Supercritical fluid extraction of heavy metals from solid matrices

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ABSTRACT

The subject matter of this review is extraction of heavy metals from solid matrices in the presence of supercritical fluids. Since solvent extraction of heavy metals is utilized on a commercial scale, the replacement of organic solvents by Supercritical fluid (SCF) has been the major driving force behind these research efforts. This review is prepared to highlight the areas important for commercial scale application of technology. This review specially focuses on extraction of heavy metals by using supercritical fluid and application field of SFE. In part 1 of this review, an introduction to supercritical fluid extraction technology is given. A brief introduction to instrumentation of supercritical fluid extraction is also presented in same part. The advantages of supercritical fluid over conventional solvent extraction have been also discussed in part 1. The second part of this review represents properties of supercritical fluids and important studies on SFE of heavy metals from solid matrices. Applications of SFE technology in various field and Raman shift study of CO_2 have been discussed in last section.
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INTRODUCTION

Recently, increasing attention has been directed towards supercritical fluid extraction (SFE) as it offers a promising alternative to the conventional process because of its inherent potential to minimize the amount of liquid waste generation and simplification of the extraction process.

When a gas is compressed to a sufficiently high pressure, it becomes liquid. If, on the other hand, the gas is heated beyond a specific temperature, no amount of compression of the hot gas will cause it to become liquid. This temperature is termed as the critical temperature (Tc) and the corresponding vapor pressure as the critical pressure (Pc).These values of temperature and pressure define a critical point, which is unique to a given substance. A substance above the critical point is said to exist in the supercritical fluid (SCF) state[1]. SCF has characteristics of liquid as well as gas.

The properties of SCF such as density, diffusivity, viscosity and surface tension are intermediate to those of liquid and gas. From the extraction point of view, the unique characteristic of SCF is its solvating property. This characteristic of SCF was discovered by Hanny and Hogarth[2] in 1879. Another unique characteristic of SCF is tenability of its solvating power by changing the density of SCFs by varying pressure/temperature conditions. Higher diffusivity of SCF than that of liquids

Review

facilitates rapid mass transfer and faster completion of a reaction. Due to low viscosity and surface tension, SCFs can penetrate deep inside the material matrix, extracting the components of interest. Hence, supercritical fluids offer faster, cleaner and more efficient extraction.

In 1962, Lovelock[3] suggested the use of SCF as a mobile phase in chromatography. In 1962, Klesper et al.[4] demonstrated chromatographic separation of nickel porphyrins employing supercritical chlorofluoromethanes as the mobile phase. Since then SCFs have been widely employed in extraction and separation of natural products. Carbon dioxide has been widely employed as supercritical fluid owing to its moderate critical parameters (Pc = 72.9 atm., Tc = 31.3°C), non-toxic nature, chemical inertness, non-flammability, environmental friendliness, radiochemical stability, inexpensiveness and easy recyclability.

In the SFE of natural products, predominantly CO_2 is being used as SCF. However, SC CO_2 could not be applied for metal ion extraction for a long time, as direct extraction of metal ions by SC CO_2 is highly inefficient owing to charge neutralization requirement and weak solute–solvent interactions. The credit for metal ion extraction by SC CO_2 goes to Laintz et al.[6] who in 1992 demonstrated the extraction of Cu^{2+}[5]. Metal ions were complexed with suitable complexing agents so that the metal complex could become quite soluble in supercritical CO_2 facilitating metal ion extraction. Demonstration of SFE of metal ions opened a new realm for metal ion extraction. Subsequently, extractions of many metal ions were reported. In 1993, Lin et al.[6] succeeded in extracting lanthanides and uranium from solid materials by supercritical CO_2 containing fluorinated β-diketone. Next year (1994), Lin et al.[7] performed SFE of thorium and uranium from solid and liquid materials with fluorinated β-diketone and tributyl phosphate.

In 1995, Lin et al.[8] carried out SFE of uranium and thorium from nitric acid solution from organo phosphorus reagent. In the literature, direct dissolution and extraction of Uranium compounds by SC CO_2 has been reported[9,10]. Kumar et al.[11,12] have carried out the SFE of uranium from a tissue paper matrix. SC CO_2 is expected to be used as alternative "green" medium to organic solvent for extraction, separation, chemical reactions, and material processing[13-15]. As mentioned

earlier the first paper dealing with the application of SCF dates from 1879[2]. They discussed the ability of an SCE to dissolve low vapour pressure solid materials. Since then a substantial amount of work has been done by many investigators to understand the basic fundamentals of fluid in supercritical region.

However the work of Francies[16] by far suppresses the work of others when one consider the extent of his work. In the single paper he present an extensive, quantitative study on the solvent properties of liquid CO_2 with hundred of compound. His work is primarily concerned on the phase behavior of ternary systems containing liquid CO_2 collected data for 464 ternary phase diagrams and determined solubility of 261 compounds in near critical CO_2.

Nearly half of these compounds are reported to be miscible with liquid CO_2. He included many classes of organic compounds, e.g. Aliphatics, Aromatics, Heterocyclics and compound with large number of functional group.

Although Francies studied solubility behavior in near critical liquid CO_2 (25°C, 655 bar), his results are generally applicable. For example he compound soluble in liquid CO_2 will also soluble in SC CO_2. Therefore from his work it is possible to extract some general rules of functional group.

The lower weight aromatic compound such as Benzene and Toluene are completely soluble in near critical carbon dioxide, however by increasing the molecular weight the solubility will drop(Bibenzyl of biphenyl).

Aliphatic compounds are completely soluble in near critical liquid CO_2, however solubility will drop with increase in molecular weight

The unbranched heterocyclic components are soluble in near critical liquid CO_2 (furfural, pyridine and thiophene). The existence of group such as methyl in heterocyclic like pyrrole (2,5-dimethyl pyrrole) causes the compound not to be completely soluble in near critical liquid CO_2.

The low molecular weight carboxylic acids are soluble in near critical liquid carbon dioxide (e.g. Acetic acid, Caproic acid). The solubility of aliphatic carboxylic acid will be marginal when both carboxylic and hydroxyl groups are present in molecule or when molecular weight increases(Oleic acid).

The halogenated substitution shows no negative in-

fluence on solubility a compound (aliphatic or aromatic). In general Meta position of substitution in aromatic compounds show higher solubility than para or ortho position.

The low molecular weight nitriles such as acetonotriles and acrilonitriles are soluble in near critical liquid CO_2.

Low molecular weight aliphatic substitution seems to enhance the solubility of components which would otherwise not be soluble. For example the solubility of N,N-dimethylaniline, N,N-diethylacetamide and N,N-Dimethylformamide show increased to completely miscible.

Several review articles have been published to cover numerous available literatures on SFE processes and its application[17-19]. C.Erkey[19] has published the first review article on the supercritical fluid extraction of heavy metals. The author has mainly focused on extraction of metals from aqueous solution. In present review new class is added to previous existing class. The new class include detailed description of Raman spectra of supercritical CO_2 it also contain some special application of SFE technique in various field.

Supercritical fluid extraction set-up

A schematic diagram of the supercritical fluid extraction set-up used for study is shown in figure 1. The set-up consists of a CO_2 delivery pump, a modifier pump, a thermostat, a back-pressure.

Regulator and a collection vessel. Each unit can be independently controlled by inbuilt microprocessors. All units together (except the back-pressure regulator) can also be controlled through a computer. The thermostat temperature control range is from room temperature –15°C to ~80°C with a temperature control precision of
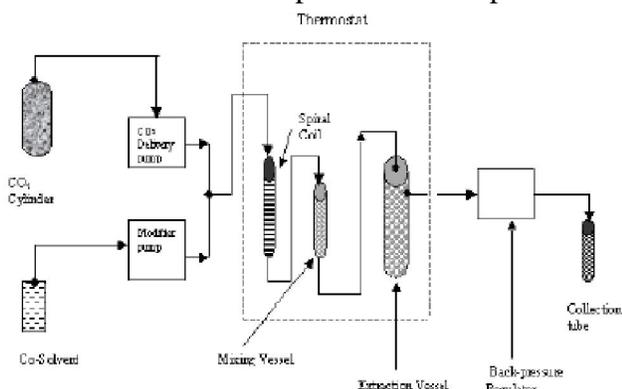

Figure 1 : A schematic diagram of the SFE set-up

± 0.1°C. The extraction vessel of a 10 ml capacity is cylindrical in shape and made up of stainless steel. The extraction vessel has an inlet tube (0.5mm ID) at the top for allowing SCF to enter the vessel and an outlet tube (0.5mm ID) for the transport of SCF to the collection vessel.CO_2 is delivered to the extraction vessel at a desired flow rate by the CO_2 delivery pump. From the cylinder, CO_2 gas is fed to the delivery pump, where CO_2 is liquefied by lowering the temperature to –10°C.

