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REVIEW PAPER

Supercritical fluid technology

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ABSTRACT

Supercritical fluids (SCFs) are increasingly replacing organic solvents, e.g., *n*-hexane, dichloromethane, chloroform, and so on, that are conventionally used in industrial extraction, purification, and recrystallization operations because of regulatory and environmental pressures on hydrocarbon and ozone-depleting emissions. In natural product extraction and isolation, supercritical fluid extraction (SFE), especially that employing supercritical CO_2, has become the method of choice. Sophisticated modern technologies allow precise regulation of changes in temperature and pressure, and thus manipulation of solvating property of the SCF, which helps the extraction of natural products of a wide range of polarities. This review deals mainly with the application of the SFE technology in the natural product extraction and isolation, and discusses various methodologies with specific examples. Supercritical fluid (SCF) technology is investigated as a dry technique for photoresist developing. Because of their unique combination of gaseous and liquid-like properties, these fluids offer comparative or improved efficiencies over liquid developers and, particularly carbon dioxide would have tremendous beneficial impact on the environment and on worker safety. Additionally, SCF technology offers the potential for processing advanced resist systems which are currently under investigation as well as those that may have been abandoned due to problems associated with conventional developers. An investigation of various negative and positive systems is ongoing. Initially, supercritical carbon dioxide as a developer for polysilane resists was explored because the exposure products, polysiloxanes, are generally soluble in this fluid. These initial studies demonstrated the viability of the SCF technique with both single layer and bilayer systems. Subsequently, the investigation focused on using SC CO_2 to produce negative images with polymers that would typically be considered positive resists.

Key Words : Super critical fluid, Phospholipids, Trace organics, Spices

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A fluid heated to above the critical temperature and compressed to above the critical pressure is known as a supercritical fluid. Frequently the term, compressed liquid, is used to indicate a supercritical fluid, a near-critical fluid, an expanded liquid or a highly compressed gas. The phenomena and behavior of supercritical fluids has been the subject of research right from 1800's.Supercritical fluid extraction technique is a new separation technique, which is developed by use of the fluid, which has the ability of dissolution at the supercritical pressure and the supercritical temperature. The supercritical fluid extraction technique has many characteristics, such as high extraction efficient, simply separation technology, no need solvent recovery equipment, easy operation condition, widely used future, etc. Supercritical fluid extraction technique is always completed in the room temperature. Since it is no poisonous, no residual, and green manufacture, there are more and more studies and applications about it home and abroad in recent

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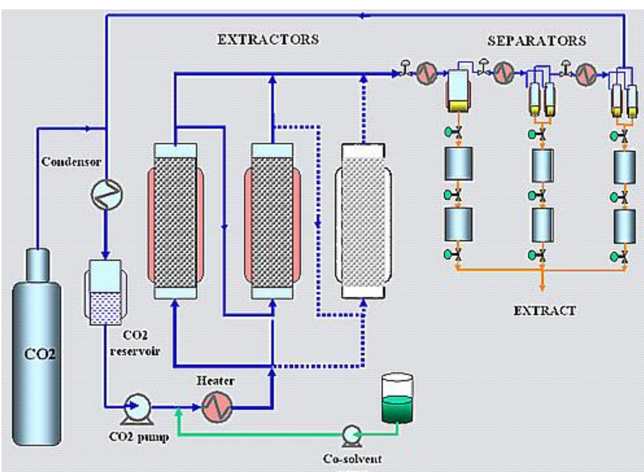
years. Two supercritical fluids are of particular interest, carbon dioxide and water. Carbon dioxide has a low critical temperature of 304 K and a moderate critical pressure of 73 bar. It is non-flammable, non-toxic and environmentally friendly. It is often used to replace certain organic solvents. Further, it is miscible with a variety of organic solvents and is readily recovered after processing. It is also a small and linear molecule and thus diffuses faster than conventional liquid solvents.Water has a critical temperature of 647 K and a critical pressure of 220 bar due to its high polarity. The character of water at supercritical conditions changes from one that supports only ionic species at ambient conditions to one that dissolves paraffins, aromatics, gases and salts. Due to this unique property, research has been carried out on supercritical water for reaction and separation processes to treat toxic wastewater. Supercritical fluids such as water and carbon dioxide are substances that are compatible with the earth's environment. However, several other supercritical fluids can be used, but the final choice would depend on the specific application and additional factors such as safety, flammability, phase behavior and solubility at the operating conditions and the cost of the fluid. In the following sections, a brief outline of the properties, fundamentals and applications of supercritical fluids is provided.



