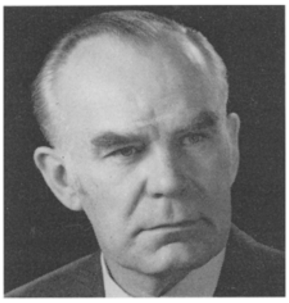
# Liquefied Gases and Supercritical Fluids in Oilseed Extraction



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## ABSTRACT

Soybean oil and numerous other vegetable oils can be extracted from crushed seeds by means of liquefied gases or supercritical fluids. The oils are recovered by lowering the pressure or increasing the temperature, or both. Supercritical carbon dioxide is ideally suited for the food industry as it is nontoxic and nonflammable. Moreover, it can be removed easily from the oil as well as the meal. The oils extracted with supercritical carbon dioxide contain much lower proportions of phospholipids than those obtained by conventional processing with hexane. The addition of acetone or another carrier or entrainer aids in the fractional extraction of lipids differing in polarity. The range of applicability of liquefied gases and supercritical fluids in the extraction and fractionation of lipids should be explored further to develop industrial processes using these solvents.


Much work on the use of liquefied gases and supercritical fluids is being done in industrial research laboratories. Thus, I can only hope that some of these colleagues will contribute to the dissemination of knowledge in the discussion following my presentation.

Carbon dioxide certainly is the most important compound used for the extraction of natural products – either as a liquid or as a supercritical fluid. The boiling point of carbon dioxide at 1 bar is -78.5 C, its critical pressure is 72.9 bar and its critical temperature is +31.3 C.

Above the critical point, CP, carbon dioxide occurs as a supercritical fluid. Although some properties of supercritical fluids have been described more than 100 years ago by Hannay and Hogarth, and although supercritical carbon dioxide has been used by Giddings for the fractionation of numerous lipophilic compounds, already in the 1960s, interest in fluid extraction has gained new impetus when Zosel as well as Vitzthum and Hubert applied for patents on the use of supercritical gases for the decaffeination of coffee beans and the extraction of hops and tobacco.

Besides carbon dioxide, nitrous oxide, and some organic compounds such as ethane, propane, and butane as well as halogenated hydrocarbons, such as chlorotrifluoromethane, have been employed as supercritical fluids for the extraction of natural products. Table I lists the boiling points as well as the critical pressures and critical temperatures of these substances.

The principle of the experimental design used in extracting natural products with liquefied gases and supercritical fluids is rather simple. As shown in Figure 1, a gas, such as

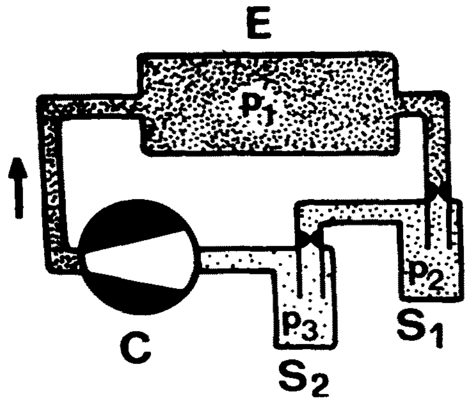


FIG. 1. Principle of the experimental design employed in extracting seed oils with liquid and supercritical carbon dioxide.

carbon dioxide, is condensed in a diaphragm compressor, C, to a pressure of 350 bar, p1; even higher pressures can be obtained by using a second compressor. The liquid or supercritical carbon dioxide flows through an extraction vessel, E, containing crushed seeds. The extracted oil is recovered from its solution by lowering the pressure in two stages, in a first trap, S1, to ~ 200 bar, p2, and in a second trap, S2, to 30-65 bar, p3, that is, below the critical pressure of carbon dioxide. The gas released is again condensed in the compressor, C, thus completing the cycle. Alternatively, the oil may be recovered by raising the temperature at constant pressure. And, of course, it is possible also to isolate the oil by decreasing the pressure and increasing the temperature simultaneously (Table II).

