SUPERCRITICAL FLUID AIDED MICRO-ENCAPSULATION OF DRY POWDERS

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Abstract

Sub micron and micron size powders of Titanium dioxide and Calcium oxide were coated in a fluidized bed. The micro-encapsulation is accomplished using a temperature swing of the bed temperature where the powders are fluidized in the supercritical CO_2, DMSO and Chitosan mixture. The analysis using AFM, SEM, TEM, and FTIR confirm uniform coatings of nano scale.

Introduction

Encapsulation of fine particles to produce tailored surface properties have extensive applications in different industries like: pharmaceutical, nutraceutical, cosmetic, agrochemical, electronic and specialty chemistry industries. There has been a continuous growth of interest in replacing conventional organic solvents with environmentally friendly supercritical fluids in chemical processes. Among them, supercritical carbon dioxide ($SCCO_2$) emerged as an excellent candidate due to its characteristics and properties: its relatively mild critical conditions (T_c = 304.1 °K, P_c= 7.38 MPa), is inexpensive, nontoxic, nonflammable, readily available, easily recycled, and as a solvent, it possesses both gas-like diffusivities and liquid-like densities and solvencies (1).

The objective of this research is to encapsulate dry powder particles with diameters on the micron and sub-micron range using a green, controllable and scalable technique (Supercritical Fluid Technology) in order to obtain a uniform and controllable coverage of particles with a biopolymer.

There are a portfolio of biodegradable polymers and selection of suitable polymers for a given application, depending on the time delivery range, the targeting objective and the delivery pH (2, 3). One of the challenging tasks on this research was finding a natural and versatile biopolymer, soluble on physiological pH, and non-toxic. Chitosan that is a modified carbohydrate polymer, derived from chitin deacetylation, was chosen as the coating material for this research because it is a natural and versatile biopolymer, soluble on physiological pH, and non-toxic (4).

Solubility in SCF

The solvent power of supercritical fluids is a function of pressure and temperature. For this reason different solubilities at different conditions can be used to solubilize or separate solutes and solvents. Usually, the solvent power of a supercritical fluid increases with density and vice-versa. Decreasing the pressure or increasing the temperature can reduce density.

Pressure reduction at constant temperature leads to lower concentrations of the dissolved substances causing it precipitation due to the lower density. In the same order of ideas but now considering the temperature effect, the density is reduced by temperature augmentation at constant pressure.

When working with a multi-component system at supercritical conditions, a separation process can be designed by studying the solubility of the mixture components at different temperatures and constant pressure. When this information is plotted the isotherms intersection at crossover points is obtained (5). Consequently, the separation conditions of a solid mixtures lie between the crossover points of the two species.

The observed retrograde behavior for solubility of multicomponent solutes mixtures is similar to the retrograde effects of pressure and temperature observed on sorption processes (6). The pressure at which the crossover occurs increases with the supercritical phase concentration for the components. This behavior was modeled (7), by coupling supercritical sorption isotherms with a conventional fixed bed desorber model, where a high-density favored desorption was predicted.

As there is no solubility data available for the system Chitosan-DMSO- $SCCO_2$, the first part of this study consisted on generating this fundamental information. The fact that DMSO solubility in supercritical CO_2 is high compared to the solubility of Chitosan Oligosaccharide Lactate in $SCCO_2$ was the reason to try a temperature change at isobaric conditions to disrupt the equilibrium of this ternary system. By increasing the temperature at constant pressure the solubility of the chitosan decreases causing it precipitation over the particles to be encapsulated while the DMSO stays soluble in the $SCCO_2$.

The solubility for the system Chitosan-DMSO- $SCCO_2$ was studied through two different experimental methods (8, 9): cloud point determination (Figure 1) and dynamic solubility (Figure 2).

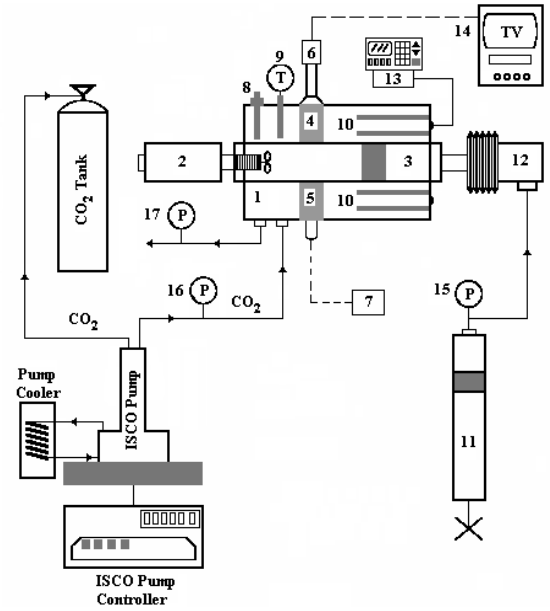


Figure 1. Phase Analyzer Setup Diagram. (1) Variable-volume cell, (2) Mixer, (3) Piston, (4) Camera sapphire window (5) Light sapphire window, (6) Camera, (7) Light source, (8) Pressure transducer, (9) Thermocouple, (10) Heaters, (11) Syringe pump, (12) Hydraulic lifting section, (13) Controller, (14) TV/VCR, (15, 16, 17) Pressure gauges at pump, cell inlet & outlet (vent).