The modifier pump is employed to add a desired percentage of the complexing agent to the liquefied CO_2 stream. The CO_2 and complexing agent streams are combined by a T-joint and fed to the extraction vessel. Prior to entry in the extraction vessel, the stream is allowed to pass through a 5m long spiral coil and then through a cylindrical vessel (10ml capacity) containing spherical teflon pebbles for acquiring thorough homogeneity. The desired pressure in the extraction vessel is maintained by opening/closing of a variable stroke needle valve of the back-pressure regulator. The pressure of the extraction vessel can be varied from atmospheric pressure to 500 atm. with a pressure control precision of ±1 atm. The extract of the extraction vessel is collected in the collection tube at atmospheric pressure while CO_2 escapes as gas. The CO_2 and solvent flow rates can be varied from 0.001 to precision of 0.001ml/min. All the operating parameters can be set, controlled and monitored by means of PC.

Properties and fundamentals of supercritical fluids[20,21]

Solvent strength

The density of a supercritical fluid is extremely sensitive to minor changes in temperature and pressure near the critical point. The densities of the fluids are closer to that of organic liquids but the solubility of solids can be 3-10 orders of magnitude higher. The enhancement of solubility was discovered in 1870's for the potassium iodide-ethanol system. The solvent strength of a fluid can be expressed by the solubility parameter, δ, which is the square root of the cohesive energy density and is defined rigorously from first principles. A plot of the solubility parameter for carbon dioxide versus pressure would resemble a plot of density versus pressure. This confirms that the solvation strength of a supercritical fluid is directly related to the fluid density. Thus the solu-

Review

bility of a solid can be manipulated by making slight changes in temperatures and pressures.

Another attractive feature of supercritical fluids is that the properties lie between that of gases and liquids. A supercritical fluid has densities similar to that of liquids, while the viscosities and diffusivities are closer to that of gases. Thus, a supercritical fluid can diffuse faster in a solid matrix than a liquid, yet possess a solvent strength to extract the solute from the solid matrix.

Phase behavior

The phase behavior of ternary systems of carbon dioxide and the solubilities of over 260 compounds in liquid carbon dioxide were studied in a monumental work published in 1954. Though this data is for liquid carbon dioxide, it provides a first approximation to solubilities in supercritical fluids. An understanding of the phase behavior is important since the phase behavior observed in supercritical fluids considerably differ from the behavior observed in liquids. One such behavior is the retrograde region. For an isobaric system, an increase in the temperature of a solution increases the solubility of the solute over certain ranges of pressure (consistent with the typical liquid systems) but decreases the solute solubility in other pressure ranges.

This anomalous behavior wherein the solubility of the solute decreases with a temperature increase is called the retrograde behavior. Thus, the following generalizations may be made regarding the solute solubility's in supercritical fluids. Solute solubility in SCF may exceed that of liquid solvents. Solubility generally increases with increase in pressure. An increase in the temperature of the supercritical fluid may increase, decrease or have no effect on the solubility of the solute depending upon the pressure.

Carbon dioxide is not a very good solvent for high molecular weight and polar compounds. To increase the solubility of such compounds in supercritical carbon dioxide, small amounts (ranging from 0 to 20 mol%) of polar or non-polar co solvents called modifiers may be added. The co solvent interacts strongly with the solute and significantly increases the solubility. For example, addition of a small amount (3.5 mol%) of methanol to carbon dioxide increases the solubility of cholesterol by an order of magnitude. Compressed gases and fluids have the ability to dissolve in and expand organic liquid solvents at high pressures (50 to 100 bar). This expansion usually decreases the solvent strength of the liquid. Eventually the mixture solvent strength is comparable to that of the pure compressed fluid. Knowledge of when a solute would precipitate can be important and helps one to determine when heavy hydrocarbons would precipitate in an oil reservoir when carbon dioxide is injected. The very special physical properties of SCF distinguish it from liquid and gases. An SCF has an liquid like density but its viscosity is more like that of a gas, resulting in a diffusion coefficients that are the phase behavior of binary systems follows the typical six classes of binary diagrams. The Class I binary diagram is the simplest case. The pressure-temperature diagram consists of a vapor-pressure curve for each pure component, ending at the pure component critical point. The loci of critical points for the binary mixtures are continuous from the critical point of component one to the critical point of component two. More complicated behavior exists for other classes, including the presence of upper critical solution temperature (UCST) lines, two-phase immiscibility lines, and even three-phase immiscibility lines.

Modeling of phase behavior cannot be done using relatively simple thermodynamics because extreme nonidealities occur in the supercritical region. One of the simplest cases of phase behavior modeling is that of modeling the solubility of crystalline solids in supercritical fluids. Thermodynamic models are based on the principle that the fugacities of a component are equal for all phases at equilibrium under constant temperature and pressure. Associations resulting from hydrogen bonding or donor-acceptor interactions can have a pronounced effects on supercritical fluid phase behavior. Understanding of hydrogen bonding among mixtures in supercritical fluids is important because of the increased interest in supercritical water solutions, and in polar co solvents for supercritical fluid carbon dioxide. Various equations of state such as the statistical association fluid theory and the lattice fluid hydrogen bonding model are often used to describe these associations.

Experimental confirmation of phase behavior is often necessary to account for unaccounted and complex behavior that can not be modeled apriori. The most useful tool for examining phase behavior is the variable-volume view cell, whose contents can be viewed

TABLE 1 : Comparison of some physical properties for gas, liquid and SCF

	Density [kg/m3]	Diffusion coefficient [m²/s]	Viscosity [Pa.s]
Gas (1 bar, 20°C)	0.6-2.0	$1\text{-}4 \times 10^{-5}$	0.01-03
Liquid (20°C)	600-1200	$0.2\text{-}2 \times 10^{-9}$	0.2-3.0
SCF	200-900	$2\text{-}7 \times 10^{-7}$	0.01-0.09

TABLE 2 : Critical temperature and pressure for various compounds

	Critical pressure[bar]	Critical temperature[°C]
Carbon dioxide	73.8	31.1
Ethane	48.8	32.1
Water	220.5	374.2
Benzene	48.9	289.0
Ammonia	111	133
Methanol	81	240

safely through a sapphire window by means of a mirror or a video camera. The apparatus contains a piston to separate the pressurizing fluid from the sample and allows for manipulation of temperature, pressure, or composition. The very special physical properties of SCF distinguish it from liquid and gases. A supercritical fluid has a liquid like density but its viscosity is more like that of a gas, resulting in diffusion coefficients that are much higher than those in liquid. TABLE 1 shows a comparison of this characteristics for a gas, liquid and SCF TABLE 2 shows critical pressure and temperature of various compounds. The solubilities of SCF appear to be virtually exponential in density, which mean small pressure change can result into enormous solubility variations. This gives the opportunity to put chemicals into the solutions or drop them out very selectively.

Advantages of SFE over conventional solvent extraction[19]

In conventional solvent extraction, since the target material must be accumulated in the organic phase during loading, the ratio of the aqueous to the organic volumes cannot usually be more than: 10. This leads to the use of large volumes of solvent, particularly when the feed is lean. This adverse effect can possibly be eliminated by the substitution of non-toxic SCFs such as SC CO_2 for organic solvents.

Residual contamination of the aqueous solution by the organic solvent may also be eliminated by substitution with SC CO_2.

In solvent extraction of metals, the chemical reactions occurring at the interfacial plane may be fast compared to mass transfer processes. Thus, depending on hydrodynamic conditions in the extraction vessel, the observed kinetics of removal may be controlled by mass transfer. Since the mass transfer characteristics of SCFs are excellent compared to those of organic solvents because of their relatively low viscosities and high solute diffusivities, the use of SC CO_2 in place of organic

solvents may enhance rates of extraction and stripping.

SCFs generally have a much lower surface tension than traditional organic solvents, resulting in an increased dispersed phase surface area, which may reduce the size of equipment required for a particular solvent-to-feed ratio.

The fact that the solvency characteristics of SC CO_2 can be varied with small changes in temperature and pressure may also be exploited in the development of selective extraction schemes.

In some nuclear applications such as uranium extraction, the solvents are degraded by hydrolysis and radiolysis and depending on the type of solvent; such attacks produce nitrato esters, nitro compounds, carboxylic acids and ketones. Using SC CO_2 may be beneficial due to its inert nature and may improve solvent Quality .As a result of these favorable properties of SC CO_2 as a solvent in extraction of metals, quite a few studies have been conducted in laboratories around the world.

The chemical structures of extractants used in these studies, together with their abbreviations are given in TABLE 3. These studies are discussed in more detail in the subsequent sections.

