

The use of supercritical fluid extraction technology in food processing

by

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There is an increasing public awareness of the health, environment and safety hazards associated with the use of organic solvents in food processing and the possible solvent contamination of the final products. The high cost of organic solvents and the increasingly stringent environmental regulations together with the new requirements of the medical and food industries for ultra-pure and high added value products have pointed out the need for the development of new and clean technologies for the processing of food products. Supercritical fluid extraction using carbon dioxide as a solvent has provided an excellent alternative to the use of chemical solvents. Over the past three decades, supercritical CO₂ has been used for the extraction and isolation of valuable compounds from natural products (Mansoori et al 1988, Martinelli et al 1991, del Valle and Aguilera 1999, Hartono et al 2001).

Supercritical CO₂ was found to be selective in the separation of desired compounds without leaving toxic residues in extracts and without the risk of thermal degradation of processed products. Through the exploitation of the solvating power acquired by fluids near their critical points and the sensitivity of this power to small perturbations in temperature, pressure and modification of the solvent with the addition of entrainers, solvent-free extracts were readily obtained due principally to the high volatility of these solvents at ambient conditions. The favorable transport properties of fluids near their critical points also allows deeper penetration into solid plant matrix and more efficient and faster extraction than with conventional organic solvents.

For the past three decades, the commercial application of supercritical fluid technology remained restricted to few products due to high investment costs and for being new and unfamiliar operation. With advances in process, equipment and product design and realization of the potentially profitable opportunities in the production of high added value products, industries are becoming more and more interested in supercritical fluid technology (Sihvonen, et al., 1999). The extraction is carried out in high-pressure equipment in batch (Figure 1) or continuous manner (Figure 2). In both cases, the supercritical solvent is put in contact with the material from which a desirable product is to be separated. The supercritical solvent, now saturated with the extracted product, is expanded to atmospheric conditions and the solubilized product is recovered in the separation vessel permitting the recycle of the supercritical solvent for further use.

Table 1 presents some of the existing commercial applications put in operation over the past few years. Supercritical fluid technology is now recognized as an effective analytical technique with favorable and comparable efficiencies to existing chemical analysis methods and when applied for the qualitative and quantitative identification of constituents of naturally occurring products and heat-labile compounds (Dionisi et al., 1999; Ibanez et al., 2000; de Castro and Jimenez-Carmona, 2000; Moret and Conte, 2000). In addition, the reduction of liquid solvent waste and the substitution of some undesirable organic substances is another advantage of supercritical fluid analytical techniques. Extraction with supercritical fluids is also a unit operation that could be employed for a variety of applications including the extraction and fractionation of edible fats and oils, purification of solid matrices, separation of tocopherols and other antioxidants, clean-up of herb medicines and food products from pesticides, detoxification of shellfish and concentration of fermentation broth, fruit juices, among others (Eggers et al., 2000; Lang and Wai, 2001, Gonzalez et al., 2002, Ibanez et al, 2000).

Supercritical fluid extraction has proved effective in the separation of essential oils and its derivatives for use in the food, cosmetics, pharmaceutical and other related industries, producing high-quality essential oils with commercially more satisfactory compositions (lower monoterpenes) than obtained with conventional hydro-distillation (Ehlers et al., 2001; Diaz-Maroto et al., 2002; Ozer et al., 1996).

Alkaloids, organic compounds with bitter taste and toxic effects on animals and humans, but present therapeutic effects when applied in moderate doses, are found in many natural plants. Alkaloids such as caffeine, morphine, emetine, pilocarpine, among others,

are the active components in a variety of stimulants and medicinal products and their recovery from natural plants is of great interest to the food, pharmaceutical, and cosmetic industries. Supercritical Carbon dioxide proved to be highly selective for caffeine prompting its use as the selected solvent in the commercial decaffeination of coffee and black tea. Recent investigations have demonstrated the potential exploration of solvent and anti-solvent properties of carbon dioxide in the recovery of alkaloids such as theophylline, theobromine and pilocarpine, among others (Saldaña et al., 2002a, Saldaña et al., 2000; Saldaña et al., in press).

