# SFE OF *CURCUMA LONGA*: SOLUBILITY OF ESSENTIAL OIL

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Solubility is one of the main parameters needed for design or operating purposes. Frequently this property is unknown and it needs to be determined. Essential oils are complex mixtures and as a consequence their solubility is not easily established from single components. *Curcuma longa* is a rhizome of interest in food processing due to its colour compounds and other solutes with very interesting beneficial properties for human health, that can be extracted as essential oils.

The aim of this study was to determine the solubility of turmeric (*Curcuma longa*) oil in supercritical $CO_2$. For that purpose an identification procedure based on mathematical models was considered. The model of Naik, was used due to the fact that solubility is one of the parameters to be identified from experimental data. The figures were compared to those obtained by least squares fitting of the initial part of the extraction curve where it is assumed that mass transfer is solubility dependent. Similar values of solubility were obtained from both methods. The identified solubilities values at different operating conditions were correlated by using Chrastil's equation. It was found that figures from both methods presented a similar agreement with this equation (VAR ˜ 0.970). As a consequence it can be concluded that the procedure using Naik's equation could be adequate for identifying solubility values.

## INTRODUCTION

*Curcuma longa* is a native plant of tropical climates, it is mainly cultivated in India and Central America. Rhizomes of *Curcuma longa* present a high interest for food processing. Traditional use of these rhizomes has been the extraction of a colorant (curcumin) [1] widely used as additive in foods. Furthermore the beneficial properties for the health of its essential oil are also important [2]: antioxidant [3], anti-inflammatory [4], antimutagenic [5], antivenom [6].

Essential oil of *Curcuma longa* rhizomes is a complex mixture [7]. The most important compounds are ar-turmerone (42 % of total fraction) and turmerone (12 %), while the rest of

compounds are found in a lower percentage to the 5% of total fraction. As a consequence its solubility is not easily established from single components.

Supercritical fluid extraction (SFE) is an alternative to traditional techniques of natural compound extraction. SFE permits to obtain free extracts of organic solvents. $CO_2$ has been traditionally the most important solvent used in SFE, because it is a non-toxic and cheap product, furthermore it presents a low critical point (Pc = 71.8 bar and Tc = 31.1 ºC) [8].

The aim of this study is to obtain the solubility of essential oil of *Curcuma longa* in supercritical $CO_2$ at different conditions of pressure and temperature.

## I. MATERIALS AND METHODS

The rhizomes of *Curcuma longa* originated from Playa Grande (Guatemala) were hot air dried and grinded (particle size lower 0.1 mm) before extraction. Essential oil was extracted in a continuos-flow extractor (Figure 1). The flow rate of $CO_2$ used was 3 kg/h. The extraction yield was measured at different times by the decrease of raw material weigh. Experiences were carried out at different conditions of pressure and temperature (Table1 and 2).
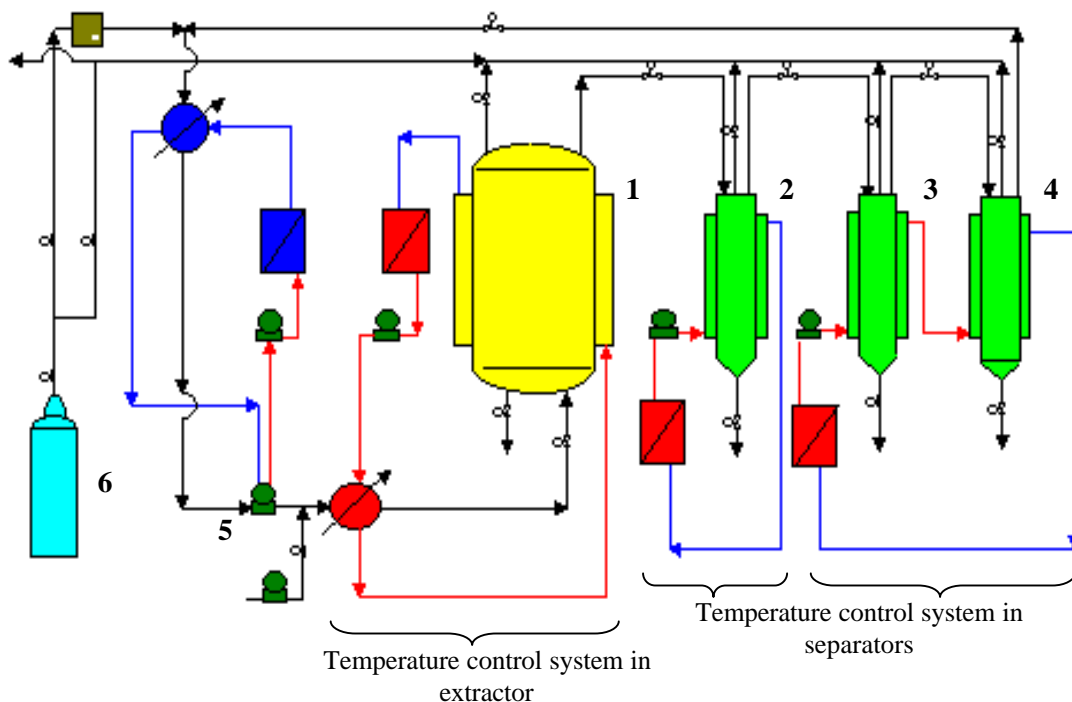


