ON-LINE SOLUTE CONCENTRATION DETERMINATION IN SC-CO_2 BY APPLYING SPECTROPHOTOMETER TECHNIQUES.

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Coating or encapsulation of fine particles can produce tailored surface properties, which is of great interest in pharmaceutical, cosmetic, food, and agrochemical industries. Encapsulation of active compounds may allow enlarging product life, preventing degradation, improving handling conditions and providing sustained release properties. Encapsulation processes based on supercritical fluids (CO_2 especially) provide important advantages compared to other methods such us smaller particle diameters, narrow particle size distribution, or the possibility of defining different morphologies as a function of process conditions.

In this context, a project was conceived to study several aspects concerning microencapsulation of substances with SC-CO_2 in order to develop an innovative process. As a result, solute concentration after microencapsulation was pointed out as an important parameter to be controlled. In this work, spectroscopy techniques have been applied on-line at a laboratory scale supercritical fluid encapsulation equipment has been used to carry out the experimental concentration measurement. Experimental research showed that the designed and built-up system may be applied at SC-CO_2.

INTRODUCTION

In last years, microencapsulation has devoted an increasing attention as number of published articles may prove. Coating or encapsulation of fine particles can produce tailored surface properties, which is of great interest in pharmaceutical, cosmetic, food, and agrochemical industries [1,2]. Encapsulation of active compounds may allow enlarging product life, preventing degradation, improving handling conditions and providing sustained release properties [3, 4].

Encapsulation processes based on supercritical fluids (CO_2 especially) provide important advantages compared to other methods [5]: smaller particle diameters, narrow particle size distribution, or the possibility of defining different morphologies as a function of process conditions. In addition, CO_2 is a GRAS substance which solvent power may be tuned by varying pressure and/or temperature, is widely available, non-toxic, non flammable, mild temperatures applicable, and does not leave residues in final products [6].

In this context, a project was conceived to study several aspects concerning microencapsulation of substances with SC-CO_2 in order to develop an innovative process. As a result, solute concentration after microencapsulation was pointed out as an important parameter to be controlled. Also, limitations to estimate it according to solubility were detected. Thus, it was decided to study the feasibility of applying a new *in-situ* instrumental non- invasive system to determine and to control quickly this parameter.

This work led to interesting qualitative conclusions, which are addressed in this paper in brief.

MATERIALS AND METHODS

Spectroscopy techniques were on-line applied at a laboratory scale. A supercritical fluid encapsulation equipment was used to carry out the experimental concentration measurement. This equipment consist of a 0,5 litres vessel (15), working at 280 bar and 50ºC, and three separation units. Figure 1 shows the experimental disposition, where on-line concentration measure (XI) is located between solubility vessels (6,7) and encapsulation vessel.

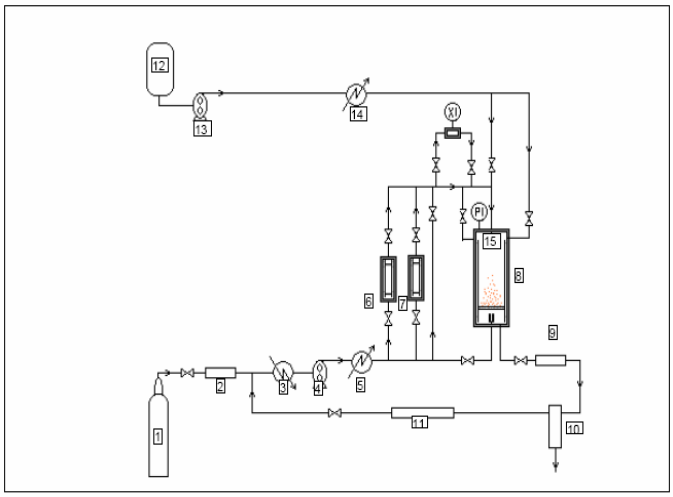

Figure 1. Installation scheme.