The association of high blood cholesterol levels with heart diseases or cancer is the motivating factor in recent works on the reduction of cholesterol levels in consumed meals that include meats, dairy products and eggs. Several methods including supercritical extraction have been proposed for the reduction of fat and cholesterol content in dairy products (Greenwald, 1991). Cholesterol was shown to be soluble in supercritical carbon dioxide and even more soluble in supercritical ethane. Extraction with supercritical fluids requires higher investment but can be highly selective and more suitable for food products. A summary of the main products containing cholesterol and their extraction with supercritical fluids is presented in Table 2. These results clearly indicate the great potential of supercritical fluid extraction in the recovery of meat products with acceptable cholesterol and fat contents.

As ethane is much more expensive than CO₂, the use of CO₂/ethane and CO₂/propane mixtures can be an attractive alternative for the removal of cholesterol from foods due to the compromise between higher ethane cost and better cholesterol removal

efficiency. Cholesterol removal was also improved through the coupling of carbon dioxide extraction with an adsorption process operating at the same extraction conditions. Literature data also point to potential fractionation of fat simultaneously with the removal of cholesterol from dairy products. The extraction/fractionation operation was also coupled with an adsorption step that uses alumina as the adsorbent (Mohamed et al., 1998, 2000). The combined extraction/adsorption operation resulted in the removal of more than 97% of the cholesterol in the original butter oil (Table 2). The operation has also resulted in the generation of butter oil fractions with characteristic properties that are distinctly different from those of the original oil.

The carbon dioxide extraction has also proved effective for the production of high quality cocoa butter from cocoa beans (Saldaña et al., 2002b). Recent investigation point to the potential use of supercritical CO₂ for microbial inactivation of foods and the implementation of an innovative technique for the sterilization of thermally and pressure sensitive materials (Spilimbergo et al., 2002).

Supercritical water oxidation, an environmentally attractive technology through which organic materials can be oxidized to carbon dioxide, water and gaseous nitrogen, is one of the new potential applications of supercritical fluid technology (Mizuno et al., 2000). In analytical applications, it has the advantage over standard methods in providing consistent qualitative and quantitative analysis and the simultaneous oxidative decomposition of the material. In addition to the homogenization of the reaction mixture, high oxygen concentrations are attained in supercritical water. The application of

supercritical water for the safe destruction of toxic materials is a viable alternative to incineration and land disposal (Moret and Conte, 2000).

The rapid expansion of supercritical solutions through small size orifices and nozzles has opened new opportunities for the formation of finely divided powders. This process has been applied for the formulation of drug particles, drug-containing polymeric particles and solute-containing liposomes (Jung and Perrut, 2001, Kompellla and Koushik, 2001). The ability of supercritical mixtures to fractionate polymers contributes to the better control of drug release in formed polymeric delivery systems.

Supercritical or gas anti-solvent precipitation were proposed in the 1980s as a promising technology for the production of micron and submicron size particles with controlled particle size and particle size distribution (Jung and Perrut, 2001). The principal features of this process is the use of supercritical carbon dioxide, the mild operating temperatures and the smaller particles (sizes down to 50 nm, 1-1.5 μ m and 0,1-20 μ m, have been reported for some operations) obtained with this process as compared to conventional milling and crystallization via liquid antisolvent precipitation. While particle morphologies that include spheres, rod-like and snowballs have been reported, the most commonly encountered is the formation of spherical particles. Supercritical CO₂ was used for protein purification through the fractional precipitation of proteinalkaline phosphatase, insulin, lysozyme, ribonuclease, trypsin and their mixtures from dimethylsulphoxide (Reverchon et al., 2000). Other investigations focused on coatings, semi-conductors and pharmaceuticals. More recently this technique has been employed for the encapsulation of micron size particles and the selective precipitation of products from reaction media.

Variations of this process include the aerosol solvent extraction system (ASES), which involves spraying the solution through an atomizing nozzle as fine droplets into supercritical carbon dioxide (Jung and Perrut, 2001). The dissolution of carbon dioxide in the liquid droplets leads to large volume expansion of the liquid and consequently the reduction of the dissolution power of this liquid and the existence of large supersaturations and thereby the formation of small solute particles.

Another variation is the solution-enhanced dispersion by supercritical fluids. In this process, the supercritical fluid is first mixed with the solution and it is the mixture that is subsequently sprayed into a vessel controlled at the operating temperature and pressure and where particle formation takes place (Jung and Perrut, 2001). Droplets formed are generally smaller than in the ASES with enhanced mixing between the supercritical fluid and the solution.

