

# A Review on Supercritical Carbon Dioxide as Green Solvent for Dairy Product Processing



Mansooreh Soleimani<sup>1</sup> and Maryam Takht Ravanchi<sup>2\*</sup>

<sup>1</sup>Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Iran

<sup>2</sup>Petrochemical Research and Technology Company, National Petrochemical Company, Iran

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\*Corresponding author: Maryam Takht Ravanchi, Petrochemical Research and Technology Company, National Petrochemical Company, Iran

## Abstract

Carbon dioxide is a non-flammable, inexpensive and non-corrosive substance that due to its properties is a suitable solvent for supercritical fluid extraction. CO<sub>2</sub> critical temperature is 31.06°C and its critical pressure is 7.386MPa. Due to its low critical temperature, thermal degradation of food components is not occurred. For extraction of compounds with high molecular weight, supercritical CO<sub>2</sub> extraction is a suitable technology. In dairy processing industry, supercritical CO<sub>2</sub> extraction, in comparison to pasteurization process, has vast applications, such as using as enzymatic and microbial inactivation agent; producing bicarbonates, carbonic acid and hydronium in milk carbonation reduced liquid production, extraction and fractionation of fat and cholesterol by which, higher quality products and solvent free residues were produced. On the other hand, supercritical CO<sub>2</sub> technology systems have the advantage of operating as batch, semi-continuous and continuous mode. In this research, different applications of supercritical CO<sub>2</sub> extraction for some dairy products are reviewed in detail.

**Keywords:** Supercritical carbon dioxide; Dairy product; Extraction; Green solvent

**Abbreviations:** PAA: Peracetic Acid; SCT: Short-Chain Triglycerides; MCT: Medium Chain Triglycerides; LCT: Long-Chain Triglycerides

## Introduction

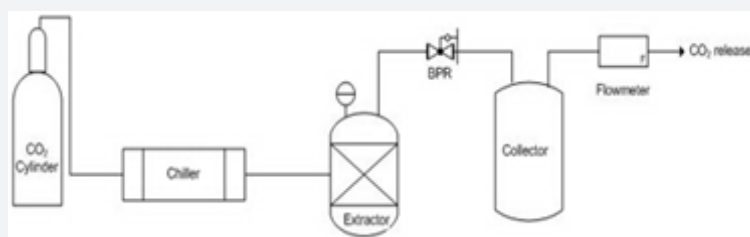


Figure 1: Schematic Diagram of a Supercritical CO<sub>2</sub> System.

In supercritical fluid extraction, under certain temperature and pressure, as some chemicals are good solvents for some solutes, the required extraction happened. For each solvent, above its critical pressure and its critical temperature, it becomes supercritical. CO<sub>2</sub> critical temperature is 31.06°C and its critical pressure is 7.386 MPa. CO<sub>2</sub> as a non-flammable, non-corrosive and inexpensive substance is a proper solvent for supercritical fluid extraction. On the other hand, as CO<sub>2</sub> critical temperature is low, thermal degradation of food components during extraction is prevented [1]. For extraction of compounds with high molecular weight, supercritical CO<sub>2</sub> extraction is a suitable technology (Figure 1). This system has CO<sub>2</sub> pump, pressure regulator, a chamber for keeping the sample, and

a collecting vessel. A heating zone is also required in which the liquid would be heated to supercritical condition and subsequently for solubilizing the sample to diffuse into it. From extraction column, dissolved material is sent to separator and extracted part was settled out. In the last stage, carbon dioxide is cooled, recompressed and discharged to atmosphere or recycled to the process [2]. In the food industry, supercritical CO<sub>2</sub> is an ideal solvent; as it is inert, cheap, available, odorless, tasteless and safe solvent. Due to its near ambient critical conditions, supercritical CO<sub>2</sub> is an appropriate choice for thermo-labile and non-polar natural products. In comparison to pasteurization process, in dairy industry, supercritical CO<sub>2</sub> process has various applications; it is suitable for reduction in microbial substances.