Properties and fundamentals of supercritical fluids:

Solvent strength :

The density of a supercritical fluid is extremely sensitive to minor changes in temperature and pressure near the critical point. The density 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 solubilities was discovered in 1870's for the potassium iodide-ethanol system. The solvent strength of a fluid can be expressed by the solubility parameter, ?, 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 that 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 solubility 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 these data are for liquid carbon dioxide, provide 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 solubilities in supercritical fluids. Solute solubilities approach and may exceed that of liquid solvents. Solubilities generally increase 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 cosolvents called modifiers may be added. The cosolvent interacts strongly with the solute and significantly increases the solubility. For example, addition of a small amount (3.5ml%) 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 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 non-idealities 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 cosolvents 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.

Extraction with supercritical fluids:

Supercritical extraction has been applied to a large number of solid matrices. The desired product can be either the extract or the extracted solid itself. The advantage of using supercritical fluids in extraction is the ease of separation of the extracted solute from the supercritical fluid solvent by simple expansion. In addition, supercritical fluids have liquid like densities but superior mass transfer characteristics compared to liquid solvents due to their high diffusion and very low surface tension that enables easy penetration into the porous structure of the solid matrix to release the solute.

Extraction of soluble species from solid matrices takes place through four different mechanisms. If there are no interactions between the solute and the solid phase, the process is simple dissolution of the solute in a suitable solvent that does not dissolve the solid matrix. If there are interactions between the solid and the solute, then the extraction process is termed as desorption and the adsorption isotherm of the solute on the solid in presence of the solvent determines the equilibrium. Most solids extraction processes, such as activated carbon regeneration, fall in this category. A third mechanism is swelling of the solid phase by the solvent accompanied by extraction of the entrapped solute through the first two mechanisms, such as extraction of pigments or residual solvents from polymeric matrices. The fourth mechanism is reactive extraction where the insoluble solute reacts with the solvent and the reaction products are soluble hence extractable, such as extraction of lignin from cellulose. Extraction is always followed by another separation process where the extracted solute is separated from the solvent. Another important aspect in supercritical extraction relates to solvent solute interactions. Normally the interactions between the solid and the solute determine the ease of extraction, i.e., the strength of the adsorption isotherm is determined by interactions between the adsorbent and the adsorbate. However, when supercritical fluids are used, interactions between the solvent and the solute affect the adsorption characteristics due to large negative partial molar volumes and partial molar enthalpies in supercritical fluids. The thermodynamic parameters that govern the extraction are found to be temperature, pressure, the adsorption equilibrium constant and the solubility of the organic in supercritical fluid. Similar to the retrograde behavior of solubility in supercritical fluids, the adsorption equilibrium constants can either decrease or increase for an increase in temperature at isobaric conditions. This is primarily due to the large negative partial molar properties of the supercritical fluids. In addition to the above factors, the rate parameters like the external mass transfer resistances, the axial dispersion in the fluid phase, and the effective diffusion of the organics in the pores also play a crucial role in the desorption process. A thorough understanding of these governing parameters is important in the modeling of supercritical fluid extraction process and in the design, development and future scale-up of the process.

Polymers and supercritical fluids:

A number of studies have examined solubilities of polymers in supercritical fluids. With the exception of a few polymers, such as fluoropolymers, most high molecular weight polymers do not dissolve in carbon dioxide. However, polymers can uptake a significant amount of the supercritical fluid. As the concentration of the compressed fluid is increased in the polymer phase, the sorption and subsequent swelling of an amorphous polymer can cause a glass- to liquid-phase transition. The glass transition temperature of the polymer may be drastically reduced and this behavior may be exploited in polymer processing to produce extremely small voids only a few micrometers in diameter.

