GENERATION AND EFFECTS OF HIGH-INTENSITY ULTRASOUND IN SUPERCRITICAL FLUIDS

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Abstract
Mass transfer processes in supercritical fluid extraction (SFE) can be enhanced by power ultrasound. This is probably the unique practical way to produce a deep agitation under the high-pressure conditions of SFE because the use of mechanical stirrers is unable on an industrial scale. For the generation of the ultrasound a 20kHz sandwich-type piezoelectric transducer for a power capacity of about 100W was designed, constructed and characterized. To drive and keep it at resonance during the trials, a specific electronic system was developed. This system permits to generate constant output power in the fluid under conditions ranging from the normal gas regime (1bar and 20ºC) up to the supercritical regimen (280bar and 55ºC). The feasibility of the ultrasonic technology to assist supercritical extraction processes was demonstrated in almond oil extraction where improvements of about 30% in the kinetic of the process were reached.

Introduction

Ultrasonic energy is a tool with a wider application potential in chemical, pharmaceutical and food industries. Supercritical fluid extraction (SFE) processes assisted by power ultrasound represent a clear example of this potential.

The term supercritical fluid (SCF) can be applied to any fluid that is compressed to a pressure greater than its critical pressure, P_C, and heated to a temperature above its critical temperature, T_C [1]. At temperatures $T>T_C$ the substance cannot be liquefied by increase the pressure. Fluids under supercritical conditions exhibit enhanced dissolving power and have transport properties that favor high extraction capabilities. In particular, supercritical fluids have a relative lower viscosity and higher diffusivity than liquid solvents. Therefore, they can penetrate into porous solid materials more effectively than liquid solvents [2].

One emergent application of power ultrasound in chemical and food industries is the enhancement of mass transfer in different processes. In this way some authors [3,4,5] recently started with the study and development of the application of ultrasonic energy in supercritical fluid extraction processes. Due to the environmental regulations, supercritical CO_2 has grown as an alternative "green" solvent to conventional solvent methods in many analytical and industrial processes. This is because it presents important advantages (cheap, recyclable, non-toxic, non-flammable, improves product quality and recovery). A difficulty when applying a supercritical fluid as solvent for extraction is the slow kinetics of the process. The traditional way to accelerate extraction processes is the application of a mechanical agitation system. The use of power ultrasound represents a potential efficient way to produce deep agitation, enhancing mass transfer processes.

Additionally ultrasonic waves can be used for determination of the critical state of the fluid by using resonance methods and through transmission techniques [6,7,8,9,10,11].

The aim of this work was to study the generation and effects of ultrasound on particulate almond oil extraction kinetics by using supercritical CO_2.

Experimental set-up and method

The basic scheme of supercritical extraction facility assisted by power ultrasound is shown in Figure 1. It consists of one high-pressure vessel with 5L of capacity, two separation units (a cyclone and a decanter), a diaphragm pump and different sensors for temperature, pressure and flow rate measurements. The fluid employed in the extractor was supercritical CO_2 (P_C=7.38MPa; T_C=31,1ºC; ρ_C=0,468g/mL) [12,13]. This fluid is the most commonly used for SFE applications due to their properties as well as its availability in high purity at low cost. The ultrasonic system includes : a) two different power piezoelectric sandwich transducers working at 18kHz and 20kHz, respectively, with a power capacity of 100W; b) an impedance matching box and a power generator unit composed by a power amplifier and a resonant frequency control system to keep constant the power applied to the transducer. This control system allows the parameters of the driving signal to be stored during the trials (resonant frequency, impedance, voltage, current phase and power). The pressure and the density of the supercritical CO_2 inside the reactor were also measured and stored into a computer. Therefore, the behavior of the ultrasonic transducer was followed during all the process. That means, from the initial instant in which the gas CO_2 was introduced into the extractor unit (at 1bar and 20ºC), during the time needed to reach the operational conditions (at 280bar and 55ºC), as well as during the extraction process. The time for each trial was of about 8 hours and 30 minutes.

