectivity is the interaction between CO<sub>2</sub> and the carbonyl groups. Such an interaction is expected to enhance the steric bulk of the carbonyl group(s) and provide conformational rigidity (inset, Figure 3). This in turn may stabilize one specific diastereomeric transition state, leading to high diastereoselectivity.

### Hydrogenation and hydromylation

Catalytic hydrogenation reactions are extensively used in the petrochemical industry. The use of organic solvents with highly flammable hydrogen gas is often a safety concern and in such situations the substitution of organic solvents by scCO<sub>2</sub> is desirable. The first report on catalytic hydrogenation in scCO<sub>2</sub> was the hydrogenation of a cyclopropene derivative using MnH(CO)<sub>5</sub> as a catalyst<sup>18</sup>. Subsequently, hydrogenation of fats and oils in a mixture of scCO<sub>2</sub> and scC<sub>3</sub>H<sub>8</sub> for better solubility (C<sub>3</sub>H<sub>8</sub> = propane) has been reported<sup>19,20</sup>. An important recent development in this area is the invention followed by commercialization of hydrogenation of specialty chemicals such as  $\alpha,\beta$ -dihydrocinnamaldehyde from cinnamaldehyde, trimethyl cyclohexanone from isophorone, and cyclohexylamine from aniline in continuous rather than batch processes<sup>21</sup>. This technology development, spanning over a period of 7 years, involved the scaling-up of operations from a 5 ml reactor to a plant with 1000 t/yr capacity<sup>22</sup>.

Closely related to hydrogenation is hydroformylation, where an alkene is reacted with a mixture of  $H_2$  and  $CO$  to give an aldehyde. The cleanest industrial hydroformylation process was developed by Ruhrchemie/Rhône-Poulenc and involves an aqueous biphasic reaction medium<sup>23,24</sup>. It may be noted, however, that Mitsubishi Chemical has patented SCF-based hydroformylation technology, although no commercialization has followed<sup>25</sup>. There are also recent reports of hydroformylation reaction carried out in a continuous process using ionic liquid and  $scCO_2$  as a biphasic medium<sup>26</sup>.

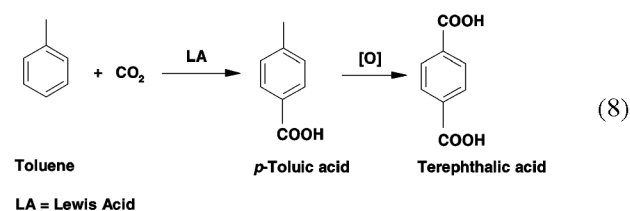
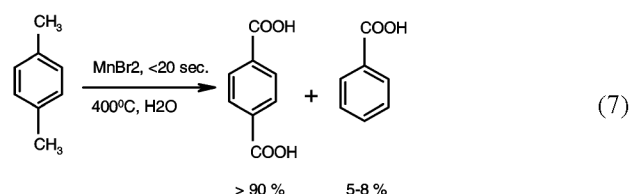
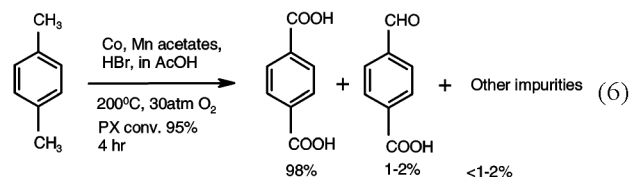
### *Oxidation, Friedel–Crafts reactions and terephthalic acid*

Terephthalic acid is one of the monomers for the production of polyesters. The most common polyester, the polymer of terephthalic acid and ethylene glycol was originally called ‘Terelyne’ and is widely used in garments. Terephthalic acid is made by the oxidation of *p*-xylene ( $\leq 200^\circ C$ ,  $\sim 30$  atm  $O_2$ ) in acetic acid, with cobalt and manganese salts as catalysts and  $HBr$  as a promoter. As shown in eq. (6), in this process 4-carboxybenzaldehyde is produced as a by-product, and its concentration must be maintained at a level as low as 20 ppm. Interestingly,  $scH_2O$  in place of acetic acid provides favourable changes in the rates of reactions and completely eliminates the formation of the undesired 4-carboxybenzaldehyde (eq. (7))<sup>27,28</sup>. Also, liquid-phase oxidation with high temperature water (HTW) and a continuous process based on  $scH_2O$  have been found to be technically feasible<sup>29,30</sup>. From recent reports it is clear that terephthalic acid and polyester manufacturers like Dupont, Invista, Ariva and Mitsubishi have serious commercial interest in this emerging technology<sup>31</sup>.

