USE OF SUPERCRITICAL CO_2 AS DISSOLVED GAS FOR THE ATOMIZATION OF ETHANOL

Giuseppe Caputo, Sara Liparoti, Renata Adami and Libero Sesti Osséo

Dipartimento di Ingegneria Industriale, Università degli Studi di Salerno.
Via Ponte Don Melillo, 84084 Fisciano (SA), Italy Email: gcaputo@unisa.it

ABSTRACT

Supercritical dissolved gas atomization (SDGA) is an atomization process in which carbon dioxide at temperatures and pressures above its critical point is used as atomizing gas. In this work SDGA has been experimentally studied when ethanol is used as the liquid to be atomized. The spray characteristics in terms of droplets size and distribution have been investigated using a droplet size analyzer based on a laser diffraction method.

Very narrow droplet size distributions were produced down to 2.5 µm. The main parameter that influences the droplets size is the gas to liquid mass ratio. From the point of view of the atomization mechanism, mean droplet diameter is mainly influenced by the two phase (gas liquid) flow formed within the atomization nozzle. The overall analysis of the experimental data confirms that dissolved gas atomization allows the formation of micrometric droplets that can be useful in fine-particles production processes.

1. INTRODUCTION

The transformation of liquids into sprays is important in several industrial processes such as agriculture, combustion, liquid-metal processes, powders production, spray drying, coating and painting, production of health-care products. Therefore, the process has been extensively studied, from theoretical and experimental point of view [1]. The selection of a particular atomization method involves the discussion of several factors that may include economic considerations, scale of production, the physical and chemical properties of the droplets/particles to be produced and the dimensions and morphologies of the droplets/particles desired. The atomization mode is also strictly connected to the application of the spray process and to the range of droplets diameter of interest for the given application. Among the various atomization processes, the gas atomization has received attention for its potentiality. Gas atomization is a special twin fluid atomization, in which a secondary fluid (atomization gas) is used to break-up the liquid jet into droplets. The twin fluid atomization method can be classified into external and internal mixing. Most airblast atomizers belong to the external mixing category, in which the bulk liquid is first transformed into a jet or a sheet, before being exposed to the atomization gas flowing at high velocity. When internal mixing is used, the contact between the gas and the liquid takes place within the atomizer body. In literature, three categories of internal mixing atomization mode are reported: effervescent atomization [1,2], flash atomization and dissolved gas atomization [1].

The basic principle of the effervescent atomization is to inject a two-phase bubbly flow through a discharge orifice. The liquid is "squeezed" by the gas bubbles into thin shreds and ligaments, which are further shattered into small drops by the rapid expansion of gas bubbles. This phenomenon occurs immediately downstream of the discharge orifice due to the sudden pressure drop [2]. In flashing atomization, a liquefied propellant is dissolved into the liquid to be dispersed [3]. Due to the high vapor pressure of the propellant, after the discharge of the solution into atmosphere, the propellant is transformed in a gas by "explosion", causing the formation of liquid droplets.

Dissolved gas atomization is widely used in commercial spray cans (aerosols, perfumes, etc.). It relies on a dissolved gas coming out from a liquid to form bubbles, therefore, this technique is applied only to a limited range of liquids that can hold significant quantity of dissolved gas. Both the effervescent and the flashing atomization can contribute to dissolved gas atomization. Indeed, the dissolved gas at the exit orifice nucleates to form gas bubbles, as in effervescent atomization or can also rapidly evaporate by flashing [4].

The mentioned limitations of dissolved gas atomization can be overcome using carbon dioxide at supercritical conditions as the atomization gas, due to its large miscibility in most of the organic liquids, among them solvents and fuels. The technique described is called Supercritical Dissolved Gas Atomization (SDGA) [5]. The solubility of supercritical CO_2 in organic liquid solvents can vary from 0.1 to 0.7 mole fraction and more, to take advantage of this characteristic, a solubilisation device can be used to put in contact CO_2 and the liquid before the atomization takes place. Therefore, the atomization apparatus is based on the use of a packed saturator characterized by a high specific surface and large residence times. In the saturator, supercritical CO_2 dissolves in the organic solvent before the atomization through a thin wall injector. The atomization is particularly efficient since CO_2 is released from the internal of the droplets and enhances their fragmentation.