Several investigators have constructed equipment for work with dense gases. Recently, an apparatus for use on a laboratory scale has become commercially available from Nova Werke, Effretikon, Switzerland. This piece of equipment is suitable for extraction on a kilogram scale. I understand that it is being used in more than 50 laboratories.

Companies that offer pilot plants of various capacities include Nova Werke, the HDA company in Konstanz, Germany, as well as Krupp and Extraktionstechnik, both in

TABLE I

Physical Constants of Some Inorganic Compounds Used as Supercritical Fluids

| Compound | Boiling point BP (C) | Critical temperature $T_c$ (C) | Critical pressure $P_c$ (atm) |
|---|---|---|---|
| Carbon dioxide | -78.5 | 31.3 | 72.9 |
| Ammonia | -33.4 | 132.3 | 111.3 |
| Nitrous oxide | -89 | 36.5 | 71.5 |
| Water | 100 | 374.4 | 226.8 |

**TABLE II**

**Extraction and Stepwise Recovery of Seed Oils**

| Extraction pressure (bar) | Temp. (C) | First fraction Pressure (bar) | Temp. (C) | Yield (%) | Second fraction yield (%) | Total yield of oil (%) |
|---|---|---|---|---|---|---|
| | | Decrease in pressure (rapeseed) | | | | |
| 300 | 50 | 180 | 50 | 28.4 | 4.4 | 32.8 |
| | | Increase in temperature (sunflower seed) | | | | |
| 300 | 40 | 300 | 75 | 34.5 | 11.7 | 46.2 |
| | | Decrease in pressure and increase in temperature (sunflower seed) | | | | |
| 300 | 40 | 200 | 60 | 36.7 | 8.8 | 45.5 |

Hamburg, Germany.

As far as I know, the use of dense carbon dioxide on an industrial scale is still limited to the decaffeination of coffee beans (HAG company in Bremen) and, more recently, the processing of hops (HEG company in Münchsmünster).

We have studied the extraction of soybeans, sunflower seed, and rapeseed in cooperation with Egon Stahl, Saarbrücken. In order to assess the solubility of seed oils in carbon dioxide, ground soybeans were treated at pressures of 300-700 bar and at a temperature of 40 C. The yield of oil extracted from ground soybeans depends on the size and shape of the meal particles. Friedrich and his colleagues at the USDA Laboratories in Peoria, IL, have found soybean flakes particularly easy to extract with supercritical carbon dioxide.

The solubility of soybean oil in liquid, that is below 31.3 C, and in supercritical carbon dioxide, that is above 31.3 C, increases with pressure, though at different rates. Figure 2 shows that at pressures below 250 bar, the concentration of oil is higher in liquid carbon dioxide, whereas above 250 bar its concentration is higher in supercritical carbon dioxide.

Obviously, the effect of pressure on the solubility of a seed oil is much more pronounced when supercritical carbon dioxide is used for its extraction. The concentration of oil in the supercritical fluid is a decisive factor in the amount of carbon dioxide needed for the extraction of oil from a certain amount of seeds. As an example, we extracted 100 g sunflower seeds at pressures of 660-700 and 250-280 bar, respectively, and at a temperature of 40 C.

At a pressure of 660-700 bar and a temperature of 40 C, the extraction of 40 g of oil requires ~ 1.1 $Nm^3$ of carbon dioxide, whereas at 250-280 bar and 40 C the extraction of 40 g of oil requires more than four times this amount of carbon dioxide (Incidentally, 1 $Nm^3$, at 293 K, 1 bar, corresponds to ~ 1.8 kg of carbon dioxide). At the higher pressure, the concentration of oil in carbon dioxide decreases rapidly after ~ 0.7 $Nm^3$ have passed through the bed of ground seeds, whereas at the lower pressure the concentration of oil in carbon dioxide remains fairly constant until ~ 1.5 $Nm^3$ have been used. Thus, an increase in pressure to over 300 bar can obviously be of advantage.