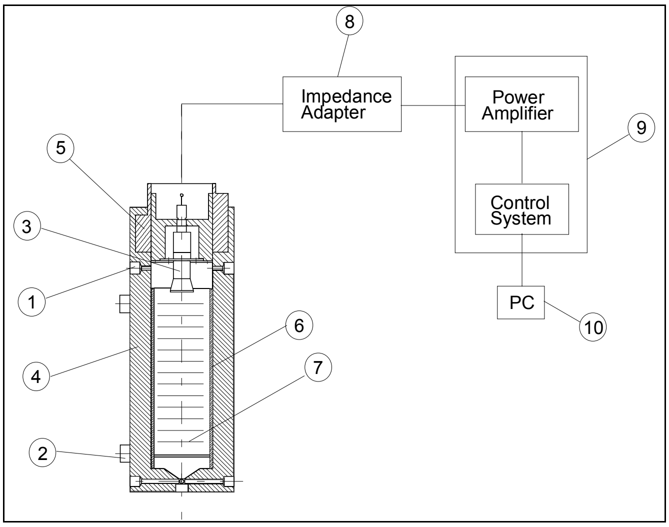

Figure 1. Scheme of the SFE reactor assisted by power ultrasound. 1) SCF input, 2) SCF output, 3) power transducer, 4) extractor, 5) upper lid of the extractor, 6) vessel, 7) acoustic field, 8) impedance adapter, 9) power generator and 10) computer.

Experimental procedure

Before to study the effects produced by the ultrasonic energy on the extraction kinetics in supercritical conditions, the behavior of the ultrasonic system was studied in water. This is due to the similarity between the characteristic impedances of the water (≈ $1,48x10^6$ Rayls at 20ºC and 1atm) and the supercritical CO_2 (≈ $5,9x10^5$ Rayls at 55ºC and 280bar). Therefore, the cylindrical vessel was filled with water. The head of the transducer was completely submerged in it and the resonance modes of the set were measured in an Impedance Analyzer HP4194A.

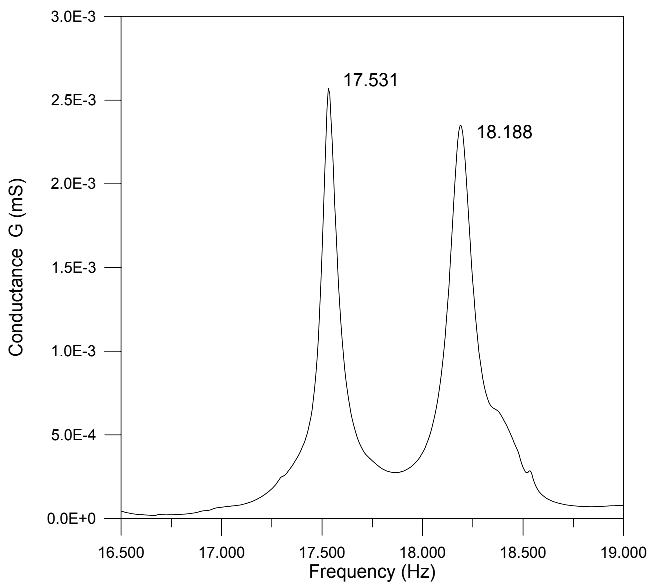

Figure 2. Modes propagating through the cylindrical rigid vessel filled with water

In Figure 2 the modes propagating through the cylindrical rigid container filled with water are shown. Both modes were also obtained considering the exact longitudinal and shear wave equations in a tube coupled with the equations describing the propagation inside the liquid [14]. The frequency of about 18200Hz corresponds to the resonant frequency of the transducer measured in air.

Next an experimental assembly (see Figure 1) based on the integration of the power transducer inside the extractor, inserted on the upper lid of the vessel, was designed and developed [4]. The transducers operated satisfactorily under high-pressure conditions along all the extraction time, although instabilities appeared during the pressurization stage, due to the changeable properties of the medium in this part of the process.

