Supercritical Fluid Technology for Separations from Solid and Liquid Feedstocks

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Supercritical fluid extraction (SFE) technology is widely used in the food and spice extraction industries, however, it is still very sparsely used in the chemical industry. To date, supercritical fluid technology applications have focused on natural product processing, (e.g. coffee and tea decaffeination; tobacco denicotination; fat extraction from cocoa, nuts, and flowers; and extraction of flavors from hops, spices, etc.). Today over thirty commercial-scale supercritical fluid solid matrix extraction plants are in operation throughout the world, but still primarily in North America and Europe. SFE has not found wide use in the chemical industry, primarily because of the cost factors associated with semi-continuous processing.

_ Non-food applications of near and supercritical fluid processing that have been commercialized, include the Residual Oil Supercritical Extraction (ROSE) process for petroleum deasphalting, the separation of ethanol from water, the removal of organic compounds from wastewater, soil remediation, fractionation of synthetic oils such as polydimethylsiloxane, fractionation of polymer solutions to reduce polydispersity, the cleaning of precision parts and plastic parts, etc. In these applications, the primary advantages of supercritical processing are the selective tuning of the solvent power for fractional extraction or separation, and the absence of an organic solvent in the residue or extract.

Semicontiuous Solid Matrix SFE vs. Virtually Continuous Stagewise Solid Matrix SFE

A major impediment for further commercial exploitation of SFE technology are the problems and costs associated with the conveyance of solid materials into and out of high pressure extraction vessels. Basically, two methods solids conveyance have evolved: 1) quick opening closures that rapidly open the tops of the extraction vessel to permit loading and

unloading, and 2) lock hopper systems to bring materials under pressure stagewise, in one or more intermediate stages. The problems associated with quick opening enclosures are: 1) they are expensive to manufacture, (up to 75% of the vessel cost); 2) they are difficult to seal; 3) they are a major source of carbon dioxide losses (after extraction of each batch the carbon dioxide in the vessel is lost to the atmosphere, or in larger SFE systems, the carbon dioxide must be collected utilizing an expensive carbon dioxide recovery system); 4) they are awkward to operate, (solids are difficult to handle in large-scale extraction systems requiring specially designed baskets or bags to be filled, in most operations utilizing manual labor representing up to 50% of the labor operating costs); 5) solid matrix extraction also requires expensive pre-treatment moisture level control steps, (such as drying or wetting to an optimal moisture level); and 6) requires multiple vessels piped in a complicated series manifold piping design, to maintain a semi-continuous operation, which is costly and complex to operate.

Lock Hoppers and Extruder Feeders

The use of lock hoppers and extruder feeders greatly reduces costs associated with semi-continuous SFE processing. Many applications that are not cost effective with semi-continuous SFE processing become cost effective with virtually continuous multi-stage SFE solid matrix processing. Lock hoppers have limitations in application which are: 1) the solids must be flowable, which eliminates many potential applications; 2) they require expensive valves and controls, which can only be justified for very large (>20 tons/day) extraction facilities; 3) the valves are subject to wear and leakage, and require significant maintenance; and 4) the plant layout sometimes dictates that large vessels be utilized, which are expensive to manufacture and erect on site. Extruder feeders also have limitations on their use, which are: 1) the solids must form a seal in the extruder, which limits applications to highly compressible materials, 2) extruder feeders are expensive, and can only be justified for large extraction facilities, 3) the extruder feeders will require significant amounts of maintenance, 4) the plant layout sometimes dictates that large vessels be utilized, which are expensive to manufacture and erect on site, and 5) the maximum pressure for an extruder feeder would be 350 bar.

All of the above problems and associated costs would be exacerbated by operating in the enhanced solubility region (>50°c and 450 bar). Therefore, almost all commercial-scale SFE plants built to-date are operating well below 350 bar extractor operating pressure, because operating in the enhanced solubility region would add exorbitant capital costs to the typical multiple vessels (with closures) design of a commercial-scale solid feedstock SFE process. Similarly, the number of lock hoppers required for a nearly continuous stagewise design, also becomes unwieldy at pressures above 350 bar.

Countercurrent Column Supercritical Fluid Extraction

The countercurrent column supercritical fluid extraction process consists of the following steps: 1) a solute-containing fluid is introduced into the extraction column at the top of the vertically oriented column; 2) simultaneously, carbon dioxide solvent enters from the bottom of the column; 3) the column's internal contacting device insures that both phases are radially dispersed throughout the column; 4) because of differing densities, the solute-containing fluid moves downward while the carbon dioxide solvent travels upward in the column; 5) the carbon dioxide solvent extracts the solute from the solute-containing fluid while traveling up the column; 6) the solution of solute and carbon dioxide solvent, when it reaches the top of the column, will exit the extraction vessel to be directed to a separation device; 7) in the separation device the solute is separated from the carbon dioxide solvent; and 8) the carbon dioxide solvent may be recovered from the separation device and directed to the recycle system for pressure and temperature adjustment prior to reintroduction into the bottom of the extraction column.

