Supercritical Antisolvent Technique for the Preparation of Nanocatalysts

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In an era where sustainability is becoming the main driving force for research and development, supercritical fluidsbased techniques are presented as a very efficient alternative technology to conventional extraction, purification, and recrystallization processes. Supercritical antisolvent (SAS) precipitation is a novel technique that can replace liquid antisolvent precipitation techniques. Additionally, through the optimization of precipitation operating conditions, morphology, particle size, and particle size distribution of nanoparticles can be controlled. As an antisolvent, supercritical carbon dioxide (scCO₂) is far more sustainable than its conventional liquid counterparts; not only does it have a critical point (304 K and 73.8 bar) on its phase diagram that allows for the precipitation processes to be developed so close to room temperature, but also its recovery and, consequently, the precipitated solute purification stage is considerably simpler. This technique can be used efficiently for preparing nanocatalysts to be used in biodiesel production processes.

supercritical antisolvent precipitation

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carbon dioxide
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ide supercritical CO2

nanoparticles

1. Introduction

Ever since Baron Charles de la Tour first theorized supercritical fluids (SCFs) in 1822 ^{[1][2][3]}, several research studies have been executed regarding its applications, resulting in several technologies such as supercritical fluid extraction, supercritical drying, supercritical dyeing, and supercritical fluid chromatography. ^[1] SCFs are characterized by having both their temperature and pressure values higher than their critical point, where a significant difference between liquid and gas does not exist ^{[2][4]}.

As these operating conditions exceed the critical point, a clear interface between the liquid and gas phases tends to disappear and, thus, becomes a mixed gas, as shown in **Figure 1**. This mixed gas has properties inherited from both gaseous and liquid states, namely: low viscosity, high density, high diffusivity, non-existing surface tension, good fluidity, heat and mass transfer characteristics, as well as an adjustable solvent selectivity ^{[1][5][6][7][8][9][10]}.



Figure 1. A brilliant orange CO_2 -philic complex of rhodium was added in order to obtain better contrast and to demonstrate the solvent behavior of the liquid and the supercritical phase in the CO_2 phase diagram, which is illustrated with figures of the transition from the liquid/gas region to the supercritical region ^[11].

Supercritical carbon dioxide (scCO₂) and supercritical water have been recognized as green solvents for the future, mostly due to their ecological benefits, as they are nontoxic, noncarcinogenic, non-mutagenic, nonflammable, and thermodynamically stable. Supercritical carbon dioxide (scCO₂), when compared to supercritical water, exists at temperatures above 647 K and pressures over 221 bar, and it is more easily accessible by having a critical temperature (TC) of 304 K and a critical pressure (PC) of 73.8 bar, as shown in **Figure 1**.

2. Preparation of Nanomaterials Using Supercritical CO₂

Nanoscale materials, often known as nanomaterials, are defined by the International Union of Pure and Applied Chemistry (IUPAC) as having organized components with at least one dimension less than 100 nm ^[12]. New nanomaterials, including nanoclays, nanofibers, nanoporous materials, carbon nanotubes, nanocomposites, and nanoparticles, have recently been used for several different applications ^[13].

The most used methods to produce nanomaterials are gas condensation, vacuum evaporation and deposition, precipitation, impregnation, chemical vapor deposition, nano-grinding, calcination-hydration-dehydration, and sol-gel techniques ^{[1][14][15][16]}. Liquid anti-solvent processes are also used in the industry, based on the miscibility between two solvents. The solute to be micronized has to be soluble in the first solvent, but not soluble in the anti-

solvent. Therefore, by adding the anti-solvent, the formation of a solution between the two liquids and the supersaturation is induced, and subsequent precipitation of the solute occurs ^[17]. This traditional micronization technique usually produces wide particle size ranges and products with an uneven morphology. The elimination of liquid solvent residues is also a matter of concern ^{[17][18]}. These limitations can be particularly pertinent for some industrial applications, such as the production of pharmaceutical compounds ^[19].

Due to the features of supercritical fluids (SCFs) that have been previously described, approaches based on SCFs have been suggested as an alternative to traditional procedures ^[5]. By adjusting the operational parameters like the temperature, pressure, and solvent flow rate, supercritical fluids like $scCO_2$ can produce nanoparticles. It is also feasible to modify the particle size as well as the morphology of nanoparticles by utilizing the unique properties of supercritical solvents ^[1]. The earliest evidence of supercritical fluids being used for particle formation upon their depressurization was found in 1879 by Hannay and Hogart ^{[20][21]}. Surprisingly, the first patent for the rapid expansion of supercritical expansion solutions by valves or other spraying devices, or Rapid Expansion of Supercritical Solutions (RESS), was not published until 1986, more than a century after the invention was made ^[21]. Since CO_2 has a low critical pressure, and particularly temperature, in addition to being abundant and reasonably non-expensive, it has several technological advantages: used CO_2 can be easily collected and reutilized ^[22], and different processes have been developed for that purpose.