When seeds are extracted with supercritical carbon dioxide at 200 bar, the yield diminishes with increasing temperature. At pressures of 300 bar and higher, however, a dramatic increase in yield can be achieved by raising the temperature. Thus, the efficiency of extraction can be improved not only by high pressure but also by high temperature.

The extraction of soybeans has been studied most extensively, but the lipids of lupins, and of seeds containing triacylglycerols of epoxy and hydroxy fatty acids have been investigated as well. It has been found that only traces of phospholipids and glycolipids are extracted when seeds are treated with supercritical carbon dioxide. Thus, the oils obtained are virtually free of lecithins and other polar lipids. For this reason, it appears that they need not be degummed.

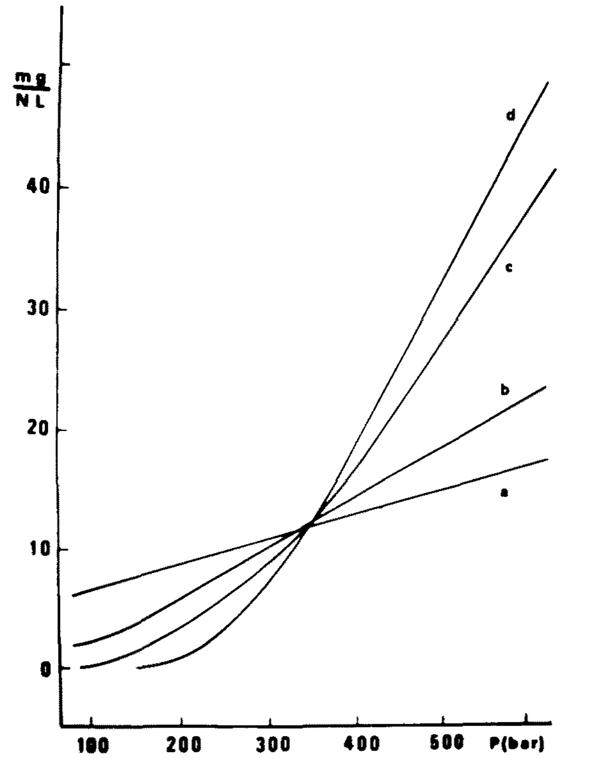


FIG. 2. Solubility of soybean oil in carbon dioxide. (a) 10 C (liquid); (b) 25 C (liquid); (c) 40 C (supercritical); (d) 80 C (supercritical).

The treatment of soybeans with supercritical carbon dioxide at 300 bar and 40 C does not alter the composition or the general properties of their protein.

I should mention that lipids less polar than triacylglycerols, such as wax esters of jojoba seeds, can be recovered in excellent yields from the ground seeds or press cakes by means of supercritical carbon dioxide. Rather polar lipids that are not completely extracted can be obtained by adding small proportions of chloroform, isopropanol, ethanol or methanol to the dense carbon dioxide.

Supercritical carbon dioxide as well as supercritical ethane and propane can be used for the deodorization of fats and oils on an industrial scale.

There is still considerable doubt whether the use of supercritical fluids will be competitive with traditional methods of processing oilseeds. Yet, if the price of hexane should increase further and if large-scale equipment could become available at reasonable cost, the deodorization of oils, and eventually the extraction of oilseeds with supercritical carbon dioxide may become competitive with steam deodorization and hexane extraction, respectively.

Of great interest is the fractionation of complex lipid mixtures with liquefied gases and supercritical fluids. It has been shown recently that butter fat can be fractionated using supercritical carbon dioxide. This process yields a fraction that contains twice as much triacylglycerols of short-chain fatty acids as the starting material. Even more promising appears a process for the removal of oil from crude lecithin by using supercritical carbon dioxide or some other supercritical fluids.