DYES MICRONISATION USING TWO SUPERCRITICAL FLUIDS BASED TECHNIQUES

E. Reverchon*, R. Adami, I. De Marco, C.G. Laudani, A. Spada

Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno,
Via Ponte Don Melillo, 84084 Fisciano (SA), Italy
Tel +39089964116 fax +39089964057
E-mail: ereverchon@unisa.it

The production of micrometric particles of some dyes (Solvent Blue 35, Solvent Yellow 56 and Disperse Red 60) was investigated using two different Supercritical Fluids based techniques: Supercritical AntiSolvent precipitation (SAS) and Supercritical Assisted Atomisation (SAA).
Using SAS technique, we obtained Disperese Red 60 nano-particles with a spherical shape and with mean diameters ranging between 50 and 100 nm. Very long needle like crystals were also obtained in some cases. Using SAA process, spherical crystals with mean diameter ranging between 0.5 and 2.5 μm were produced.
The two processes demostrated to be complementary: nanometric particles can be obtained using SAA, whereas micronic particles were produced using SAA.
We also studied the influence of some process parameters on the final product: mainly the variation of the dye concentration in the solvent in the SAS technique and the increase of supercritical fluid/liquid solvent flow ratio in SAA. These parameters mainly control the particle size of the produced powders.

INTRODUCTION

Dyes are largely used in the formulation of paints, inks, toners and photographic emulsions and their production in the micronic range with controlled particle size distribution can largely improve their performance. When they are used as pigments, dimensions and regularity of the particles are among the major quality characteristics of the pigment; when they are dissolved, their very low solubility in the medium can be a major problem in processing.

Several micronization techniques were proposed that try to take advantage of the specific characterics of supercritical fluids. They can be classified in two groups: supercritical antisolvent processes and supercritical assisted atomization techniques. The first group uses CO_2 as the supercritical antisolvent and is formed by discontinuous processes like GAS (Gas Antisolvent) [1-3] or semi-continuous processes like SAS (Supercritical Antisolvent) [4-6], SEDS (Solution Enhanced Dispersion by Supercritical Fluids) [7, 8] and ASES (Aerosol Solvent Extraction System) [9, 10]. The second group of techniques produces an enhancement of the atomization process solubilizing supercritical CO_2 in molten solids (PGSS, Particles from Gas Saturated Solution) [11, 12], mixing it in liquid solutions (CAN-BD, Carbon dioxide Assisted Nebulization with a Bubble Dryer) [13, 14] or solubilizing it in liquid solutions (SAA, Supercritical Assisted Atomization) [15-17].

Supercritical antisolvent processes were largely proposed for the micronization of several kind of compounds: pharmaceuticals, polymers, explosives, superconductor and catalyst precursors [4, 18, 19]; whereas only some attempts were performed in pigments micronization [20, 21].

No attempts have until now performed to micronize colouring matter by supercritical atomisation processes.

Therefore, the scope of this work is to propose the micronization of some dyes: Disperse Red 60, Solvent Yellow 56 and Solvent Blue 35. They will be processed using SAS and SAA to assess if

both techniques can be used to micronize these pigments. The micronization performance of the two techniques will also be evaluated.

I - MATERIALS AND METHODS

Solvent Blue 35 (SB35) with a purity of 99.9% (MW = 350.4, MP = 134 °C), Disperse Red 60 (DR60) with a purity of 99.9% (Mw = 331.3, MP > 300 °C) and Solvent Yellow 56 (SY56) with a purity of 99.9% (Mw = 253.3, MP = 153 °C) were supplied by Sun Chemicals (USA). Acetone (Ac, purity 99.8%), Methanol (MeOH. 99.8%), N-methyl-pirrolydone (NMP, purity 99.5%) and Dymethylsulfoxide (DMSO, purity 99.5%) were supplied by Carlo Erba Reagenti (Italy). CO_2 (purity 99.9%) was purchased from SON (Naples, Italy). The solubility of these dyes was measured at room temperature. The solubility of DR60 in Ac, DMSO and NMP is 17, 25 and 33 mg/mL, respectively. The solubility of SY56 in Ac, MeOH, DMSO and NMP is 40, 8, 35 and 33 mg/mL, respectively. The solubility of SB35 in Ac, NMP is 11 and 33 mg/mL, respectively. Untreated DR60 and SY56 consisted of irregular crystal with particle sizes ranging between 10 and 30 μm; instead Untreated SB35 consisted of irregular crystal with particle sizes ranging between 40 and 600 μm. All products were used as received.