Biocatalysis and supercritical fluids:

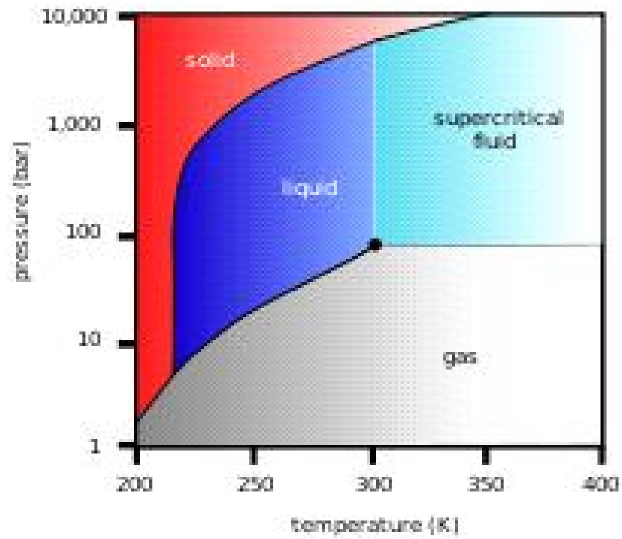
The advantages of using enzymes in supercritical fluids have been investigated. The densities of supercritical fluids are comparable to that of liquids, while the viscosities and diffusion coefficients are comparable to that of gases. This enhances the rates for diffusion controlled reactions. The low water activity environment will shift the thermodynamic equilibrium of hydrolytic reactions to favor synthesis. Also, reactions in which water is a product can be driven to completion. Gaseous reactants are completely miscible in supercritical fluids and thus reactions involving gaseous substrates will not be limited by solubility.Since enzymes are insoluble in supercritical fluids, recovery is straightforward and immobilization is unnecessary. Further, product fractionation, purification etc. from the reaction mixture are feasible by reducing the pressure in a sequence of separators. Enzyme catalysis has been well characterized for physical properties of aqueous systems and detailed reaction mechanisms have been derived. However, knowledge of aqueous systems can not be extrapolated to supercritical fluid catalysis because the physical properties of the solvent such as dielectric constant, viscosity, diffusivity etc. are widely different.Enzymatic reactions in non-aqueous media, especially supercritical fluids, are gaining acceptance. The initial paper on this subject appeared in 1985 in which a study of the hydrolysis of p-nitrophenyl phosphate to p-nitrophenol with alkaline phosphatase was reported. Subsequently, rates of oxidation of cholesterol with cholesterol oxidase were determined. It was also found that cosolvents facilitate cholesterol aggregation in supercritical carbon dioxide and the enzyme is known to be more active toward aggregates than cholesterol monomers. The most extensively studied enzymatic reactions in supercritical carbon dioxide systems have involved lipases. However, the use of supercritical fluids as the reaction media for enzymatic catalysis is still in its infancy.

Dispersions in supercritical fluids:

The ability to design surfactants for the interface between water (or organics) and supercritical fluids offers new avenues in protein and polymer chemistry, separation science, reaction engineering, waste minimization and treatment. Surfactant design, which is reasonably well understood for conventional reverse micelles and water-in-oil microemulsions for alkane solvents, is more difficult for carbon dioxide because the properties of carbon dioxide are much different from those of water or nonpolar organic solvents. Carbon dioxide has no dipole moment and weaker van der Waals forces than hydrocarbon solvents. It is possible, however, to form dispersions of either hydrophilic or lipophilic phases in a carbon dioxide continuous phase. Organic-in-carbon dioxide dispersions may be stabilized using surfactants like fluorinated compounds, which are carbon dioxide-philic.

Applications and commercial processes of supercritical fluids:

Any commercialization of a process that uses



Supercritical carbon dioxide

supercritical fluids must involve a cost analysis that should indicate that the advantages in the new process offset the penalty of high pressure operations. A variety of supercritical fluid processes have been commercialized. Details of a few such processes are given below. Many other processes have been investigated on a lab or pilot plant scale and have the potential to be scaled up in the near future.

Food applications :

Extraction of natural spicey:

A very successful application of supercritical fluid extraction technique is the distillation of natural spicery. For example, the distillation of rare spicery such as jasmine cream, rosa rugosa thunb, clove oil, and rosemary, etc. Because the supercritical fluid has the ability of high dissolution, and has high extraction yield and efficient, and because CO_2 is used as the extraction agent, so the products are no poisonous, no residual, their color and fragrance are sterling. The product price is higher than that made from common means by 20-25%, and the extraction ratio is higher than common means by 20-100%, which will bring huge economic benefits. The extraction substances completed now include: jasmine cream, rosa rugosa thunb, clove oil, rosemary, osmanthus fragrans lour, epidendreae, etc.

