FE 483-Food Operations Laboratory
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SUPERCRITICAL CO_2 EXTRACTION SYSTEM
MILK FAT FRACTIONATION

Introduction

Many technologies have been developed for the separation and fractionation of different food compounds in the food industry. Conventional processes such as crystallization, filtration, distillation or precipitation are being substituted by new processes that use membranes or supercritical fluids. Supercritical fluid extraction (SFE) is a separation process where the substances are dissolved in a fluid which is able to modify its dissolving power under specific conditions above their critical temperature and pressure (supercritical region). The properties of a supercritical fluid are used to extract selectively a specific compound or to fractionate mixtures by changing the temperature and pressure without any phase change. A supercritical fluid is a liquid or a gas at atmospheric conditions which is operational when compressed above its critical pressure (50–250 bar) and heated above its critical temperature (20–60^{o}C). The most important property of these fluids is the dissolving power in their supercritical region.

In the phase diagram for a pure compound, it is possible to distinguish the three material states: solid, liquid and vapor. There are also two important points: the triple point and the critical point. The triple point is the point at which the three states coexist. The critical point lies at the end of vaporization curve, where the gas and liquid phase merge to form a single homogeneous fluid phase, and beyond this point is the supercritical fluid region. A supercritical fluid exhibits physicochemical properties between those of a gas and a liquid, and has the capacity to dissolve compounds that may only dissolve poorly or not at all in the gas or liquid state. The dissolving power of a supercritical fluid increases with increasing density depending on increasing in pressure. These properties of supercritical fluids provide a good extraction of the compounds due to their high dissolving power at high densities, and consequently a good fractionation and separation of the compound from the fluid (at lower densities) by reducing the pressure or changing the temperature in a separator. Another important factor is the penetrating power based in the high mass transfer rate of the solutes into the fluid. The low viscosity and high diffusivity of the supercritical fluid enhance this property allowing an efficient extraction of the compounds from the raw material.

Supercritical extraction is not widely used yet, but as new technologies are coming there are more and more viewpoints that could justify it, as high purity, residual solvent content and environment protection. The basic principle of SFE is that when the feed material is contacted with a supercritical fluid than the volatile substances will partition into the supercritical phase. After the dissolution of soluble material the supercritical fluid (SCF) containing the dissolved substances is removed from the feed material. The extracted component is then completely separated from the SCF by means of a temperature and/or pressure change. The SCF is then may be recompressed to the extraction conditions and recycled. Some of the advantages and disadvantages of SCFs compared to conventional liquid solvents for separations:

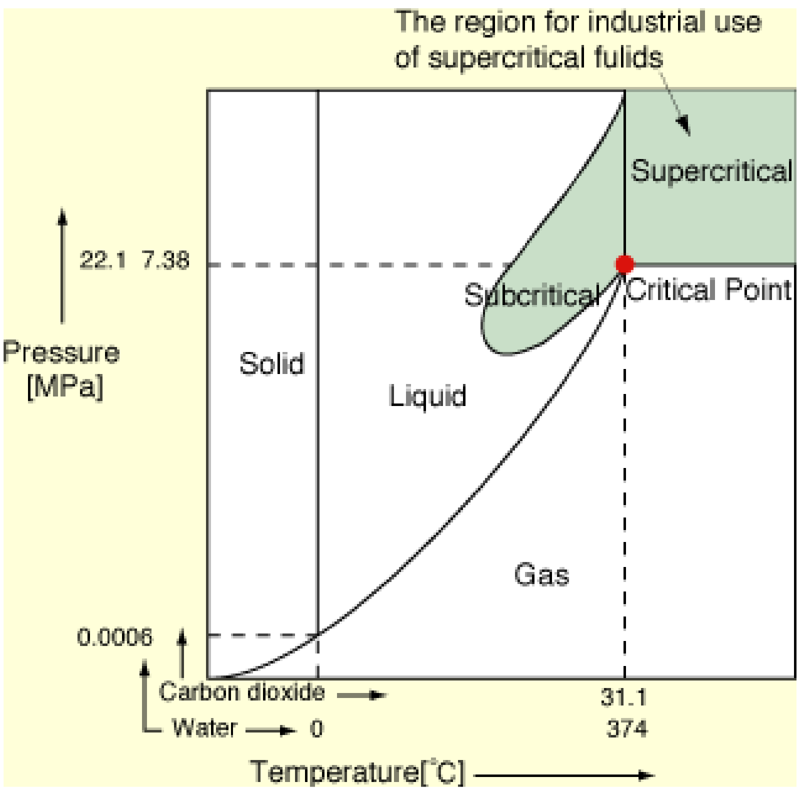
Advantages

- Dissolving power of the SCF is controlled by pressure and/or temperature
- SCF is easily recoverable from the extract due to its volatility
- Non-toxic solvents leave no harmful residue
- High boiling are extracted at relatively low temperatures
- Separations not possible by more traditional processes can sometimes be effected
- Thermally labile compounds can be extracted with minimal damage as low temperatures can be employed by the extraction

Disadvantages

- Elevated pressure required
- Compression of solvent requires elaborate recycling measures to reduce energy costs
- High capital investment for equipment

Carbon dioxide is the most commonly used SCF, due primarily to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity.



