

Extraction of active principles from tobacco with supercritical CO₂: Use of crops from Northwestern Argentina.

Gerardo TITA^a, Alexander NAVARRETE^b, María José COCERO*^b

^a Faculty of Engineering.
Catholic University of Salta
A4400ANG Salta, Argentina

^b Department of Chemical Engineering and Environmental Technology
University of Valladolid
Calle del Dr Mergelina s/n.
47011 Valladolid, Spain
* mjcocero@iq.uva.es

ABSTRACT

Tobacco compounds such as solanesol have interesting applications in food, pharmaceuticals and cosmetics, particularly as a precursor in the synthesis coenzyme Q10. Supercritical CO₂ extraction of tobacco were made using plant from Northwestern Argentina (Flue-cured leaves, Virginia variety). Two types of plant material were used: dried and as-received. When compared with total extract, the extraction of solanesol was affected in major degree by the drying. The model described the extraction evolution showing fast depletion of the extract evidenced by the flat profiles of solute concentration in the bed.

INTRODUCTION

The prejudicial effects on the health that result from smoking tobacco makes it imperative for industry to look for alternative uses of the plant. Tobacco compounds such as solanesol have interesting applications in food, pharmaceuticals and cosmetics, particularly as a precursor in the synthesis coenzyme Q10 [1, 2]. The content of solanesol in different species of tobacco can be between 0.4% and 3.0% [3]. The extraction methods involves, solvents such as hexane, methanol, ether and ethanol. Extracts obtained have to be further purified and a solvent elimination stage has to be included in order to obtain solanesol for a further process. An alternative technology for green production of extracts is the use of supercritical fluid extraction (SFE).

Supercritical CO₂ (SCCO₂) has been widely explored owing to its inertness, and low critical point (304.15 K, 7.38MPa). Thus, once the extract is obtained, the CO₂ can be expanded leaving no solvent traces in the final extract. SCCO₂ tobacco extracts have been already obtained using several pretreatment conditions and extraction methods [4, 5]. These studies have shown the potential of this method to obtain solanesol but a major scale production of solanesol needs insight in the process evolution both in the solvent and in solid material. This insight can then be used to properly design and scale up an extraction method based on SCCO₂.

The aim of this work is to provide an initial understanding for the design of an industrial process to obtain solanesol from tobacco leaves based on SCCO₂. Process design and scale up require to predict the evolution of the amount of the extract in the solid as well as in the

solvent. Here, a desorption model will be applied to predict the evolution in time of extraction profiles along the packed bed (in the solid and the fluid)[6]. Data on the evolution of the extraction were obtained by means of supercritical CO₂ extraction of tobacco leaves and the result were used to adjust the model parameters.

MODEL DESCRIPTION

The axial mass balance model along the bed is based in the following assumptions[6].

1) Pseudo-component representation of the global behavior. 2) A system comprised of two phases: First, a solid static phase containing an inert matrix and a solute. Second, a fluid phase containing the solvent and the solute. 3) Constant flow rate and transport properties (density, viscosity, etc.) of the fluid phase during the extraction. Head losses, temperature gradients and mixing heat are neglected. 4) Velocity based on the constant CO₂ flow. 5) Constant void fraction in the solid phase. 6) The conditions measured in the separator are assumed to be equal to those at the exit of the bed. 7) Axial and radial dispersions are neglected. 8) Linear relationship between the solid's surface equilibrium concentration and the fluid concentration of the solute.

The model can then be represented by the equation system below:

$$\varepsilon \frac{\partial y}{\partial t} = -\frac{u_z}{L} \frac{\partial y}{\partial x} - (k_g a)(y - y^*) \quad (1)$$

$$(1 - \varepsilon) \frac{\partial y_s}{\partial t} = (k_g a)(y - y^*) \quad (2)$$

$$y_s = h \cdot y^* \quad (3)$$

$$x = \frac{z}{L} \quad (4)$$

$$y = \frac{c}{c_0} \quad (5)$$

$$y_s = \frac{c_s}{c_0} \quad (6)$$

ε , is the bed porosity (void volume in cm³/total bed volume in cm³). $k_g a$, mass transfer coefficient (min⁻¹). u_z , axial velocity (cm/min). c , concentration of solute in the fluid phase (g solute/ cm³ of solution). c_s , concentration of solute in the solid phase (g solute/ cm³ of bed). c_0 , initial concentration of solute in the solid phase (g solute/ cm³ of bed). L , is the length of the bed (cm). t , is time (min). And h , is the equilibrium parameter.