Extraction of caffeine, theobromine, and cocoa-butter from Brazilian cocoa beans using supercritical CO_2 and ethane:

Supercritical extraction using ethane and CO_2, acceptable solvents for food products, was explored for the recovery of the methylxanthines caffeine and theobromine and cocoa butter from cocoa beans using a high-pressure apparatus. Continuous extraction of cocoa beans was performed at 343.2 K using CO_2 at pressures of 20 and 40 MPa and ethane at pressures of 15.2, 24.8, and 28.3 MPa. The extraction yields of cocoa butter obtained with ethane were much higher than those obtained with CO_2 because of the higher solubility of this fat in ethane. A pronounced effect of pressure on the extraction of methylxanthines and cocoa butter was observed for both solvents. Extraction curves revealed the greater facility of these solvents to extract cocoa butter followed by caffeine and theobromine. This behavior suggests a range of possible conditions under which the extraction and isolation of cocoa butter, caffeine, and theobromine from cocoa beans can be achieved. The methylxanthines in cocoa beans were slightly more soluble in ethane than in CO_2 probably because of co-solvency effects of cocoa butter, which was extracted more easily using supercritical ethane. Despite the higher cost of ethane, its critical pressure is lower than that of CO_2, and the higher butter solubility could render ethane a viable solvent through lower energy costs.

Cocoa beans, *Theobroma cacao*, a source of a variety of products such as cocoa powder, chocolate, etc., contain mainly cocoa butter (45-54%), proteins (11.5%), a significant amount of theobromine (1.2-1.8 wt %), and caffeine (0.26 wt %). The presence of these two alkaloids, theobromine and caffeine in common beverages such as coffee, tea, and cocoa is of concern to some consumers because of their potentially adverse health effects at certain levels of consumption. The U.S. Food and Drug Administration have recently warned pregnant women to avoid or minimize their intake of caffeine, as studies in animals have suggested a relationship between birth defects and caffeine intake. Theobromine, present in large amounts in chocolate, has been reported to cause physiological effects similar to those observed for caffeine, namely, strong diuresis and cardiac stimulation as well as arterial dilation. Cocoa butter is not only an important product for the food industry but also an ingredient of many cosmetic and pharmaceutical products.The extraction of cocoa butter and methylxanthines (caffeine and theobromine) from natural plants is a potentially attractive process for the recovery of alkaloids as ingredients in the formulation of different pharmaceutical products as well as for the production of high-value methylxanthine-free fat products for human consumption and cosmetic formulations. Dimethyl chloride, chloroform, and water have been employed for the removal of methylxanthines from natural plants, with hexane and petroleum ether reserved for oil recovery. Chemical solvents, however, require a long time for a complete extraction and almost always carry with them the risk of toxic residue in the extracted products. Water, although is an excellent solvent for methylxanthines, is not very selective and is immiscible with fats and oils under normal conditions. Mechanical expulsion has also been employed for obtaining fats and oils from natural products. This technique often introduces waste solid contaminants into the produced butter, thus necessitating the use of other processes for their removal. Low critical temperature, nontoxicity, and low cost have rendered supercritical CO_2 a suitable and environmentally benign solvent for food products, that has been successfully used for the extraction of oils and fats.Supercritical CO_2 extraction is successfully used on a commercial scale for the decaffeination of coffee beans.The application of supercritical fluid technology in biotechnology and the prediction of the solubility of biomolecules in supercritical solvents have been reported. Ethane, also an acceptable solvent for food products, has approximately the same critical temperature as CO_2. Despite its higher cost, it has a lower critical pressure than CO_2 and could, therefore, be used as a supercritical solvent at lower operating pressures and consequently lower energy costs. In this work, we present new experimental data on the extraction of cocoa butter and methylxanthines from Brazilian cocoa beans using dry and water-saturated supercritical CO_2 as well as ethane.