Recently, new proposals and developments have been made concerning various micronization technologies aiming to benefit from the peculiarities of fluids at supercritical conditions: new approaches for particle formation methods focused on the use of scCO₂ have started to be designed, developed, and tested, such as solvent (RESS), antisolvent (supercritical antisolvent (SAS)), aerosol solvent extraction system (ASES), precipitation with compressed antisolvent (PCA), gaseous antisolvent (GAS), supercritical antisolvent using enhanced mass transfer (SAS-EM), solution enhanced dispersion by supercritical fluids (SEDS), suspension-enhanced dispersion by supercritical fluids (SEDS), and co-solvent ^[21]



Figure 2. Conceptually distinct particle precipitation mechanisms are represented using scCO₂: (**a**) Formation of particles from gas-saturated solutions (PGSS). (**b**) Expansion (rapid) of supercritical solutions (RESS). (**c**) Expansion (rapid) of a supercritical solution into a liquid solvent (RESOLV). (**d**) Precipitation using a compressed anti-solvent (PCA)/Aerosol solvent extraction system (ASES). (**e**) Supercritical antisolvent with enhanced mass transfer (SAS-EM). (**f**) Solution-enhanced dispersion by supercritical fluids (SPEDS) ^[24].

3. Supercritical Antisolvent (SAS) as a Micronization Technique

Supercritical antisolvent precipitation (SAS), is a novel, ecologically benign method of creating nanomaterials that may be used as a substitute for liquid solvent precipitation since it is far more efficient. scCO₂ has been extensively used for producing a variety of materials, such as polymers, biopolymers, superconductors, explosives, colouring agents, active pharmaceutical ingredients (APIs), and catalysts, using an antisolvent for the controlled precipitation of solids dissolved in conventional solvent, if the processed compounds do not dissolve in the supercritical medium [5][19][26][27][28][29][30].

Additionally, the size and morphology of the resulting solids precipitated by SAS technologies are usually correlated with the system solvent/antisolvent high-pressure VLEs (vapour-liquid equilibrium), or the position of the SAS operating point around the critical point of the mixture (MCP) $^{[7][25]}$. For instance, if the process is being conducted as a single-phase method with no interface between the solution and the antisolvent, this indicates that micronization is occurring at supercritical conditions, i.e., above the MCP, and the very fast diffusion of scCO₂ into

the liquid solvent causes its expansion, thus producing the solute's supersaturation and resulting in forming nanoparticle morphologies that are not typically achieved by traditional catalyst preparation methods ^{[22][29]}. This phenomenon, adding to the quasi-zero surface tension of $scCO_2$, allows for obtaining particles of smaller size and having a narrow particle size distribution (PSD) with the complete elimination of the solvents, when compared to the traditional micronization techniques ^{[19][27][31][32]}; or, if the process shows a two-phase mixing, the micronization is occurring at subcritical operation conditions, i.e., in the biphasic region below the MCP, resulting in the production of microparticles ^{[21][25]}.

The success of SAS precipitation techniques is strongly dependant on the affinity between the solvent and the supercritical antisolvent, i.e., the solubility of the liquid solvent in the supercritical CO_2 and the quick gas-like diffusion of the scCO₂ in the solvent ^{[18][25]}, as shown in **Figure 3**. Several organic liquids that are completely miscible with scCO₂ under process conditions have been used, such as acetic acid, acetone, chloroform, dichloromethane, dimethyl formamide, dimethylsulfoxide, ethanol, ethyl acetate, formic acid, isopropanol, methanol, N-methyl pyrrolidone, and tetrahydrofuran. In some other cases, mixtures of two of the indicated solvents have also been used ^{[21][30]}.



Figure 3. Schematic diagram of the supercritical antisolvent (SAS) apparatus, composed of: BPV: Back-pressure valve; LS: Liquid separator; MV: Micrometric valve; P1, P2: Pumps; PC: precipitation chamber; RB: Refrigeration bath; S1: CO₂ supply; S2: Liquid solution supply; R: Rotameter ^[18].

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