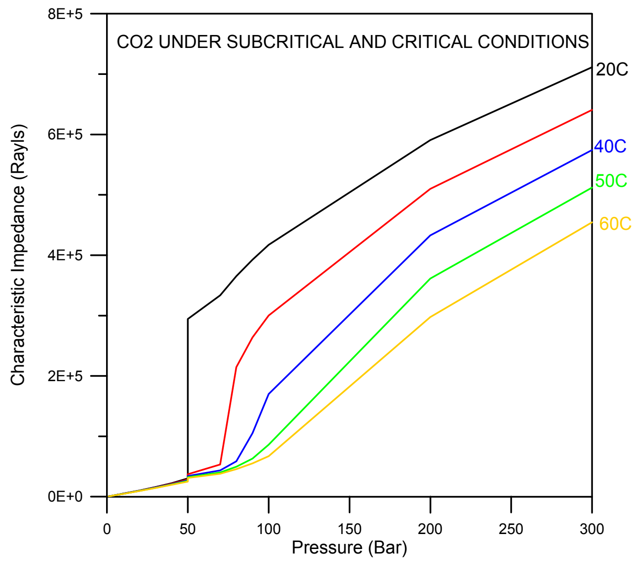

Figure 3. Characteristic impedance of the CO_2 under subcritical and supercritical conditions

The high-pressure values reached in the extractor during the process affected the frequency and the electrical impedance of the modes shown in Figure 2. In this case the lower mode was located at 18100 Hz with a Z_e≈1000Ω, whereas the upper mode was at 18350Hz with a Z_e of 400Ω.

The frequency control system allows keeping constant the power input applied to the transducer. This is an essential device because of the changes of the SCF characteristic impedance. In fact it can be seen in Figure 3 the variation of the characteristic impedance of CO_2 with the pressure at different temperatures (from 20ºC up to 60ºC).

The evolution of this parameter plotted below and above of the operational conditions, shows that it varies in the wide range of about from 500 Rayls up to $5x10^5$ Rayls. The data stored in the computed from both, the transducer and the supercritical CO_2 were analyzed. In this way, Figures 4, 5 and 6 present respectively the evolution in the SCF extractor of the transducer impedance, the pressure and the density of the CO_2 during trials. In all of them, a power of 50W was applied to the transducer.

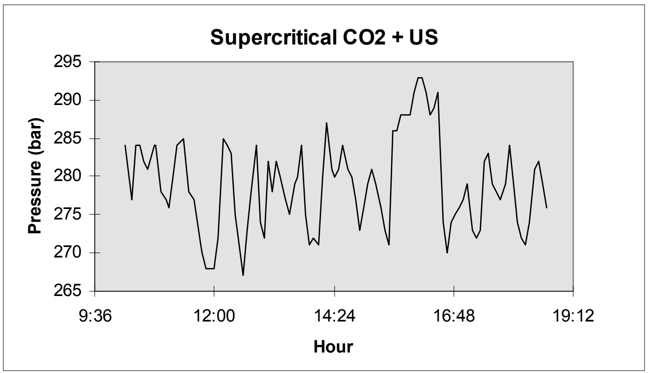

Figure 4. Evolution of the pressure inside the SCF extractor versus time during the SFE process

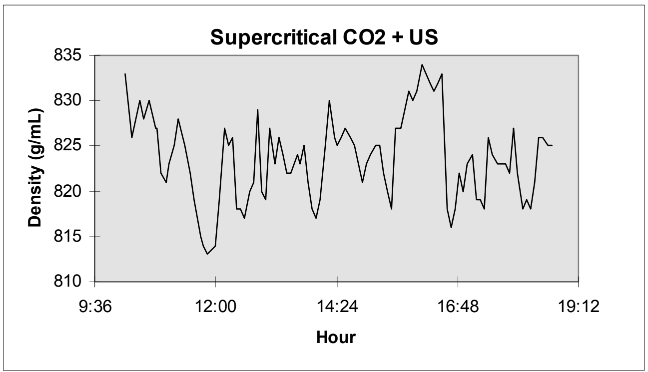

Figure 5. Evolution of the density inside the SCF extractor versus time during the SFE process