Given the commercial importance of terephthalic acid, it is not surprising that alternative routes involving Friedel–Crafts reaction have also been explored for its manufacture. Carboxylation of toluene using  $scCO_2$  to give *p*-toluic acid is an approach that avoids the use of *p*-xylene as the raw material (eq. (8))<sup>32</sup>. Oxidation of toluic acid to terephthalic acid is well studied because the conversion of *p*-xylene to terephthalic acid involves the formation of toluic acid as an intermediate.

It has been shown recently that a mixture of aluminum chloride and aluminum powder activates  $CO_2$  at 5.7 MPa and 353 K to form *p*-toluic acid from toluene, with excellent yield and selectivity<sup>33</sup>. The reaction mechanism probably involves the formation of a  $CO_2-Al_2Cl_6$  adduct followed by other steps. The complexity of the reaction mechanism is apparent from the observation that other Lewis acids such as  $ZnO$  and  $SnCl_4$  are also effective, but only if these Lewis acids and  $CO_2$  are incubated first, i.e. treated at optimized condition before addition of toluene. Furthermore, the order of addition of the reactants and the

Lewis acid catalyst seems to have a remarkable effect on the selectivity of the reaction<sup>34,35</sup>.

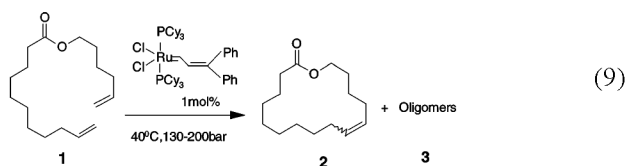


Two other important applications of  $scH_2O$  are: treatment of wastewater containing organic pollutants, and precious metal recovery from spent catalysts<sup>36,37</sup>. The short residence time (at  $\sim 500^\circ C$ ,  $<1$  min) of the former process is a notably attractive feature<sup>38</sup>.

As the solubility of oxygen is approximately ten times more in  $scCO_2$  than in organic solvents, oxidation reactions of other substrates by oxygen in  $scCO_2$  have also received attention<sup>39,40</sup>. With  $CO_2$ , activated oxygen under certain conditions can form peroxycarbonate, which is a better oxygen transfer agent than oxygen itself. Generation of hydrogen peroxide in  $scCO_2$  has also been suggested as an area of exploratory research. Such a process may have potential use in the oxidation of cyclohexane to adipic acid<sup>41</sup>, a co-monomer of Nylon 6,6.

### *Metathesis*

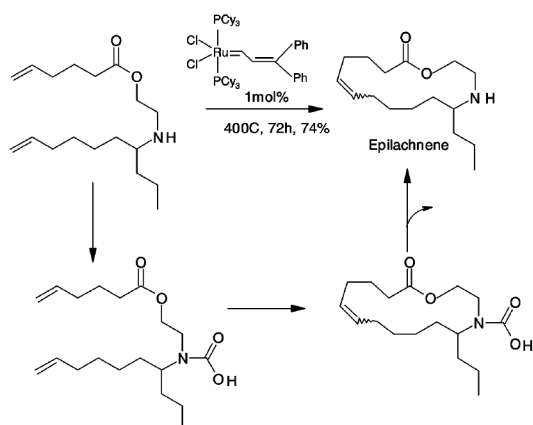
Olefin metathesis (eq. (9)) is a heterogeneous catalytic reaction that has been practised in the chemical industry for many years. However, its versatility as a synthetic tool with soluble catalysts (homogeneous catalysts) has only recently been recognized by chemists. The feasibility of both ‘ring closing metathesis’ (RCM) and ‘ring open metathesis polymerization’ (ROMP) with homogeneous catalysts in  $scCO_2$  has been established<sup>42</sup>. An important finding is that the selectivity of these reactions can be controlled by the  $CO_2$  pressure. Thus the RCM of **1** at 130 bar  $CO_2$  provides 8% of **2** and 68% of **3**, an intermolecularly formed oligomer, whereas at 200 bar 87% of **2** and 2% of **3** are obtained.