Proposed mechanism[22]

In order to study the mechanism of SCFE using ligand assisted SC CO_2, the following sequential steps are considered essential:

1. Conversion /ionization of metal oxide to metal cations.
2. Complexation of metal cations with ligands.
3. Extraction of metal chelate / adduct by SC CO_2.

It is hypothesized that SCFE for the extraction of metal ions directly from their oxides involves several sequential phenomena of mass transfer and reaction
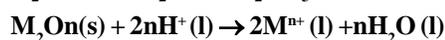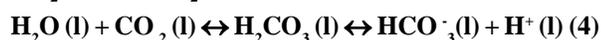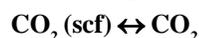
Review

TABLE 3 : Chemical structures and abbreviations for extractant used in SC CO$_2$

R$_1$ = CH$_3$, R$_2$ = CH$_3$	Pentane = 2,4-dione	ACAC
R$_1$ = C$_2$H$_5$, R$_2$ = C$_3$F$_7$	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione	HFOD
R$_1$ = CF$_3$, R$_2$ = CF$_3$	1,1,1,5,5,5-hexafluoro-2,4-pentanedione	HFAC
R$_1$ = CF$_3$, F$_2$ = CH$_3$	1,1,1-trifluoro-2,4-pentanedione	TFA
R$_1$ = (thienyl), R$_1$ = CF$_3$	thenoyltrifluoroacetone	TTFA
tributyl phosphate, R = CH$_3$(CH$_2$)$_2$CH$_2$	tributyl phosphate	TBP
di(2-ethylhexyl)phosphoric acid, R = H$_3$C—(CH$_2$)$_3$—CHCH$_2$ / C$_2$H$_5$	di(2-ethylhexyl)phosphoric acid	DEHPA
R—C(=O)OH, R = CF$_3$(CF$_2$)$_7$	pentadecafluorooctanoic acid	HPFOA
di(2,4,4-trimethylpentyl)dithiophosphonic acid, R= H$_3$C—CH(CH$_3$)—CH$_2$—C(CH$_3$)(CH$_3$)—CH$_3$	di(2,4,4-trimethylpentyl)dithiophosphonic acid	CYANEX 301

kinetics governed by their respective phase and reaction equilibria. When SC CO$_2$ is passed through a bed of powdered metal oxide mixed with water, carbonic acid is formed thereby lowering its pH in the liquid film around the solid particles.

This carbonic acid is presumed to facilitate the ionization of metal oxide to metal cations. This phenomenon is explained as

$$CO_2 \text{ (scf)} \leftrightarrow CO_2$$

$$H_2O \text{ (l)} + CO_2 \text{ (l)} \leftrightarrow H_2CO_3 \text{ (l)} \leftrightarrow HCO^-_3 \text{(l)} + H^+ \text{ (l)} \quad (4)$$

$$M_2On(s) + 2nH^+ \text{(l)} \rightarrow 2M^{n+} \text{ (l)} + nH_2O \text{ (l)}$$

Where (s) represents solid phase, (l) represents liquid phase, (scf) represents supercritical fluid phase, M$_2$O$_n$ represents metal oxide where valence of metal is 'n'. Thus, Step I, i.e., conversion of metal oxide to cations in aqueous film surrounding the solid particle involves:

- Dissolution of SC CO$_2$ in water.
- Formation of carbonic acid.
- Diffusion of carbonic acid and its reaction with oxide at the solid–liquid interface.

Recently many studies have been focused on the production of high quality thin films by using organometalic compound and SC CO$_2$ as carrier medium. Many researchers successfully applied the SFE technique for the removal of heavy meals from solid matrices such as fly ash, soil sample, solid tissue paper and sludge samples.

Shaofen and his co-worker[23] in 2008 carried out the supercritical fluid extraction of chromate copper arsenate from wood waste. In this paper, SFE of Cr, Cu and As from wood wastes using organophosphorus reagent Cyanex 302, in SC CO$_2$ are surveyed and the

extraction efficiencies of CCA with other chelating agent are also compared. The extraction was carried out in different mode i.e. single batch extraction, dynamic extraction and continues extraction. The extractor is charged with 50mg of wood sample and 1gm of cyanex 302 was loaded in a small boat like glass container. The extraction include 20 min static extraction followed by 40 min dynamic extraction. 5% MeOH modified CO_2 was used as the extracting fluid. The extracting conditions was 60°C temp. And 200 atm. Pressure.

Galy et al.[24] in 2007 studied the decontamination of solid substrates using supercritical carbon dioxide with trade hydrocarbonated surfactants. The solvation of PEO-PPO-PEO trade hydrocarbonated surfactant in CO_2 has been studied in this work by cloud point measurement. This study improve the knowledge of the surface active properties of a special kind of hydrocarbonated surfactant in a SC CO_2 medium. attention is focused on a special class of pluronics molecule which contain a central poly (propylene oxide) block (PPO) or $(PO)_y$ where y is integer number average degree of polymerization of propylene oxide inserted between polyethylene oxide blocks.

P.Kumar and his co-worker[25] in 2008 investigated the extraction of Uranium and Thorium from solid matrices using TBP-HNO_3 as complexing agent at 60°C and 150 atm. Pressure. UO_2 and U_3O_8 powder (0.02-0.05) along with 2ml of TBP-HNO_3 complex were taken in extraction vessel and CO_2 was fed until 150 atm. Press. After 20 min of static extraction, dynamic extraction is carried out by continuously flowing supercritical fluid mixture of CO_2 and 10% TBP. Uranium extraction efficiency for U_3O_8 was $97.05 \pm 3.73\%$ and for UO_2 was 98.07 ± 4.76.

C.Kersch[26] reported on supercritical fluid extraction of heavy metals from fly ash using Cyanex 302 and TBP-D_2EHPA as extractant. Extraction were conducted in 12L revolving cylinder designed to work at pressure unto 35 Mpa. Two different fly ashes were used for the experiment: alkaline CFP fly ash originating from an electric power plant in Netherland and MSWI fly ash, which was supplied by a municipal waste incinerator. The metals such as V, Sb, Ni, Mo, Cr, Co, V, Pb, Mn, Cu and Zn could be removed efficiently. The maximum extraction values were obtained after 1h for most cations when using D_2EHPA or TBP-D_2EHPA

mixture, an EE of more than 90% was obtained for z obtained for V, Sb, Ni, Mo, Cr, and Co while for Pb, Mn and Cu only 40-60% was achieved.

Direct insitu supercritical fluid extraction of Neodymium ion from its oxide using TTA-TBP-MeOH in carbon dioxide have been reported by T.Vencent[27]. The mechanism has been established by analyzing the conversion of Neodymium oxide to Nd^{+3} and metal complex. Ionization studies under supercritical conditions reveal that ionization is a P^H dependent process and conversion of Nd into ions increasing in pressure and decreases with an increase in temperature. Parametric studies on chelation with TTA-TBP show that the amount of adduct is a function temperature, pressure and contacting time.

Coal treatment[28] for the removal of metal is considered to be a challenge over recent year. Supercritical fluid technology solved the problem of metal extraction. Many researchers used relatively expensive chelating agent which may be difficult to be applied for coal treatment[28] but Iwai et al carried out the extraction of iron and calcium from low rank coal with supercritical carbon dioxide and entrainer. The entrainer used was Methanol, Ethanol, Acetic acid and Acetyl acetone or mixture of Acetyl acetone and water. The low rank coal used in this study was Berau coal from Indonesia. The coal was ground and screened to prepare 18-30 mesh size particles. The experimental condition were 313.2K and 15.0 MPa. The flow rate of CO_2 was 0.025 mol/min. Author found that coupled entrainers of acetyl acetone + water and acetic acid + ethanol are effective in supercritical carbon dioxide extraction of Fe and Ca, Resp. The flow rate of carbon dioxide and particle size of coal affected the recovery rate of Fe.

Recovery[29] of palladium from spent catalyst with supercritical CO_2 chelating agent have been investigated by Iwao et al. the experiment were carried out at pressure and temperature ranging from 8 to 20 MPa and 313 to 333 K resp. The effect of three different ligands was investigated; acetyl acetone, Cyanex 302 and TBP/HNO_3/H_2O complex in which was prepared to have 1:1 weight ratio of the TBP to HNO_3 solution. The effect of temperature, pressure, extraction time, SC CO_2 density and the type of chelating agent on the extraction efficiency of Pd were studied. Cyanex 302 gave the maximum extraction efficiency of almost 100% in 10

Review

min at pressure and temperature ranging from 8 to 20 MPa and 313-333K.

