Food Chemistry 45 (1992) 189–192

Supercritical fluid extraction of vegetable and animal fats with CO_2—A mini review

M. T. G. Hierro & G. Santa-María

Instituto de Fermentaciones Industriales (CSIC), Juan de la Cierva 3, E-28006 Madrid, Spain

(Received 5 November 1990; revised version received 7 January 1992; accepted 16 January 1992)

The application of supercritical fluid extraction techniques in vegetable and animal fats is reviewed.

Most of the published work has dealt with applications of supercritical CO_2 to extract vegetable oils. In general, the efficiency of the extraction increases with pressure as well as with temperature, provided the pressure is higher than 345 bar. The use of entrainers to enhance the extraction of lipids was also taken into account.

Since the glycerides containing polyunsaturated fatty acids have important pharmacological applications, some procedures have been developed for extraction of these compounds from animal fats.

Considerable work has been carried out on the extraction of cholesterol from fat. Fractionation of milk fat yields fractions with short- and medium-chain fatty acids enriched in cholesterol and fractions with medium- and long-chain fatty acids low in cholesterol.

INTRODUCTION

Supercritical fluid extraction (SFE) is a newly developed technique that studies the solvent properties of a fluid near its critical point.

Supercritical fluids have physicochemical properties intermediate between those of liquids and gases (Rizvi *et al.*, 1986). These properties, chiefly density, can be altered by varying the pressure and temperature. Thus, a certain selectivity for a specific compound can be conferred upon the solvent. The separation of the substances dissolved in the supercritical fluid can be carried out in three ways: depressurization at constant pressure, heating at constant pressure, or adsorption on an appropriate adsorbing agent at constant pressure and temperature (Hubert, 1989).

The solvent most often used is carbon dioxide, which possesses a number of properties that make it ideal for such applications: it is non-explosive, inexpensive, readily obtainable and plentiful in nature, non-toxic, and easily separated from the substances extracted. These last two characteristics are extremely important for applications of this technology in the food processing industry.

CO_2 exhibits a polarity classifiable in between that of dichloromethane and that of ethyl ether (Hubert, 1989). Consequently, non-polar compounds like fats, oils and aroma components, such as terpenes, dissolve quite readily. Other compounds displaying a certain degree of solubility are low molecular weight compounds with average polarity, such as caffeine, nicotine, cholesterol and alcohols.

VEGETABLE OILS

The food processing industry is one of the sectors in which the most important applications have been developed. These include extraction of the constituents of resins and spices (Hubert & Vitzthum, 1978).

Most of the work published on supercritical fluid extraction in the food processing industry has dealt with applications to extract vegetable oils (Hubert & Vitzthum, 1978; Stahl *et al.*, 1980; Bulley *et al.*, 1984; Christianson *et al.*, 1984; List *et al.*, 1984*a*,*b*; Taniguchi *et al.*, 1985; Lee *et al.*, 1986; Dakovič *et al.*, 1989).

Friedrich *et al.* (1982) and Zhao *et al.* (1987) reported that soybean and rice bran oils, obtained using supercritical CO_2, afforded a series of advantages over oils obtained using organic solvents such as hexane. Thus, the iron and phosphorus contents were lower, mainly because of the low solubility of the phospholipids compared to that of the triglycerides in supercritical CO_2. In addition, the oil was lighter in colour, thereby reducing the need for refining. This was due also to the low solubility of carotenes and other pigments in supercritical CO_2.

Food Chemistry 0308-8146/92/$05.00

In general, the solubility of vegetable oils varies considerably with temperature and pressure. The efficiency of the extraction increases as the pressure increases, basically in the range of 345–550 bar (Christianson *et al.*, 1984). The solubility increases as temperature increases, provided the pressure is higher than 345 bar; conversely, this effect does not take place at pressures lower than 345 bar (Friedrich & Pryde, 1984). This behaviour is probably related to the density of the supercritical CO_2. CO_2 is highly compressible between the critical pressure and approximately 414 bar, which makes its density highly changeable; above 414 bar the change is not so rapid, and therefore the increase in solubility with increasing temperature is observed in this range.

ANIMAL FATS

Few papers in the literature describe the extraction of animal fat or its components with supercritical CO_2.

Studies have mainly focussed on extractions using fish and eggs (Ikushima *et al.*, 1985; Yamaguchi *et al.*, 1986; Hardardottir & Kinsella, 1988; Froning *et al.*, 1990). The interest in these foods is in part due to the fact that certain types of fish contain substantial quantities of glycerides with polyunsaturated fatty acids, which have important pharmacological applications (Hirai *et al.*, 1980). It is also due partly to the fact that the egg production industry is suffering from a serious slump in consumption because of the high cholesterol content in eggs.

Hardardottir & Kinsella (1988) extracted the lipids from fish muscle with supercritical CO_2. They worked with pressures ranging between 140 and 345 bar and reported that extraction efficiency was not enhanced by varying the pressure within that range and was similar in all cases. However, they indicated that increasing the temperature (40–50°C) brought about a slight increase in the solubility of the lipids in the supercritical CO_2.

This behaviour agreed with the results for the extraction of vegetable oils obtained by Friedrich & Pryde (1984). Working at pressures below 414 bar, they found that the expected increase in solubility with increasing temperature was masked by the variation in solvent density, since the gas is highly compressible at these pressures.

Thus, the effect of temperature variations on the solubility of the different components making up the lipid fraction at pressures higher than 414 bar still requires study.

On the other hand, the use of entrainers such as ethanol considerably enhances the solubility of the lipids in supercritical CO_2. Thus, 78% of the lipids was extracted with supercritical CO_2 at 275 bar and 40°C, while 97% of the lipids was extracted when 10% ethanol was added (Hardardottir & Kinsella, 1988).