CO<sub>2</sub> can also act as temporary protecting group. Secondary amines tend to poison the ruthenium catalyst, but in scCO<sub>2</sub> carbamic acid derivatives (Scheme 2) are formed and no such poisoning is observed. Upon depressurization, the carbamic acid derivatives are converted to the desired metathesis products. This is shown by the synthesis of epilachnene, an insect repellent, using ruthenium-catalysed RCM in scCO<sub>2</sub>. The commercial viability of the SCF-based RCM process for the manufacture of pharmaceutical products is apparent from a recent report<sup>43</sup>.

### Switchable surfactant

The clever design of a switchable surfactant system consisting of an alcohol and a two-nitrogen atom containing an organic base has been recently reported. Although the design is based on gaseous CO<sub>2</sub> and does not require it to be in the supercritical state, for completeness we include this important finding here. The surfactant system is activated by CO<sub>2</sub>, deactivated by air (N<sub>2</sub>) and can be used to mix and unmix polar and non-polar mixture. This type of surfactant system is a potentially useful tool for the oil industry as it does not require metals or acids, and provides a cheap, non-toxic and environmentally benign separation method<sup>44,45</sup>. The exposure of a 1 : 1 mixture of the two non-ionic liquids, namely DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) and 1-hexanol, to gaseous CO<sub>2</sub> at one atmosphere and room temperature causes the conversion of the non-ionic liquid mixture to an ionic form (Figure 4). This is because in the presence of the nitrogen base, the electrophilic carbon atom of CO<sub>2</sub> undergoes attack by the alkoxy ion. This leads to the formation of an

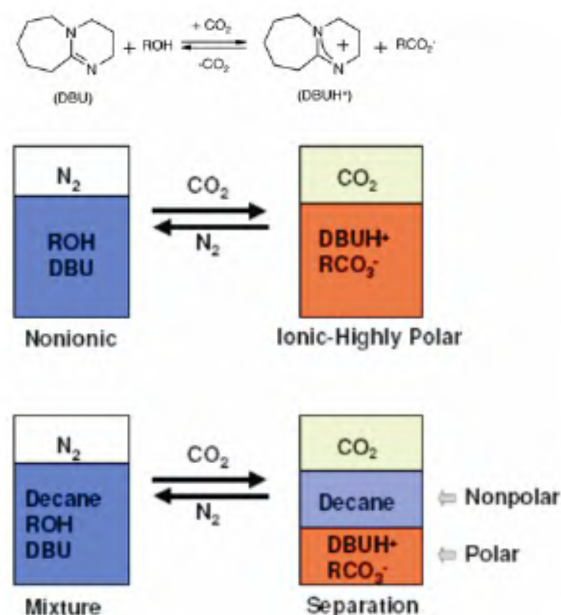


**Scheme 2.** Metathesis under supercritical CO<sub>2</sub>. No protection of secondary amine is required.

ion-pair between the protonated nitrogen base and the conjugate base of carbonic acid. A non-polar substance such as decane is immiscible with the ionic form of the mixture of 1-hexanol and DBU, i.e. if the mixture is placed under a CO<sub>2</sub> atmosphere. However, if CO<sub>2</sub> is replaced by nitrogen the ionic form reverts back to the non-ionic form and decane becomes miscible with the mixture.

### Polymerization and solubility of polymers

The solubility properties of monomers and polymers in scCO<sub>2</sub> determine the types of polymerization technique potentially applicable for polymer syntheses in this medium. Many low molecular weight nonpolar substances, and a few polar substances have moderate to good solubilities in scCO<sub>2</sub>. However, scCO<sub>2</sub> is a poor solvent for most high molecular weight polymers under mild conditions (<100°C, <350 bar). This excludes its use for the manufacture of such polymers by solution polymerization. The only polymers that show good solubility in CO<sub>2</sub> under mild conditions are fluoropolymers and silicones, both of which have been successfully synthesized in scCO<sub>2</sub>. The critical importance of the solubility properties of polymers in scCO<sub>2</sub> has been the motivation behind many studies that aim to rationalize and predict such solubility properties. Thus, based on thermodynamic reasoning and empirical observations, a series of poly(ether-carbonate) copolymers have been made and shown to be readily soluble in scCO<sub>2</sub> at low pressures<sup>46</sup>. These polymers are easily synthesized from inexpensive precursors (propylene and CO<sub>2</sub>; Figure 5).