As a consequence, a product with better shelf life and greater organoleptic properties would be obtained.

### Dairy Products

Dairy products are consumed all around the world. Due to their high nutritional value, they were considered as healthy choices. It is predicted that by 2024, approximately 36% increase in global consumption of different dairy products would be observed [3]. In order to have safe milk consumption and stable shelf-life, milk must undergo thermal processing. As conventional high-temperature processes may lead to change in nutritional and organoleptic characteristics, in recent years, alternative non-thermal technologies are required; such as supercritical carbon dioxide. In order to destroy microorganisms (while keeping nutritional content), supercritical carbon dioxide technology is used. Although due to high equipment and operational cost, industrial application of supercritical processes could be an obstacle [4-6].

In conventional food/medicine pasteurization process, bioactive compounds may be destroyed by conventional thermal process. In the food industry, various compounds at their supercritical state were used; the most common one is CO<sub>2</sub>. By reducing pressure, it can be omitted from food matrix and be circulated to the system. This is the main reason that supercritical CO<sub>2</sub> technology is known as an environmentally friendly one.

Due to low critical temperature of CO<sub>2</sub>, this technology can be used near room temperature which minimizes any probable changes in the nutritional and physicochemical characteristics of food and prevents degradation of thermosensitive and volatile compounds. Moreover, as CO<sub>2</sub> has moderate critical pressure, minor investment costs are required for this process.

In dairy processing, supercritical CO<sub>2</sub> technology has many applications; such as [7-11]:

- a. Using as enzymatic and microbial inactivation agent.
- b. Producing bicarbonates, carbonic acid and hydronium in milk carbonation reduced liquid production.
- c. Extraction and fractionation of fat and cholesterol by which, higher quality products and solvent free residues were produced.

Supercritical CO<sub>2</sub> technology systems have the advantage of operating as batch, semi-continuous and continuous mode. An effective contact between CO<sub>2</sub> and dairy sample was occurred in semi-continuous and continuous systems. As CO<sub>2</sub> saturation is very rapid, enzymatic and microbial inactivation was more effective; as a consequence, operating time and manufacturing costs were reduced. CO<sub>2</sub> pump and pressure regulator are main compartments of a batch system. An exhaust system is also implemented to release the pressure after the process. For controlling the cooling or heating temperature, a temperature

control apparatus is established which could be a water bath, oven or autoclave. In semi-continuous process, vessels are connected in series; some of them are pressurized and the rest are in constant pressure. In this configuration, processing time was reduced, and energy recovery was allowed. In continuous apparatus, dairy sample and CO<sub>2</sub> is mixed and passed through the high-pressure pump. Praxair developed a high-pressure CO<sub>2</sub> pilot plant for milk treatment at different temperatures, pressures and CO<sub>2</sub> concentrations.

### Cheese

As CO<sub>2</sub> can have influence on the quality of semi-hard cheese, current researchers were focused on its use in modified atmosphere packaging. Recently, the effect of ripening condition and composition on CO<sub>2</sub> solubility was studied [12]. It was observed that in temperature range of 2-25°C, there is a linear relation between CO<sub>2</sub> solubility and temperature. Moreover, salt content was increased from 0 g/100 g to 2.7 g/100 g, by which CO<sub>2</sub> solubility was decreased. On the other hand, fat content has influence on CO<sub>2</sub> solubility coefficient [13] which confirmed that CO<sub>2</sub> has effect on aqueous and fat phase, for the latter CO<sub>2</sub> solubility was increased with temperature. Another application of supercritical CO<sub>2</sub> technology is for microbial growth control in mozzarella cheese. Using 100ppm of peracetic acid (PAA) in combination with supercritical CO<sub>2</sub>, yielded maximum reduction of *Geobacillus stearothermophilus* spores. As mozzarella cheese has worldwide popularity and consumption, these findings have vast application for the cheese industry [14]. Supercritical CO<sub>2</sub> technology is also applicable in low-fat cheeses production; such as Cheddar and Parmesan [15,16] and Gouda-type [17]. Cheese matrix, temperature, pressure and CO<sub>2</sub> mass flow are important parameters that affect lipid removal.