The concept of SDGA has been applied in Supercritical Assisted Atomization process (SAA) technique, developed for the production of fine particles of pharmaceuticals and chemical products [5].

In this work SDGA technique has been explored, using ethanol as the liquid to be atomized. Indeed, ethanol is an important solvent in a large variety of pharmaceutical and common good processes aimed at the production of micrometric particles.

Besides being of the practical importance of ethanol, this study is aimed to investigate the mechanism of droplets formation and particularly the role played by the two-phase flow at the nozzle exit. This work is a part of a larger study on dissolved gas atomization that comprises also the study of the atomization of water as a solvent [5].

The effect of gas-to-liquid mass ratio (GLR), nozzle diameter, gas velocity and atomization pressure on drop mean size and size distribution has been studied.

2. MATERIALS AND METHODS

Ethanol (EtOH, purity 99.8%) were supplied by Sigma–Aldrich and Carbon Dioxide (CO_2) (purity 99%) was purchased by SOL.

The SDGA apparatus is illustrated in Fig 1. It mainly consists of two feed lines, used to deliver the CO_2 and the liquid to a mixing vessel. Carbon dioxide, stored in a vessel (C), is preheated in a water bath and delivered to the mixer (M) by a volumetric pump (P1). The liquid is delivered to the mixer by a membrane pump (P2) from a 500 mL graduated cylinder

(L). The two streams are fed to the mixer through a three-way connection. The mixer is a high-pressure vessel with an internal volume of 0.15 dm^3 heated by thin band heaters and is packed with stainless steel perforated saddles with a high specific surface area. It provides a large contacting surface and an adequate residence time (3-5 min depending on the flow rates) for the mixing of the liquid and supercritical CO_2. Therefore, an efficient, continuous solubilisation of supercritical CO_2 in the liquid solution is allowed. As a result, CO_2 dissolves in the liquid and tends to form a fluid phase near the saturation limit in terms of the operating conditions of temperature and pressure. The pressure in the mixer is measured by a pressure gauge mounted on the top of the mixer. The liquid-gas solution at the exit of the mixer is sprayed into the atmosphere using a single plain orifice. The orifice has a diameter of 120 μm and length to diameter ratio of 6.67. The orifice dimensions were selected to obtain pressure values above the critical pressure of CO_2 (7.38 MPa) at the given flow rates of gas.

The characteristics of the spray were investigated using a laser diffraction technique. A Mastersizer S (Malvern Instruments, Malvern, U.K.) particle size analyzer fitted with a 300-mm-focal-length lens was used to measure the spray droplet size distribution. This provides a lower droplet size boundary of about 0.5 μm. The technique is based on measuring the scattered light intensity caused by the drops as they pass through the analyzer sampling area using a series of semicircular photodiodes housed in the detector unit. The effect of CO_2 on the refractive index of the liquid droplets was not considered because the gaseous CO_2 is transparent to laser light. The instrument-reported obscuration was used to indicate the presence of multiple scattering due to dense spray. Instrument software compensates for multiple scattering and it works satisfactorily up to 95% obscuration (according to manufacturer). Droplet size measurements were carried out at distances of 7.5 and 13.5 cm downstream the nozzle exit with the laser beam passing through the centre line of the spray. The recirculation of fine droplets was kept to a minimum by absorbing the spray on an adsorbent located about 40 cm downstream of the nozzle exit. Each experiment consisted of a set of five consecutive analyses, each composed of 10000 data points acquired by the analyzer. In the atomization literature, the Sauter mean diameter (SMD) is frequently used to represent the mean droplet diameter of a spray because it expresses the fineness of a spray in terms of the surface area produced by the spray. The SMD is defined as the volume-to-surface mean diameter. The amplitude of the droplet size distribution was evaluated using the SPAN parameter, defined as

$$SPAN = \frac{D_{0.9} - D_{0.1}}{D_{0.5}}$$

where $D_{0.9}$, $D_{0.1}$, and $D_{0.5}$ are the droplet diameters of 90%, 10% and 50% by volume of the drops in the population.

When pure ethanol is injected, the plain-orifice atomizer produces only a solid jet of liquid. With the addition of SC-CO_2, the jet disintegrates into a fine spray in which it is not possible to visually observe any phase separation between gas and liquid. The spray appears like a homogeneous jet with well defined conical shape and in a full developed atomization regime.

