Proceedings of 20th International Congress on Acoustics, ICA 2010

23-27 August 2010, Sydney, Australia

Effect of High Power Ultrasounds on mass-transfer zone in Supercritical Fluid Extraction processes

Miguel Blasco (1), José García-Reverter (1), Elvira Casas (1) and Enrique Riera (2)

(1) ainia, technological centre, Technological Park of Valencia, Benjamin Franklin 5-11, 46980 Paterna (Valencia), Spain
www.ainia.es, +34 96 136 60 90
(2) Power Ultrasonics Group, CSIC, Serrano 144, 28006 Madrid, Spain

PACS: 43-35-Zc

ABSTRACT

Supercritical fluid extraction (SFE) is a recent technology that is based on the solvent power that some fluids exhibit under pressure and temperature above certain values named as critical point. This process, using supercritical CO_2 as solvent, has gained wide acceptance in the last decades, because of its advantages compared to conventional solvent extraction ones (high selectivity, non toxic, inert, suitable to extract thermolabile substances, cheap, recyclable). One of the main difficulties of SFE is to achieve favourable kinetics due to the fact that mechanical stirring is not easyly applied to an extractor vessel operating at high pressures. In this context, an interesting alternative is the use of power ultrasound. Ultrasonic radiation represents an efficient way to enhance mass transfer processes, because of some mechanisms such as microstirring, compressions and decompressions in the material, heating, and/or cavitation. Previous works of this research group pointed out the feasibility of integrating an ultrasonic field inside a supercritical extractor without losing a significant volume fraction. Moreover, a new self-controlled prototype, robust enough to fulfill industrial requirements to produce it commercially was developed and tested under supercritical conditions, giving rise to a non-antecedent patent. This new ultrasonic device led to notable enhancement both on extraction yields at certain times and on required time to achieve a certain extraction yield when applied on SFE almond oil. Some experiments carried out gave rise to yields 20% greater than those without ultrasounds. In order to deepen in the knowledge of this new technology, the aim of this work was to study the effect of High Power Ultrasounds (HPU) on mass transfer zone (MTZ) in the supercritical extraction. For this purpose, different tests have been performed to assess the effect of HPU on SFE of oil from milled almonds (3-4 mm particle size). To examine the effect of the acoustic waves all experiments were performed with and without ultrasound at identical pressure, temperature and flowrate conditions. In this work, the effect of high-intensity ultrasonic waves on mass-transfer zone based on oil concentration profiles at different times and bed heights are discussed.

INTRODUCTION

When a substance (typically a gas) is under conditions above its critical point (which is located for each substance in a certain value of temperature and pressure) it is said that is in supercritical state and behaves exhibiting a behaviour joining some liquid-like and some gas-like features. In this state, the fluid is named as “supercritical fluid” (SCF).

Supercritical fluid extraction (SFE) using CO_2 as solvent, has gained wide acceptance in the last decades as an alternative to conventional solvent processes. This interest stands on sound advantages of SFE extraction versus traditional extractive techniques involving organic solvents. For example, the extract is easily separated from the extraction agent: only a change in pressure and/or temperature conditions may be enough to get the extract. Thus, it is not necessary to perform long, energy-intensive and costly post-processing separation steps that generally imply high temperatures that may damage valuable active principles. Also, future extracts uses are not legally limited as it occurs with organic solvent trace regulations, since final SCF extract is solvent-free, which make it very interesting for high added applications. Moreover, when the SCF is carbon dioxide, additional advantages apply such as: low extraction temperature that makes it suitable for thermolabile substances; inert, non-toxic, non-flammable, non-explosive, recyclable, etc. that simplifies handling security and diminish health exposure risk; world-wide available at affordable prices, that makes it a suitable candidate for industrial uses, etc.[1].

Nevertheless, SFE implies some special requirements inherent to its own nature. In case of CO_2, although critical value is not very high, many extraction processes reach pressures over 10 or even 40 MPa. Under these operating conditions, it is significatively more difficult to increase mass transfer coefficients and to cut down processing times by using mechanical stirring systems than in traditional extraction processes [2],[3]. Economics and/or productivity of SFE may be clearly affected in cases with non-favourable kinetics and may be worthwhile to look for other options to enhance them.

In this context, an interesting alternative is the use of power ultrasound. Ultrasonic radiation represents an efficient way to enhance mass transfer processes, because of some mechanisms such as microstirring, compressions and decompressions in the material, heating, and/or cavitation. Previous works of this research group pointed out the feasibility of integrating an ultrasonic field inside a supercritical extractor without losing a significant volume fraction [4], [5].