The Particles from gas-saturated solutions involves the dissolution of supercritical carbon dioxide in melted or liquid-suspended substance and thereby generating the denominated gas-saturated solution or suspension, which is subsequently expanded through an orifice or a nozzle to produce the desired fine solid particles or droplets. This process allows the formation of particles of substances insoluble in supercritical carbon dioxide (Jung and Perrut, 2001).

Finally it is important to mention that supercritical fluids are known to provide good reaction media due to their capacity to homogenize a reaction mixture, high diffusivity and controlled phase separations and distribution of products (Phelps, et al., 1996).

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Table 1: Industrial Applications (Phelps, et al., 1996)

Year	Operating company	Processed material
1982	SKW/Trotsberg	Hops
1984	Fuji Flavor Co.	Tobacco

	Barth and Co. Natural Care Byproducts	Hops Hops, Red Pepper
1986	SKW/Trotsberg Fuji Flavor Co. CEA	Hops Tobacco Aromas, Pharmaceuticals
1987	Barth and Co. Messer Griesheim	Hops Various
1988	Nippon Takeda CAL-Pfizer	Tobacco Acetone residue from antibiotics Aromas
1989	Clean Harbors Ensco, Inc	Waste waters Solid wastes
1990	Jacobs Suchard Raps and Co. Pitt-Des Moines	Coffee Spices Hops
1991	Texaco	Refinery wastes
1993	Agisana Bioland	Pharmaceuticals from botanicals Bones
1994	AT&T	fiber optics rods

Table 2: Supercritical fluid extraction of cholesterol with CO₂ from products of animal origin.

Product	Reference	P (MPa)	T (°C)	Cholesterol (mg/g)		Yield (%)
				Before	After	
Dried egg yolk	(Froning, et al., 1990)	16.5-37.8	40-55	18.52	6.34	65.8
Dried egg yolk	(Bohac, 1998]	24.1-37.8	45-55	18.94	0.38	98.0
Dehydrated beef	(Lim, 1992]	23.4-38.6	45-55	1.56	0.19	87.8
Beef patties (cooked)	(Fenton and Sim, 1992]	17.2-55.1	40-50	1.94	0.12	93.8
Pork (cooked)	(Lin, et al., 1999)	7.3-34.4	50-150	0.80	0.22	70.1
Dried chicken meat	(Froning, et al. 1994)	30.6-37.6	45-55	4.96	0.54	90.0
Milk fat	(Mohamed, et.al., 1998)	10.1-36.4	40-70	2.50	0.21	91.5
Milk fat *	(Mohamed, et al., 2000)	8.0 -24.0	40-70	2.50	0.20	93.4