The system was fitted based on the experimental data of total extract in order to determine the equilibrium parameter (h) and the mass transfer coefficient ($k_g a$). The initial conditions to solve the system are: $t = 0 \rightarrow y = 0; x \rightarrow y = 1$. The properties of SCCO₂ were determined by means of the PC-SAFT equation as described in [7].

EXPERIMENTAL METHODOLOGY

The tobacco was supplied by COPROTAB cooperative in Salta (Argentina). Flue-cured tobacco leaves from the Virginia variety (superior quality) were used. Fresh and oven-dried (24hours, 60C) leaves were milled to obtain two fractions. One fraction (F1) was retained between 500 and 100 μ m sieve; the second one (F2) was bigger than 500 μ m. 200g of sample

were introduced in the extractor. 150g of F1 were first introduced and deposited in the bottom of the vessel (5L) and then 50g of F2 were added to the top. Two moisture levels in the plant used were established. The first was the moisture content in the plant as-received (14.3%). The second set of samples were dried at 60°C during 24 hours getting a final average moisture content of 7.1%.

A circulation unit was used which comprises an extractor and separator working together with a Dosapro pump (MB 140 SL-10) and regulated by a back pressure valve (GO BP-66). During the process CO₂ at 30.0 MPa and 55.0 C was introduced at the bottom of the extractor. The extract was periodically (15 min) withdrawn from the bottom of the separator (4.50 MPa) and weighted. The separator walls were kept at 45C by means of a flow sent from a water bath. In doing so, the extract was kept in liquid state and was easily withdrawn. The extracts were preserved in dark conditions at 4.0 °C. Their analyses were performed in the following two weeks. HPLC (solanesol) analyses were performed in the samples obtained. To performed the analyses c.a. 100 mg of extract were diluted in 20 ml of analytical grade hexane (isomers mixture). The eluent was a mixture of acetonitrile and isopropanol (60:4, v/v) and flowed at a rate of 1 ml/min. The column used was a symmetry C18 (Waters 5µm 4.6 x 150mm) kept at 30°C. The UV detector was set at 210 nm.

RESULTS AND DISCUSSION

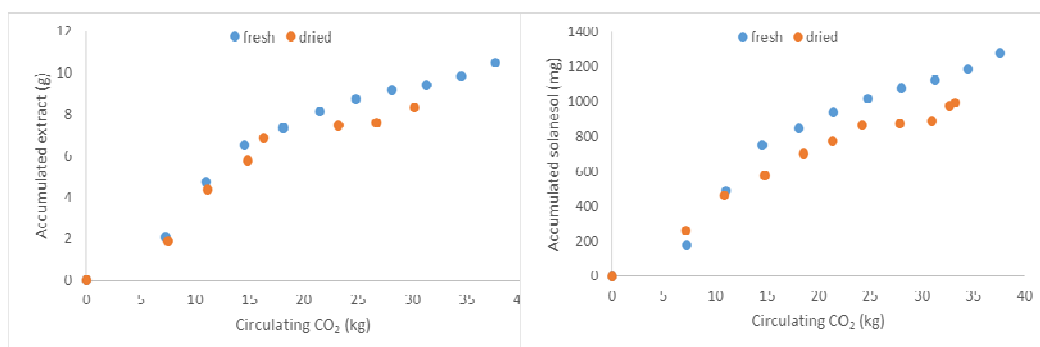


Figure 1. Evolution of the extraction (Left). Accumulated solanesol during the extraction (right)

The extracts obtained during the extraction with SCCO₂ were weighted and their content of solanesol was determined. Figure 1 presents the evolution of both extract and solanesol for the dried and as-received plant. The influence of drying in the total extract is lower than in the solanesol evolution. This is an indication of the losses of solanesol during drying. Initial content of extract was assumed to be equal to that of hexane extracts owing to the low polarity of SCCO₂[8]. Based on the results obtained by Ellington et al. (1978) on hexane extracts from tobacco leaves the content of initial extract in the solid will be considered to be 7.0% in dry basis [9]. With this the fitting of the experimental data to the model was made. For this task the “fminsearch” function of Matlab® was used. The flat extraction profiles predicted in the solid show that the fluid velocity is high relative to the sample amount. This can be confirmed by the small change on solute concentration in the fluid. The equilibrium constant and mass transfer coefficient were respectively 0.0814 and 0.001 min⁻¹ for the fresh sample and 0.0632 and 0.001 min⁻¹ for the dried sample. This indicates that equilibrium plays major role in these experiments as a consequence of the small sample used.