Moreover, a new self-controlled prototype, robust enough to fulfill industrial requirements to produce it commercially was developed and tested under supercritical conditions, giving rise to a non-antecedent patent [6]. This new ultrasonic device led to notable enhancement both on extraction yields at certain times and on required time to achieve a certain extraction yield when aapplied on SFE almond oil. Some experiments carried out gave rise to yields 20% greater than those without ultrasounds [7]. Nevertheless, there is not previous information regarding potential differences between zones along the process.

In order to go further in the knowledge of this new technology, the aim of this work was to study the effect of High Power Ultrasounds (HPU) on mass transfer zone (MTZ) in the supercritical extraction. For this purpose, different tests have been performed to assess the effect of HPU on SFE of oil from milled almonds (3-4 mm particle size), at different times and zones inside the extractor vessel.

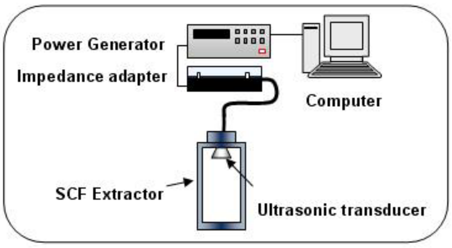
MATERIALS AND METHODS

Raw material

Peeled Marcona Almonds *(Prunus amygdalus)* were used in this investigation. Raw almonds were acquired as already peeled and grounded before the extraction process. The particle size was commercially typified as 3-4 mm and corroborated with different mesh sizes.

Equipment description

The experiments were carried out in the PFS20 planta designed and built up by Ainia technological centre, where it is also located. This SFE pilot plant has 4 extractors (5 litres each), two separation units (a cyclone and a decanter), and three diaphragm pumps. A special cover design was carried out to apply the ultrasonic equipment to one of the extractors. The ultrasonic equipment, consisting of a power ultrasound generator, an impedance adapter, transducer and a control computer with specific software developed by the Institutes of Acoustics and the Applied Physics of the CSIC, was used to control the ultrasonic parameters and to monitor the process. A scheme of this device is shown in figure 1.



Source: (Riera, 2003)

Figure 1. Ultrasonic device used for the SFE assisted by ultrasonic waves.

Methodology

An identical mass of almonds was used in every test (1500 g). Extractions were carried out at a temperature of 45ºC and a pressure of 33 MPa. Also, CO_2 flow rate was kept constant at 15 kg/h for all experiments. As the main target is to study how extraction process progress, is affected by ultrasounds along time, it would be necessary to take out samples from different places along the extraction vessel at different times. However, whereas this methodology is easily applied in traditional extractions, it is not feasible to follow the same procedure for SFE. This is due to the fact the extractor needs to be opened for samples to be taken out and this implies stopping the SFE process and depressurising the vessel. As an alternative, different experiments at identical conditions except time were performed. This way it may be possible to obtain samples at different stages of extraction to represent the whole process. Tests were performed with and without ultrasounds along different times (from 1 hour up to 5 hour). For each test, samples at different heights inside the extractor vessel were taken. In the ultrasonic assisted tests, the resonant frequency of the transducer used was 20 KHz, and the power applied was 75 W.

RESULTS AND DISCUSSION

Tests reliability

Table 1 shows the experimental conditions of the tests performed. As it has already been said, rest of key variables was kept constant (15 kg/h, 45ºC, 33 MPa).

Table 1. Experimental conditions of tests

Test Code	Time (h)	Ratio CO almond (Kg CO_2/kg almond)	US (Yes/No)
IAsin1	1	10	No
IAcon1	1	10	Yes
IAsin2	2	20	No
IAcon2	2	20	Yes
IAsin3	3	30	No
IAcon3	3	30	Yes
IAsin4	4	40	No
IAcon4	4	40	Yes
IAsin5	5	50	No
IAcon5	5	50	Yes

As it is shown in the figures 2 (with ultrasounds) and 3 (without ultrasounds), data from successive curves of extraction at different times describe the same curve. This fact points out that the results are grouped and the tests are repetitive. This suggests that expemiments carried out at different times can overcome the impossibility of direct and continuous sampling inside the extraction vessel. This is a very important point, it means that the basis of the experiments was validated and confirmed the protocole chosen to assess the effect of HPU on extraction yield and mass transfer zone.

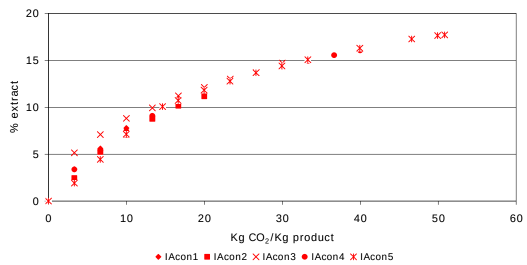


Figure 2. Repeatability. Kinetics of SFE tests with HPU.