The effect of adding entrainers to the supercritical CO_2 was studied in depth by Ikushima *et al.* (1985) for admixtures of simple triglycerides, using ethanol, acetone, ether, dichloroethylene and ethyl acetate as entrainers. These authors concluded that only dichloroethylene substantially enhanced the extraction of the triglycerides.

Extraction using supercritical CO_2 has been put forward as a method of producing foods that are low in cholesterol. Froning *et al.* (1990) showed that attempts to extract the total lipids from egg yolk brought about a considerable decrease in the total lipids and that cholesterol was the lipid that underwent the greatest reduction, chiefly under conditions of high pressure and temperature.

Another feature reported for lipid extractions has been the low solubility of phospholipids in supercritical CO_2. In this regard, Yamaguchi *et al.* (1986) extracted the oil from Antarctic krill using supercritical CO_2. Krill oil has an extremely high phospholipid content, and for that reason it is not widely used, since it deteriorates rapidly. Application of extraction using supercritical CO_2 to krill yielded an oil composed almost exclusively of non-polar lipids, devoid of contamination by phospholipids.

MILK FAT

Recently there has been considerable interest in the treatment of milk fat. The reason for this is not only to try to achieve new products low in cholesterol or in saturated fats but also to obtain other products, such as butter, that are more frigo-spreadable without being subject to flavour losses (Shishikura *et al.*, 1986).

The treatment processes employed include:

(a) hydrogenation,
(b) interesterification,
(c) mixtures with other acids and fats,
(d) enzymic treatment, and
(e) fractionation.

This last method affords a major advantage in that, since milk fat is essentially a mixture of different triglycerides with differing physical properties, it is technically possible to divide the milk fat into fractions with distinct chemical compositions and different melting points. Fractionation has been carried out by a variety of methods: crystallization, distillation and extraction with supercritical CO_2.

Arul *et al.* (1987) studied the fractionation of milk fat by means of supercritical fluid extraction using CO_2. Extraction of the triglycerides with supercritical CO_2 was carried out at temperatures of 50–70°C over a range of pressures between 100 and 350 bar and yielded eight fractions. The first two fractions were liquids, the next three were intermediate in consistency, and the

Table 1. Supercritical conditions applied in the treatment of the milk fat

Reference	Food	Pressure (bar)	Temperature (°C)
Shishikura *et al.* (1986)	Butter	150–350	40–60
Kankare *et al.* (1989)	Milk fat	100–400	50
Arul *et al.* (1987)	Milk fat	100–350	50–70
Bradley (1989)	Milk fat	160–414	80

last three were solids. The first fractions were mainly made up of triglycerides with short- and medium-chain fatty acids, the percentage of which decreased in the fractions as their melting point increased. For the triglycerides with long-chain fatty acids, the converse was true. These same profiles were recorded for the free fatty acids.

The above trends in the composition of the fractions were similar to those observed in the fractions obtained by distillation and crystallization (Arul *et al.*, 1988).

Also, in a study of the distribution of cholesterol in each of the fractions, Arul *et al.* (1988) found that the liquid fractions were enriched in cholesterol, which decreased as the melting point of the fractions rose. Similar results were reported by Kaufmann *et al.* (1982), who, working at a pressure of 200 bar and a temperature of 80°C, obtained only two fat fractions, and by Kankare *et al.* (1989) for the range of pressures between 100 and 400 bar.

According to these results, low cholesterol milk fat could then be produced by recombining these triglyceride-rich fractions while discarding the cholesterol-rich fractions (Bradley, 1989).

All the published work dealing with milk fat has examined the influence of pressure and temperature on the efficiency of the extraction, but in no case has the use of organic entrainers such as those employed for vegetable oils been considered. Studies of the influence of entrainers on extraction efficiency are therefore called for.

On the other hand, the absence of investigations into the use of organic entrainers with supercritical CO_2 for milk fat is not surprising, since CO_2, as a solvent that is only slightly polar, extracts non-polar or only slightly polar compounds best. Organic entrainers are usually added to increase solvent polarity, thereby facilitating the extraction of polar compounds. This does not appear to be particularly necessary when working with milk fat, in which most of the components are non-polar.

The supercritical conditions applied in the treatment of the milk fat are summarized in Table 1. Pressures have ranged between 100 and 414 bar, temperatures between 40 and 80°C.

However, papers examining alterations in the solubility of the different components of milk fat in supercritical CO_2, with variations in pressure at constant temperature or with variations in temperature at constant pressure, are lacking. Procedures employed to separate the milk fat extract from the supercritical fluid have been based on depressurization at constant temperature or on heating at constant pressure. No papers considering the application of adsorbents have been discovered.

SAMPLE PREPARATION

In many cases, suitable preparation helps to enhance the efficiency of the extraction.

Most of the preparation required for extracting vegetable oils has consisted simply of crushing/comminuting the raw materials (Zhao *et al.*, 1987) or of reducing them to flakes measuring 0·038–0·051 cm in thickness (Friedrich *et al.*, 1982). It seems reasonable to suppose that the rate of oil extracted will be greater at smaller particle sizes, where the amount of surface area that comes in contact with the supercritical gas rises. On the other hand, Taniguchi *et al.* (1985) achieved a satisfactory extraction of wheat germ oil without any preparation at all.

Similarly, no laborious sample preparation is required in the case of milk fat. Sometimes extraction has been performed using protein residues obtained by centrifugation of milk fat melted at 55°C for 20 min (Arul *et al.*, 1988). Starting with butter fat, Shishikura *et al.* (1986) carried out successive extractions of the melted butter with *n*-hexane, dehydrated the extract, and subsequently evaporated the residue at low pressure.

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