Samples of the processed powder were observed by Scanning Electron Microscopy (SEM, mod. LEO 420). SEM samples were covered with 250Å of gold using a sputter coater (Agar mod. 108A). Particle Size (PS) and Particle Size Distributions (PSDs) were measured using the Sigma Scan Pro software (Jandel Scientific). SEM images from samples collected at different levels in the precipitator were used in PSD calculations. About 1000 particles were considered in each calculation of PSD, to obtain results that are representative of the whole precipitate.

II - SAA AND SAS APPARATUSES AND PROCEDURES

The apparatus used for SAA mainly consists of three feed lines used to deliver supercritical CO_2, the liquid solution and an inert gas. CO_2 and the liquid solution are sent to the saturator using two high-pressure pumps (Gilson, mod. 305), a high-pressure vessel loaded with stainless steel perforated saddles. The high surface packing favours the contact between CO_2 and the liquid solution obtaining the dissolution of the gaseous stream in the liquid. Then, a spray is produced from a 80 μm nozzle diameter and droplets are formed in the precipitator operated at atmospheric pressure (I.V. 3 dm^3). A flow of heated N_2 is also delivered to the precipitation with the scope of favouring the evaporation of the liquid solvent. SAA process efficiency is based on a two step atomisation process: primary droplets are formed at the exit of the nozzle. Then, CO_2 is released from the primary droplets and secondary, smaller droplets are produced [22]. More details on the SAA apparatus and experimental procedure were previously published [15-17].

The SAS laboratory apparatus consists of an HPLC pump equipped with a pulse dampener (Gilson, model 805) used to deliver the liquid solution, and a diaphragm high-pressure pump Milton Roy (model Milroyal B) to deliver supercritical CO_2. A cylindrical vessel with an internal volume of 500 cm^3 is used as precipitation chamber. The liquid mixture is delivered to the precipitator through a 200 μm diameter stainless steel nozzle. A second collection chamber located downstream is used to recover the liquid solvent. SAS apparatus and procedures were detailedly described elsewhere [4-6].

III - RESULTS AND DISCUSSION

Some authors measured the solubility of various dyes in supercritical CO_2 and in some cases solubility correlations were proposed [23-27]. As a general consideration, solubilities of the dyes range between $1*10^{-6}$ and $1*10^{-5}$ mole fraction. These solubility data were mainly produced to evaluate the possibility of supercritical dyeing, bur are of interest in our work since SAS micronization is based on the mutual miscibility between the organic solvent and the supercritical antisolvent; but, also requires the non-solubility of the solute in the antisolvent.

SAS micronization experiments

SB35, RD60 and SY56 were processed by SAS using NMP, DMSO and Ac. All SAS experiments were performed at 150 bar and 40°C; these process parameters were selected on the basis of solubility data binary systems solvent- CO_2 and of our experiences in this process [4-6].

