Potential Applications of Supercritical Fluid Extraction Technology in the Oils and Fats Industry

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RINGKASAN

Teknologi Ekstraksi Bendalir Superkritikal (EBSK) adalah satu teknik ekstraksi menggunakan bendalir superkritikal sebagai pelarut. Teknologi ini adalah dianggap menarik terutamanya dari kacamata penggunaan tenaga dan alam sekitar. Karbon dioksida adalah satu bendalir yang kerap digunakan dalam teknologi ini kerana ialah ury murah, tak-toksik, takmudah-terbakar, tidak menjejaskan alam sekitar dan sesuai untuk bahan yang taktahan-haba. Satu kelemahan teknologi ini ialah ianya memerlukan modal yang besar dan oleh sebab itu ekstraksi bahan-bahan komoditi mungkin tidak berdaya maju. Walau bagaimanapun, teknologi ini mempunyai potensi yang besar untuk menjadi teknologi ekstraksi bahan-bahan nilai tinggi atau bahan-bahan yang susah diproses dengan cara biasa. EBSK telah dikomersialkan dalam proses pengnyahkafen kopi dan dalam ekstraksi hops. Dalam industri minyak dan lelemak, bidang-bidang yang menggunakan EBSK termasuklah dalam pengeluaran bahan-bahan nilai tambah seperti minyak mutu tinggi (untuk makanan kesihatan dan kosmetik), asid oleik, karoten dan vitamin E.

INTRODUCTION

A supercritical fluid (SCF) is a gas or a liquid that is held above its critical temperature and pressure. The existence of the critical point of a substance was discovered by Baron Cagniard de la Tour in 1822. Supercritical fluid technology encompasses supercritical fluid extraction (SCFE) and supercritical fluid chromatography (SCFC) and it is based on the fact that a supercritical fluid has the ability to act as a solvent. This property was first observed by Hannay and Hogarth who in 1879 reported that solids such as metal halides are soluble in ethanol or tetrachloromethane under conditions above the critical point (McHugh and Krukonis, 1986).

Even though the principle of SCFE technology was discovered more than a century ago, great interest developed only in the last decade or so, as indicated by the large number of publications and patents related to applications in various fields including foods, pharmaceuticals, biochemistries and essential oils (e.g. Zosel, 1978; Bott, 1980; Hubert and Vitzhum, 1978; Larson and King, 1986; McHugh and Krukonis, 1986; Nakamura et al. 1986). This renewed interest was partly prompted by the prospect of this technology providing an alternative to conventional extraction methods in terms of energy saving, and by the possibility of using physiologically inert supercritical fluids for applications in the food and pharmaceutical processing industries.

This paper is a short review of the current status of SCFE technology with emphasis on the progress of research and development related to applications in oils and fats. An attempt is also made to identify areas in which this

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technology might have potential applications in the palm oil industry.

**CHARACTERISTICS OF SUPERCRITICAL FLUIDS**

The region in which a substance exists as a supercritical fluid is defined by the critical pressure and critical temperature of the substance. The critical temperature and critical pressure of some gases are given in Table 1 (McHugh and Krukonis, 1986). The pressure-temperature phase diagram of pure carbon dioxide is shown in Figure 1 (Brogle, 1982). When a gas is heated above its critical temperature, it cannot be liquefied, regardless of the pressure applied. The reduced pressure-reduced density phase diagram of any fluid carbon dioxide is given in Figure 2 (Filippi, 1982). The supercritical region is that which lies above a reduced pressure of 1.0, and above the reduced temperature isotherm of 1.0.

The physicochemical properties of supercritical fluids tend to be intermediate between those typically associated with gases and liquids (Schneider, 1978; Willson, 1985).