A few large-scale supercritical fluid countercurrent column extraction plants are in operation in the United States, Europe and Japan. Applications include separating organics from wastewater; ethanol from an aqueous stream; terpenes from citrus peel oils; and some fatty acid mono-, di-, and tri-glyceride fractionations. The major impediment to further commercial exploitation of this technology has been the perception that countercurrent column technology should be utilized for fractionation of two or more components within a liquid stream. These applications are limited because other fractionation technologies are highly competitive. Although SFE countercurrent column technology has been applied in a few applications for total

extraction of all organic components from an aqueous stream, the process economics have been somewhat disappointing due to the low solubility of solutes in carbon dioxide at low column operating temperatures and pressures.

Potential Applications of SFE Countercurrent Column Technology

The feed fluid may take the form of a solution, multiphase liquid dispersion, slurry, or combination thereof. The feed fluid, in all of the above cases, must have hydrodynamic characteristics that will allow it to flow through the extraction column. Also, in all cases, the feed fluid must contain at least one or more solute(s) that will transfer from the feed fluid to the dense gas solvent. The feed fluid may be in the form of a solution such as an aqueous solution with: oxides, alcohols, citrus oils, pesticides, organic acids, crude oils, aldehydes, ketones, lactones, esters, dyes, carboxylic acids, amino acids, antibiotics, pyrazines, terpenoids, anthraquinones, sesquiterpenes, hydrocarbons, carotenoids, tocopherols, curcumoids, chelated metals, and other soluble extractable components or mixtures thereof. Additional examples include decaffineation of liquid coffee and teas and dealcoholization of beers and wines. The fluid feed may also be in the form of multiple liquid phases that may be in the form of an emulsion, such as aqueous phase(s) in contact with immiscible organic phase(s). Examples include: egg yolks, hydrous milkfat, petroleum and other organics products in sea or fresh water, i.e. any organic system that forms an immiscible system with the aqueous phase, or combinations thereof. The fluid feed may also be in the form of a slurry where a solid is dispersed in the aqueous phase. US 3,477,856 and US 5,178,735 describe the utility and benefits of forming a slurry prior to extraction. Examples of the dispersed solid phase include: algae, fungi, cells from a fermentation or enzyme broth, ground plant matter, ground animal matter, ground mineral matter, ground polymers and plastics, ground seeds, fruit or vegetable pulps, or mixtures thereof. The water or brine slurry must be pumpable, and the solids must be able to flow through the extraction column without accumulating inside the column to the point of causing clogging of the liquid flow down the column. Conversely, the solute concentration must be high enough to make the extraction economically feasible. The addition of salts to the aqueous feed stream has been shown in US 5,116,508 to have a beneficial effect on the extraction of organics with dense

gases. Cosolvents may be added to either the fluid feed or to the dense gas to enhance recovery of the solute(s) in the dense gas. The fluid feed may also be an azeotropic mixture that is to be separated as discussed in US 4,349,415. Furthermore, an extraction aid (such as polyhydric alcohol, propylene glycol, glycerol, or glycol, etc.) having a greater affinity for water than for the solute, may be used to enhance the separation of the solute from the aqueous carrier, as described in US 4,956,052.

Commonly the solute or solutes transfer from the fluid phase to the dense gas phase. The selectivity, S, is defined as the distribution coefficient of the solute between the extract and raffinate phases, Ks, divided by the distribution coefficient of the carrier fluid between the extract and raffinate phases, Ka.

$$S = Ks/Ka$$

Ks = solute "s" concentration in the extract phase/ solute "s" concentration in the raffinate phase.

Ka = carrier fluid "a" concentration in the extract phase/ carrier fluid "a" concentration in the raffinate phase

The distribution coefficient of the solute is defined as the concentration of the solute, (component "s"), in the extract phase divided by the concentration of the solute, (component "s"), in the raffinate phase at a specified temperature and pressure. Likewise, the distribution coefficient of the carrier fluid, often water, is defined as the concentration of the carrier fluid, (component "a"), in the extract phase divided by the concentration of carrier fluid, (component "a"), in the raffinate phase. For the extraction to be successful, the selectivity, as defined above, must be greater than unity.

Advantageous of Countercurrent Column SFE Technology

When compared to traditional supercritical extraction of a solid substrate, countercurrent column SFE should have a major impact on processing costs, because this process would allow for continuous operation of many applications by slurrying the solids. Thus, for the same

throughput volume, the cost of SFE processing with countercurrent column technology, will be significantly lower when compared to solid substrate SFE, because: 1) efficient usage of the solvent translates to reduced solvent usage and associated costs per pound of product processed, will significantly reduce both the capital and operating costs; 2) a continuous operation will significantly reduce solids handling, and will considerably reduce associated labor costs; 3) faster processing cycles will reduce product degradation; 4) expensive drying pretreatment steps will be eliminated; 5) high capital cost quick closures will be eliminated; and 6) eliminating temperature and pressure swings will the extend the life of pressure vessels.

Conclusions

1. For larger applications of extraction from a solid matrix, virtually continuous multi-stage SFE process should be considered utilizing lock hopper or extruder feeders.

2. For liquid feedstocks, countercurrent column SFE could prove to be a cost effective alternative to conventional liquid/liquid extraction and distillation technology.

3. Consideration should be given to grinding solid feedstocks and slurrying them through a countercurrent column SFE process to take advantage of the lower capital and operating costs associated with the countercurrent column SFE process, when compared to the semi-continuous solid matrix extraction process.

References

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