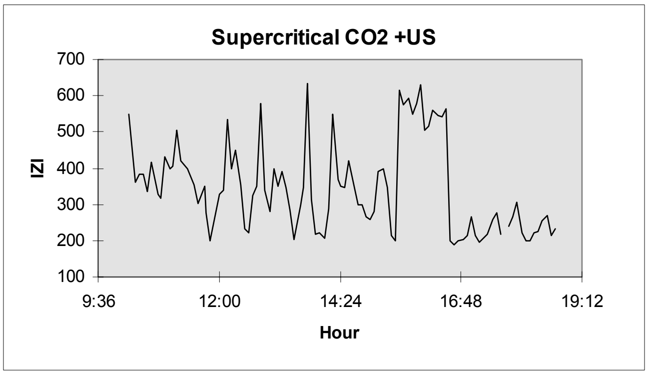

Figure 6. Evolution of the electrical impedance of the transducer inside the SCF extractor versus time during the SFE process

Although the temperature and the flow rate of the CO_2 also varied during the process, their fluctuations were less significant than those detected in the pressure and the density. From the graphics it is clear that a narrow correlation exists between the pressure and the density of the fluid. In parallel, the fluctuations detected in the electrical impedance of the transducer also suggest that some kind of correlation exist with the characteristic impedance of the supercritical CO_2.

Therefore, it can be said that the transducers can works, simultaneously, as a probe and as a power source. As a probe for monitoring operational conditions of supercritical process, and as power source to enhance the mass transfer processes.

Results and Discussion

The experiments on the effects of power ultrasound in supercritical fluids were carried out through the study of the mass transfer processes in SFE. In particular on the almonds oil extraction kinetics by using supercritical CO_2. For this purpose grounded almonds (Marcona comuna) were used in this investigation. The raw almonds were blanded, pealed, dried and grounded before the extraction process.

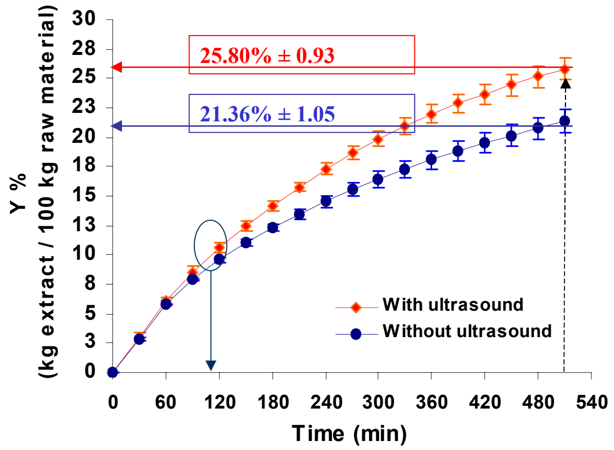

Figure 7. Effect of ultrasound on the yield of extracted oil from particulate almonds.

SFE was performed in all cases with 1500 g of grounded almonds. The solvent was CO_2 99.9% purity. The pressure, the temperature and the flow rate of the process were 280bar, 55ºC, and 20kg/h, respectively. To analyzed the effect of the ultrasonic waves in all trials were carried out with (+US) and without (-US) ultrasound application and replicated twice. The experimental curves on the yield extracted were fitted to several mathematical modes and analyzed in [15].

At the end of the extraction time (see Figure 7), the yield of the oil was significantly increased by using ultrasound. The improvement was about the 21%, which also means that the process was speeded up. In fact, to obtain the same amount of yield the ultrasound reduces the treatment time in about 35%.

Conclusions

In this paper the generation and effects of power ultrasound on the SFE has been study.

The power ultrasonic system developed has worked satisfactorily in two different ways: a) as a probe for monitoring the operational conditions of the supercritical CO_2 in the extractor during all the process; and b) as an efficient power agitator capable to accelerate the almond oil extraction kinetics in about 35% which represents a very promising result.

For future work specific stepped plate transducers for a 20-50 kHz frequency range and with higher power capacities will be developed for industrial purposes in bigger volume extractors.

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