### Milk

Different researchers studied supercritical CO<sub>2</sub> technology effects on milk properties. For food products, supercritical CO<sub>2</sub> technology reduced the pasteurization or sterilization time and minimized thermal degradation of thermo-labile compounds (such as vitamins) [18]. It is worth mentioning that for milk, its effect on vitamins degradation must be studied in detail. Acidified milk, in comparison to heat-treated milk, showed better preservation to retinol,  $\alpha$ -tocopherol and  $\beta$ -carotene [19]. Due to acidification and solvation properties, supercritical CO<sub>2</sub> affect milk protein as well; the probable mechanism for this phenomenon is binding the obtained carbonic acid with calcium ions [20]. In the process of supercritical CO<sub>2</sub> treatment of milk, casein precipitation is an obstacle after which a dairy product containing cheese would be obtained [21,22]. The precipitated casein has industrial application. It was reported [21] that for fractionation and precipitation of concentrated protein solution, supercritical CO<sub>2</sub> technology is a suitable method. All around the world, whey beverage consumption is increasing [23,24]. It is reported [25] that whey proteins, in comparison to casein

are more resistance to high pressure and supercritical CO<sub>2</sub> technology is capable of changing the structure of whey proteins. Alkaline phosphate (as a milk endogenous enzyme) is used as a criterion of effectiveness in milk pasteurization. Centi et al. [26] used supercritical CO<sub>2</sub> to inactivate alkaline phosphate in milk. They studied the effect of pressure (8-18MPa), temperature (30, 50, 70°C) and mass ratio of CO<sub>2</sub> to milk (0.05 and 0.45 wt.%) during 30 min. At 70°C, 80 MPa and 0.45 wt.% the best inactivation rate of alkaline phosphate was obtained as 98.2%. This finding confirmed that supercritical CO<sub>2</sub> technology is applicable for alkaline phosphate inactivation in milk.

### Roles of Supercritical Carbon dioxide

#### As shelf life improver

In 1987, for increasing shelf life of dairy products, supercritical CO<sub>2</sub> use was proposed [27]. In recent years, in dairy (with emphasis on milk) products, the use of supercritical CO<sub>2</sub>

**Table 1:** Supercritical CO<sub>2</sub> Application in Milk Microbial Inactivation.

Product	Microorganism	Pressure (MPa)	Temperature (°C)	Time (min)	Reference
Raw skim milk	Native psychrotrophs	20.7	35	10	[28]
	<i>Pseudomonas fluorescens</i>	20.7	35	10	
Raw milk	Aerobic Bacteria	25	50	70	[29]
	Coliforms	25	40	50	
	Yeast and molds	25	40	50	
	Aerobic Bacteria	4	45	1	[30]
UHT milk	<i>Escherichia coli</i>	4	50	5	[31]
Whole milk	<i>Escherichia coli</i>	8	70	1	[32]

#### As cholesterol remover

Chitra et al. [35] used supercritical CO<sub>2</sub> technology to develop dairy product with healthier lipid profile. Temperature (40-80°C) and pressure (15-25 MPa) were considered as operating parameters; the optimum values for cholesterol removal from whole milk powder were 68°C, 20.7 MPa, 6 lit/min of CO<sub>2</sub>. Approximately 22.8% of cholesterol content was removed, while free fatty acids, lightness amount and solubility indicator were kept unchanged. In recent years, various methods were investigated for cholesterol removal from foods [36-38]; such as blending animal and vegetable fat with each other, steam distillation, supercritical CO<sub>2</sub> extraction, silica gel- or carbon active- based adsorption, complexation with  $\beta$ -cyclodextrin, enzymatic treatment by cholesterol oxidase and cholesterol reductase for cholesterol degradation and use of cholesterol decomposing microorganisms such as *Nocardia* and *Rhodococcus*. Among these methods, supercritical CO<sub>2</sub> technology has various advantages, the most important of which are high efficiency, rapid extraction fluxes, lower risk for thermal product degradation, and higher nutrient retention [39,40]. It was reported that at moderate dynamic time increasing operating pressure and decreasing extraction temperature enhanced cholesterol removal [41-43]. For instance, increasing pressure from 100 bar to 250 bar, cholesterol extraction was