In this context, possibilities to apply an on-line spectrophotometry-based measurement systems to a supercritical process were studied. First step was related to probe optic fiber selection. In order to get this goal, spectrophotometric system had to satisfy quite extreme constraints for a transmitter: to be connected and performed without fluid or mechanical problems up to 30 MPa and up to 353K.

In experimental test, both for checking set up performance and on-line measurement test, CO_2 with purity higher than 99% was used. Also, linen oil from seeds was used as example substance to correlate absorbance and solute concentration

RESULTS AND DISCUSSION

First of all, a deep search was performed to look for commercially available and potentially applicable solutions. A system was found in one supplier commercial information and contacts were established to check detailed specifications. Although it was said that this element may be feasible, at the end the manufacturer pointed out that the element could not be served and ad hoc designed equipment was suggested. A specific cell with fitted specifications to process requirements was proposed, but neither configuration nor budget allocated for this item fitted expected features. Another local supplier was contacted in order to design and build up flow cell similar in concept to that previously rejected but more accurate to initial expectative. Even in this case, final specifications led to doubts related to feasibility for the implementation of spectrophotometric methods to this supercritical process.

This way, an alternative approach was required. A deep review of available commercial elements for high pressure applications was carried out in order to identify compatible elements

and devices with required materials, configuration and/or dimensions. With regard to spectrophotometric elements, technical specifications were analysed to perform measuring adequately. On the other hand, a bibliographic search was realised for selecting the proper spectrophotometer to acquire data within the most common spectra BANDAS related to the most probable absorbance peaks. As a result, it was deduced that near-infrared may exhibit the best combination of intense enough absorbance peaks with a reasonable costs. For this reason, a spectrophotometer performing between 1100 and 2000 nm was selected (NIR256L-2.2T2-20 de Sentronic).

Once configuration was defined and elements were available, set up was built up as it is showed in figure 2.

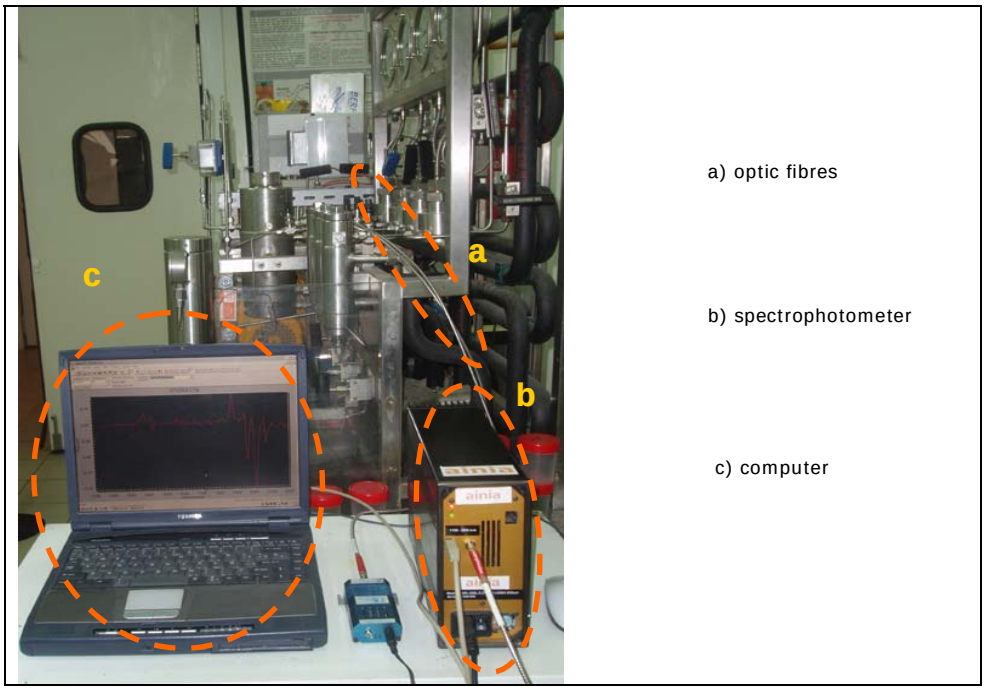

Figure 2: Elements for acquisition of absorbance spectra in SCF medium.