The common fluid flows encountered in gas assisted spray atomization are classified in three main regimes: bubbly flow, slug flow (also called transition regime) and annular flow. In the bubbly flow that occurs at very low GLR single bubbles form a "train" through the exit orifice. As the jet discharges from the orifice the bubbles expand rapidly and shatter the jet into ligaments and drops. Increasing GLR, the number of bubbles increases until a GLR is reached; above which the bubbles start to coalesce and form voids in the liquid flow.
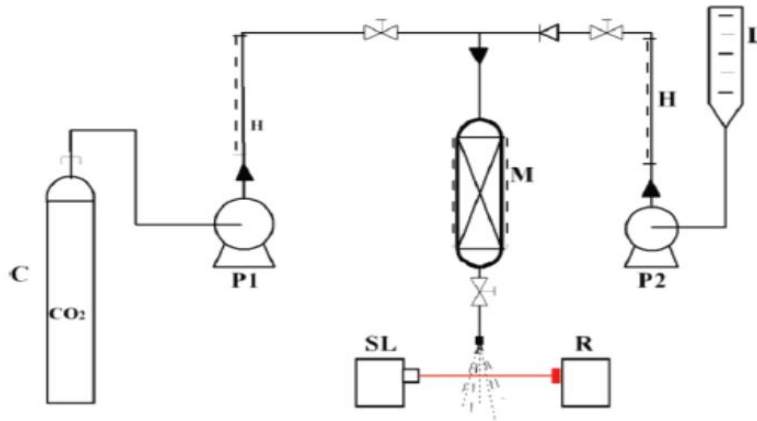
Figure 1. SDGA apparatus: C, CO_2 vessel; P1, CO_2 pump; M, mixer; H,
electric heating; L, liquid vessel; SL, laser source; R, receiver.

This phenomenon marks the onset of the slug-flow regime, characterized by unsteadiness due to voids. A further increase in GLR suppresses instabilities and a new steady flow is formed in which a central round jet of gas is surrounded by a thin annular sheet of liquid. At very high values of GLR, as in the case of this work, the two phase flow inside the nozzle is fully dispersed and discharges in the form of drops suspended in the atomizing gas [2]. At these conditions, the jet appears like a gaseous plume in which no phase separation can be visually observed, but it has a white colour as a result of visible light scattering produced by the droplets. In addition, in the case of supercritical atomization, liquid drops contain carbon dioxide that after phase separation may contribute to the formation of smaller droplets.

3. RESULTS AND DISCUSSION

All the experiments were performed at steady-state conditions with the injector spraying into the atmosphere. The spray characteristics reported here include the mean droplet size (SMD) and the droplet size distribution curves. The variations with the GLR, temperature and injector downstream distance were studied. Experimental observations are presented in this work as function of GLR, because it is the most relevant parameter controlling this atomization process.

3.1 Ethanol-CO_2 Phase Equilibria

Knowledge of the phase equilibrium is fundamental in dissolved-gas atomization because it provides information on the maximum quantity of gas that can be dissolved in the liquid.

The compositions of the liquid and gas phases can be determined from thermodynamic phase diagrams representing, on a pressure-mole fraction (p-x) diagram, the miscibility curve of the binary system CO_2-solvent. Miscibility curves of the system CO_2-ethanol [6] at 40 and 80 °C were reported in Fig. 2. To understand the role played by dissolved CO_2 in the atomization process, in Fig. 2 the operating points in term of GLR along with the solubility data are reported. As shown in the figure, the operating points have been properly selected to cross the miscibility curves. Thus, in the hypothesis that equilibrium conditions hold in the saturators, the system changes from two-phase to one-phase flow. In this way we can study the effect of