However, several other SCFs have been used in both commercial and development processes. The critical properties of some commonly used SCFs are listed in Table.

Table. Critical conditions for various supercritical solvents.

Fluid	**Critical Temperature (K)**	**Critical Pressure (bar)**
Carbon dioxide	>304.1	> 73.8
Ethane	>305.4	>48.8
Ethylene	>282.4	>50.4
Propane	>369.8	>42.5
Propylene	>364.9	>46.0
Trifluoromethane	>299.3	>48.6
Chlorotrifluoromethane	>302.0	>38.7
Trichlorofluoromethane	>471.2	>44.1
Ammonia	>405.5	>113.5
Water	>647.3	>221.2
Cyclohexane	>553.5	>40.7
n-Pentane	>469.7	>33.7
Toluene	>591.8	>41.0

Beside CO_2, water is the other increasingly applied solvent. One of the unique properties of water is that, above its critical point, it becomes an excellent solvent for organic compounds and a very poor solvent for inorganic salts. This property gives the chance for using the same solvent to extract the inorganic and the organic components, respectively.

Milk Fat Fractionation

Fractionation of milk fat permits to obtain fractions with variable triglycerides compositions and melting points. Thus, fractionation of milk fat and recombination of the fractions allow the control and the improvement of the thermal and physical properties, i.e. its consistency, and the development of new products.

The high melting fractions have found extensive use as shortening in puff pastry imparting a desirable butter flavour, fat bloom inhibitors in chocolate, hard stock for ghee production, cocoa butter replacement in confectionary products, edible films and frozen desserts.

Other potential applications for low melting fractions include biscuits, short breads, cold spreadable butter, pourable frying oils and improving the reconstitutibility of milk powder.

Historically, milk fat has been a part of human diets through consumption of:

Fluid milk, butter and cheese

Commercially prepared foods that contain milk fat-based ingredients such as:
Baked goods and bakery mixes
Confectionery items, frozen dinners and entrée mixes
Soups and snacks

Milk fat is obtained from milk by first separating the cream and churning to butter
• It is the most varied among all fats in its chemical and physical characteristics
• It possesses a uniquely pleasing flavour not found in other fats
• Its higher proportion of short-chain fatty acids contributes to ease of digestibility

Melting Characteristic of Milk Fat

Milk Fat Fraction	**Melting Temperature Range (ºC)**
Very High Melting Fraction	>50ºC
High Melting Fraction	35 - 50ºC
Middle Melting Fraction	25 - 35ºC
Low Melting Fraction	10 - 25ºC
Very Low Melting Fraction	<10ºC

Low Melting Fraction <15ºC
– Has strong butter flavour
– Can be incorporated into milk powder to improve functionality
– Has applications in confectionery products
– Can be used to make normal butter spreadable at refrigerator temperatures

Medium-Melting Fraction 15-30ºC
– Can be used as shortening to provide a crusty, flaky texture to croissants and pastries
– Can be used in making cakes and biscuits such as shortbread

High-Melting Fraction > 30ºC
– Hard fraction can be used in chocolate manufacturing instead of cocoa butter
– Has been reported to act as bloom inhibitor in dark chocolate
– Can be used as a flavour and texture agent in milk chocolate
– Hard fraction can improve the whipping properties of cream which is desirable in ice cream manufacturing

Fractionation Technology of Milk Fat
• Crystallization from Melted Milk Fat
• Crystallization using Solvents
• Short-Path Distillation
• Supercritical Fluid Extraction

Experimental

Supercritical Fluid Extraction System: Thar SFE 100 Model
Components of SFE:

1. Three fractionation vessels
2. High Pressure CO_2 pump
3. Heat Exchanger
4. Automated Back Pressure Regulator

Pressure set up values of vessels:
360 bar (high melting fraction)
300 bar (medium melting fraction)
100 bar (low melting fraction)

Temperature: 40-60^{o}C
Fractionation time: 1 hour

Differential Scanning Calorimeter (DSC): to determine the melting and crystallization characteristics of milk fat and its fractions between +60 and -40^{o}C.