In SAS experiments using SB35 in NMP (concentrations between 5 and 20 mg/mL), needle like long crystals were (10 ÷ 50 μm) produced together with nano-particles. An example of needle like long crystals is reported in **Figure 1**. SAS experiments on SB35 using Ac, instead, produced nano-particles ranging between about 50 and 100 nm, as shown for example in **Figure 2.** However the dye was recovered only in very low percentages in the precipitation chamber.
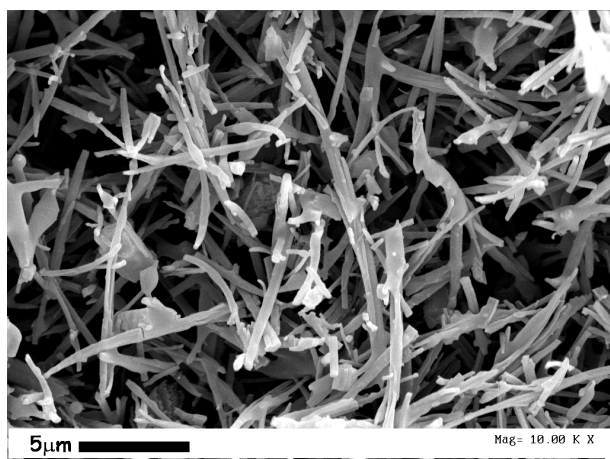

Figure 1: SEM image of SB35 crystals precipitated by SAS from NMP; the concentration of liquid solution is 20 mg/mL.
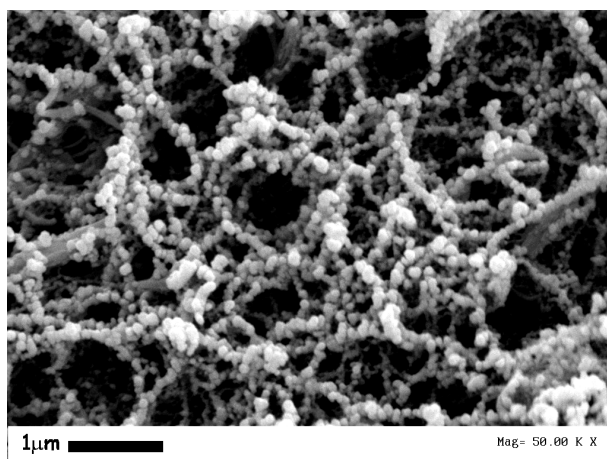

Figure 2: SEM image of SB35 nano-particles precipitated by SAS from Ac; the concentration of liquid solution is 5 mg/mL.

The experiments on RD60 in NMP were performed at concentrations between 1 and 15 mg/mL. Operating at concentrations of 1 to 2 mg/mL RD60 was completely extracted; at concentrations up to 15 mg/mL particles smaller than 100 nm were produced similar to those produced in SB35 experiments. Particle size distributions demonstrate that the mean particle size increase from about 50 nm to about 100 nm when the concentration in NMP is increased from 5 to 10 mg/mL. Particle size distribution also enlarges with the concentration increase. Using concentrations larger than 10 mg/mL, needle like long crystals were produced together with nano-particles. The yield of the micronization process, however, was low, ranging between 30 to 40 % by weight of the injected dye.

The behavior observed for RD60 in NMP was also obtained in SAS experiments performed using RD60 in DMSO: nano-particles at concentrations up to 15 mg/mL and needle-like crystals together with nano-particles, for concentrations larger than 15 mg/mL. The yield of the process was low.

SAS experiments performed on SY56 using DMSO were unsuccessful in producing micrometric particles; whereas, when Ac was used nanometric particles smaller than 100 nm were obtained; but almost all the material was recovered in the separator located downstream the precipitation vessel.

Summarizing, during the SAS experiments on RD60, SB35 and SY56, nano-particles were produced for all of them at some process conditions; but, in the case of SB35 and SY56 the dye was extracted due to an increase (co-solvent effect) of the dye solubility in supercritical-CO_2.

The possible effect of the concentration increase in producing a variation in the ternary system vapor- liquid equilibria (VLE) was previously observed and can be put in the framework of VLE interactions that can interfere with SAS micronization process [28, 29]

SAA micronization experiments

The conditions useful for SAA processing are: limited solubility between supercritical-CO_2 and the liquid solvent and efficient contact between the two phases (in the packed saturator). Moreover, liquid solvents like DMSO e NMP are not suitable for SAA processing since their low vapour pressures obstacle the droplets evaporation. Values of CO_2 solubility under pressure in different liquids are available only for a limited number of CO_2-liquid systems [30]. Due to the uncertainties in these solubility limits, we as a rule operate with a moderate excess of supercritical-CO_2 with respect to the evaluated saturation value.