![Figure 1. Pressure-temperature phase diagram of carbon dioxide.](image_url)

**TABLE 1. CRITICAL-POINT DATA OF SOME POSSIBLE SUPERCRITICAL SOLVENTS**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Critical Temperature (°C)</th>
<th>Critical Pressure (Atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>31.1</td>
<td>72.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.3</td>
<td>48.2</td>
</tr>
<tr>
<td>Ethylene</td>
<td>9.3</td>
<td>49.7</td>
</tr>
<tr>
<td>Propane</td>
<td>96.7</td>
<td>41.9</td>
</tr>
<tr>
<td>Propylene</td>
<td>91.9</td>
<td>45.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>280.3</td>
<td>40.2</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>235.2</td>
<td>47.0</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>198.1</td>
<td>43.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.5</td>
<td>111.3</td>
</tr>
<tr>
<td>Water</td>
<td>374.2</td>
<td>217.6</td>
</tr>
</tbody>
</table>
For example, supercritical fluids are generally found to have values for transport properties such as viscosity and diffusivity that are more gaslike than those typical of liquids. On the other hand, as one applies increasing pressure, the densities of supercritical fluids can approach those of liquids, of the order of 0.2 to 0.9 grams per cubic centimetre. Because of these liquid-like densities, supercritical fluids have liquid-like solvating power which can also be changed by the addition of co-solvents (entrainers or modifiers).

**SUPERCRITICAL FLUID EXTRACTION (SCFE)**

**Principle of the Process**

A supercritical fluid (SCF) has solvating properties approaching those of the liquid state, and high diffusivity and low viscosity resembling the gaseous state. This unique combination of properties makes supercritical fluids attractive in solvent for extraction processes. By varying such parameters as temperature and pressure, selected components can be differentially extracted from a mixture, somewhat as in fractional distillation. The thermodynamic principles of SCFE have been discussed (Peter, 1983; Starling *et al.*, 1985).

Supercritical fluid extraction, which can be carried out at lower temperatures than those used in conventional extraction methods, is often a less energy-consuming process. Many of the common inexpensive substances often used as solvents in SCFE processes are in the gaseous state below room temperature so that upon depressurization, the extracted product can be obtained virtually free of solvent.

Supercritical carbon dioxide (SC-CO$_2$) is one of the most widely used supercritical fluids, and is especially useful in the extraction of nonpolar substances (Filippi, 1982; Blenford, 1983). It is a choice solvent as it is non-toxic, nonflammable, inexpensive and environmentally acceptable. It is also applicable for the extraction or processing of heat-labile compounds because it has the mild critical temperature of 31°C (Kamihara *et al.*, 1987; Taniguchi *et al.*, 1987).

A major technical drawback to the use of SCFE technology in the separation of natural products is the low solubility of many biochemicals in supercritical fluids, which necessitates the use of a large fluid:feed ratio (Wong and Johnston, 1986). Compounds having low or medium polarity are more soluble in supercritical fluids than highly polar materials. The use of entrainers (co-solvents) may improve selectivity and solubility (Walsh *et al.*, 1987).

**Equipment**

A schematic diagram of a typical laboratory apparatus used for SCFE extraction is shown in Figure 3 (Shishikura *et al.*, 1986; Zhao *et al.*,
The samples are placed in the extractor (EX) which is a stainless steel cyclinder (4 cm i.d., 20 cm height) having a working pressure of 500 kg/cm² G at 100°C. Pure CO₂ which is supplied from a cylinder (CY), is subjected to cooling (GC), filtration (F), compression (C) to the required pressure, and heating (HE) to the required temperature, after which the compressed CO₂ is passed through the extractor. The extract is recovered by depressurization of the SC-CO₂ via a metering valve (MV) and collected in a receiver (RE).

The development and some applications of countercurrent SCFE equipment have been reported (e.g. Peter and Brunner, 1978; Bondioli et al., 1992; Brunner et al., 1991).

**R&D ON APPLICATIONS OF SCFE TECHNOLOGY IN OILS AND FATS**

**Fundamental Data**

Fundamental data on properties such as viscosity and solubility in supercritical fluid (SCF) system are required for the design and scaling-up of SCFE processes, but the availability of such data in the literature is still limited.

Kashulines et al. (1991) reported the viscosities at 40 and 60°C of oleic acid and linoleic acid saturated with SC-CO₂ from 85 to 350 bar and of their respective methyl esters from 90 to 170 bars. The viscosity of anhydrous milk fat saturated with CO₂ was also measured from 100 to 310 bars at 40°C.