**Figure 4.** 'Switchable surfactant'; switching from polar to nonpolar on demand.



The inherent insolubility of most polymers in  $\text{scCO}_2$  also means that dispersion, emulsion or precipitation rather than solution polymerization are viable options for synthesizing high molecular weight, morphology-controlled polymers. Syntheses of novel surfactants that help overcome the solubility problem have thus emerged as an important area of research. These surfactants form complex micellar structures in  $\text{scCO}_2$  and make it possible for dispersion or emulsion polymerization reactions to be carried out in such a medium. 'Solubilization' of the otherwise insoluble material takes place in the microphase-separated environment, which is stabilized within the continuous solvent phase of  $\text{scCO}_2$ . The direct structural characterization of spherical micelles resulting from specially designed block copolymer surfactants in  $\text{scCO}_2$  by small angle neutron scattering (SANS) has been reported<sup>47</sup>. More specifically, polystyrene-*b*-poly(1,1-dihydroperfluorooctyl acrylate) copolymers have been shown to self-assemble into polydisperse core-shell-type micelles in  $\text{CO}_2$  (Figure 6). Such a micellar solution of  $\text{scCO}_2$  is capable of emulsifying a  $\text{scCO}_2$  insoluble hydrocarbon material such as hydrogenated polystyrene<sup>48</sup>.

Apart from these basic studies, significant advances have also been made in the use of SCF-based polymerization technologies. A  $\text{scCO}_2$ -based process, the so-called UniCarb Process, has been reported for the coating of polymers, which is claimed to reduce the levels of volatile organic chemicals by almost 60%. Dupont<sup>49</sup> is going

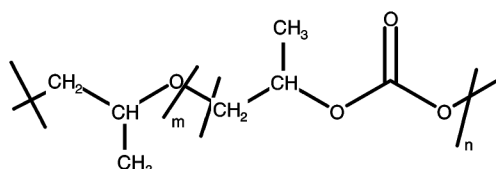


Figure 5. Structure of  $\text{CO}_2$  philic poly(ether-carbonate) copolymers.

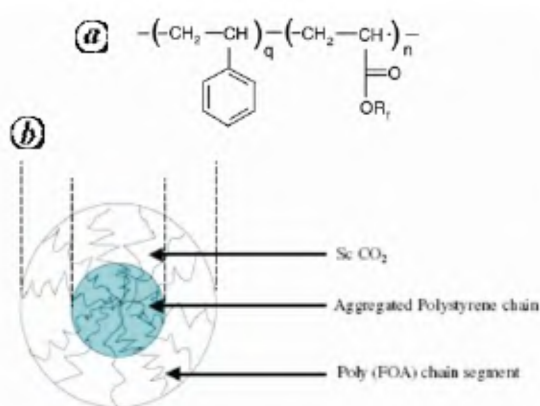
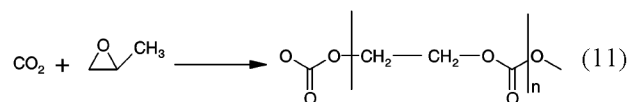
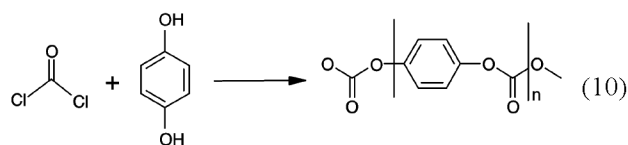


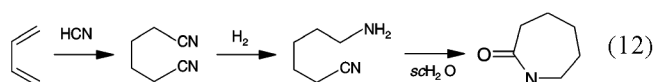
Figure 6. *a*, Structure of polystyrene-*b*-poly(1,1-dihydroperfluorooctyl acrylate; PFOA). *b*, Core-shell-type micelles of PFOA in  $\text{CO}_2$ .

to start a plant of 1000 t annual capacity of fluoropolymers and has scaled up  $\text{scCO}_2$ -mediated polyacrylic acid formation by precipitation polymerization<sup>50,51</sup>.

A significant technological achievement is the implementation of 50,000 t/yr of polycarbonate manufacture from alkene oxide and  $\text{CO}_2$ , under liquid or supercritical conditions by Asahi Kasei Corp. (AKC). This environment-friendly manufacturing process not only avoids the use of highly hazardous phosgene, but also reduces  $\text{CO}_2$  emissions<sup>52</sup>. The basic chemistry of the conventional phosgene-based process and Asahi Kasei's process are indicated by eqs (10) and (11) respectively.