Meguro et al.[30] studied the new method of extraction, reffered as supercritical CO_2 fluid leaching(SFL), which is based on selective dissolution of Uranium oxide with the supercritical CO_2 fluid containing the HNO_3–Tri-n butyl phosphate complex the UO_2 and U_3O_8 powder efficiently react with the HNO_3-TBP complex in the supercritical CO_2 medium to form a U(VI)-TBP complex, $UO_3(NO_3)_2(TBP)_2$ which is soluble in the CO_2 phase. The rate of the complexation of the UO_2 or U_3O_8 powder is high enough when the content of HNO_3 in the HNO_3-TBP complex is high. In particular, when ratio of mole fraction of HNO_3 to that of TBP is larger than ca.1. i.e., content of 2:1 complex $(HNO_3)_2$ TBP becomes large, the complexation rate increases remarkably, the complexation rate decreases slightly with an increases of the pressure in range between 12.5 and 25 MPa. The water molecule contained in the HNO_3-TBP complex enhance the complexation rate of uranium oxides. Here water dissolved in the supercritical CO_2 phase is as a component of the mixed complex of HNO_3-TBP-H_2O. Large production of $UO_2(NO_3)_2(TBP)_2$ as well as the HNO_3-TBP complex remained with the synthetic solid waste sample after the SFL at 12.5MPa though more than 99.4% of Uo2 or 99.8% of U_3O_8 was reacted to the complex.

Shimizu et al.[31] successfully applied the technique of supercritical fluid extraction for the removal rare earth element from luminescent material in waste fluorescent lamps. Rare earth element were extracted from luminescent material in waste fluorescent lamps using supercritical carbon dioxide (SC-CO_2) containing tri-n-butyl phosphate (TBP) complexes with HNO_3 and H_2O. The CO_2–soluble TBP complexes, however, is problematic in that an excess amount of water is generated from the reaction of complex with metal oxide. The complex is prepared by a vigorous mixing of TBP and concentrated nitric acid, which is a mixture of HNO_3 and H_2O, therefore, the complex gets saturated with water. The excess water separates, forming small droplets in the supercritical fluid . when the metal ions are distributed into the droplets, effective extraction is not achieved. Droplets formation was prevented by controlling of the molecular ratio.

Fox et al.[32] studied the Holmium nitrte

complaxation with tri-n-butyl phosphate in supercritical carbon dioxide. When TBP is added to SC CO_2 and the organophosphorousrate reagent contacts the solid Holmium nitrate, a chemical reaction occur leading to formation of Ho-TBP complexes. As the amount of a TBP added to the system increases , the amount of complexed holmium nitrate dissolved in the supercritical fluid phase increases. The complexation reaction between Holmium nitrate and TBP was studied in SC CO_2 at 308K and found to produce Ho-TBP complexes having 1:2 and 1:4 stochiometries. Conditional extraction coefficient were calculated from uv-vis data. The value for log k_{ex2} = 5.8±0.1 and value for logk_{ex4} = 3.1±0.1, giving a value of log k_{ex} = 8.9±0.1 where K_{ex} is the extraction coefficient. The result found in this study demonstrate that metal complexation reaction in supercritical fluid solvent can produce multiple ML_n complexes. The different ML_n species formed are a function of the system.

Y.Takeshita and Y.Sato[33] constructed a new flow type apparatus to measure the solubility of solid samples in supercritical fluid. Author ascertained the validity of this apparatus and procedure by measuring the solubility of naphthalene in supercritical CO_2 at 508 K and from 9.8 to 24.5 MPa. The solubility of naphthalene in supercritical carbon dioxide was determined by the following equations.

$$Y_2 = \frac{(W2/M2)}{\{(p-p_w)V_1/RT\} + (W2/M2)}$$

Where W_2 is the weight of the trapped naphthalene, p the atmospheric pressure, p_w the vapour pressure of water, V_1 the gas volume measured by the meter at temperature T, R the gas constant, and M_2 the molar mass of naphthalene. Author mainly focused on copper compounds and used a flow type apparatus to measure the solubility of a model copper compound fixed in wood. The model compound used in this study was CuH_2SO_4, which is believed to exist in CCA-treated wood. The $CuHAsO_4$ solubility was of the order 10^{-9}.

Chang et al.[34] designed and synthesized new CO_2 soluble, 4-aminopyridine derivatives a chelating agent by modifying conventional chelating agents with 'CO_2-philic' moieties, such as carbonyl, ether, and fluoroalkyl or amide group. Comparison of tertiary amide group moiety with secondary amide group moiety of amide

Review

group containing pyridine derivatives for CO_2 solubility and the extraction of Copper, Cobalt, Zinc newly and Strontium with newly synthesized pyridine derivative into SC CO_2 are described. Newly prepared pyridine type chelating agent show good or moderate extraction efficiencies for several metal ions (Cu^{2+}, Co^{2+}, Zn^{2+}, Sr^{2+}) in 50-90% yield with Co-ligand.

Joung et al.[35] reported the extraction of lanthanide ions from aqueous solution by modified supercritical CO_2 with Tri-n-butyl phosphate and bis-2-ethylhexyl phosphoric acid. To find information of phase transition from subcritical to supercritical phase of TBP+CO_2 and B2EHPA+CO_2, phase behavior of this mixture was measured at various temperature (313.15, 323.15 and 333.15 K) and pressure (ambient to 25 Mpa). It was found that a single phase was easily reached for TBP+CO_2 even at low pressure. However in case of B2EHPA+CO_2 system, the phase behavior was very complicated by variation with pressure. By a variable-volume view –cell apparatus, the phase transition pressure of each system were measured. The effect of conditions such as temperature, pressure and concentration of HNO_3 on SFE of Lanthanide have been studied.

Yamini et al.[36] successfully applied the orthogonal array design for the optimization supercritical carbon dioxide extraction of Platinum (IV) and Rhenium (VII) from solid matrix. OAD is type of fractional factorial design in which orthogonal array is used to assign factors to series of experimental combination whose result can be analyzed using common mathematical procedure. Recently several application of this method have been reported . More detailed description of an OAD was reported by H.B.Wan. effect of five experimental factors: pressure, temperature, volume of 20% (w/v) cyanex 301 solution in methanol, static and dynamic extraction time on SFE of these ions were studied and optimized. The effect of this parameter were investigated using the analysis of variance (ANOVA). The result showed that Pt (IV) and Re (VII) could be quantitatively extracted from solid matrix at 308 K, 202 bar.

C.Kersch and his co-worker[37] further studied the leachability of heavy metals from fly ash. After leaching of heavy metals from fly ash they carry out the supercritical fluid extraction. Paper focuses on the metal leachability and the effect after extraction in a 12L re-

volving vessel with supercritical CO_2 with fly ash from municipal waste incinerator as model compound. Pre-leaching removed the major part of the water soluble compound while the undesired removal of heavy metals through pre-leaching was low for the studied fly ash.

To use SFE as a analytical or industrial scale process, both the extraction and collection efficiency of the procedure need to be determined. M.D.Burford and his co-worker[38] performed detailed study to evaluate both the extraction and collection efficiency. The non fluorinated metal β-diketons and dithiocarbamates had a greater tendency to dissociate and /or degrade in supercritical fluid than the corresponding fluorinated metal complex. The collection efficiency (per cent recovered in the collection solvent) is assessed by spiking the analyte to be collected onto an inert matrix and extracting the sample with CO_2.

C.Y.Tai, G.S.You and S.L.Chen[39] performed the kinetics study on supercritical fluid extraction of Zinc(II) ion from aqueous solution. This work studies the kinetics of metal ion extraction using an in situ chelation-SFE method. The extraction was carried out in 1.3 dm3 batch stirred tank. The effect of pressure and stirring rate were investigated. The result show that the extraction rate of Zn(II) ion with increase in stirring rate , but
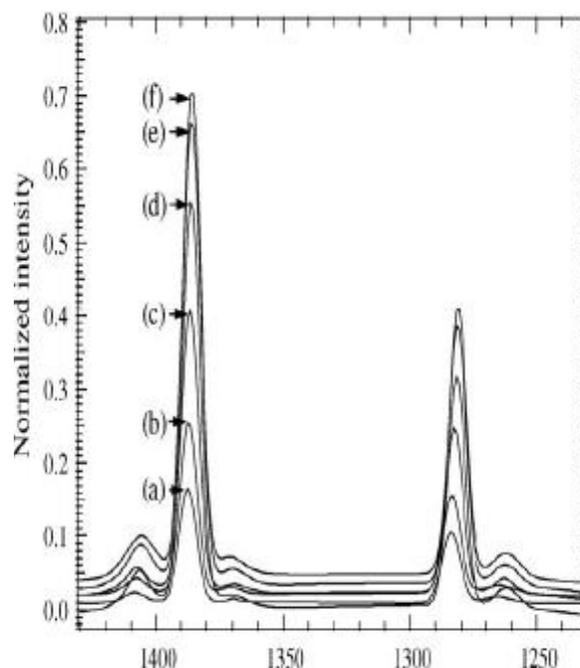

Figure 2 : Raman spectra of CO_2 in neat sc-CO_2 measured at 40°C under various pressures. (a) 8.0MPa, (b) 9.0MPa, (c) 10.0MPa, (d) 15.0MPa, (e) 20.0MPa, and (f) 25.0MPa

Review

decreases with pressure. The effective mass transfer coefficient at 313 K and 8.3 MPa varies from 0.4 5 to $2.6 \times 10^{-3} s^{-1}$ when the stirring rate increases from 7.2 to $17.7 s^{-1}$.