The first selection of SAA parameters was based on our previous experience on this process [16, 17]. The complete set of SAA process parameters includes: saturator pressure and temperature, precipitator temperature, liquid solution concentration, feed ratio CO_2/liquid solution (R) and injector diameter. Saturator pressure, temperature and composition play an important role in the feasibility of the process since high-pressure vapour-liquid equilibria (VLE) of the ternary solvent-solute-CO_2 system are influenced by these parameters. Indeed, they define the possibility of the formation of a ternary homogeneous mixture in the saturator.

Experiments on SB35 were performed using Ac that is the only solvent that can be used for SAA in which this dye was a relatively good solubility (11 mg/mL). We fixed saturator temperature and pressure at 80 bar and 80 °C; precipitator temperature was set at 65 °C and SB35 concentration in Ac at 8 mg/mL. A series of experiments was performed varying R between 1.2 and 1.8. We obtained crystals with an ellipsoidal shape as shown in the SEM image reported in **Figure 3** and the crystal size and the crystal size distribution were influenced by the feed ratio. The mean dimensions of these crystals ranged from about 4 to 7 µm on the minor axis and from 9 to 12.5 µm on the major axis. Then, we fixed R = 1.2 and using the same process parameters as in the previous set of experiments, we studied the effect of the concentration on the morphology and shape of SB35 powders. Again we obtained ellipsoidal particles; but, at lower concentrations, nearly spherical crystals were obtained. An increase of the concentration of the liquid solution produced an enlargement of particles. At the lowest concentration studied (5 mg/mL) crystals with mean values of 4 to 6 µm on the minor axis and major axis were obtained, respectively. The results are reported in from of distributions, expressed of number of particles in **Figure 4.** In this case, form the point of view of the process, the precipitation was successful, but the dimensions of precipitates were larger with respect to our target.
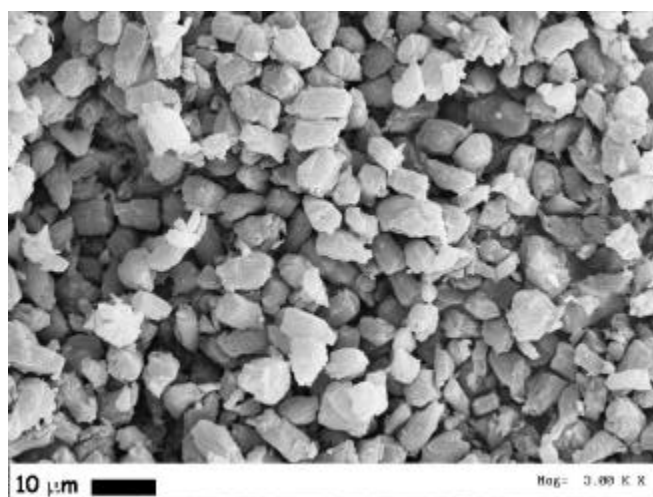

Figure 3 SEM image of SB35 precipitated by SAA, at a feed ratio of 1.2.
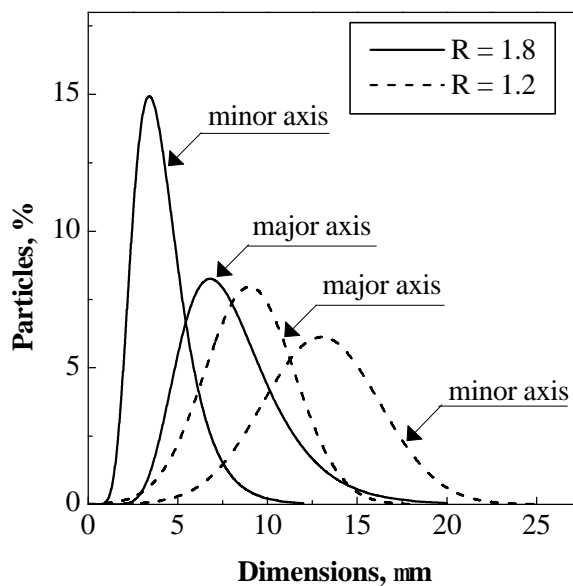
Figure 4 PSDs of SB35 produced by SAA varying the feed ratio (R) from 1.2 to 1.8.