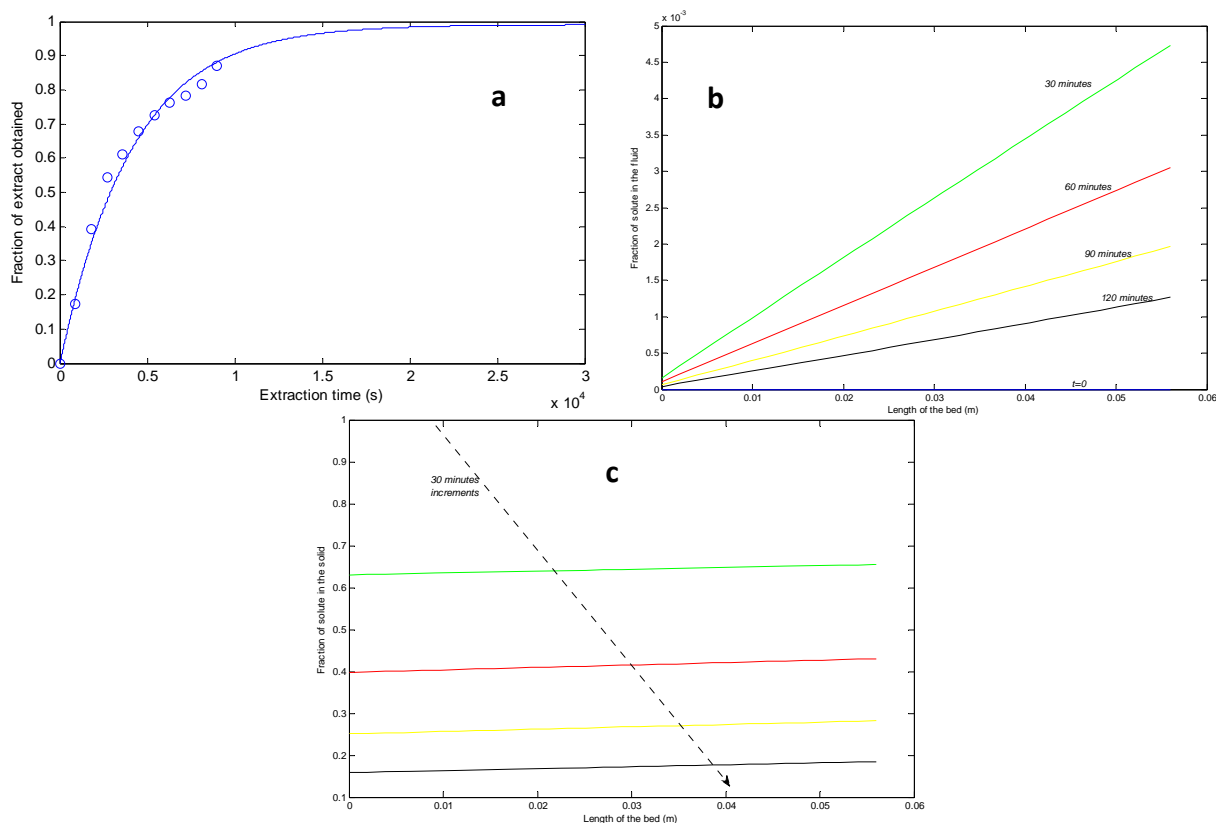


Figure 2. Model predictions of the fraction of solute extracted (a), the fraction in the present in the fluid (b) and the fraction remaining in the solid (c).

CONCLUSIONS

1) The extraction of tobacco was modelled. 2) The profiles show a fast extraction possible owed to the small amount of sample relative to the fluid velocity. 3) More studies are necessary varying the amount of sample and the fluid velocity.

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