Glenon et al have reported the extraction of Au(III) from cellulose paper using new fluorinated macrocyclic reagents based on calixarene molecular baskete[40]. High extraction percentage were obtained at 60°C temperature and 200 atm pressure. Wai et.al.[56] have described the extraction of Au(III) from cellulose paper using bistriazolo-crowns in supercritical CO_2 in the presence of 5% methanol as a modifier and the addition of microlitre quantities of water, up to 80% of the spiked gold was extracted.

Vencent et al.[41] successfully studied the in-situ chelation and extraction of heavy metal oxide using modified supercritical carbon dioxide. Cerium oxide has been considered as a candidate material to carru out feasibility studies along with TTA as chelating agent for extraction. Solubility of Ce $(TTA)_3$-chelate has been investigated in the pressure range of 150-350 bar at 400°C. it is noted that Ce (TTA)-chelate is quite soluble

Figure 3 : Plots of wavenumbers for v_l and v_u bands of neat SC-CO_2 (O) and SC-CO_2 containing Hacac (●), Htfacac (_), and Hhfacac (■) of $1.3 10^{-1}$ moves. Density experimental conditions: temperature = 40°C; pressure = 8.0–25.0 MPa

in SC CO_2.

T.Wang and Y.Guan in 2003[42] investigated the new method for the removal of the arsenic in the form of anions such as arsenite and arsenate, from solid sample by supercritical carbon dioxide coupled with ion pairing . Tetrabutylammonium bromide (Bu_4Nbr) was used as the ion pairing reagent. Bu_4Nbr is insoluble in SC CO_2. The arsenic in the form of anion from solid sample can be effectively removed by supercritical CO_2 extraction with ion pairing.

Raman spectral shift of CO_2

In order to study the intermolecular interactions of SC CO_2 with solute, Kachi et al.[43] have measured the Raman spectra of CO_2 in neat SC CO_2 and SC CO_2 containing β-diketons [acetylacetone (Hacac),trifluoro-acetylacetone (Htfacac), hexafluoro- acetylacetone (Hhfacac)], uranyl β-dikatanato complex [$UO_2(hfacac)_2$ DMSO] (DMSO:dimethyl sulfoxide) by changing the pressure from 8.0 to 25MPa at 400 (density in gm/cm^3 : 0.28 author have also observed Raman spectra of CO_2 in SC CO_2 containing compounds [acetic anhydride (Ac_2O), methyl acetate (MeOAc), ethanol (EtOH), N, N dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), tetramethylurea (TMU), Hexamethyl phosporamide (HMPA), and Acetonitrile (AcN)] with different donicity or (DN) to understand strength of their CO_2 philicity.

Raman spectra of CO_2 in SC-CO_2 and SC-CO_2 containing β-diketones

The Raman spectra of pure gaseous CO_2 are well-known to have two narrow bands at about $1286 cm^{-1}$ (v_l) and $1388 cm^{-1}$(v_u), which are due to a Fermi resonance between the harmonic $2v_2$ of the bending mode and the symmetric stretch v_1[44–46]. Author measured Raman spectra of CO_2 in neat SC-CO_2 at 40°C in the pressures range from 8.0 to 25.0 MPa to examine the dependence of v_l and v_u bands on density. The results are shown figure 2. The plots of v_l and v_u bands versus density are shown in figure 3. As seen from figure 3, the peaks of v_l and v_u bands of sc-CO_2 shift linearly to lower wavenumbers with increasing intensity, i.e., the red-shifts are about $3.0 cm^{-1}$ for v_l and $1.5 cm^{-1}$ for v_u. These results are consistent with those reported previously[47-49] and indicate that the experimental method is
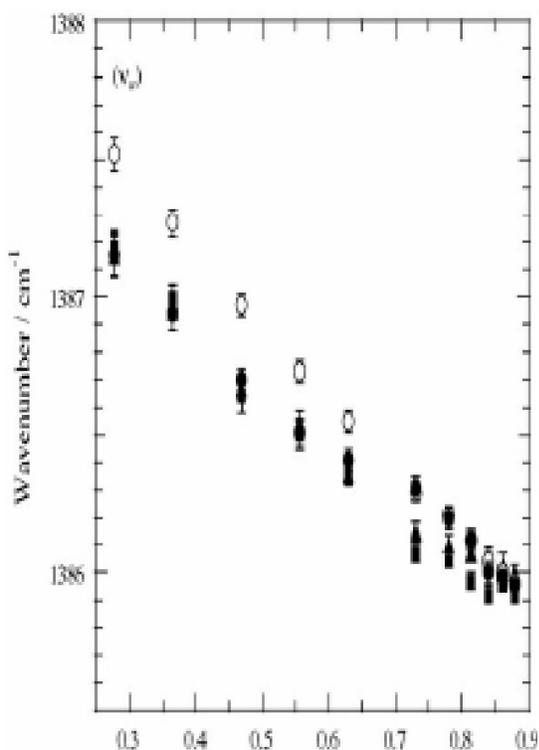
effective. On the basis of confirmation for validity of experimental procedures, authors measured the Raman spectra of CO_2 in SC-CO_2 containing Hacac, Htfacac, and Hhfacac of 1.3×10^{-1}M (M: mol dm^{-3}) to examine effects of added solutes on the structures and vibrational motions of sc-CO_2. Figure 3 displays the plots of wavenumbers corresponding to the v_l and v_u bands of sc-CO_2 containing β-diketones against the densities of SC-CO_2. Both bands are found to shift to lower wavenumbers as as in neat SC-CO_2, that is, the red-shifts for the $\_l$ and v_u bands are about 2 and 1cm^{-1}, respectively.

Furthermore, it was found that the v_l and v_u bands of SC-CO_2 containing β-diketones are observed at different wavenumbers from those of neat SC-CO_2 in the low density region, and approach to those of neatsc-CO_2 with an increase in density. These phenomena suggest the existence of solute–solvent interactions such as the LA–LB interactions and OH⋯O and/or CH⋯O proposed by Wallen et al. The C = O bond length of CO_2 molecules should become long with an increase in the interactions of β-diketones with CO_2 accompanied by the LA–LB interactions between the C = O oxygen atoms as electron donor and the carbon atom of CO_2 molecules as electron acceptor.

The C = O bond of CO_2 molecule is also affected by the OH⋯O hydrogen bonding between enolic proton of β-diketone and the oxygen atom CO_2, hence it is considered that the red shift from wavenumber of neat SC CO_2 in lower density region shown in figure 3 is due to the relatively larger ratio of β-diketone to CO_2 molecules interacting with β-diketone is relatively larger than that in higher density region.

Application fields of supercritical fluid technology

Experience accumulated in recent years on the use of SCF and SCF process have reached the step that it is possible to explore and envision their uses beyond the common practice of extraction. In recent year supercritical fluids (SCF) have gained considerable importance as media in various field of application such as extraction, fractionation, chemical and enzymatic reaction.

Sarrade et al.[50] in his presentation reviewed the new ideas recently proposed in the field of supercritical fluid and membrane coupled processes or membrane preparation one of the most important application include coupled supercritical CO_2 extraction with nanofiltration separation to purify low molecular weight compounds. another more significant potential application includes:

- Ceramic filtration membrane prepared using supercritical CO_2 route.
- Solvent recovery or separation of CO_2 from complex mixtures.
- CO_2 extraction coupled with. Cross flow filtration.
- CO_2 fludification of viscous fluids during cross filtration.
- Membrane cofactor/ reactor operated under SC CO_2 conditions.

