Extraction with Supercritical Fluids: A Progress Report from Germany

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ABSTRACT

This review of research in Germany on the use of supercritical fluids for extraction and fractionation covers work on vegetable fats and oils, butterfat, and other lipids. The future commercialization may depend on the cost of alternative procedures and the cost of equipment for large-scale processes involving supercritical fluids.

It is known for over a quarter of a century that numerous natural products can be extracted with liquified gases and supercritical fluids (1,2). The results of some studies on the extraction of lipids with such solvents have been reviewed (3,4).

The various parameters influencing the extraction can be investigated on a laboratory scale using an apparatus developed by Stahl and Schülz (5). A similar piece of equipment is commercially available (Nova Werke AG, CH-8307 Effretikon, Switzerland). Pilot plants of various capacities are being offered by the latter company as well as several others (HDA Hochdruckextraktion Anlagenbau GmbH, D-6000 Frankfurt 70, Germany; Extraktionstechnik Gesellschaft für Anlagenbau mbH, D-2000 Hamburg 76, Germany; Friedr. Krupp GmbH, Krupp Industrie- und Stahlbau, Werk Harburg, D-2100 Hamburg 90, Germany).

Carbon dioxide has been studied most extensively; it has a critical temperature of 31.2 C and a critical pressure of 73.8 bar. This inorganic compound appears to be the ideal solvent for the food industry because it is neither toxic nor inflammable.

Systematic studies on the extraction of oil from soybean, sunflower seed, rapeseed, and lupinseed with liquid, as well as supercritical carbon dioxide, have been done using the aforementioned apparatus (6,7). It has been found that the solubility of oil at a pressure of about 300 bar is almost equal in liquid (<31.2 C) and supercritical (>31.2 C) carbon dioxide. A much more efficient extraction is achieved, however, with supercritical carbon dioxide above 600 bar and 40 C (6). Besides pressure and temperature, particle size and shape of the seed meal plays a significant role in extraction (6). The oils are obtained in yields ranging from 95 to 98.5%; they are virtually free of phospholipids and glycolipids, whereas those obtained with hexane contain between 1 and 3% of these polar lipids (7). The fatty acid compositions of oils extracted with supercritical carbon dioxide are almost identical to those extracted with hexane (6,7). The fractionation of oils by a stepwise reduction of the pressure or an increase in temperature, or both, has been described (6).

The content and composition of alkaloids in lupin oil extracted with either supercritical carbon dioxide or hexane are similar; the water content of the ground seeds does not influence the extent of extraction of the alkaloids (7).

A recent patent application describes a process for the removal of oil from "crude lecithin" by using supercritical carbon dioxide, as well as several other supercritical fluids (8).

The treatment of various oilseeds with supercritical carbon dioxide at 300 bar and 40 C does not alter the composition or the general properties of their proteins (9). To assess the influence of carbon dioxide on enzymes, the composition, structure and properties of ribonuclease were studied before and after exposure to supercritical carbon dioxide. It was found that polymerization occurred under some conditions together with a small increase in the rate of digestion by trypsin (10).

Supercritical carbon dioxide, as well as supercritical ethane or propane, can be used for the deodorization of crude fats and oils (11).

Of particular interest is the fractionation of lipid mixtures with liquified gases and supercritical fluids. A process for the fractionation of butter fat using supercritical carbon dioxide yields a mixture which contains twice as much triacylglycerols of short-chain fatty acids as the starting material (12).

The extraction of acylglycerols and diacylglycerols can be enhanced by the addition of a carrier or entrainer, such as acetone, to the supercritical fluid (3,4). The effects of organic solvents and solvent mixtures on the extraction and fractionation of less common and unusual lipids has been studied (13).

The solubility of minor constituents of natural fats and oils in supercritical gases is certainly of interest. Therefore, the solubility of a great number of sterols in supercritical carbon dioxide has been determined (14). Moreover, the extraction and fractionation of essential oils has been investigated (15).

In the author's opinion, the range of applicability of liquified gases and supercritical fluids in the extraction and fractionation of lipids needs to be explored further before industrial processes using these solvents can be evolved. In Germany, the use of "dense gases" on an industrial scale is still limited to the decaffeination of coffee beans (2) (HAG A.G., Bremen); the processing of hops (2) will be realized in the near future (HEG Hopfenextraktion GmbH, Münchsmünster).