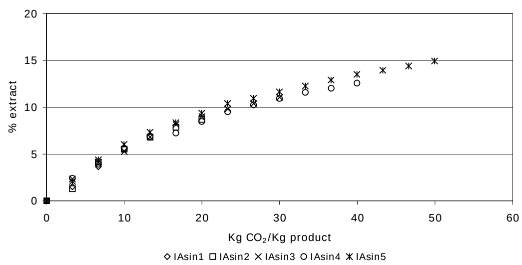


Figure 3. Repeatability. Kinetics of SFE tests without HPU.

Influence of HPU on SFE kinetics

Extraction experiments with ultrasounds exhibited faster kinetic curves and higher extraction yields as it is shown in figures 4, 5, 6, 7 and 8.

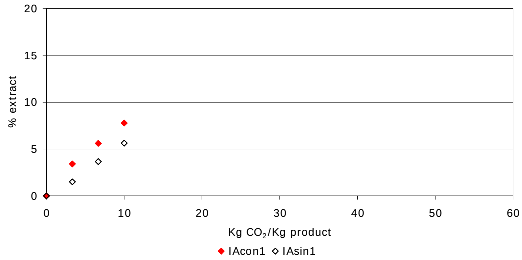


Figure 4. Effect of HPU on SFE yield (amount of extracted almond oil). Extraction time =1 h.

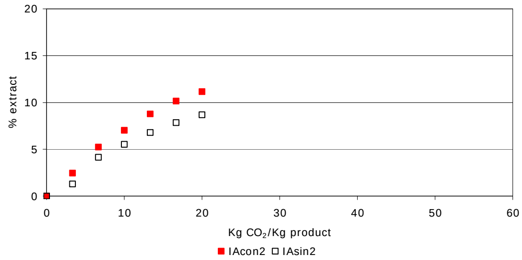


Figure 5. Effect of HPU on SFE yield (amount of extracted almond oil). Extraction time =2 h.

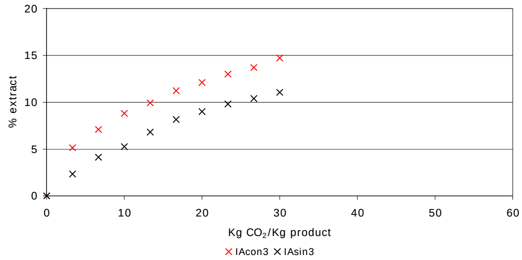


Figure 6. Effect of HPU on SFE yield (amount of extracted almond oil). Extraction time =3 h.

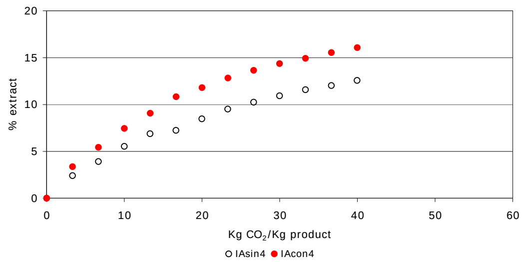


Figure 7. Effect of HPU on SFE yield (amount of extracted almond oil). Extraction time =4 h.

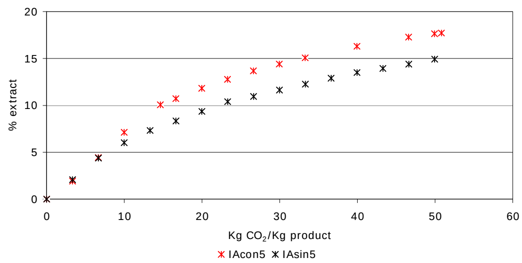


Figure 8. Effect of HPU on SFE yield (amount of extracted almond oil). Extraction time =5 h.

Both the kinetics of the processes and the yield at the SFE were enhanced due to the application of HPU. Improvements on yield were between 19% and 37% depending on the test. These results were in accordance to the results obtained in previous works of this group [7], [8].

Effect of HPU on SFE mass transfer zone (MTZ)

The effect of high-intensity ultrasonic waves on mass-transfer zone based on oil concentration profiles at different times and bed heights was studied. For that purpose, after every test the material remaining inside the extractor was divided into five equal parts in height. The section at the bottom of the extraction basket was numbered as “1” and labelled as “bottom”; the section in the middle of the five was “3· and named “medium” and the upper section was numbered as “5” and called “top”.

Results regarding the concentration in oil remaining in almonds after the SFE test are addressed in figures 9 (SFE with HPU tests) and 10 (SFE without HPU tests).