Progressive increasing pressure tests were performed in order to verify correct plant behaviour and safety measurements. Next, spectra measurements were performed with CO2 at different pressures to register SC- CO_2 spectra at different pressures, as it is showed in Figure 3.

As it may be seen, there were significant differences among absorbance curves observed under various pressure conditions between 1,5 and 25 MPa. This fact may be directly related to properties changes in the fluid as a result of operating conditions variation. In the same way, tabulated values of CO_2 absorbance at a certain wavelength (2011 nm) showed clear changes along the sub-critical range whereas slighter variations were observed above 9 MPa (table 1). This circumstance may be very interesting in order to monitor critical point, which is a clear innovation with respect to published information up to date.

Figure 3: On-line CO2 absorbance spectra

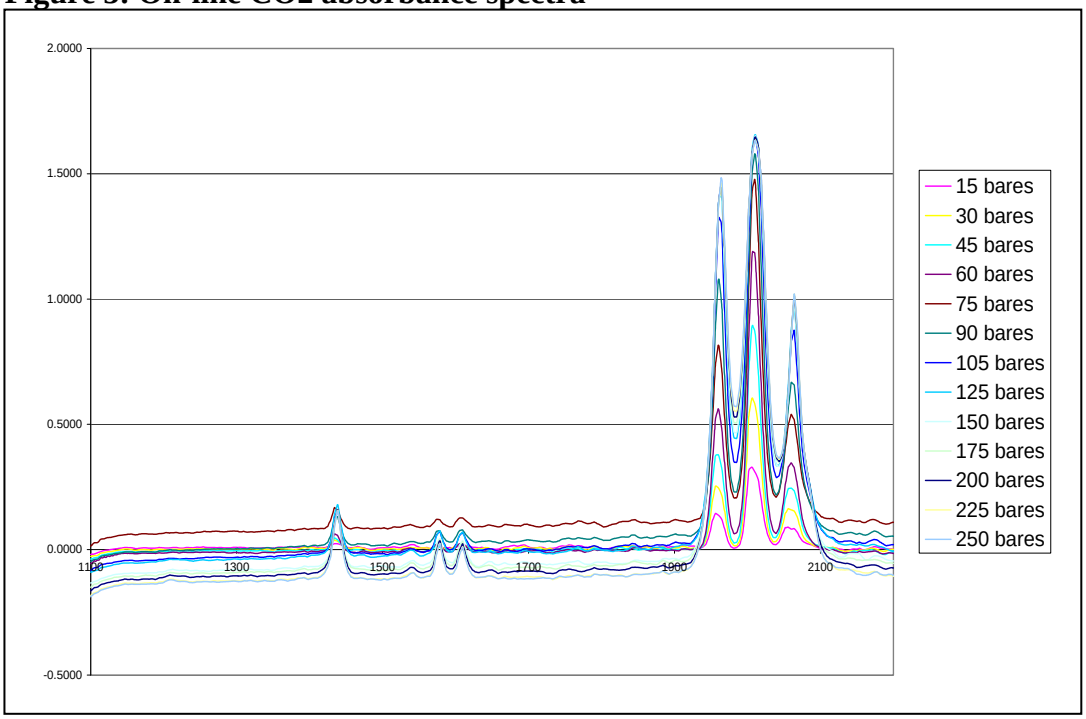

Table 1. CO_2 absorbances at different pressure conditions, from sub-critical up to supercritical ones

Pressure (MPa)	Absorbance @ 2011 nm
1,5	0.3062
3,0	0.5703
4,5	0.8525
6,0	1.1528
7,5	1.4572
9,0	1.5748
10,5	1.6396
12,5	1.6556
15,0	1.6509
17,5	1.6394
20,0	1.6471
22,5	1.6338
25,0	1.6316

Following, experiments with different substances which may be used as cores to be encapsulated were performed. For this purpose, first of all, measurements with reference solutions with an organic solvent were performed to correlate absorbance signal and solubilised substance concentration. A special procedure for signal treatment was developed, taking CO2 spectra as internal reference and integrating along time and as a result, a suitable wave length for estimation of concentration was determined (figure 4). Finally, it was possible to establish a certain relationship between spectrophotometric values and concentration. These related values may be observed in table 2.