**Figure 1**. Schematic representation of the SFE apparatus. 1 Extractor vessel, 2, 3, 4 separators, 5 High pressure pump, 6 $CO_2$ cylinder.

Three stages where mass transfer is controlled by different parameters can be found in a theoretical extraction curve. The first period is controlled by solubility, extraction rate is non-dependent of supercritical fluid flow. So a linear relation appears between extraction yield and the amount of supercritical fluid. The first period is approximately extended to reach 50 % of

maximum yield [9]. Solubility can be calculated as the slope of extraction curve in this first stage [7]. In the second stage mass transfer is controlled by solubility and diffusion of solutes from inside particle. In the final period mass transfer is only dependent on diffusion.

Two methods were used to calculate solubility by using first period kinetic data. The first method consists on the conventional measure of the slope, experimental data were fitted by least squares in the range of the curve where mass transfer is controlled by the solubility. The second method applied was the mathematical model of Naik (equation 1) [10]:

$$Y = \frac{Y_\infty \cdot t}{B + t}$$
(1)

Where: Y = the extraction yield $\left(\dfrac{kg_{extract}}{kg_{Curcuma}}\right) \cdot 100$

t = the $CO_2$ mass $\left(\dfrac{kg_{CO2}}{kg_{Curcuma}}\right)$

$Y_\infty$ = the extraction yield at equilibrium

B = the $CO_2$ mass needed to reach the half of $Y_\infty$

The fraction $\dfrac{0.5 \cdot Y_\infty}{B}$ can be used as an approximation of the slope of extraction curve in the first stage.

The solubilities calculated by using both ways were correlated with operating conditions, Pressure and Temperature, using Chrastil's equation (2) [11]:

$$S = d^K \cdot \exp\left(\frac{a}{T} + b\right)$$
(2)

Where: S = the solubility $\left(\dfrac{g_{extract}}{L_{CO2}}\right)$

d = the density of supercritical $CO_2$ $\left(\dfrac{g}{L}\right)$

T = the temperature (K)

a, b and K are model parameters, related to chemical properties. a = ?H/R where ?H is the total heat of reaction and R is the universal constant of gases. b is a constant related to molecular weigh of solute and solvent and K is the association number, number of molecules of solvent needed to solvate a molecule of solute.

Solver (Microsoft Excel-Microsoft Corporation) was used to optimize the non-linear regression models. Lineal regression coefficient ($R^2$) was calculated to determine the agreement on linear regression models while VAR (explained variance) (equation 3) was useful to determine the agreement for non-linear correlations.

$$VAR = 1 - \frac{S^2_{yx}}{S^2_y} \tag{3}$$

Where: $S^2_{yx}$ = the standard deviation of the estimation.
$S^2_y$ = the standard deviation of the sample.

## II. RESULTS AND DISCUSSION

Naik's model was useful to describe the extraction kinetics, it presented a good agreement with experimental data (Figure 2, Table 1).
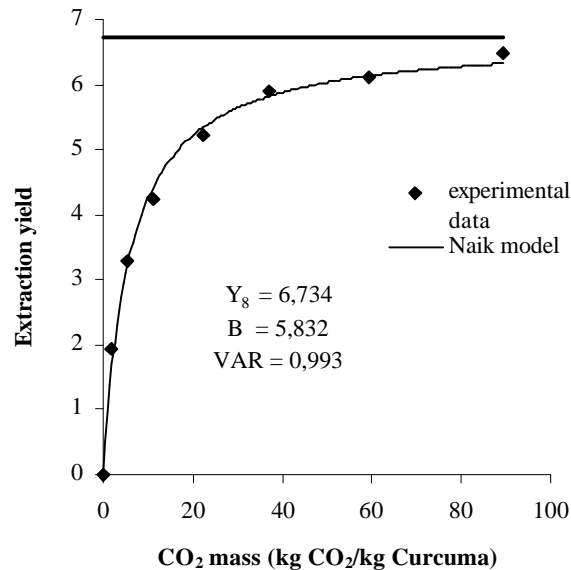


Y_8 = 6,734
B = 5,832
VAR = 0,993

**Figure 2**. Extraction curve of essential oil of *Curcuma longa* at 40 °C and 150 bar. Experimental data and fit from Naik's model.