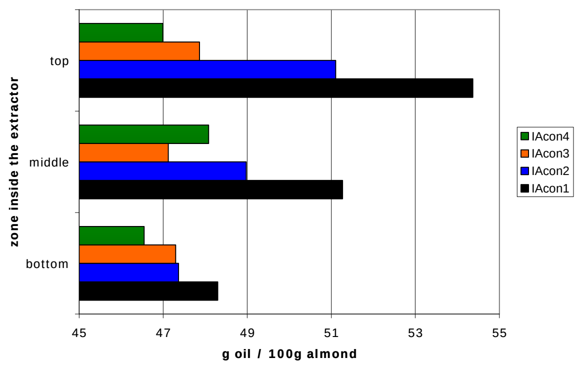


Figure 9. Almond oil content in different sections along time (SFE with HPU experiments)

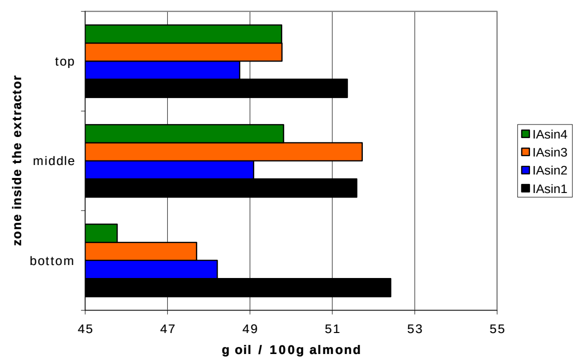


Figure 10. Almond oil content in different sections along time (SFE without HPU experiments)

As it may be seen on figure 9, when the time of extraction is short (IAcon1), the highest rate of extraction occurs in the section where the supercritical CO_2 enters the extraction vessel (bottom section). This behaviour is consistent with the theory: the oil extracted at the bottom saturates the CO_2 step by step and thus, the capacity to extract when it reaches the upper zone becomes very small. As the process continues, the amount of extractable almond oil in the bottom zone decreases and thus, extraction gets more intense in the medium and top section. It is confirmed with data from 1 hour to 2 and 3 hours of extraction, when almond oil content got more similar among the three sections. Finally, when the easily accessible almond oil reduces, it gets harder to extract it. As a result, although there was still an important amount of almond oil inside the extracted almonds, extraction process became slower as it was shown in figures 7 and 8.

On the other hand, the extraction yield is more similar along the whole extractor and along time in extraction tests performed without HPU (figure 10). In the first two hours of process (IAsin1 and IAsin2), there were not important differences between oil remaining in almonds in the top, in the middle and in the bottom of the vessel. During the third and the fourth hour of process, there was an important extraction yield in the bottom of the extractor.

Comparison between figures 9 and 10 may be also complemented with figures 11 (top), 12 (medium) and 13 (bottom), where with and without SFE results are presented jointly.

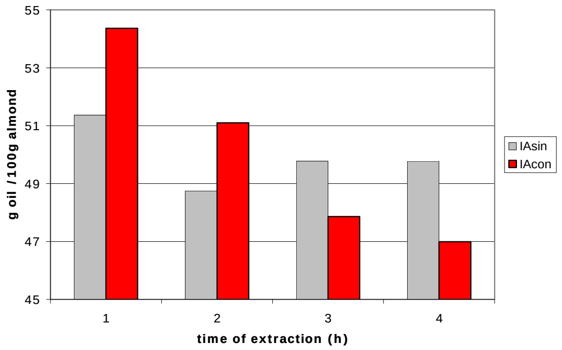


Figure 11. Influence of HPU in the content of oil remaining in almond at the top zone of the extractor

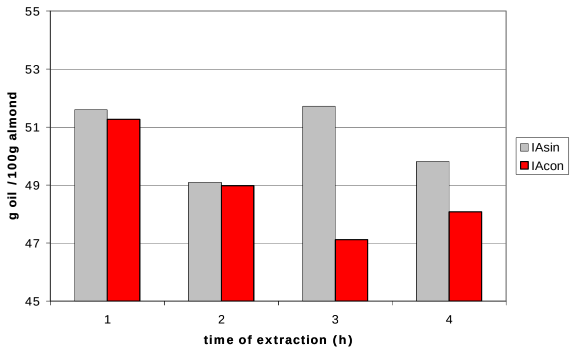


Figure 12. Influence of HPU in the content of oil remaining in almond at the middle zone of the extractor