There are also reports on the use of SCF other than  $\text{scCO}_2$  in polymer manufacture. Thus the conventional manufacture of lactum, the precursor for Nylon 6, consists of two steps: reaction of cyclohexanone with hydroxylamine followed by Beckman rearrangement. The amount of ammonium sulphate produced as a by-product (5 kg per kg lactum) is large; consequently, this process has a large E-factor. An alternate route (eq. (12)) reported by Invista has a much lower E-factor as it involves the formation of lactam from 6-aminocapronitrile<sup>53,54</sup>, followed by hydrolysis in  $\text{scH}_2\text{O}$  in <2 min.



Post-synthesis processing of polymers is often critically important for their practical applications and  $\text{scCO}_2$  finds an important role in many post-polymerization processing. Although most polymers are insoluble in  $\text{CO}_2$ , the converse is not the case, i.e.  $\text{CO}_2$  does have good solubility in many polymer melts. This reduces the glass transition temperature ( $T_g$ ) of these polymers and has significant 'plasticizing' effect. Plasticization and solubility of  $\text{CO}_2$  are important in many polymer processing operations such as polymer impregnation, extraction, chemical modification and foaming.

A particularly active area of research is the foaming of polymers with  $\text{CO}_2$  instead of chlorofluorocarbons, which are known ozone-depleters. Trexel has licensed a continuous processing of microcellular and supermicrocellular foaming technology developed at MIT<sup>55</sup>.

## SCFs in other industries

### *Supercritical fluid extraction*

As mentioned earlier, decaffeination of coffee beans was the first successful technological application of  $\text{scCO}_2$ . In this process the coffee beans are soaked in water before roasting. This helps to make them swell and allow the  $\text{scCO}_2$  to penetrate more easily. In a high-pressure extraction chamber,  $\text{scCO}_2$  is circulated through the pre-soaked beans and in a second vessel water and the caffeine-rich carbon dioxide are passed in opposite directions. The caffeine dissolves in water and carbon dioxide is repressurized and reused. A concentrated water solution of caffeine is finally obtained using one of a range of processes, including reverse osmosis. The successful decaffeination of coffee beans triggered much research directed towards the selective extraction of many other substances, including natural products such as food colour, essential oil, natural dye and fragrances<sup>56</sup>.

Applications of supercritical fluid extraction (SCFE) for oil remediation, pre-treatment of waste sludge, sterilization and recovery of organics from oil shale have also been explored. An important example in the hydrocarbon processing area is the Residual Oil Supercritical Extraction (ROSE) technology. This helps to separate out bitumen into its base components (resins, asphaltenes and oils) that are excellent feedstock for fluid catalytic crackers or hydrocrackers. Bitumen is the semi-solid residue obtained from crude oil after removal of lower hydrocarbons and is basically a mixture of organic and inorganic components. The techno-commercial superiority of ROSE over the conventional thermal process is primarily due to the easy mass transfer property of the SCF, which in turn allows efficient (heat transfer and energy) recovery<sup>57</sup>.

### *Supercritical fluid chromatography*

Supercritical fluid chromatography (SCFC) is an elegant, commercialized, analytical application, where the advantages of high diffusivity, low viscosity and low surface tension of SCF are taken into consideration. These properties of the SCF allow high flow rates of components compared to those obtained by conventional liquid chromatography. Faster recoveries of the components are thus possible. The solvating power of the SCF can also be tuned by changing the pressure, and the analyte that cannot be vapourized in gas chromatography can be analysed by exposing it to a detector like FID<sup>58,59</sup>.

Briefly, a SCF chromatograph consists of a gas supply unit, a pump, the column in a thermostat-controlled oven, a restrictor to maintain the high pressure in the column, and a detector. Both capillary GC and packed LC columns can be used, and although FID is the most common detector, other GC or LC detectors can also be used. Cold

liquid  $\text{CO}_2$  is pumped and before entering the column by heating is converted to the supercritical phase. Low viscosity implies little pressure drop between the column outlet and inlet. The mobile phase is depressurized and heated at the column outlet and for preparative work, products are recovered in cyclones, while the gaseous  $\text{CO}_2$  is cleaned, cooled and returned to the tank.