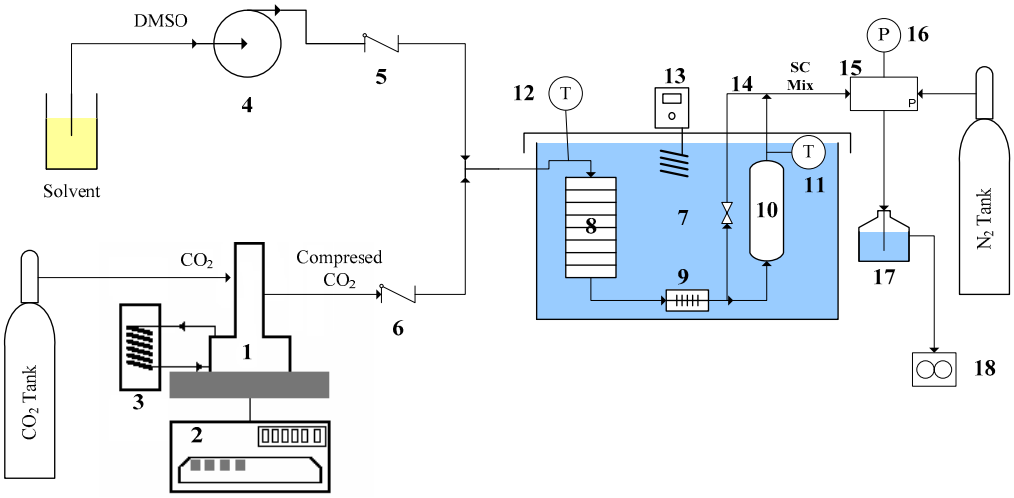


Figure 2. Dynamic Solubility Setup Diagram.(1) ISCO pump, (2) ISCO pump controller, (3) pump chiller, (4) HPLC pump, (5, 6) check valves, (7) water tank, (8) coil heat exchanger, (9) inline mixer, (10) extraction vessel, (11, 12) thermocouples, (13) Immersion circulator, (14) bypass line, (15) back pressure regulator, (16) pressure gage, (17) collection vessel, (18) wet test meter.

The cloud point information obtained from the static set-up or solubility cell correspond to the unique point where the ternary system co-exist in equilibrium, , and the solubility data obtained on the dynamic set-up shows the conditions where the ternary system behave as one single phase. These results are interrelated and they should be very

similar but not necessarily an exact match. Even though as can be confirmed in Figure 3 for a temperature of 35 °C both results present the same behavior, as the pressure increase for an isothermal system the solubility increase.

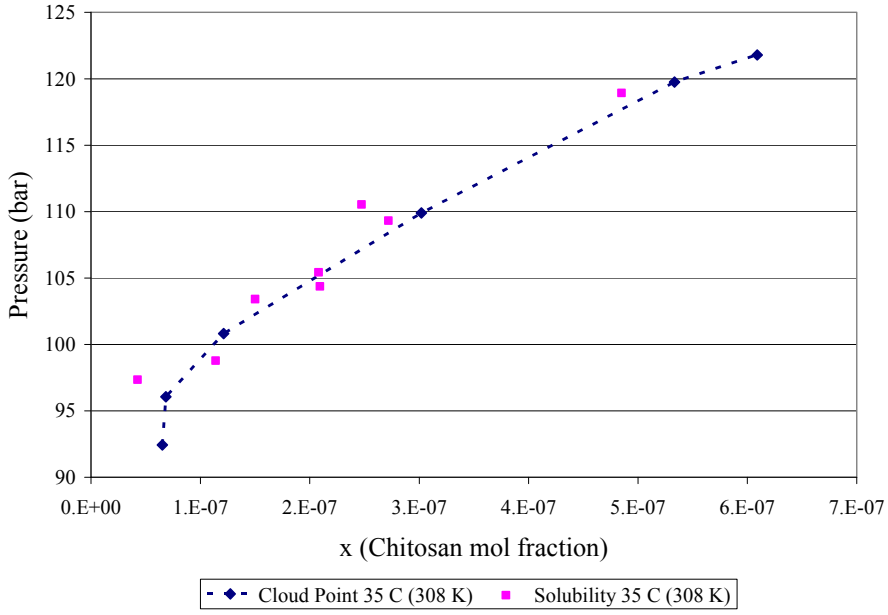


Figure 3. Solubility and Cloud Point Data for the Ternary System Chitosan-DMSO-CO_2 at 35 °C (308 °K).

Encapsulation Process

With the static and dynamic solubility data generated for the ternary system, the encapsulation experiments were performed in a pressure range of 110-120 bars and a temperature range of 41-50°C (314-323 °K), using different contact periods and particles sizes.