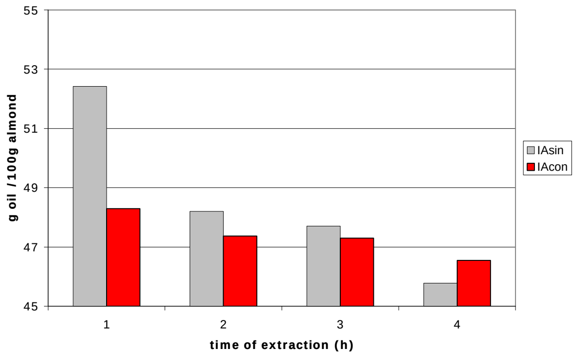


Figure 13. Influence of HPU in the content of oil remaining in almond at the bottom zone of the extractor

Although HPU device is placed in the upper part of the extractor, it seemed that transmission was good enough to enhance mass transfer at the bottom to saturate the CO_2 and to reduce rapidly the oil content inside the almonds in the bottom section. In cases of experiments without ultrasounds, as CO_2 still had extraction capacity at top section, the oil concentration remaining in the almonds was smaller at the beginning of the process (1 hour extraction time). However, as time passed and MTZ advanced from bottom to top in SFE tests with HPU, oil quantity remaining in almonds was lower than in experiments without HPU carried out during the same extraction time.

CONCLUSIONS

It was proved the positive effect of HPU coupled to supercritical fluid extraction, giving rise to extraction yields up to 37% higher than without ultrasounds. Also, it was confirmed that the protocol developed to take data regarding the material inside the extraction vessel is valid, since the reliability of the results was proved.

Regarding the mass transfer zone (MTZ), it has been shown how it moves forward from bottom to top sections along time in all experiments. However, its shape and evolution is different depending on HPU are being applied or not. At the beginning HPU made the extraction to take place preferably where CO_2 started to be in contact with the raw material, since HPU helped the CO_2 to extract the oil more easily and quickly and thus, it had less capacity to continue extracting through the extraction vessel. As the extraction time continued, MTZ moved forward from bottom to top and at last, oil content remaining in extracted almonds was similar in all sections. This behaviour proved that the HPU are effectively transmitted along the extraction vessel.

ACKNOWLEDGEMENTS

The authors are grateful to the Ministry of Science and Innovation for its support through the **USTRAMAS project**: **USDEG subproject** *"Estudio del efecto de los ultrasonidos de potencia en procesos de transferencia de materia. Mejora de procesos de extraccion con gases densos"* (DPI2009-14549-C04-03). **PUSO subproject** "*Estudio de los efectos de los ultrasonidos de potencia en procesos de transferencia de masa. Diseño, desarrollo y validación de sistemas ultrasónicos de potencia"* (DPI2009-14549-C04-01).

REFERENCES

1 Q. Lang, C.M. Wai, "Supercritical fluid extraction in herbal and natural product studies - A practical review" *Talanta*, 53, 771-782 (2001)

2 H. Sovova, J. Kucera, J. Jez, "Rate of vegetable oil extraction with supercritical CO2.II extraction of grape oil" *Chem.E.Sci*. 49, 415 (1994)

3 A. Berna, A. Tàrrega, M. Blasco, S. Subirats, "Supercritical CO_2 extraction of essential oil from orange peel; effect of the height of the bed" J. Supercritic. Fluids 18, 227 (2000)

4 E. Riera, A. Blanco, J. García, J. Benedito, A. Mulet, J.A. Gallego-Juárez, "High-power ultrasonic system for the enhancement of mass transfer in supercritical CO2 extraction processes". *Ultrasonics*, 50(2), 306-309 (2010)

5 E. Riera, Y. Golás, A. Blanco, J.A. Gallego-Juárez, M. Blasco, A. Mulet, "Mass transfer enhancement in supercritical fluids extraction by means of power ultrasound". *Ultrasonics Sonochemistry*, 11(3-4), 241-244 (2004)

6 E. Riera, J.A. Gallego-Juárez, F. Montoya, A. Blanco, A. Mulet, J.J. Benedito, R. Pena, Y. Golas, A. Berna, S. Subirats, M. Blasco, J. García. (2004) Patent WO2004012859 (EP1547679 A1)

7 J. García-Reverter, C. Redón, J. Benedito, E. Riera. "Development of a new and robust ultrasonic device for supercritical extraction processes" *11th European Meeting on Supercritical Fluids* (Barcelona, 2008)

8 E. Riera, Y. Golás, A. Blanco, J. A. Gallego, J. García-Reverter and S. Subirats, "Effect of high-intensity ultrasound on the particulate almonds oil extraction kinetics using supercritical CO_2" *Sixth International Symposium on Supercritical Fluids* (Versalles, 2003)