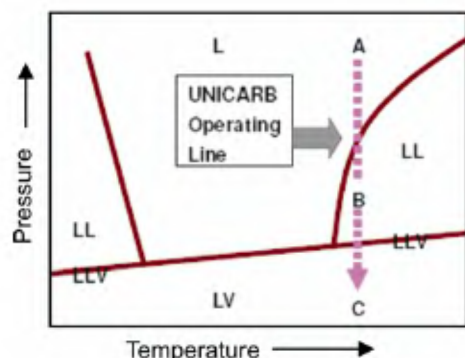
### *Particle design*

SCFs have been used successfully to produce solid phases of unique morphologies<sup>60-62</sup>. This is of importance to many technologies, including pharmaceutical formulations. This is because in most drug-delivery systems, the dimensions of the particles of the pharmaceutical products are of importance. Alternative solvent-based processes are often damaging to the product and require stringent removal after use. Rapid expansion of supercritical solutions (RESS), and supercritical/gas anti-solvent (GAS) are two widely used SCF-based technologies currently utilized by many companies in the commercial manufacture of pharmaceutical products<sup>63</sup>.

Synthesis and crystallization of Cu-Indo, a nonsteroidal antiinflammatory drug, involves multiple operations with solvents, and a long filtration step. Applying GAS technique, crystallization and separation of the crystals become easy. Once the reaction is complete, the expanded solution is filtered. The reduced viscosity and increased diffusivity of the expanded solution make filtration considerably easier. The antisolvent  $\text{CO}_2$  is then removed from Cu-Indo by simple depressurization. Importantly, crystal morphologies are found to be dependent on the rate of expansion. With slow expansion rhombic crystals, and with fast expansion a mix of rhombic and bipyramidal crystals are obtained<sup>64</sup>.

### *Painting and dyeing*

The use of 1 litre of paint results in the release of approximately 1/2 kg of volatile organic chemicals in the atmosphere. SCF can therefore play an important role in reducing VOC level provided, of course, the paint is soluble in such a medium. The normal paint-spraying process is based on a three-component system that consists of polymers or pigments with two solvents. The two solvents act as diluents and one of them helps reduce the viscosity of the mixture, which in turn facilitates the even coating of paints. Thus if  $\text{CO}_2$  is to be used as the viscosity reducer, the phase behaviour of the polymer- $\text{CO}_2$ -solvent ternary system needs to be critically studied<sup>65</sup>. The UniCarb process mentioned earlier is an example of SCF-mediated painting process, where the ternary mixture is initially pressurized at ~100 bar. Under these conditions there is a single liquid phase which on reduction of pressure passes into a binary liquid-liquid region, and



**Figure 7.** Schematic phase diagram of UNICARB process. L, Liquid; V, Vapour. Pressure is reduced along A–B–C.

on further reduction of pressure passes through a ternary liquid–liquid–vapour line into a binary liquid vapour region (Figure 7, line ABC).

The potential of  $\text{scCO}_2$  in dyeing textiles, both synthetic and natural, has been investigated in considerable detail, as the amount of water required for conventional dyeing is considerable ( $\sim 100$  kg/kg of textile), and the dye-contaminated wastewater is hazardous<sup>66</sup>. Solubility of the dye in  $\text{scCO}_2$  is obviously a critical parameter. Non-polar or so-called disperse dyes are generally used due to their acceptable solubility in  $\text{scCO}_2$ . However, the pressure and temperature dependence behaviour of solubility of such dyes in  $\text{scCO}_2$  is a complex phenomenon and not fully understood.

At a molecular level the ability of the dye to adhere to the fibre depends on the type of functional groups that are present in the fibre. For polyester,  $\text{scCO}_2$  penetrates and swells the fiber, which helps the non-polar dye molecules to diffuse through the polymer. On depressurization the fibres shrink, and the dye molecules remain trapped within the fibres. For nylon, silk and wool, textile materials with amino functionalities, non-polar dyes that have reactive groups towards amino functionalities are used. Here, unlike polyester, the dye is bound to the matrix through chemical bonds. There are reports that Samsil Industries Ltd., South Korea, has developed a supercritical dyeing machine, where apparently no dispersing agent is required<sup>67</sup>.