** Using supercritical ethane as solvent*

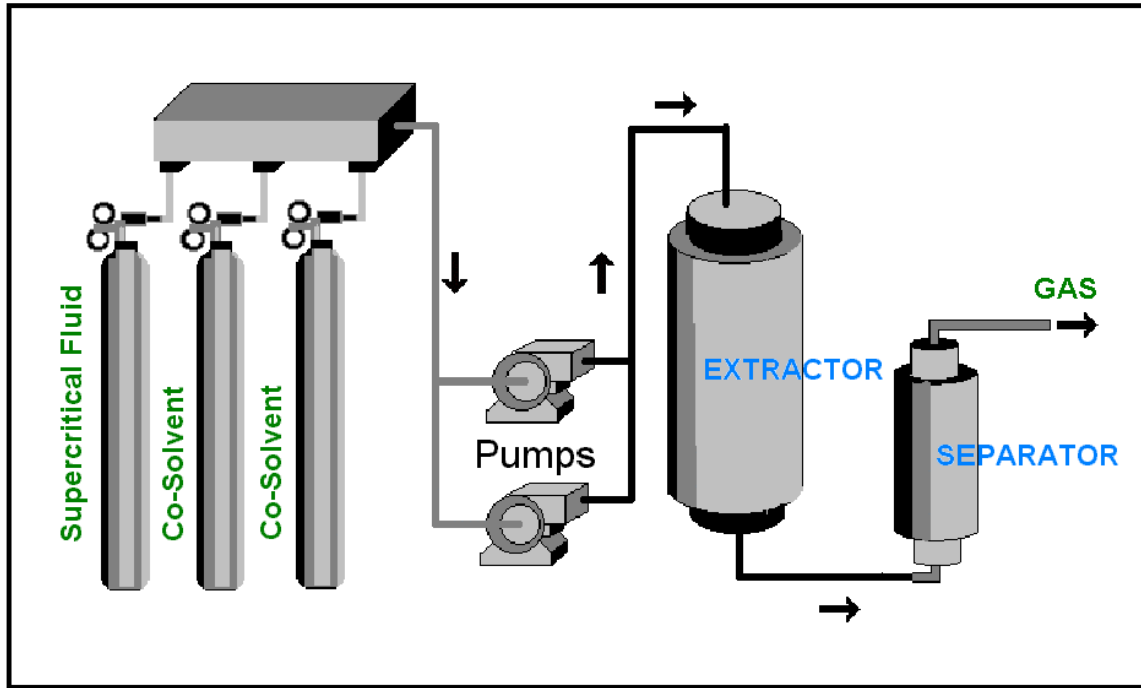


Figure 1: A schematic diagram of a supercritical fluid batch extraction.

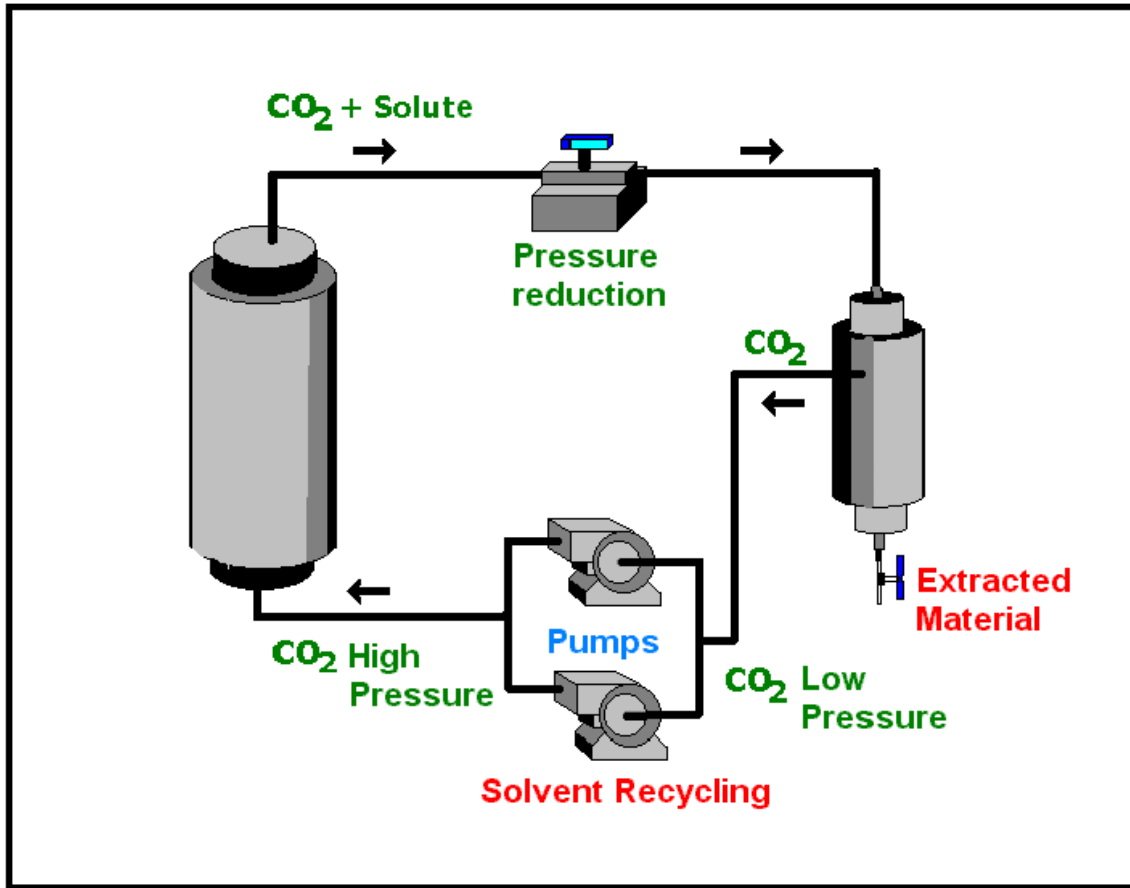


Figure 2: A schematic diagram of a supercritical fluid continuous extraction.