Supercritical fluids can dissolve a wide variety of substances but the extractability of particular substances by SCFE technology obviously depends very much on the degree of solubility of the substances in particular supercritical fluids. Chrusti (1982) determined the solubility of tocopherol, several fatty acids and their corresponding triglycerides in SC-CO₂ at different pressures and tempera-

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**Figure 3. Schematic Diagram of SC-CO₂ Extraction Apparatus.**

CY, CO₂ cylinder; PG1, pressure gauge; GC, gas cooler; F, gas filter; C, Compressor; RV, back pressure-regulating valve; precise pressure gauge; SV, shut-off valve; CV, check valve; PS pressure sensor, HE, heater; EX, extractor; RD, rupture; MV, metering valve; FM, flow meter; RE, receiver.

...
these data were compared with calculations based on the Peng-Robinson equation and on an equation of state containing a theoretically-realistic repulsive term.

**Processing**

Studies on the applications of SCFE technology to the extraction of oils from oil seeds have been reported (Mangold, 1983; Stahl et al., 1980). The performance of SC-CO₂ extraction of soyabean flakes has been compared with that of hexane extraction in terms of the yield and quality of the extracted oil, and it was found that the oil yields by SC-CO₂ extraction were comparable and that SC-CO₂ extracted oils showed significantly lower refining loss and phosphorus content than those extracted with hexane, and that they were light coloured and essentially degummed (Friedrich and List, 1982; Friedrich et al., 1982).

Christianson et al. (1984) applied SC-CO₂ to the extraction of dry-milled corn germ and found that the oil obtained was lower in free fatty acids and refining loss, and lighter in colour by comparison with a commercial expeller-milled crude oil.

Taniguchi et al. (1985) extracted oil from wheat germ oil by SC-CO₂ and found that the oil was lighter in colour and contained less phosphorus than that extracted with hexane but contained a comparable amount of tocopherols to those in hexane-extracted oil.

It has been reported that SC-CO₂ extraction of evening primrose oil is faster and more efficient than hexane extraction, and at 122°C and 10 000 psi, recovery was more than 95% in 10 minutes (Latta, 1990).

Yamaguchi et al. (1986) reported the extraction of oils from Antarctic krill and found that the oils were composed solely of nonpolar lipids, mainly triglycerides which were relatively rich in eicosapentaenoic acid (EPA) and free of phospholipids.

Turpin et al. (1990) obtained triglycerides which were free of free fatty acid, mono- and diglycerides, iron, triterpene acetates, triterpene cinnamates and polysoprenoid gum from crude shea nut oil by SC-CO₂ extraction at temperatures of 40°C-80°C.

The process produced triglycerides which were more stable to oxidation than the crude oil, and were partially fractionated according to their carbon numbers. Zhao et al. (1987) applied SC-CO₂ to the extraction of rice bran oil at pressures of 150kg/cm² to 350kg/cm² at 40°C and found that the SC-CO₂ extracted oil was of a lighter colour than that of hexane-extracted oil and that it had a very low content of iron and phosphorus. They also reported that the fractions obtained at higher pressures contained less free fatty acid and waxes.

The effect of pressure and temperature on the rate of extraction of triglycerides from plant tissue by SC-CO₂ was studied by Brannolte et al. (1983). Recently, Cygnarowicz-Provost et al. (1992) extracted lipids from a filamentous fungi (S. parasitica) using SC-CO₂ and CO₂ mixed with 10 wt% ethanol at temperatures from 40°C to 60°C and pressures from 205 to 680 bar. It was found that the recovery of lipids increased with increasing pressure, and higher recoveries were obtained when a mixture of CO₂ with ethanol was used as the solvent.

Lee et al. (1986) carried out experiments to obtain equilibrium data and extraction rates at 55°C and 36MPa using solvent velocities ranging from 0.04 to 2.8mm/s in a system for the SC-CO₂ extraction of oil from fixed beds of crushed canola seeds. A one-dimensional, unsteady state mathematical model was used to obtain the oil concentration profiles in both the solvent and solid phases, and to determine the overall volumetric mass transfer coefficients, and it was found that the calculated concentrations and extraction rates were in good agreement with experimental results.