The extraction and fractionation of fats and other lipids is being studied at the Universities of Erlangen-Nürnberg (G. Brunner and S. Peter) and Saarbrücken (E. Stahl), as well as the Federal Dairy Research Center, Kiel (W. Kaufmann) and the Federal Center for Lipid Research, Münster (H.K. Mangold in cooperation with E. Stahl, Saarbrücken). Industrial research and development work is being carried out by HAG A.G., Bremen (P. Hubert and O.G. Vitzthum), Kali-Chemie Pharma GmbH, Hannover (W. Heigel and R. Hüschens), Fried. Krupp GmbH, Essen (H. Coenen and E. Kriegel), Thyssen Industrie A.G., Witten (R. Eggers), and Unilever Research, Hamburg (G. Biernoth and W. Merk).

The properties of supercritical gases and various theoretical aspects are being investigated at the Universities of Bochum (G.M. Schneider) and Karlsruhe (E.U. Franck).

There is still some doubt whether the use of supercritical fluids will be competitive with traditional methods of processing oilseeds and oils. In the near future, the use of supercritical carbon dioxide and other dense gases will probably be limited to a few special applications, such as the deoiling of crude lecithin and the fractionation of butter fat. Yet, if the price of hexane should increase dramatically and if large-scale equipment should 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.

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Biorenewable Solvents for Vegetable Oil Extraction[1]

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ABSTRACT

A review of the literature pertaining to possible alternatives for hexane as solvent in the extraction of vegetable oils was made. The review was restricted to solvents obtainable from renewable resources and included the most recent technological advances in oil extraction processes. The most promising systems surveyed were based on the use of water, alcohols, ketones, halocarbons, or of liquified and supercritical gases as solvents for oils.

INTRODUCTION

Over 14 billion lb of edible vegetable oils (soybean, cottonseed and sunflower) was produced in 1979 in the U.S. mostly by direct solvent or prepress-solvent extraction methods (1). The major portion (86%) of this oil was produced from soybeans with hexane as the extraction solvent. With a crush of over 1 billion bushels of soybeans in 1979 and a conservative estimated solvent loss of 0.15% of the total soybeans processed (2), ca. 16 million gal of hexane was lost. A report (3) in the spring of 1980 confirmed the fact that hexane was in short supply and demonstrated to edible oil producers that an alternative solvent, less dependent on petroleum for its source, was needed. Additionally, with the price of hexane approaching $1.70/gal and both federal and state authorities enforcing emission standards, solvents and/or extraction systems once considered uneconomical have begun to attract renewed interest. McGee (4), in 1947, and Price (5), in 1965, reviewed a list of potential vegetable oil extraction solvents; now it is timely to update their work and to concentrate on the potential of renewable solvents or extraction systems currently available to processors.

This is a review of potential biorenewable solvents, the basic processes for each, and the advantages and disadvantages of the proposed solvents compared to the present hexane system.

Water

Water, known as the universal solvent, is immiscible with vegetable oil and therefore is a poor solvent for the oil. Nevertheless, many researchers have used water systems in the extraction of oil and protein from soybeans, cottonseed, peanuts, sunflowers and coconuts (6-14). The aqueous process, as shown in the flow diagram (Fig. 1) consisted basically of the following steps—grinding, mixing, and extracting with water-containing additives, solid-liquid and liquid-liquid separations, and drying. The mechanics of oil extraction with aqueous solutions are unique in that it is critical to all the processes that a majority of oil cells in the raw material be ruptured during the grinding step. This is necessary to free the oil globules and to allow them to emulsify with water, under agitation, and thus be "extracted." Insufficient grinding results in low oil recoveries and corresponding high residual oils in meal or protein fractions. Excessive grinding yields "mayonnaise-like" emulsions that are difficult to break and call for specialized

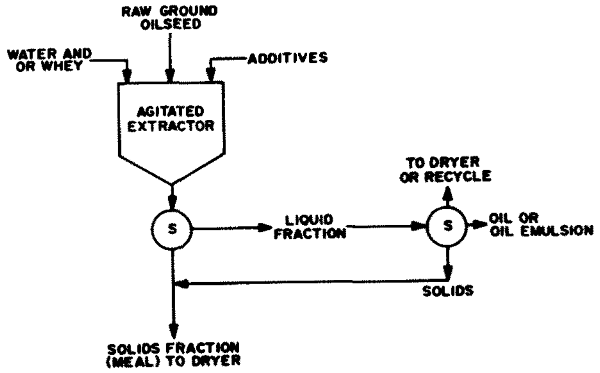

FIG. 1. Simplified flow diagram for aqueous extraction of vegetable oil.

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[1] Presented at the 31st Oilseed Processing Clinic March 1982, New Orleans, LA.