#### *Nanotechnology, microelectronics and enzymatic reactions*

There are many reports on the syntheses of nanostructured materials, particles, fibres, wires, tubes and films in SCF<sup>68</sup>. Silver nanoparticles may be made in compressed propane by reducing  $\text{AgNO}_3$  with  $\text{NaBH}_4$  in reverse micelles stabilized by anionic surfactants, where growth is found to be faster compared to conventional micellar systems. Titanium hydroxide nanoparticles have been produced in a continuous plant<sup>69</sup> by hydrolysis of titanium tetra-isopropoxide in  $\text{scCO}_2$ . Nanoporous materials can also be generated in  $\text{scCO}_2$  by impregnating metal pre-

cursors into activated carbon with micro or mesopores, and removing the activated carbon by calcination or oxygen plasma treatment<sup>70</sup>.

On an average, electronic microchips require about 130 solvent-rinsing steps in a single wafer-manufacturing process. This contributes substantially to the energy cost of the microelectronic industry and provides motivation for replacing solvents with SCF<sup>71,72</sup>. High penetrating ability and easy mass transfer properties of SCF facilitate deposition or cleaning at very low nanometric levels and successful applications in photo lithography, spin-coating and deposition have been reported<sup>73</sup>.

Enzymatic reactions in  $\text{scCO}_2$  were first reported more than 20 years ago and have also been reviewed<sup>74–78</sup>. A recent review highlights the advantages and challenges associated with SCF-based enzymatic reactions<sup>79</sup>. Lipases, cutinases, D-galactosidase and subtilisin Carlsberg are among many enzymes that have been found to be stable, active and enantioselective in  $\text{scCO}_2$ .

The degree of enzyme hydration plays a critical role in the specific activity of the enzyme in a given SCF. An example of this is the behaviour of cholesterol oxidase in  $\text{scCO}_2$ , which shows a ten-fold drop in rate in dry  $\text{CO}_2$ , but regains its activity upon addition of water. However,  $\text{CO}_2$  reacts with water to give carbonic acid, and with the amine groups of an enzyme to form carbamates. This may lead to a substantial reduction in enzyme activity, as has been observed in cutinase catalysed transesterification. Because of this, enzymatic reactions in other SCFs such as  $\text{sc}$ -ethane are often found to be much faster than in  $\text{scCO}_2$ . In theory, the native state of the enzyme could be stabilized and the solubility issue of the substrate could be addressed in a multicomponent mixture of  $\text{scCO}_2$ , water and a  $\text{CO}_2$ -philic surfactant of the type discussed earlier. Indeed a recent molecular dynamics simulation of random quaternary mixtures of protein–water– $\text{CO}_2$ –fluorosurfactants shows the self-assembly of reverse micelles in  $\text{scCO}_2$ , where the protein becomes entrapped inside the aqueous pool and maintains its native state<sup>80</sup>. Finally, from the point of view of potential technology, ring open polymerization (ROP) of  $\epsilon$ -caprolactone to polycaprolactone in  $\text{scCO}_2$  by Novozyme, and the several advantages claimed over the conventional solvent-based process, is to be noted<sup>81</sup>.

#### **Cost and safety**

From what has been discussed so far, it is apparent that SCF offers attractive technological alternatives to many of the existing industrial processes and unit operations. A reasonable question to ask then is why is it not adopted more widely in the industry? Apart from a few intrinsic limitations, such as limited solubilities of reactants for specific reactions, there are also economic issues. The cost of reactor design for SCF involving processes must



be carefully considered, as otherwise the alternative technology becomes commercially unviable. Minimizing the size of the reactor for high-value products may minimize the cost, as the relative cost of a SCFE process is estimated to scale as  $(V^*Q)^{1/4}$  ( $V$  is the column volume,  $Q$  the flow rate)<sup>82</sup>.

As high pressures are involved, the safety aspects of SCF-based processes must also be carefully considered, especially while planning for scale-ups<sup>83</sup>. A parameter used for measuring the safety limit of any solvent is the 'threshold limit value time weighted average' (TLV-TWA). Basically for a 40 h work-week, it is the concentration of the solvent vapour to which all healthy workers may be repeatedly exposed without any adverse effect. Such data for SCF must be generated before it is widely adopted by the industry. These issues have received enough attention and it is reasonable to expect a healthy growth of SCF-based industries<sup>84–87</sup>.

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