Carbon dioxide is the only fluid which has been applied in producing composite particle. M. Bahrami and S. Ranjbarian[50] have published the review article on the production of micro- and nano- composite particles by supercritical carbon dioxide. Composite particle are produced for many purposes such as controlling the release of active material in desired quantity and location, increasing the dissolution rate of slightly water soluble material and modifying the surface properties of particles used in pharmaceutics, catalysts, cosmetics and energetic material. Several review paper have been published to cover numerous literatures on particle design by SCF method.[50-59]

Many nonvolatile solutes are insoluble in CO_2 because of the weak van der Waal forces and lack of a dipole moment. Thus many recent advancements in supercritical fluid science and technology starting in the late 1980s have utilized collide in carbon dioxide to take advantage of insoluble phases such as water, polymer latexes, metals and semiconductors. Water-in-CO_2 (W/C) and CO_2-in-water (C/W) micro emulsions and emulsions have the ability to function as a universal solvent medium by solubilizing high concentrations of polar, ionic and no polar molecules within dispersed and continuous phase[60]. W/C or C/W dispersions in the form of micro emulsions and emulsions offer a new possibilities in waste minimization for the replacement of organic solvent in field including chemical processing, pharmaceuticals, microelectronics, for solubilizations and separation, particle formation, organometallic catalysis and synthesis of polymer collide and inorganic nanoparticles[61-65]Additional applications include photo

Review

resist drying[66,67], and cleaning of low k dielectrics in microelectronics[68,69], emulsion templating in polymerization[70], drug delivery[71] and enzymatic catalysis[72,73].

R.L.Smith and Z.Fang in (2009)[74] have described the new area of supercritical fluid technology. In his review, diamond anvil type cells (DACs) are reviewed as a method for supercritical water system. The diamond anvil cell (DACs) is a remarkably device for studying high pressure phenomenon that was inspired by studies of Bridgeman[75] who used large high pressure press apparatus. The essential feature of the DAC are a miniature mechanical press that applies a balanced force onto two opposing small area (ca.1 mm diameter) anvils typically made of diamond and a metal sheet containing a w hole that is placed between the anvils, which allows confinement of liquids and solutions. Figure 1a shows a simplified diagram of the DAC proposed by Basette et al.[76] in 1993 and figure 1b shows an annotated photograph.

Application of hydrothermal DAC

hydrothermal DAC has been used to study many properties and phenomenon in geology, Physics, chemistry, engineering and material sciences. TABLE 4 shows selected topics in geology, biomass, energy, environmental, polymer and material.

Beside above mentioned applications, large amount of literature is available on application of SFE. To be able to handle systematically this large amount of information available in literature, this information will categorized under the following application field of SCF.

1. Rate processes: Crystallization.
2. Extraction processes in food, Pharmaceuticals and environmental applications.
3. Chemical reactions.
4. Polymer processing technology.
5. Fractionation.
6. Analytical supercritical extraction.
7. Supercritical water oxidation.

Each application field will be treated in a separate paragraph and a review will be given of so far explored information in open literature. Because most of the information and research work found in literature is limited to technical aspects and/or possible new application fields of SCF and does not treat the cost or industrial experiences, this aspect is not included unless it

TABLE 4

Research topics	Conditions	
	T(°C)	P(atm)
Polymer related		
Depolymerization of polyethylene terphthalate (PET)	490	l<173
Depolymerization of Nylon66	264-425	30-900
Reaction of polyethylene	423-670	<2600
Decomposition of polystyrene	400-570	453-958
Liquification of styrene- Butadiene	450-686	860-969
Rubber degradation of polyvinylchloride	400-500	16-688
Material related		
Formation of boehimite from $Al(NO_3)_3$	431	<850
Formation of erbium nanoparticles	300	<444
Formation of Zn_2Sio_4:Mn^{2+} (ZSM) phosphor	650	<1250

was mentioned. Finally an overview of possible mathematical methods will be presented and discussed regarding the estimation and simulation of technical aspects of SCF such as the solubility, influence of cosolvent, etc. which are available in literature.

Rate process

Crystallization

The particle size and size distribution of solid materials formed in industrial processes is frequently not the size that is desired for subsequent reaction or the use of these materials. Crushing, grinding, ball milling and precipitation from the solution are examples of the methods for particle size redistribution applied to chemicals, pharmaceuticals, dyes and polymers. There are many solids that are difficult to process by grinding or by solution techniques for one reason or another. For example certain dyes and explosive compounds. The use of SCF in this field has recently been under the attention, especially the GAS and RESS process as will be described below.

Gas anti-solvent (GAS) recrystallization

Gallagher et al.[77], describe a new process to recrystallize compounds insoluble in SCF, so called GAS (Gas Anti-Solvent) Recrystallization. In their study this process has been used for recrystallization of nitroguanidine from n-methylpyrrolidone and N,N-dimethyl formamide using SCFs. The type of SCF used is not mentioned in the paper. The investigation was directed to a specific explosive, nitroguanidine, but the process has been reported to be general in its applica-

tion. In this process, gases that are soluble in liquid can be admixed through complete expansion which causes an extremely high level of super saturation and nucleation rate resulting in the formation of extremely small particles which are not readily achievable by other processes. This process can not be used to recrystallize solids which are "too" soluble in the gas.

Crystallization through rapid expansion of supercritical solvent (RESS)

In the RESS process super saturation is caused by a mechanical perturbation, contrary to the conventional process wherein super saturation is caused by a thermalperturbation. The speed with which perturation propagates in the RESS process gives rise to a narrower particle size distribution compared to the conventional method. Halverson et al., investigate the influence of pre-and post-expansion condition on the crystallinity and particle size distribution. Their studies concern the continuous expansion of mixtures of naphthalene in SC-CO_2. It seems that the particle size and shape are a sensitive function of pre and post expansion temperature and solute concentration in SC mixture. Although the Gas Recrystallization and the RESS process is in developing status, it seems to be an effective process for (re)crystallizing of solid material within a controlled particle size distribution. There is no information reported regarding the process conditions. Application of these techniques for a new process should be subjected to a careful case-by-case evaluation for its economic and environmental factors compared with other recrystallization processes.

Extraction processes in pharmaceuticals, food and environmental

In recent years much research has been done on the application of SCF in the food, pharmaceutical and environmental field. Schaeffer et al.[78], report extraction of pyrrolizidine alkaloids (anti-cancer agent) from seeds of Crotalariaspectabilis which is difficult to extract and isolate from the plant material without degradation or use of toxic solvents. In this process oil of crushed seeds of Crotalarias extracted using SC-CO_2 with addition of ethanol and water as co-solvents. There are no data reported regarding the process conditions and/or the physical parameters such as solubilities. Ex-

traction of chemotherapeutic agents from the plant materials like maytansine and rollinia papillionela with SC-CO_2 also has-been mentioned[88].

Use of SC-CO2 as a replacement of hexane in soybean-oil extraction recently is being considered. Data on the extraction and oil composition of soybean oil have been described by Friedrich et al.[79] He showed that the separation of oil from CO_2-oil stream at 800 bar can be carried out by dropping the pressure by only 150 or 200 bar at 70°C.

Other development work on a SC-CO_2 process for extracting oils from potato chips and extension of seed- and fish-oil extraction has been reported[80] It is reported that potato chips containing about 45-50 wt% oil can be extracted of about 50% of their oils while retaining the original flavour and texture.

Robey et al.[81] describe a SC-CO_2 process to concentrate aromatic constituents in lemon oil. The conventional process which is based on either steam distillation or liquid-liquid extraction suffers from certain drawbacks such as product degradation and requirement of subsequent removal of solvent. It is reported that a tenfold concentration of aromatics can be achieved in a single extraction stage with a superior result concerning the flavour compared to the conventional method.

The extraction of alcohol from water using SCF has been described in some detail by Kuk et al.[82] It has been suggested that the compressibility of SCF solvent and the differences in the liquid phase no ideality exhibited by the binary alcohol-SCF and alcohol-water mixtures are two major factors for controlling the selectivity and loading of the solvent. These two factors determine whether the alcohol water-SCF mixture will split into an LLV mixture.

Extraction of phenol from soil and water using near critical and SC-CO_2 has been reported by Roop et al.[83] They report extraction of phenol from water using SC-CO_2 at pressures up to 310 bar for isotherms 25 and 50°C. Benzene has been reported as suitable co-solvent since its solubility in water is very small and it enhances the distribution of phenol into the SC phase. The presence of methanol was found to have no effect; since methanol is polar and completely soluble in water, it favours the aqueous phase and therefore does not change the characteristics of the SC phase. The

Review

two soil systems they have investigated were contaminated dry and wetted soil. They found that the SC-CO_2 was able to remove phenol from both systems equally effectively. For contaminated soil both co-solvents, benzene and methanol, increased the distribution coefficient of phenol, whereas methanol has been reported by far the most effective. The presence of moisture in the soil was found to have no effect on the extraction of phenol using pure CO_2. While the influence of water has been shown to have a dramatic impact on the effectiveness of the entrainers.

The benzene/CO_2 has been reported to be able to remove all of the phenol from the wetted soil while the methanol/CO_2 offered no enhancement over that of the pure CO_2. From the results it can be concluded that the choice of a co-solvent is not independent of the contaminated matrix or in the case of soil, its moisture content. Data regarding the process conditions and physical parameters were missing in this report.