Figura 4: On-line CO_2 + linen oil absorbance spectra with CO_2 as internal reference.

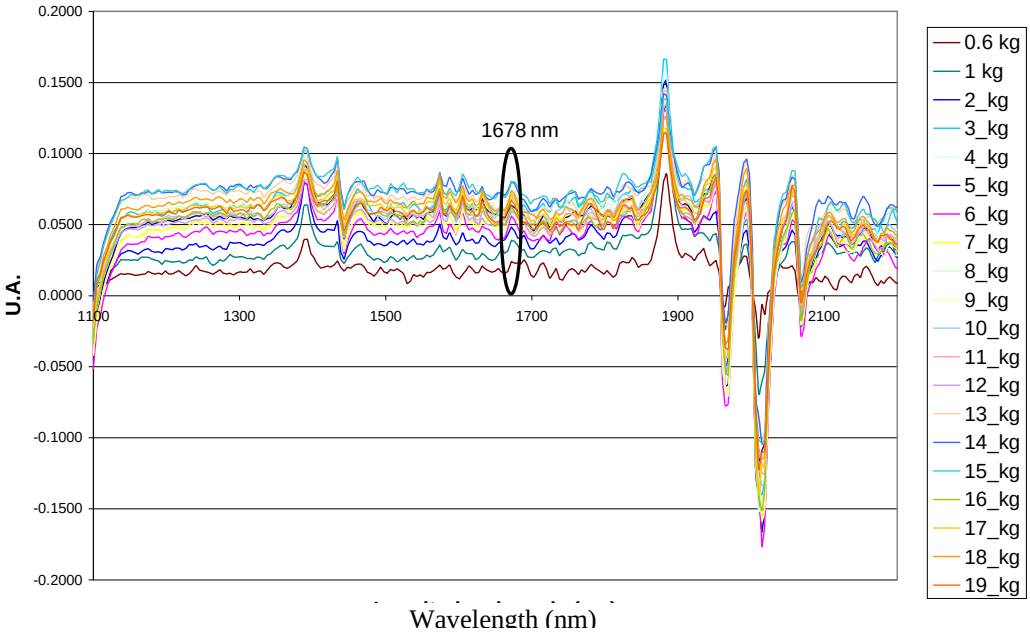

Table 2: Estimation of linen oil concentration in SC-CO_2

Kg CO_2	Absorbance at 1678nm	% Concentration
0.6	0.0229	3.96
1	0.0371	4.98
2	0.0436	5.44
3	0.0689	7.23
4	0.0622	6.76
5	0.0613	6.70
6	0.0512	5.98
7	0.0579	6.45
8	0.0722	7.47
9	0.0554	6.28
10	0.0681	7.19
11	0.0577	6.44
12	0.0568	6.38
13	0.0692	7.26
14	0.0768	7.80
15	0.0790	7.95
16	0.0575	6.43
17	0.0652	6.97
18	0.0686	7.22
19	0.0617	6.73

Values estimated by spectrophotometric measurements ranged within the same order of magnitude than estimated concentration from registered extract weights along time. This fact showed that it could be feasible to apply spectrophotometry to supercritical processes. Nevertheless, deeper studies should be carried out in order to improve aspects such as reference measurement, stability of spectrophotometric signal along time, data filtering, etc. As a result, more accurate and versatile procedures may be defined.

CONCLUSIONS

Experimental research showed that the designed and built-up system may be applied at SC-CO_2, so it may be feasible to performed spectrophotometric measurements in supercritical conditions by means of some equipment adaptations. Although some difficulties were faced, a special measuring procedure was developed and certain correlation between spectrophotometric data

and solute concentration were found for linen oil. Estimated concentration with spectrophotometric values ranged the same order of magnitude than those calculated from gravimetric data. Further studies may include improvements to enhance the system and procedures.

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