DR60 was processed in Ac and the influence of the feed ratio, temperature and solute concentration was studied. The influence of the feed ratio was studied operating at 10 mg/mL, saturator pressure of 76 bar, saturator temperature of 82 °C and precipitator temperature of 62 °C. The experiments were performed at R-values ranging between 0.9 and 1.8. In all cases, the same morphology was observed: micrometric nearly spherical particles. Crystals dimensions decrease with increasing R as observed for the SAA experiments performed on SB35.

From the point of view of the diameter of the particles and of the regularity of produced particles (that are the major characteristics for the improvement of disperse dyes) the optimum R-value is 1.8 since in this case the mean diameter of DR60 particles is 0.6 μm and the size distribution ranges from 0.25 to 1.3 μm.

Some experiments were performed at the previously described SAA conditions, at 10 mg/mL and changing the precipitation temperature between 40 and 80 °C. The same morphology and similar particle size distributions were observed. Therefore, in this case the effect of temperature is negligible. Fixing R at 1.2, several experiments were performed at different concentrations of the liquid solution. The same morphology was observed in all the experiments: single particles having well defined boundaries were produced. Tests performed at 10 and 15 mg/mL showed that RD60 mean particle size increases with concentration from 0.9 to about 1.1 μm. This dependence of particle size on liquid concentration was also observed in previous works performed using SAA [17, 22]. It was attributed to an increase of liquid viscosity when concentration is increased. Therefore, larger droplets are produced and as a consequence larger particles are precipitated.

SY56 was processed in Ac and MeOH. The influence of these solvents and of the feed ratio was studied. Ac-SY56 solutions with feed ratios, ranging between 0.9 and 1.5 were tested, operating the saturator at 75 bar and 80 °C, the precipitator at 72°C and at a solute concentration of 30 mg/mL. In all the experiments very large crystals were obtained, indicating a substantial failure of the atomisation-precipitation process.

CONCLUSIONS

The results show that SAA and SAS micronization was completely successful only in the case of RD60. Moreover, it is possible to obtain products with very different characteristics. In general, SAS technique produces very small particles, indeed nanometric particles for all the tested dyes were produced; using SAA, instead, crystalline particles of micrometric size were obtained. But, we obtained a low yield for SAS micronization because of the enhancement of the solubility of the dyes

in supercritical-CO_2 due to the co-solvent effect; whereas, the yield of SAA process was not affected by this problem.

Therefore, from a general point of view, the results obtained can be considered complementary: when nanometric particles of DR60 are required SAS is the technique of election, though a relatively low yield characterizes the process; when micrometric particles of DR60 are of interst, SAA process is with no doubt the most effective.

REFERENCES

[1] WEBER, A., NOLTE, C., BORK, M., KÜMMEL, R., Proceedings of the 6t[th] Meeting on Supercritical Fluids, Chemistry and Materials, **1999**, p. 181.

[2] THIERING, R., DEHGHANI, F., DILLOW, A., FOSTER, N.R., Journal of Chemical Technology and Biotechnology, Vol. 75, **2000**, p. 29.

[3] FORTER-BARTH, U., TEIPEL, U., KRAUSE, H., Proceedings of the 6th Meeting on Supercritical Fluids, Chemistry and Materials, **1999**, p. 175.

[4] REVERCHON, E., J. Supercrit. Fluids, Vol. 15, **1999**, p. 1.

[5]REVERCHON, E., DE MARCO, I., DELLA PORTA, G., J. Supercritical Fluids, Vol. 23, **2002** p. 81.