for microbial inactivation was studied (Table 1).

In dairy products, spore-former is an important contaminant as it affects food quality. Moreover, it facilitates product spoilage as it decreased its commercial shelf life [33]. The effect of supercritical CO<sub>2</sub> on milk spore's inactivation was reported in some researches. Werner and Hotchkiss [34] evaluated the existence of *Bacillus cereus* spores at different operating conditions (i.e. temperature: 15, 30, 35 and 40°C; pressure: 10.3, 24.1, 48.3 MPa; CO<sub>2</sub> concentration 0, 3.66, 132 g/kg milk). All researches proved that supercritical CO<sub>2</sub> technology has the ability to inactivate microbial contaminants in milk; although milk fat content, bacteria age, equipment type, and operating parameters are important factors that have influence on microbial inactivation rate. Hence, in dairy production, for the application of supercritical CO<sub>2</sub> technology, the knowledge of microbial inactivation mechanism is vital.

increased. On the other hand, by raising temperature from 40°C to 57.5°C, cholesterol extraction was decreased and beyond 57.5°C a slight increase was observed in cholesterol extraction. For dynamic extraction time, an increase from 2.5 h to 3 h resulted in higher cholesterol extraction yield and from 3 h to 3.5 h yielded to lower insignificant cholesterol extraction yield. As a concluding remark, for cream powder, optimum operating parameters are 75°C, 204 bar and 3.5 h by which 39% reduction in cholesterol content was observed [44].

#### As lipid fractionator and vitamin isolator

Supercritical fluid extraction is a technique for lipid fractionation and vitamin isolation. It was reported that supercritical CO<sub>2</sub> technology is applicable to dairy products for vitamins A and E removal from powder [45,46]. In order to reduce the negative effect of water content of milk on extraction, Berg et al. [45] tested Hydromatrix as a water adsorbent. As a result, in 80min, from 0.5 g sample, all vitamins A and E were extracted. Ramos et al. [47] used supercritical CO<sub>2</sub> technology by which milk fat was fractionated into four different parts; namely short-chain triglycerides (SCT), medium-chain triglycerides (MCT), long-chain triglycerides (LCT) and cholesterol. It was found that polychlorinated biphenyls are predominantly in SCT, MCT and cholesterol fraction of milk fat.

Yu et al. [48] reported the application of supercritical CO<sub>2</sub> technology for anhydrous milk fat. Milk fat obtained by supercritical CO<sub>2</sub> technology affected rheological and physicochemical properties of butter. Shukl et al. [49] reported that the resultant butter has lower moisture content and cholesterol and higher melting points.

In order to produce valuable substances that have industrial application, supercritical CO<sub>2</sub> technology is a good candidate as it is capable of extracting lipophilic food compounds [50]. Moreover, supercritical CO<sub>2</sub> technology has the capacity to effectively inactivate microorganisms [51].

### Concluding Remarks

Supercritical fluid extraction as a green technology is following all future regulations of health, safety and environment. Supercritical fluid extraction has the ability to provide high solubility, improved mass transfer rates and increased selectivity, hence it has application in many industries. As a concluding remark, in dairy industry, supercritical CO<sub>2</sub> technology is a good option for keeping nutritional quality and inactivating important enzymes. More research is needed to evaluate supercritical CO<sub>2</sub> influence on main intrinsic factors of dairy food processing such as decreasing milk protein allergenicity.

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