Cholesterol extraction from food :

The association of high blood cholesterol levels with heart diseases or cancer is the motivating factor in recent works on the reduction of cholesterol levels in consumed meals that include meats, dairy products and eggs. Several methods including supercritical extraction have been proposed for the reduction of fat and cholesterol content in dairy products (Greenwald, 1991). Cholesterol was shown to be soluble in supercritical carbon dioxide and even more soluble in supercritical ethane. Extraction with supercritical fluids requires higher investment but can be highly selective and more suitable for food products. A summary of the main products containing cholesterol and their extraction with supercritical fluids is presented in Table 1. These results clearly indicate the great potential of supercritical fluid extraction in the recovery of meat products with acceptable cholesterol and fat contents. As ethane is much more expensive than CO_2, the use of CO_2/ethane and CO_2/propane mixtures can be an attractive alternative for the removal of cholesterol from foods due to the compromise between higher ethane cost and better cholesterol removal efficiency. Cholesterol removal was also improved through the coupling of carbon dioxide extraction with an adsorption process operating at the same extraction conditions. Literature data also point to potential fractionation of fat simultaneously with the removal of cholesterol from dairy products. The extraction/fractionation operation was also coupled with an adsorption step that uses alumina as the adsorbent (Mohamed *et al*., 1998, 2000).

The combined extraction/adsorption operation resulted in the removal of more than 97% of the cholesterol in the original butter oil. The operation has also resulted in the

Table 1 :

Product	Reference	P (MPa)	T (°C)	Cholesterol (mg/g)		Yield (%)
				Before	After	
Dried egg yolk	Froning *et al.*, 1990	16.5-37.8	40-55	18.52	6.34	65.8
Dried egg yolk	Bohac, 1998	24.1-37.8	45-55	18.94	0.38	98.0
Dehyrated beef	Lim, 1992	23.4-38.6	45-55	1.56	0.19	87.8
Beef patties (cooked)	Fenton and Sim, 1992	17.2-55.1	40-50	1.94	0.12	93.8
Pork (cooked)	Lin *et al.*, 1999	7.3-34.4	50-150	0.80	0.22	70.1
Dried chicken meat	Froning *et al.*, 1994	30.6-37.6	45-55	4.96	0.54	90.0
Milk fat	Mohamed *et al.*, 1998	10.1-36.4	40-70	2.50	0.21	91.5
Milk fat	Mohamed *et al.*, 2000	8.0-24.0	40-70	2.50	0.20	93.4

*using supercritical ethane as solvent

generation of butter oil fractions with characteristic properties that are distinctly different from those of the original oil. The carbon dioxide extraction has also proved effective for the production of high quality cocoa butter from cocoa beans (Saldaña *et al*., 2002b). Recent investigation point to the potential use of supercritical CO_2 for microbial inactivation of foods and the implementation of an innovative technique for the sterilization of thermally and pressure sensitive materials (Spilimbergo *et al*., 2002).

Supercritical fluid extraction of dry-milled corn germ with carbon dioxide:

Dry-milled corn germ was extracted with supercritical carbon dioxide ($SCCO_2$) at 5.000-8.000 psi and 50^0T. CO_2 -extracted oil was lower in free fatty acids and refining loss. and was lighter in color when compared with a commercial expeller-milled crude oil. Total unsaponifiable and tocopherol contents were similar for both oil types. The defatted. highly friable flour has a shelf-stable moisture content of 2-3% and good flavor quality. The flour contains 20% protein with good amino acid balance. Meeting FAO specifications for food protein supplements. High pressure SC-CO_2 extraction also denatures the proteins. including oxidative enzymes. Peroxidase activity is reduced tenfold in SC- CO_2 extracted flour when compared with hexane-extracted flours. Storage tests for 5 wk at 38^0C and for 2 months at 25^0C show that flavor quality of untoasted SC-CO_2 -defatted germ flour is maintained even under these extreme conditions.