In the field of refining of oils and fats and
related activities, SC-CO₂ extraction has been found to be a suitable technique for the deacidi-
fication of olive oil (Brunetti et al., 1989) and palm oil (Peter, 1984). Recently, Waldmann and Eggers (1991) applied SC-CO₂ to the ex-
traction of oil from spent bleaching earth and showed that oil of good quality could be re-
covered, and that the bleaching earth still had an activity about 50% of that of fresh earth. SCFE has also been applied to the extraction of polychlorinated biphenyls from fish oils (Krukonis, 1989). Decholesterolization of but-
ter oil has been shown to be possible by an SC-
CO₂ extraction followed by the passage of the extract through a silicic column (Shishikura et al., 1986).

Nutritional interest in tocopherols has at-
tracted researchers to investigate the tech-
nical feasibility of extracting this product from natural sources by SCFE technology (Lee et al., 1991; Brunner et al., 1991). Shishikura et al. (1988) succeeded in obtaining a concentra-
tion of more than 64% tocopherols from soyabean sludge. The application of an SC-
CO₂ technique to the extraction of alpha-toco-
pherol from palm leaflets has been demon-
strated. At 40°C and 200 kg/cm² pressure, and using a dry sample, the results showed that the concentration of alpha-tocopherol in the extract could be >9% and the yield >90% (Ab Gapor Md Top et al., 1990).

Eicosapentaenoic (EPA) and docosahexaenoic acid (DHA) are important nutritionally; in order to obtain these compounds with a purity of more than 90%, Nilsson et al. (1988) subjected menhaden oil fatty acid ethyl esters to urea fractionation followed by fractionation of the esters according to carbon number using SC-CO₂. In another re-
port, they demonstrated that incremental pressure programming was an effective tech-
nique for increasing the yield of 90% pure all cis-5,8,11,14,17-ethyl eicosapentanoate (EPA) in the fractionation of urea-crystallized fish oil

ethyl esters using SC-CO₂ (Nilsson et al., 1989).

In a study of the fractionation of fatty acids by extractive crystallization using SC-
CO₂, Arai and Saito (1986) found that the separation of C18 fatty acids on the basis of their degree of unsaturation seems possible. Brunner and Peter (1982) reported that stearic monoglyceride could be successfully separated from stearic diglyceride and stearic triglyceride. SC-CO₂ was also found by Nilsson et al. (1991) to be a good medium for the removal of mono- and diacylglycerol by-prod-
ucts from synthetic triglyceride reaction mixture at moderate temperatures.

The use of SC-CO₂ as a medium for the lipase-catalysed interesterification of triolein and stearic acid was studied by Nakamura et al. (1986). Nippon Oil and Fats Co. Ltd. of Japan has been granted a patent for the manufacture of EPA- or DHA- enriched fats and oils using lipase in SC-CO₂ (Latta, 1990).

**SOME CONSIDERATIONS IN THE DESIGN OF SCFE PLANT**

SCFE is a high-pressure separation process and hence the design of the equipment draws heavily on the existing techniques of high pressure technology and the experience in this field. The first task in process development is to select the most suitable solvent for the particular separation process in the laboratory or pilot plant; this is followed by optimization of the process parameters (including solvent to feed ratio, temperature and pressure) with due emphasis on minimizing the energy requirement. The results will serve as the basis for designing the industrial plant (Coenen et al., 1985).

Eggers and Tschiersch (1979) reviewed the criteria underlying the design of plants for the recovery of carrier material or extract including the parameters to be determined in
the planning of a large-scale plant. Plant components and equipment are described together with particular processes and construction materials. Marentis and Vance (1989) gave an overview of the general and specific criteria for the selection of equipment and components for SCF food processing plants.

ISSUES RELATED TO COMMERCIALIZATION

A decisive part of development work is economic optimization, and several process parameters have to be considered in this connection (Beutler et al., 1988). In addition to the high capital cost of high pressure equipment, the major economic drawback to the use of SCFE in the recovery of natural products is the generally low solubility of many biochemicals in supercritical solvents, necessitating the use of large solvent:feed ratios. In order to design and scale-up SCFE processes effectively, fundamental physical properties such as mixture viscosities need to be known but such data are limited or unavailable in the literature (Kashulines et al., 1991).

