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SCIENCE DIRECT

Powder Technology 154 (2005) 110 – 115

POWDER TECHNOLOGY

www.elsevier.com/locate/powtec

Micronization of the natural pigment-bixin by the SEDS process through prefilming atomization

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Received 10 January 2005; received in revised form 17 March 2005; accepted 2 May 2005
Available online 2 June 2005

Abstract

Bixin was micronized from dichloromethane solution using Supercritical CO_2 (SC-CO_2) as antisolvent by the SEDS process through Prefilming Atomization (SEDS–PA) with the aim of evaluating the efficiency of the supercritical fluid precipitation technologies in processing natural pigments and studying the effects of operating variables in the SEDS–PA process. Morphologies and sizes of microparticles were analyzed using scanning electron microscopy. This study has shown that the sizes of the bixin microparticles could be substantially reduced by the SEDS–PA process. The precipitates obtained at all experimental conditions were needle-like or coalesced net-like particles. With the increase of SC-CO_2 flow rate the impingement of SC-CO_2 on the liquid film and the consequent mixing of SC-CO_2 and droplets are reinforced, producing smaller particles. For constant SC-CO_2 flow rate, with the increase of solution flow rate the impingement of SC-CO_2 on the liquid film becomes weak leading to formation of bigger particles. Higher solution concentration results in formation of bigger particles and increase of agglomeration. Sizes of bixin microparticles decrease with pressure. Serious agglomeration and coalescence phenomena at the high operating temperature result in precipitation of net-like products.

Keywords: Supercritical fluid; SEDS–PA process; Micronization; Microparticle; Bixin

1. Introduction

Increasing reports of health hazards and toxicity of synthetic pigments are driving the food industry towards application of natural colourants in an increasing number of processed food products. Annatto extracts are orange/red natural carotenoid colouring agents obtained from the outer coats of the seeds of *Bixa orellana* L. and have been widely used in the food industry for the colouring of many commodities including flour and sugar confection, dairy and savoury products, soft drinks and fish [1]. The principal colouring component of annatto is the liposoluble diapocarotenoid 9′-*cis*-bixin, the mono methyl ester of the water-soluble 9′-*cis*-norbixin [2].

The application properties and the final colour value of pigmented systems are a function of the physical properties of the pigment (including the particle size distribution, morphology, and crystal configuration) and are dependent on the way the pigment is made. For instance, to ensure a maximum colour value, the pigment should be in the optimum size range according to the Mie theory [3]. Besides colour strength, other properties such as transparency, opacity, and flow are known to be a function of the pigment particle size. Generally, in industrial production recrystallization from organic solution, spray drying and machinery comminution (crushing, grinding, milling,

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doi:10.1016/j.powtec.2005.05.001

etc.) are used for the manufacture of pigment particles. However, these methods suffer from some drawbacks such as a wide particle size distribution and an environmental pollution problem associated with the use of an organic solvent for the pigment solution [4,5], etc. During the recent years Supercritical Fluid Precipitation (SFP) technologies used for formation of microparticles, due to their distinct advantages such as producing micro- or even nanoparticles with a narrow particle size distribution, reducing the residual solvent in the product to very low concentration, largely conditioning the final results and so on, are attracting widespread attention and have been applied in explosives [6], polymers [7], inorganic materials [8], organic materials [9] and pharmaceutical compounds [10], etc.

The Supercritical Fluid (SF) state is that attained by gases and liquids when subjected to temperatures and pressures above their critical parameters (T_c and P_c), and exists as a single phase characterized by a continuously adjustable solvent power/selectivity obtained by careful control of changes in the temperature and pressure. The diffusivity of SFs is similar to that of gases and about two orders of magnitude larger than that of liquid solvents. As a result, SF based processes can have very fast mass transfer and can produce outstanding size selectivity that cannot be obtained by conventional solvents [11]. Of the many possible SFs, CO_2 is the most widely used. It has low critical points (T_c=304.1 K and P_c=7.38 MPa), and as a process solvent offers the additional benefits of being non-toxic, non-flammable, environmentally acceptable, inexpensive, and can be used at a mild critical temperature suitable for the processing of thermally labile compounds.

Among all the SFP technologies, the Gas (or Supercritical fluid) Anti-Solvent (GAS or SAS) process is the most often used. The process exploits the ability of gases or SFs to dissolve in organic liquids and to lower the solvent power of the liquid for the solid in solution, thus causing the solid to precipitate. In the general SAS/GAS process an organic solution of solute is atomized through a nozzle into a high pressure vessel containing a near critical or supercritical fluid, causing intimate mixing of the solution and the fluid and resulting in solution expansion and particles precipitation [12–16]. One of the key processes that can condition the evolution of SAS/GAS precipitation is droplet formation due to jet break-up at the exit of the atomizer [17,18]. Smaller liquid droplets allow for an increase in the two-way mass transfer rates between the solvent and antisolvent, resulting in larger nucleation rates and smaller particles. With atomization mechanisms as a guide, attempts have been made to control particle size and size distribution [19–24]. Solution Enhanced Dispersion by Supercritical (SEDS) fluids is a novel SFP technology developed based on the principle of SAS. In the process, a nozzle with two coaxial passages allows introducing SC-CO_2 and a solution of active substance(s) into the particle formation vessel where pressure and temperature are controlled. The high velocity of SC-CO_2 allows breaking up the solution into very small droplets. Moreover, the conditions are set up so that SC-CO_2 can extract the solvent from the solution at the same time as it meets and disperses the solution. This technique has been used for the processing of diverse materials including low molecular weight substances, proteins and polymers [23–29].

In our previous work [30], based on the mechanisms of atomization a prefilming twin-fluid atomizer was designed and applied to the SEDS process to optimize the atomization and mixing of SC-CO_2 and solution for increased mass transfer rates through the impingement of dense gas (SC-CO_2) on the liquid film and the use of swirl; ephedrine and natural carotene crystals were successfully micronized by the SEDS process through Prefilming Atomization (SEDS–PA) [30,31].

The structure of the atomizer is illustrated in Fig. 1. Solution to be atomized is driven along a coaxial annular passage and formed to a thin swirl film (thickness 10 μm) by the liquid distributor with spiral slots, inclined at an angle of 45° relative to the central axis of the atomizer. The outlet diameter of the coaxial annular passage is 2 mm. The SC-CO_2 is driven through an inner capillary (80 μm internal diameter) to form a jet stream with high velocity. At the exit of the atomizer, the atomizing SC-CO_2 stream impinges on the swirling film at 45° and interacts with it to generate shear force on it. Upon violent interaction with the jet stream, the annular liquid sheet is disintegrated into fine drops and the mixing of the SC-CO_2 and the solution is intensified.

In the present work, the SEDS–PA process was used to micronize the natural pigment-bixin with the aim of evaluating the efficiency of the SFP technologies in processing natural pigments, overcoming the drawbacks in the existing industrial pigment postprocessing and studying the effects of operating variables (SC-CO_2 flow rate,

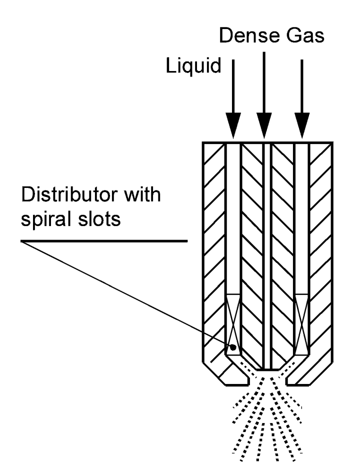

Fig. 1. Prefilming twin-fluid atomizer.