Preparation of natural food:

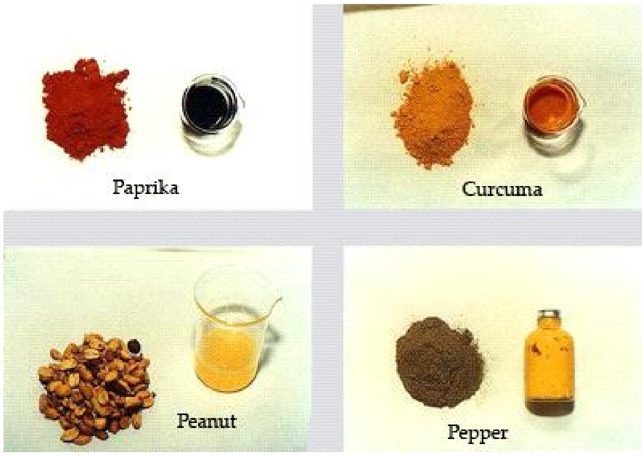
Take advantage of supercritical fluid extraction technique, we can extract the paprika pigment, carotene, tomato red element, hop, caffeine, etc. These are well-rounded technique, the products are no poisonous, no residual, and are the natural nutritious component. We can also extract nicotine from tobacco, in order to produce cigarette without nicotine. These techniques are welcome to the company.

Extraction of the biochemical components:

Using the supercritical fluid extraction technique to distill the health compounds such as depth fish oil, vitamin E, vitamin C, etc., not only it is natural, green, no poisonous, no residual, high purity, etc. but also it has a high extraction yield and a good benefit. Besides, this technique can be used to distill taxol, flavones, glucide, and alkaloids. The components after being separated are used for pharmacy, which makes great progress and change in the realm of medicine. For example, the DNA can lower the blood pressure, prevent thrombosis, and even strengthen the intelligence, while the taxol is the only medicine, which specially has good effect on remedying some cancers at present. The extraction techniques completed now include: deep sea fish oil (EPA, DHA); vitamin E; vitamin C; etc.Products have been extracted are as follows: paprika pigment, carotene, lycopene, soja oil, wheat germ oil, safflower oil, etc. Carbon dioxide is the most common supercritical fluid in the food industry. Due to the non-toxicity and low critical temperature, it can be used to extract thermally labile food components and the product is not contaminated with residual solvent. Further, the extract's color, composition, odor, texture are controllable and extraction by supercritical fluid carbon dioxide retains the aroma of the product. Supercritical carbon dioxide extraction is used as a replacement for hexane in extracting soybean-oil and has been tested for extraction from corn, sunflower and peanuts. Supercritical fluid extraction provides a distinct advantage not only in the replacement but also extracts oils that are lower in iron and free fatty acid. To satisfy the consumer's need for 'lighter' foods, developmental work on supercritical extraction of oils from potato chips and other snack foods are been carried out. In addition, supercritical carbon dioxide has also been used to extract lilac, essential oils, black pepper, nutmeg, vanilla, basil, ginger, chamomile, and cholesterol.

Supercritical Extraction of natural products:

Many molecules can be extracted or refined by



supercritical fluid processes : colorants (deodorization of blue color from red cabbage juice, orange color from pot marigold flower, carotenoids from palm oil or shellfish or carrots…), antioxidant preservatives (deodorization of rosemary extract), or texture agents (lecithin purification from vegetal oil). fish oils or derivatives deodorized and purified by SFF ; moreover, some stuffs are treated for elimination of pesticides (ginseng) or toxaphenes (fish oils).

Supercritical water oxidation, an environmentally attractive technology through which organic materials can be oxidized to carbon dioxide, water and gaseous nitrogen, is one of the new potential applications of supercritical fluid technology (Mizuno *et al*., 2000 and Phelps *et al*., 1996). In analytical applications, it has the advantage over standard methods in providing consistent qualitative and quantitative analysis and the simultaneous oxidative decomposition of the material. In addition to the homogenization of the reaction mixture, high oxygen concentrations are attained in supercritical water. The application of supercritical water for the safe destruction of toxic materials is a viable alternative to incineration and land disposal (Moret and Conte, 2000).

Supercritical fluid chromatography:

Supercritical fluid chromatography is now often used as an analytical tool. The density is used as the controlling feature. Separations are based on a user programmed density profile with the supercritical fluid as the mobile phase. This analytical technique has been successfully used to separate oligomers and high molecular weight polymers. Supercritical fluids are used as the extracting solvents for the removal of polyaromatic hydrocarbons from soil. It is now a standard method for gas chromatography sample preparation because the extraction is considerably faster than Soxhlet extraction.

Fractionation:

Supercritical fluids can be used to fractionate low vapor pressure oils and polymers. This fractionation is difficult to achieve in distillation because the impurities have about the same volatility as the primary components reducing the overall selectivity. Kerr-McGee Inc. has developed a commercial process for the separation of heavy components of crude oil. Fractionation with respect to chemical composition is possible and has been investigated to produce polymer fractions of low polydispersity starting from a parent material of high polydispersity.