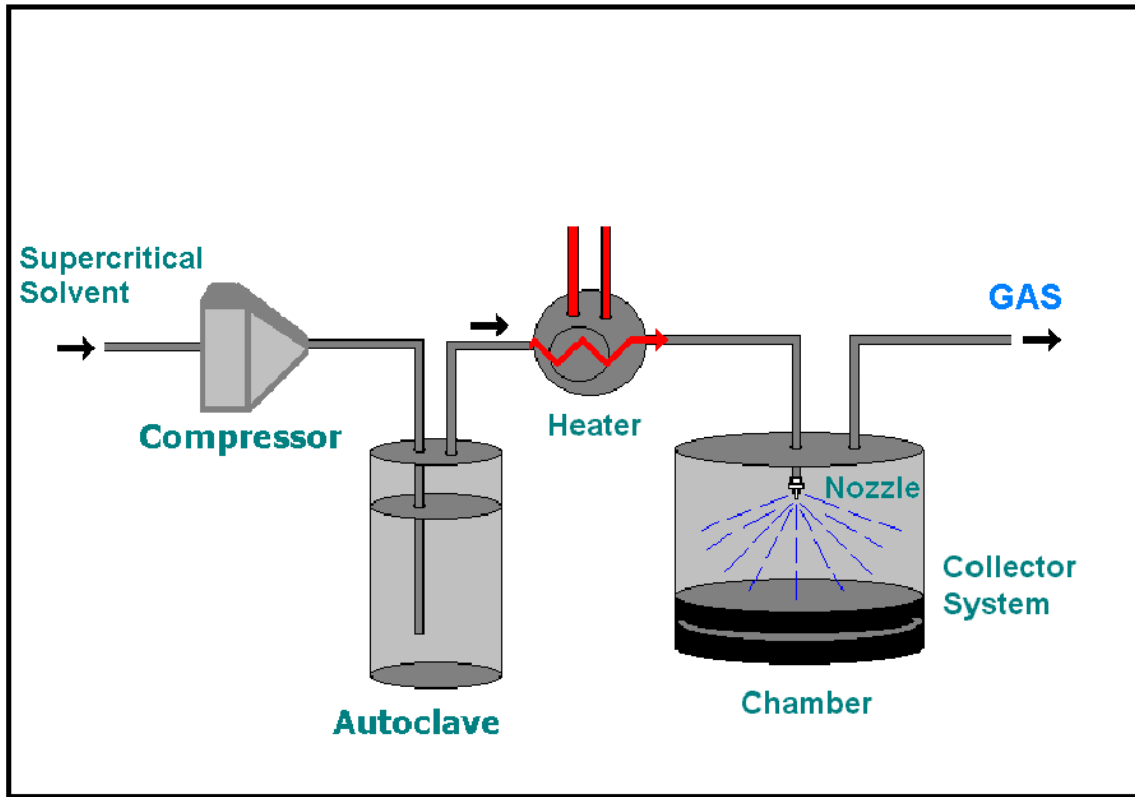


Figure 3: A schematic diagram of the Rapid Extraction of Supercritical Solutions process.