Marentis (1988) has summarized the steps towards developing the commercialization of an SC-CO₂ processed food product under five areas of activities. These are 1) application of high pressure CO₂ phase equilibria and fluid dynamics theory; 2) knowledge of the structure and chemistry of the substances of interest; 3) performance of the process design protocol; 4) preliminary process design and economic evaluation; and 5) design, construction and start-up of the commercial-scale plant.

Process economics are a very important factor in assessing the feasibility of applying SCFE on a commercial basis. Ramachandran et al. (1992) developed a dynamic SCFE process simulator and found it to be ideally suited for studies on control and process optimization. Cygnarowicz and Seider (1989, 1990) studied the economic aspects of the design of the SCFE process using steady state simulations and have demonstrated that SCFE can be competitive for the recovery of high-value products like beta-carotene.

CURRENT INDUSTRIAL APPLICATIONS OF SCFE TECHNOLOGY

Even though the technology has been available for some time, its commercialization seems to be relatively limited. This may be due partly to the high capital cost of installing SCFE plant and partly to lack of technical information such as equilibrium data. Currently, several commercial SCFE plants are known to be operating successfully in industrial countries and new ones are being constructed.

The first SCFE plant was opened in 1981 by HAG (General Foods) in Bremen, Germany for the decaffeination of coffee by SC-CO₂. A second plant followed in 1988 in Houston, USA. A plant for the decaffeination of black tea was installed in 1988 by SKW of Germany (Voeste et al., 1988).

Plants for the production of hop extract are operated by Barth, Wolnzach, and SKW in Germany (Voeste et al., 1988). Pfizer has a hops SCFE facility in Nebraska, USA and SKW Chemicals, Inc in Marietta, Georgia, USA uses supercritical fluids to extract hops, essential oils and spices (Latta, 1990). It has recently been reported that John I. Hass, Inc. at Yakima, Washington has just completed the installation of an SC-CO₂ plant for producing hop extract and other food products (Pitt-Des Moines, Inc., 1992). Hop extract is also produced with liquid carbon dioxide in a virtually critical state in England and Australia (Voeste, 1988).
In view of the growing concern about environmental and health issues, SCFE technology provides a potential alternative to conventional extraction processes; it is expected that this technology will play an important role and that more commercial plants will be set up in the future, including some for the production of specialty or value-added products from oils and fats.

**POTENTIAL APPLICATIONS OF SCFE TECHNOLOGY IN PALM OIL INDUSTRY**

It is recognized that at present SCFE belongs in the high-value or high profit margin sector, and accordingly R&D activities in this area should be directed towards the processing of value-added products for a specific market (e.g. health-foods, cosmetics) or development of new processes which are techno-economically competitive with the traditional methods. It is thought that SCFE technology has a wide range of potential applications in the palm oil industry. Some of the projects which might be worth pursuing, at least at the R&D levels are:

- extraction of palm oil for health-food applications
- separation of monoglycerides, diglycerides and triglycerides.
- extraction of oleic acid
- deacidification and deodorization processes for palm oil
- concentration and purification of palm minor components e.g. carotenes and vitamin E
- supercritical fluid as a medium in processes for the modification of palm oil.

It is to be noted that some of these projects are currently being carried out in PORIM.

**CONCLUSION**

The ability of supercritical fluids to act as solvents is the basis of SCFE technology. Most of the substances used or considered for use as supercritical fluids are cheap and environment-friendly. Applications of SC-CO$_2$ for the extraction or separation of edible oils and fats or their components in the laboratory or pilot plant have been reported. SCFE technology is capital-intensive, and is therefore only useful for the extraction or processing of high value products. In the oils and fats industry, examples are jojoba oil, evening primrose oil and carotenoids. For commercialization, it is certainly necessary to consider the techno-economic feasibility of the project. In view of the fact that awareness regarding the environment and health is growing, it might be worthwhile exploring the potential of this technology.

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