[6] REVERCHON, E., DE MARCO, I., DELLA PORTA, G., International J. of Pharmaceutics, Vol. 243 (1-2), **2002**, p.83.

[7] PALAKODATY, S., YORK, P., HANNA, M., PRITCHARD, J., Proceedings of the 5th Meeting on Supercritical Fluids, Vol. 1, **1998**, p. 275.

[8] HANNA, M., YORK, P., Patent WO 95/01221, **1994**.

[9] DEBENEDETTI, P.G., LIM, G.B., PRUD'HOMME, R.K., European Patent EP 0 542 314, **1992**.

[10] WEBER, A., WEISS, C., TSCHERNJAEW, J., KÜMMEL, R., Proceedings of the High Pressure Chemical Engineering, **1999**, p. 235.

[11] WEIDNER, E., STEINER, R., KNEZ, Z., High Pressure Chemical Engin., **1996**, p. 223.

[12] KNEZ, Z., WEIDNER, E., High pressure technology, fundamentals and applications, Vol. 9, **2000**, p. 587.

[13] SIEVERS, R.E., KARST, U., MILEWSKI, P.D., SELLERS, S.P., MILES, B.A., SCHAEFER, J.D., STOLDT, C.R., XU, C.Y., Aereosol Sci. Tech., Vol. 30, **1999**, p. 3.

[14] SIEVERS, R.E., HUANG, E.T.S., VILLA, J.A., ENGLING, G., BRAUER, P.R., J. Supercrit. Fluids, Vol. 26 (1), **2003**, p. 9.

[15] REVERCHON, E., Process for the production of micro and/or nano particles, Swiss patent 1209/01, **2001**.

[16] REVERCHON, E., Ind. Eng. Chem. Res., Vol. 41, **2002**, p. 2405.

[17] REVERCHON, E., SPADA, A., Powder Technol., in press.

[18] JUNG, J., PERRUT, M., J., Supercrit. Fluids, Vol. 20, **2001**, p. 179.

[19] FOSTER, N., MAMMUCARI, R., DEHGHANI, F., BARRETT, A., BEZANEHTAK, K., COEN, E., COMBES, G., MEURE, L., NG, A., REGTOP, H. L., TANDYA, A., Ind. Eng. Chem. Res., Vol. 42, **2003**, p. 6476.

[20] GAO, Y., MULENDA, T.K., SHI, Y.F., YUAN, W.K., J. Sup. Fluids, Vol. 13, **1998,** p. 369.

[21] HONG, L., BITEMO, S.R., GAO, Y., YUAN, W.K., Proceedings of the 5th International Symposium on Supercritical Fluids, **2000**.

[22] REVERCHON, E., SPADA A., Proceedings of the 6th International Symposium on Supercritical Fluids, Vol. 3, **2003,** p. 1665.

[23] GORDILLO, M:D., PEREYA ,C., MARTINEZ DE LA OSSA, E.J., J. Sup. Fluids.,Vol. 27 **2003**, p. 31.

[24] LEE, J. W., MIN, J. M., BAE. H. K., J. Chem. Eng. Data, Vol. 44, **1999**, p. 684.

[25] LEE, J. W., PARK, M., BAE, H. K., Fluid Phase Equilibria, Vol. 173, **2000**, p. 277.

[26] SAFA ÖZCAN, A., CLIFFORD, A. A., BARTLE, K. D., J.Chem. Eng. Data, Vol. 42, **1997**, p. 590-592.

[27]GAO, Y., MULENDA, T. K., SHI, Y., YUAN, W., J. Sup. Fluids, Vol. 13, **1998**, p. 369.

[28] REVERCHON, E., Proceedings of the 4th Internat. Symp. On High Pressure Process Technology and Chemical Engineering, BERTUCCO, A., (Ed.), **2002**, p. 1.

[29] REVERCHON, E., DE MARCO I., J. of Supercritical Fluids, in press.

[30] OHE, S., Vapour-Liquid Equilibrium Data at High Pressure, **1990**.