Oudkerk et al. estimated the cost for the handling of 10 tons of sludge per hour, based on 5000 h/a, to be $ 26-53/ton with investment costs of about $M 3. It concerns a continuous SC-CO_2 extraction process where no co-solvent has been used. The sludge is assumed to be polluted with polycyclic aromatic hydrocarbons (PAH's), polychloric biphenyls and pesticides.

Chemical reactions

In the recent years much investigation has been done to understand the influence of SCF on the reaction rate, conversion and reaction pathway[84-86]. The major reasons for carrying out chemical processes in SCF phase are: The availability of an extended pressure and temperature range provides the opportunity to operate the reaction under conditions which are optimal with respect to kinetics and selectivity; The Solvent properties are easily varied and may be adjusted to special requirements, e.g. homogeneity is often easily reached. These make it possible to precipitate the product from the reaction mixture as the reaction proceeds. In this manner unwanted side-reactions may be avoided if the product species is immediately removed from the reacting system as it precipitates from solution.

The product recovery may be achieved by simply decompressing the system; - The heat and mass trans-

fer are very efficient in SCF state.

Occhiogrosso et al.[87] studied the oxidation of cumene in a homogeneous phase in SC-CO_2. The oxidation reaction which is normally carried out in the liquid phase suffers from the occurrence of side reactions. Application of SC-CO_2 has been reported to decrease the formation of byproducts and enhance the selectivity. The application of SC-CO_2 for the production of furfural from xylose has been reported by Sako et al.[88]. The conventional method for the production of furfural has a low selectivity due to the high reactive character of furfural and so the appearance of side reactions such as decomposition and polymerization. Use of SC-CO_2 makes it possible to extract the furfural out of the reactor as soon as possible and so increase the selectivity. The authors carried out experiments at 150°C and 200 bar.

Srinivas et al.[89] studied the oxidation of cyclohexane in SC-CO_2 for production of cyclohexanone and cyclohexanol. In general the oxidation of cyclohexane is carried out in the liquid phase at 393-413 K and pressures up to 20 bar with air or oxygen as co reactant under several oxidation conditions, such as uncatalyzed, catalyzed by transition metals or promoted by initiators. The vapour phase oxidation requires high temperatures in the range of 320-340°C, which leads to degradative oxidation and formation of by-products. The mechanism of oxidation reaction in a SC-CO_2 is proceeded by free radical as in the case of liquid phase oxidation. The temperature and pressure effects on the reaction rate constant are described by Arrhenius type of equation.

The conversion of oxidation reaction in SC-CO_2 is low compared to the liquid phase oxidation because of dilute concentrations of the reactants. The cyclohexanone is more selectively formed and favoured by increasing of pressure than cyclohexanol. An increase of 20% in pressure results in reduction of the induction period by 50%, an increase in activation energy, an increase in the preexponential factor by 5 orders of magnitude and an increase in the first order rate constant by about 70%.

These studies show that the reaction rates can be manipulated by adjusting the operating conditions of temperature, pressure and feed composition near the mixture critical point.

Use of an SCF reaction medium to lower the operating temperature of pyrolysis reaction is mentioned by McHugh et al.[88] Use of SCF reaction medium suppresses the formation of carbon that occurs at the high temperatures in pyrolysis reactions. Therefore an improved yields, selectivity and product separation can be attained as compared to conventional pyrolysis methods. Koll et al., 1978, report the pyrolysis reaction of cellulose in the presence of SC acetone (Tc = 235.7°C, Pc = 47 bar) operating at 250 atm and 150-290°C. At SCF conditions, the yield of glucosan is about 38.8% which is 72% higher than the yield obtained with conventional pyrolysis. This increase in yield is explained by the increase of density of the reacting mixture with pressure. At higher densities the intermolecular reaction proceeds at a much higher rate.

Titscher et al. describe the influence of an SCF reaction medium on the activity of a heterogeneous catalyst. They studied the catalytic isomerization of 1-hexene (Tc = 231°C and Pc = 30.7 bar) on σ-Al2O3 with 2-chlorohexane as a co catalyst where by cis and trans-2-hexene are the desired products. The catalyst normally is deactivated after 1.5 hours (operating conditions: 250°C and 14.8bar) and a maximum conversion of 20% has been reached. They show that the conversion slowly drops to 12% after 12 hours. The deactivation of the catalyst is a result of accumulation of oligomeric compounds (C12-C30) on the surface of the catalyst. By increasing the pressure up to 493 bar the authors have observed that the conversion increases up to 40% after 1.5 hours, and also remains at the same level after 12 hours reaction time.

Alexander et al.[90] described a reaction/separation scenario for the Diels-Alder reaction of isoprene with maleic anhydride in $SC-CO_2$. They find that the product precipitates as a solid from the reaction mixture as the reaction proceeds. In this case the reaction is run at fairly low concentrations of reactants in $SC-CO_2$.

Use of $SC-CO_2$ for the neutralization and strengthening of old paper has been reported by Perre et al.[91] The fabricated paper from wood pulp deteriorates with age through degradation of cellulose molecules by oxidation and hydrolysis reaction which results into formation of acid substances. To treat deteriorated paper documents and reverse the damage, $SC-CO_2$ has been showed to offer many advantages compared to the avail-

able processes based on the use of organic solvents. This not only from the environmental point of view but also from the quality of printed document (damage of inks or bindings) and cost of operation. In the process suggested by the authors the books (closed) are stacked in the autoclave and submitted to $SC-CO_2$ at a pressure of 200 bar and a temperature of 40°C. The flow rate of $SC-CO_2$ is reported to be 25kg CO_2 per kg of books. The acidification treatment has been carried out using dissolved methyl ethyl magnesium carbonate in $SC-CO_2$. Residence time of 4 hours has been reported to be sufficient to increase the pH level to alkaline range (> 8). Strengthening of the paper has been reported through impregnation of paper with components like grafted silica or polymers transported by $SC-CO_2$. Further details regarding this technique are missing in the paper.

Bhise[92] describes a multistep process for the production of ethylene glycol in near-critical to $SC-CO_2$, whereby much less high glycols have been produced compared to the conventional method.

Poliakoff et al.[93] explored several organometallic systems in SC fluids. Organometallic complexes are used in many homogeneous reactions, and volatile organometallic components may be used in chemical vapour deposition processes for the production of thin films for micro electrconic applications. The inertness of CO_2 and Xe and the complete miscibility with other permanent gases such as N_2 and H_2 offer significant benefits. Both N_2 and H_2 are used in organometallic chemistry. The limited solubility of these gases in liquids limits the generation of potential useful organometallic components and limits the rate of reaction. In addition since Xe is completely transparent for UV, visible and IR radiation, it is pre-eminently useful in spectroscopic reaction studies. By performing the reactions in SC-Xe, high concentrations of both N_2 and H_2 could be obtained facilitating and stabilizing the formation of new complexes. The progress of the reaction was studied using time-resolved IR-spectroscopy. The UV photolysis of η_5-$C_5H_5M(CO)^3$ with M being Mn or Re, was studied in a supercritical Xe / H_2 mixture. Both complexes reacted differently. The Mn complex formed a di hydrogen complex whereas the Re complex formed a di hydride complex. The Mn-H_2 complex was stabilized by the presence of the

Review

hydrogen in the reaction medium. Replacing H_2 with N_2 leads to a rapid H_2-N_2 exchange in the metal complex.

Polymer processing technology

The major activities relating use of SCF in polymers relate from the 1980s with one exception: polyethylene. The development of the high pressure polymerization process in the 1940s represents the first commercialized SCF process. In the recent years a growth of activities in SCF-polymer processing technology can be observed, as in other fields of application of SCF processing. This in the light of increasingly stringent regulations and bans of organic solvent use("motivation").

The dissolution of an SCF into a polymer melts results in modification of both thermodynamic and rheological properties.

Recent activities on the use of SCF in polymer lie in two fields: fundamental studies and applied process development studies. The fundamental studies recover the following areas.

Thermodynamics (phase equilibria, polarity effects, reaction kinetics, co solvent effects, etc); Transport properties (diffusion, viscosity, etc.); Predictive modeling (binary diffusion coefficient, solubility, distribution coefficient, etc.); Equipment related (chromatography, mass transfer, etc.).