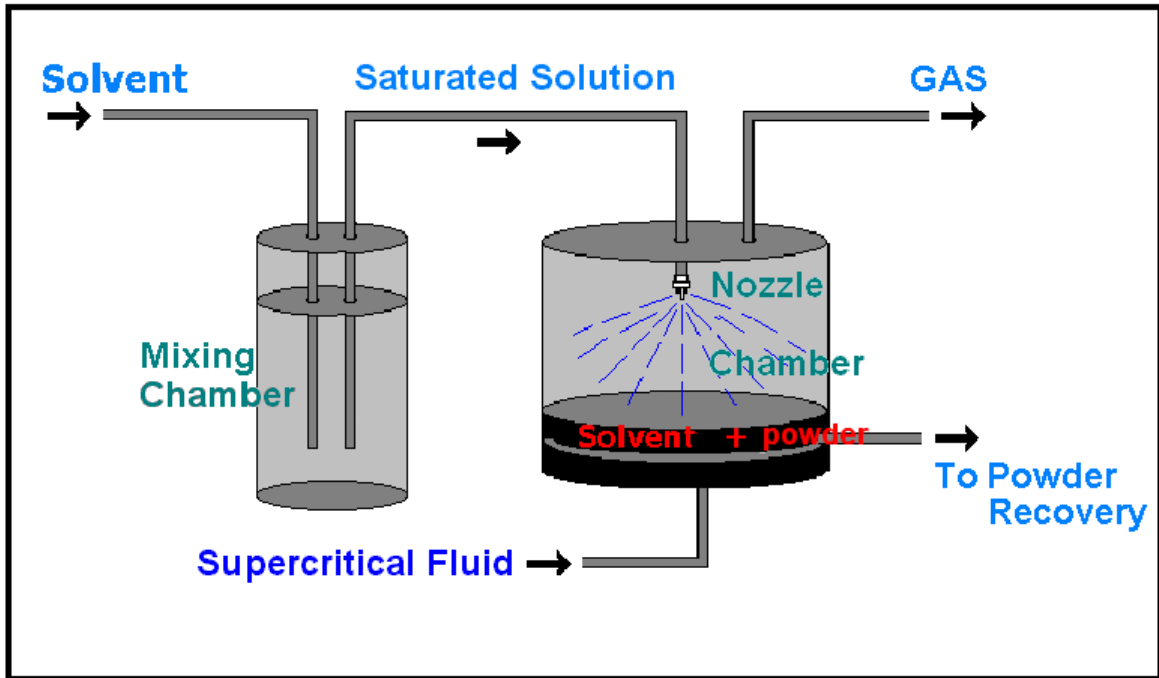


Figure 4: A schematic diagram of the Solvent or Gas Anti-Solvent process.

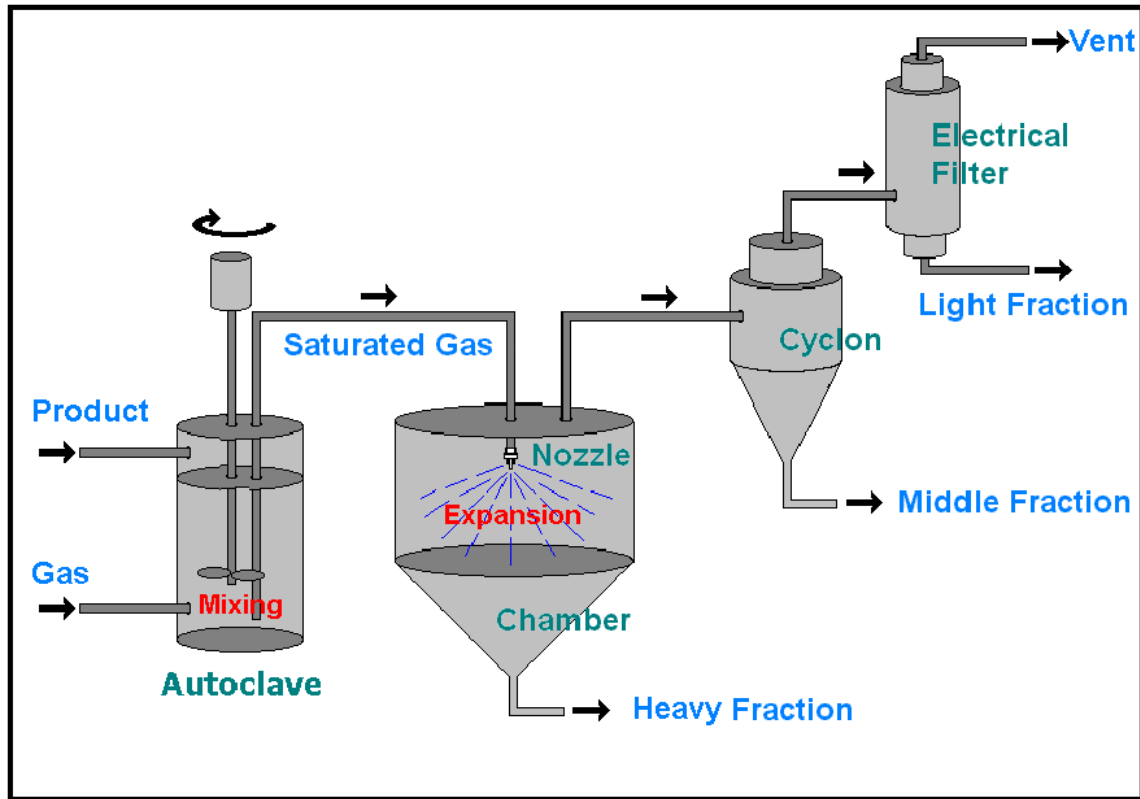


Figure 5: A schematic diagram of Particle from Saturated Solutions process.