The encapsulation set-up was built from a Jerguson gage with a visualization window. The core materials used were titanium dioxide (TiO_2) and calcium oxide (CaO), the coating was chitosan and the solvent $SCCO_2$ and DMSO as co-solvent. Figure 4 describes graphically the encapsulation process step by step considering each factor by separate, pressure, temperature and carbon dioxide flow rate as a function of time.

FTIR and EDS confirmed to be valuable techniques to verify the presence of Chitosan in the encapsulated particle and also shows that almost all DMSO was removed during extraction. TEM analysis provided visually confirmation (Figure 5) that CaO and TiO_2 particles of 1 micron or less were encapsulated with thickness of 5 nm and less, and these results coincided with SEM and AFM analysis.

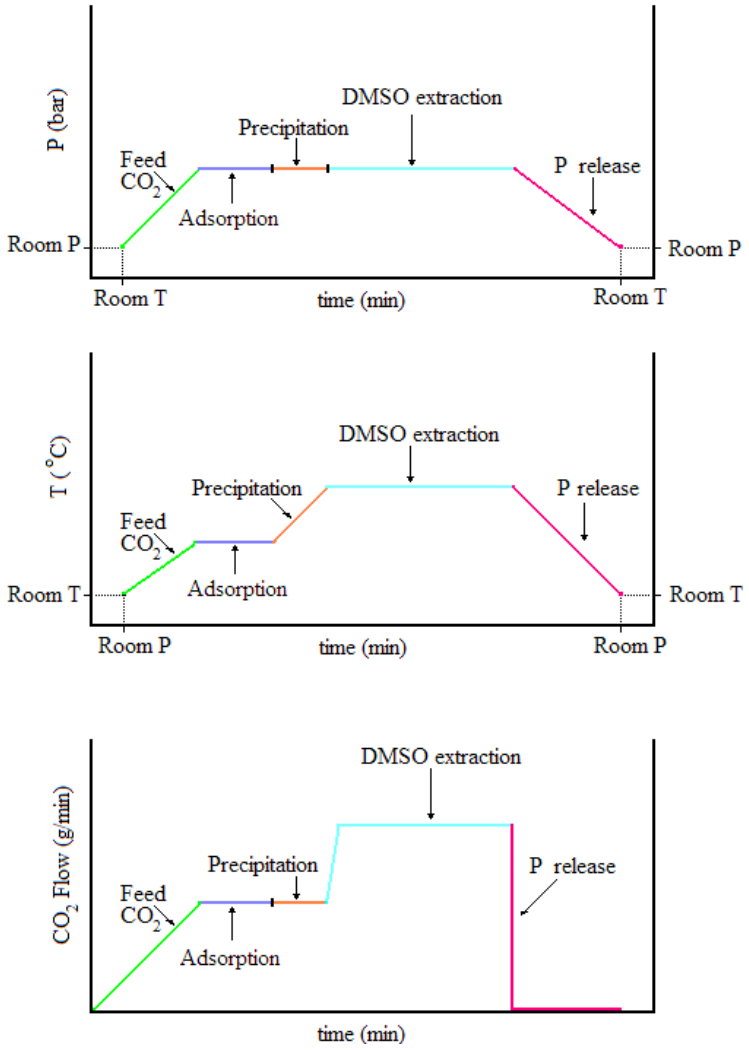
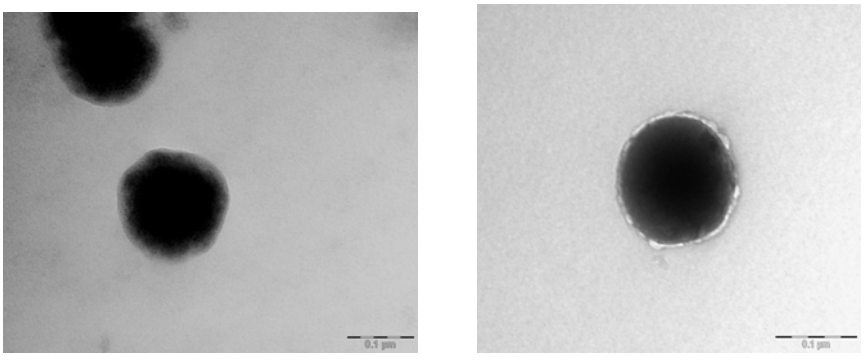


Figure 4. Coating Process Diagram.



(a) (b)

Figure 5. TEM for Particles Coated with Chitosan, (a) CaO Particles, (b) TiO_2 Particles.

SEM samples of 477 to more than 900 particles provided a particle size distribution, where more than 90% of the CaO and TiO_2 particles had been confirmed to have a diameter under one micron.

AFM showed particle roughness of 2-4 nm for the encapsulated samples and 36 to 46 nm or higher for uncoated ones, proving the particles were encapsulated since the surface is smoother after the coating is applied; also the uncoated particles presented a crystal angular shape structure when compared to the encapsulated ones with a rounded coated shape.

References

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