The applied process development studies lie in the field SCF fractionation of polymers and copolymers by molecular weight and chemical composition. Bangert et al.[94] describe a process for spinning polymer fibers from a supercritical solution. This process entails dissolving a polymer in a high pressure fluid and extruding the gaseous solution through a die. Polymers studied are polypropylene, polybutene-1 and Nylon-6. The solubilities of these materials in CO_2 and n-butane are shown TABLE 5. Diameters ranging up to 25 microns have been reported to spun from polypropylene dissolved in supercritical propylene. The pressure levels needed to dissolve a polymer are directly related to the molecular weight of the polymer. Polymer solubility in SCF is also related to polymer tacticity Data is presented in TABLE 5.

The fractionation of a high molecular-weight silicone oil, a poly(dimethyl)siloxane using SC-CO_2 has been reported by McHugh et al.[88]. The polymer was extracted at 80°C over a pressure range from 121 to 440 bar. Six fractions have been reported to be separated from low molecular weight cyclic sand liners to high molecular weight oligomers. The replacement of methyl group in poly (dimethyl) siloxane with phenyl group lowers the solubility dramatically. In the same article, the fractionation of a perfluoroalkylpolyether, ($[CF(CF_3)$-$CF_2O]nC_2F_5$), in SC-CO_2 has been reported. Perfluoroalkylpolyether is resistant to corrosive or oxidizing materials and is being used as a diaphragm fluid, in computer disc lubricant and as a seal fluid for computer disc drives. The fractionation of perfluoroalkylpolyether is carried out at 80°C over a pressure range from 81 to 271 bar. Further the fractionation of polystyrene, photo resist polymer (polysilastyrene, $(CH3)_3$ $Si[C_6H_5SiCH_3]$ × $[CH_3Si$-$CH_3]y$ $Si(CH_3)_3$), polymeric surfactant (carboxylic acid-terminated perfluoralkyl polyether, HOOC $[CF(CF_3)CF_2O]n$ C_2F_5) and polyisobutylene-succinic have been reported[88]. More data regarding these processes are missing in the articles.

Reactive monomers which are used in applications that require high purity but which are difficult to process by distillation because of their sensitivity to temperature, can be purified by SCF processing techniques[88]. One of the examples is silicon monomer for the use in soft contact lenses or BisGMA monomer for the use in hard dental structures. These monomers have been purified with SC-CO_2 at 60°C and 94.6 bar. More data regarding these processes are missing in the article.

Another field of application of SCF in polymers are the RESS and the GAS recrystallization techniques. These techniques offer precipitation of polymers which are difficult to handle by traditional means or provide the possibility to alter the morphologies of polymers which can have advantage on further processing (e.g. in membranes). Within this concept use of SCF for modification of polymer surfaces can be mentioned.

Fractionation

Use of SCF for regeneration of activated carbon is reported by McHugh[88]. The advantages of SCF regeneration of activated carbon are reported to be lower energy requirements and carbon loss as compared to the thermal regeneration process.

Review

An Indian Journal

Design procedure and economic attraction of the use of SC-CO_2 for the fractionation of mixtures containing a homogenous series of hydrocarbons at low temperatures (25-100°C) is mentioned by De Haan. As a case model he took a process with a feed capacity of 10 kton/year for the fractionation of a mixture containing 25 wt% tetradecane, hexadecane, octadecane and eicosane into its 99wt% pure constituents.

The fractionation column used was equipped with Sulzer BX gauze packing. The required vapour-liquid equilibrium data were either measured or calculated by Peng-Robinson equation of sate. The extraction of the alkane mixture is carried out through three extraction units whereby tetradecane, hexadecane and octadecane are obtained as top products respectively and eicosaneas bottom product of the last unit. The extraction temperature was set up on 80°C and pressures obtained were 170 bar, 190 bar and 210 bar respectively in the first, the second and the third column. After extraction the CO_2 is being separated by isothermal pressure reduction to 70 bar and recycled.

In the first column the feed is pumped up to the extraction pressure (170 bar) and contacted counter currently with the SC-CO_2. After leaving the top of the column the pressure is reduced isothermally to 70 bar to separate the CO_2 and the tetradecane. The gaseous CO_2 is recompressed to 170 bar and after being cooled to 80°C with cooling water, recycled to the bottom of the column. Most of the produced tetradecane, which contains 20 wt% CO_2 is returned to the top of the column as a reflux. The remaining raffinate which contains less than 1 wt% tetradecane and 40 wt% CO_2 is drawn off from the bottom and pumped to the second column. In this column the hexadecane is separated from the alkane mixture at 190 bar. In the third column a pressure of 210 bar is used to separate the octadecane and eicosane. The produced eicosan is first expanded to 70 bar to recover the major part of the dissolved CO_2 and is expanded to 1 bar before further use. The gaseous CO_2 from both stages was recompressed and recycled to the first column. TABLE 5 shows the pressures, temperatures, flow rates and compositions of the most important streams in figure 2.

The cost of fractionation of alkane mixture into 99

TABLE 5

Polymer	SCF	Pressure [bar]	Temperature [°C]	Solubility [wt%]	Polymer melting point [°C]
Polypropylene	CO_2	450-850	163-208	6-38	162-176
Nylon-6	CO_2	400-510	233-241	13-16	212-225
Polybutene-1	CO_2	300-900	131-150	6-38	126
Polybutene-1	n-Butane	120-170	167-190	5-21	126
Polypropylene	n-Butane	130-190	166-186	5-20	162-176

wt% pure constituents comes from \$0.65/kg to \$ 0.71/kg which is much higher compared to for instance high vacuum distillation (0.02 bar) of approximately from \$ 0.09 to 0.12/kg. However the detailed design and cost evaluation of high vacuum distillation are missing in the paper of De Haan, he concluded that SC fractionation of hydrocarbon mixtures is an expensive technique. The only advantage of this technique upon the distillative workup is reported to be lower operating temperatures, 80°C compared with the range of 100-400°C, which can be important for the components integrity.

Supercritical water oxidation

Supercritical water oxidation (SCWO) is a waste treatment technology being developed for the ultimate destruction of organic materials. The technology involves the complete oxidation of organic compounds in an aqueous phase at conditions that exceed the critical point of water (Tc = 374°C, Pc = 218 bar). Supercritical conditions are attractive because organic compounds, oxygen and water can exist in a single homogeneous phase. Consequently the rapid oxidation reactions can proceed unaffected by the transport limitations that may occur at sub critical conditions. While SCW is a strong solvent for organic compounds, it is a poor solvent for inorganic salts. The oxidation process produces CO_2 and water but no NOx, SOx or dioxins. Compounds containing halogens, sulphur, phosphorus and nitrogen produce their corresponding inorganic acids (corrosion).However nitrogen compounds can also produce ammonia, nitrogen or N_2O. The SCWO can handle a wide range of aliphatic and aromatic organic compounds. For example polychlorinated biphenyls (PCBs), dioxins, the pesticides DDT and aldrin, etc. The SCWO can proceed autogenously with no need for an external energy supply at COD values of 5-10g/l.

Despite of two major drawbacks of the process,

Review

corrosion and precipitation of inorganics, this year Texaco Chemical Company decided to start the first SCWO plant worldwide in Texas. However MODEC (Modell Environmental Cooperation's) claims a new type of reactor which has no zones where solid deposits can build up.

The reactor (Texaco) which is 4 meter tall and 2 meter wide handles $1.5 m^3/h$ of aqueous waste containing some 10% organic compounds. The degree of purification has been reported to be higher than 99.5%. The new SCWO plant is expected to have a payback time of 2 years. The main application field of SCWO is expected to be for aqueous wastes that are too difficult to handle by conventional methods or wastes that are too exp.

CONCLUSIONS

The future of SFE technology is very bright and it can be envisioned that considerable opportunity still exist in developing unit operations for SCF and in the synthesis of new flow sheet. As it is evident from the information presented in this article, the SC CO_2 extraction of metals from solid matrices can be considered to in very early stage of development. The insufficient solubility of metal complexes in SC CO_2 formed by using commercial extractant is a major driving force for the development of new extractant, specifically for SC CO_2. In future a researchers can incorporate a CO_2 philic group in common extractant and can enhance the extraction efficiency. Beckmen's group have tried to accomplish this by attaching fluoropolymers to various chelating agent. The amount of metal extracted from the sample matrix did not necessarily correspond to the concentration of metal recovered in the collection solvent, as the chelated metal complex could partially degrade and /or dissociate in the supercritical fluid prior to collection to use SFE as an analytical or industrial scale process, both the extraction and collection efficiency need to be determined. To obtain quantitative metal recoveries in an SFE apparatus series of conditions must be met, namely: (i) the ligand must be sufficiently soluble and stable to be adequately solvated in the SF; (ii) the metal ion must be efficiently chelated so that charge neutralization is achieved. (iii) the resulting metal complex must be sufficiently soluble and stable in the SF to be rapidly extracted and effectively swept out of extraction cell; and (iv) the complex must be quantitatively trapped in collection devise.

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