Solubilities calculated with both methods (Table 1) were similar enough. Although significant differences were found in some experiments (30 °C-100 bar, 50 °C-250 bar, 50 °C-280 bar). They could be linked to the subjectivity in determining the extent of the initial linear part of the experimental curve to be fitted by least squares. One must choose the experimental points to consider for computing the solubility. Naik's model removes the subjectivity and it permits carrying out solubility identifications in an easy and systematic way.

For both models, solubility increased when the pressure increased. The influence of temperature in solubility was not well established.

| T (°C) --- P (bar) | 100 | 150 | 200 | 250 | 280 |
|---|---|---|---|---|---|
| 30 | 0,39 | 0,82 | 0,87 | 0,95 | |
| VAR | 0,942 | 0,997 | 0,980 | 0,989 | |
| 40 | 0,17 | 0,58 | 1,24 | 1,67 | 1,88 |
| VAR | 0,995 | 0,993 | 0,940 | 0,991 | 0,998 |
| 50 | 0,19 | 0,77 | 1,51 | 2,54 | 2,80 |
| VAR | 0,992 | 0,992 | 0,955 | 0,997 | 0,996 |
| 35 | | | | | 1,59 |
| VAR | | | | | 0,998 |

**Table 1**. Solubilities (g essential oil/100 g $CO_2$) calculated from parameters of Naik's model and explained variance (VAR).

| T (ºC) --- P (bar) | 100 | 150 | 200 | 250 | 280 |
|---|---|---|---|---|---|
| **30** | 0,67 | 1,00 | 1,12 | 1,20 | |
| $R^2$ | *0,999* | *0,999* | *0,999* | *0,999* | |
| **40** | 0,20 | 0,63 | 1,34 | 1,51 | 1,74 |
| $R^2$ | *0,947* | *0,882* | *0,835* | *0,825* | *0,949* |
| **50** | 0,31 | 0,89 | 1,53 | 1,96 | 2,16 |
| $R^2$ | *0,971* | *0,971* | *0,802* | *0,813* | *0,936* |
| **35** | | | | | 1,54 |
| $R^2$ | | | | | 0,911 |

**Table 2**. Solubilities (g essential oil/100 g $CO_2$) calculated from the slope of extraction curves and linear regression coefficient ($R^2$).

The solubilities obtained with both methods are lightly higher than those presented by Gopalan et al [7].

When using Chrastil's model to describe the influence of operating conditions the results from both identifying solubility methods were equally good (Figure 3 and Table 3). However the parameters obtained with both methods are different, this could be linked to the numerical procedure, at least for parameter "a" where the differences are higher. All the Chrastil's equation parameters were found to be higher when using Naik's model data.



**Figure 3**. Solubilities obtained with Naik's model and calculated with Chrastil's model.
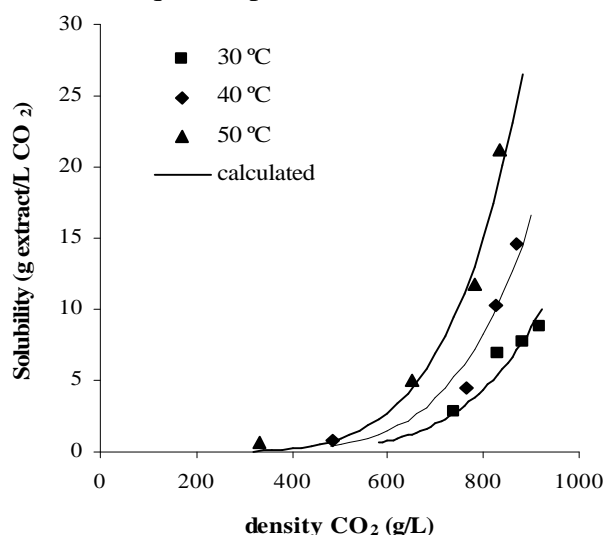
| Parameters | Naik | Slope |
|---|---|---|
| **a** | -6083,07 | -3629,1 |
| **b** | -18,0 | -15,3 |
| **K** | 5,92 | 4,3 |
| **VAR** | 0,970 | 0,969 |

**Table 3**. Parameters of Chrastil's model for both methods used to calcultate solubility.

## CONCLUSIONS

Solubility of essential oil has been calculated using two different methods. Small differences have been found between both methods. So Naik's model can be presented as a new way to determine the solubility of a compound in supercritical $CO_2$. This equation permits making this calculation in an easy, fast and adequate form.

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