Reactions:

Supercritical fluids are attractive media for several chemical reactions. The properties of supercritical fluids mentioned earlier can be used to advantage. By small adjustments in pressure, the reaction rate constants can be altered by two orders of magnitude. Equilibrium constants for reversible reactions can also be changed 2-6 fold by small changes in pressure. This dramatic control over the reaction rates has led to the design of several reactions in different areas of biochemistry, polymer chemistry and environmental science. In bioreactions, increased solubilities of hydrophobic material and the potential to integrate the separation and reaction steps has led to research in this area. The use of lipase and synthesis of mondisperse biopolymers holds commercial promise. Carbon dioxide has also been extensively studied for homogeneous polymerization of a few polymers such as fluoroacrylates. The feasibility of free radical polymerization of polystyrene and the polymerization of polyethylene has also been investigated. Carbon dioxide is also often used as a swelling agent for a polymer substrate. Though highly corrosive and a high critical temperature and pressure, supercritical water has been one of the most studied medium for chemical reactions. Supercritical water has the ability to dissolve many nonpolar organic compounds such as alkanes and chlorinated biphenyls and can dissolve in several gases. It is thus an attractive media for oxidative reactions and has been used to treat a wide variety of waste water streams from chemical, petroleum, textile industries. Huntsman Corporation has commercialized a hydrothermal oxidation unit to treat alcohol and amine contaminated water.

Preparation of nano-material :

Take advantage of supercritical fluid extraction technique, solve solid granule into supercritical fluid, the anti-solvent method or fast expand method is adopted, make fluid expand and at state of low pressure, it's too late for crystal nucleus to grow up, so it will be crystaled to separate out within 10^{-7}~10^{-5} minutes, and can be made into super fine granule of 10~50nm. At present there are a few methods to prepare nano-material, but supercritical fluid extraction technique may take place at normal temperature, so its energy consume is low, this method is one of the best competitive technique. The other method to prepare nano-material using supercritical fluid is to solve the substances saturated in the solvent, when the solution is joined to the supercritical fluid, the solvent is solved in it but the solute is not, so we can gain the solid solute of nano-level.

Pharmaceutical applications :

Since the residual solvent present in the extracted material is of critical importance in the pharmaceutical industry, supercritical fluid carbon dioxide has found several applications. The extraction of vitamin E from soybean oil and a purification method for vitamin E has been well studied. The latter process avoids the step of vacuum distillation, which usually results in the thermal degradation of the product. Solubilities and recrystallization of various drugs has been demonstrated in supercritical fluids.

When organic flotsam is put in the supercritical fluid with oxygen, oxygenation reaction will be very quickly, it can change the organic flotsam into CO_2 and water within a few minutes. When meeting with organic flotsams difficult to transform, such as hydroxybenzene kind, chlorin-hydrocarbon kind, nitrogen containing compound, organic compound, martial material, etc., supercritical fluid technique shows incomparable superiority, especially to dioxin. Dioxin originates from the war between America and Vietnam in 1960s, is a multi-ring compound damaging physical nerve system, it exists at ashes after setting on fire, so setting on fire can't eliminate it. It may accumulate in person, fish and other animals, and experiments show that dioxin can be decomposed 100% in the supercritical water, which approved the advantage of the technique in environment protection. Besides, taking advantage of supercritical fluid extraction technique, we can degradate macromolecule material, such as polyethylene, PVC, polypropylene, nylon-66, etc. Thus it brings the hope for man to settle white pollution. Due to strict environmental regulations, supercritical fluids are used as replacements for conventional hazardous chemicals such as hexane. Supercritical fluid extraction has been proposed as an alternative technique for soil remediation and activated carbon regeneration. Over 99% of a majority of organics can be removed from contaminated soil. Organics that have been successfully extracted include PAHs, PCBs, DDT and toxophene. Carbon dioxide has been used with entrainers for the extraction of highly polar compounds. A commercial process to separate oils from refinery sludge and contaminated soil has been developed by CF Systems Corporation, USA. Chelating moieties that dissolve into carbon dioxide have been developed for the extraction of heavy metals from soil.

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