a change of phases on the droplet size and, moreover we can study the role played by the dissolved gas on the atomization.
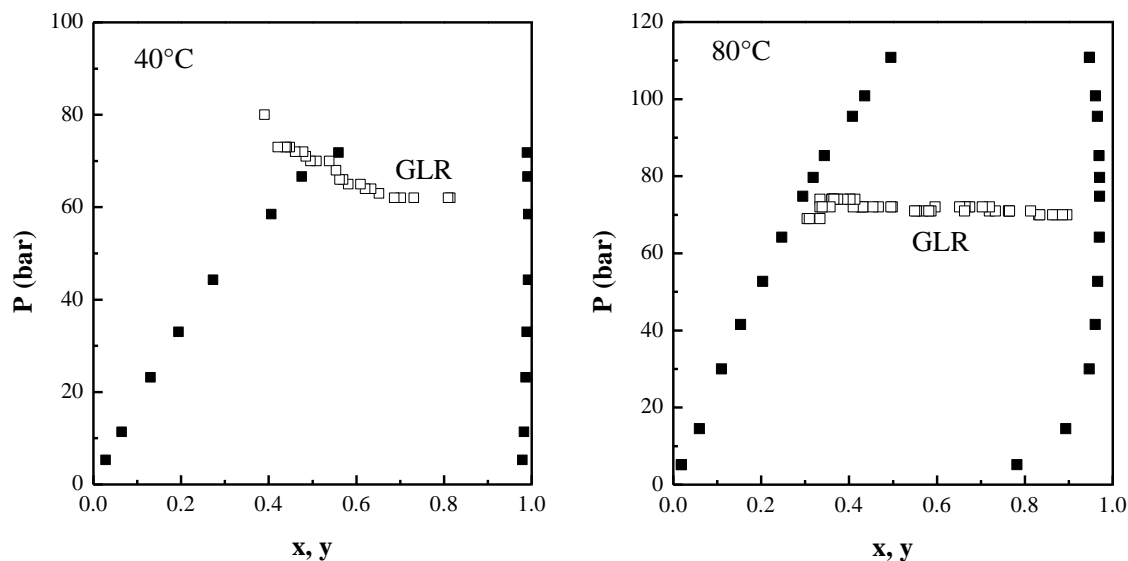

Figure 2.   VLE diagrams of the system Ethanol-CO_2 at 40°C (left) and 80°C (right).

3.2 Influence of Atomizing Gas-to-Liquid Ratio

It is common practice to present droplet size distribution data as a function of the gas-to-liquid mass flow rate ratio (GLR). SMD data were acquired for GLR values from 0.7 to 8 to explore a large range of flow conditions. The experiments were performed temperature of the mixing vessel of 80°C and 40°C. Because the experiments were performed at constant CO_2 flow rate of 14 g/min, an increase of in the GLR was necessarily accompanied by a decrease in the liquid flow rate from 3 to 42 ml/min.

As mentioned before, the experiments have been carried out at GLR that allowed to form a two phases (liquid + gas) or one-phase flow. Therefore, it has been possible to study the effect of the change of phase on the size of the droplets. Representative examples of the effect of the GLR and temperature on SMD are reported in Fig. 3.

The results show that SMD is a non-linear function of GLR: drop size decreases rapidly as GLR is increased to around 2.5-3; then, it decreases at a slower rate with further increase in GLR. Considering the region of the diagram at low GLR, a change of the slope can be observed at GLR of about 0.5 in the diagram at 80°C and about 0.9 in the diagram at 40°C that corresponds to CO2 molar fractions of 0.3-0.5, respectively. The temperature has a minor effect, but a slight decrease of the size was detected when the temperature was increased from 40 to 80°C.

To understand this behavior the miscibility curves of Fig. 2 must be taken into account. Indeed, the mole fraction values of 0.3 and 0.5 corresponds, for the curves at 40 and 80°C respectively, to the transition points from the two-phase region to the one-phase region. Thus, the change of slope shown in Fig. 3 is due to the phase change. Particularly in the curve at

40°C of Fig. 2, it is evident a step increase of the droplet size in correspondence of the phase change, likely due to the loss of the undissolved gas phase.
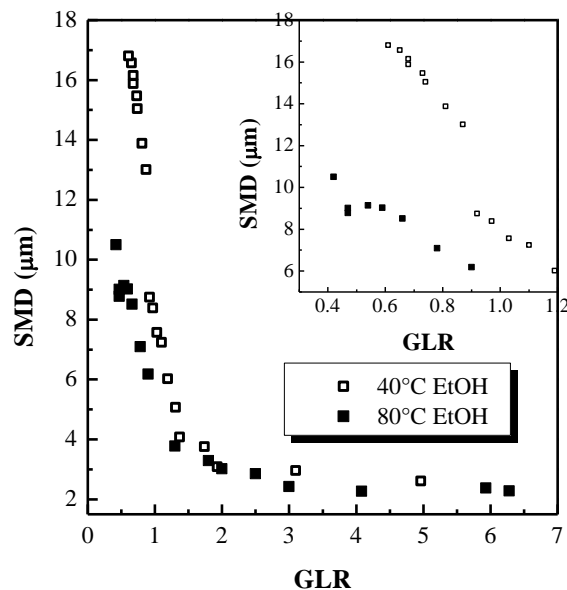

Figure 3. Influence of the GLR on the SMD of the droplets at different temperatures. CO_2 flow rates = 16 gr/min. Exit orifice diameter = 120 μm; axial distance from nozzle = 13.5 cm.

It is interesting to observe the size distribution of the droplet when the mixer-saturator operating conditions are selected to be inside or outside the two-phase region. Fig. 4 reports two representative examples of droplet size distributions (by volume) with respect to selected operating conditions, respectively inside and outside the two-phase region. The droplets produced starting from mixer-saturator operating condition resulting inside the two phase region, show a well-shaped and narrow size distribution. On the contrary, the droplets formed starting from mixer-saturator operating condition resulting inside the one-phase region, have a larger mean diameter and are characterized of two main sizes (bi-modal behavior).

The experiments also clearly show a continuous increase of the percentage of smaller droplets at higher GLR, if operation is performed in the two-phase region.

The basic atomization mechanism has not yet been studied in detail however, since both liquid and atomizing gas exit through the same orifice, an important role is played by the area available for the liquid flow. In the presence of the gas this area is reduced, causing the liquid to be discharged at a higher velocity. At the same time the liquid is "squeezed" by the gas bubbles into thin shreds and ligaments which are further shattered into small drops by the rapid expansion of gas bubbles which occurs immediately downstream of the discharge orifice due to the sudden pressure drop. In this mechanism the major role is played by the undissolved part of the gas, while the dissolved one has the role to reduce the density and viscosity of the liquid. From the data acquired in this work, it seems that the presence of undissolved gas is fundamental to obtain fine atomization. Indeed, operations at low GLR, in the region of one-phase flow do not allow to obtain small droplets. On the contrary, the best conditions for atomization falls in the two phase region at relatively lower gas to liquid ratio.
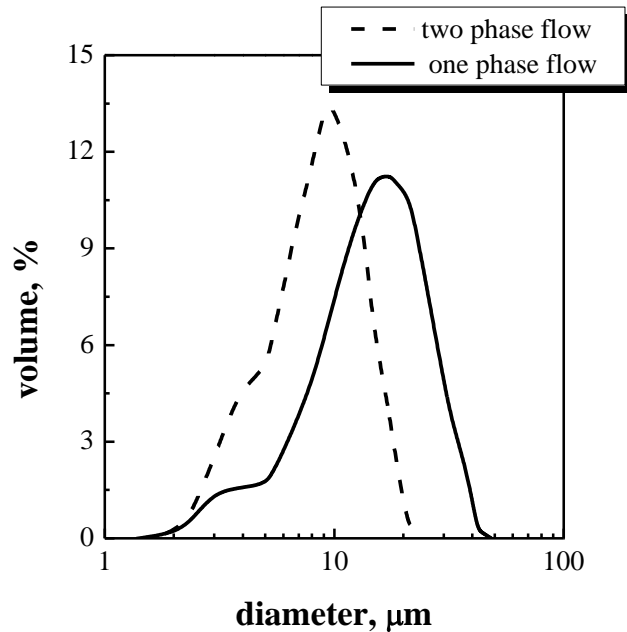
Figure 4. Droplet size distribution for experiments carried at 40°C, at GLR=0.92 (two-phase flow) and GLR=0.68 (one-phase flow).

4. CONCLUSIONS

It has been shown that supercritical dissolved gas atomization has the potentiality to produce very fine spays of ethanol with droplet dimensions down to about 2 μm and with very narrow droplet size distributions. Droplets diameters typical of SDGA are usually not attainable with the other twin-fluid atomization processes at comparable pressures. For what concerns the atomization mechanism, SDGA of ethanol is a complex process in which gaseous CO_2 acts on the liquid break-up with two different mechanisms: 1) by squeezing the liquid into ligaments as it flows through the injector orifice and 2) by exploding downstream of the nozzle exit to shatter these ligaments producing small droplets. Smaller droplets are obtained at high gas rates in the two phase region of the system CO_2-ethanol. On the contrary, within the one-fluid phase region large droplets with bimodal distribution are formed and a sudden increase of droplet size was observed as large as 4 μm.

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