

Fractionation of Copaíba Oil resin (*Copaifera officinalis*) by Supercritical Desorption in Packed Columns with γ -Alumina as Adsorbent

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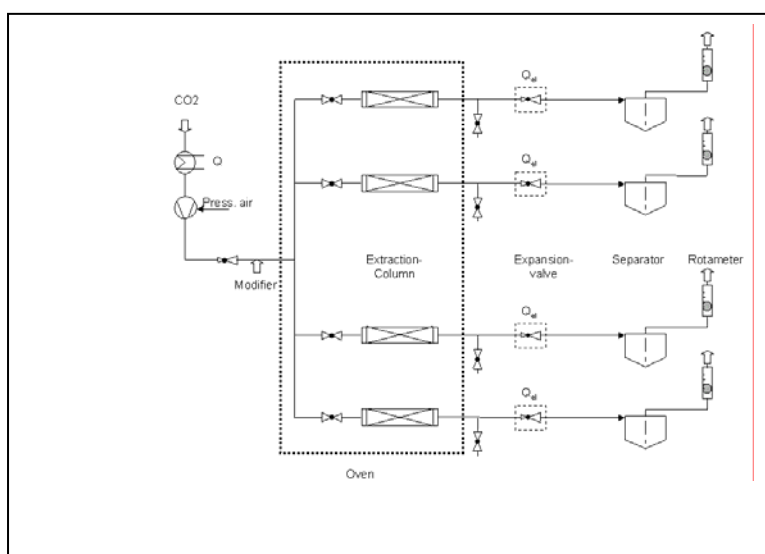
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ABSTRACT - In this work, γ -Alumina adsorbents loaded with Copaíba oil resin, a real liquid system, were submitted to desorption with supercritical CO₂ in order to investigate the feasibility of fractionating the terpene compounds. The desorption experiments were carried out in a Speed SFE Unit (Applied Separations, USA) by stepwise pressure increase (8, 12, 15, 25, and 40 MPa), temperature of 323 K, and solvent flow rate of $Q_{CO_2} = 9.0$ L/min, as shown in Figure 1.



Aluminum hydroxide Al₂O₃ (*Gibbsite*), the precursor of γ -alumina, was submitted to thermal transformation, carried out at 723 (AG.45) and 923 K (AG.65) during 01 hour in an electrical furnace (Químis, SP, Brazil, Model: 5B), to produce predominately alumina of γ type as shown in Figure 2. The adsorbent was characterized by X-ray Powder Diffraction, Scanning Electron Microscopy, Particle and Pore Size Distribution, Particle Porosity and Specific Area.

Figure 1: Experimental set-up of the Supercritical Fluid Extraction Unit.

The adsorbent was filled into a 10 ml column (20 cm length; 0,5 cm² cross-sectional area). The supercritical CO₂ flows upwards through the fixed bed. At the column outlet, the gas flow is de-pressurized by an expansion valve, where the stream is separated in a volatile CO₂ stream and a less volatile extract. The samples were collected in small glass tubes. For a gravimetric determination of the amount of separated species, the tubes were weighed after certain time slices. The flow rate of the supercritical gas was measured by rotameters at normal conditions [l/min].

The chemical analysis of Copaíba oil resin used the procedure as follows. Initially 01 (one) μ l of the solution containing the mixture was injected into a gas chromatograph (HP, Wilmington, Model: 5890A) equipped with a capillary column, a FID detector and an automatic injector (HP, Wilmington, USA, Model: 7673). The column was a 30 m x 0.245 mm ID fused silica open tubular

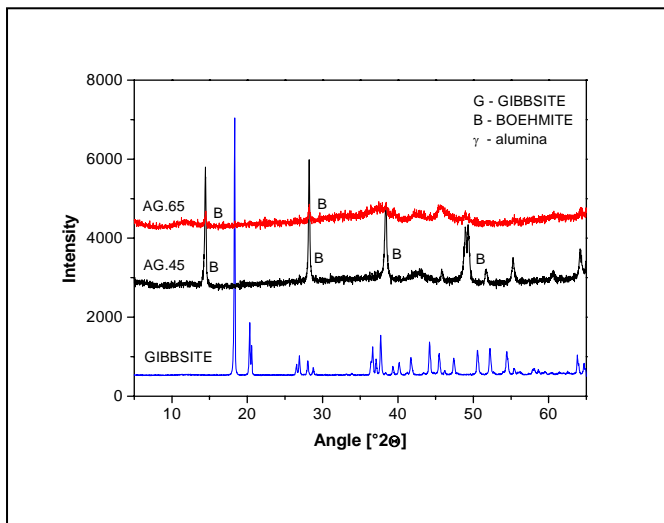


Figure 2: Diffractogram of gibbsite and γ -alumina of type AG.45 and AG.65.

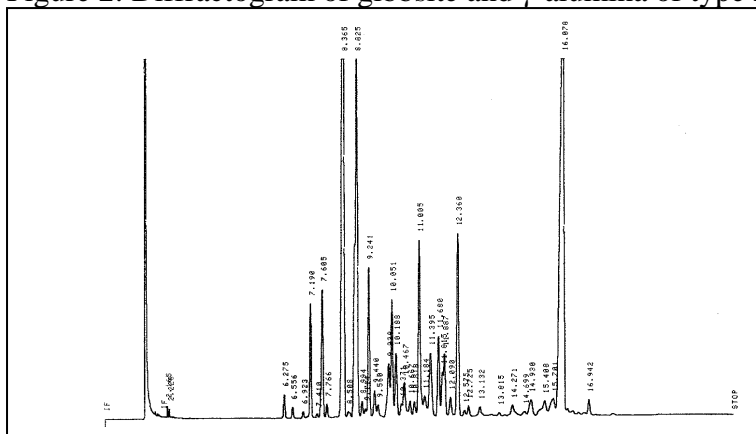


Figure 3: Chromatogram of Copaiba oil resin.

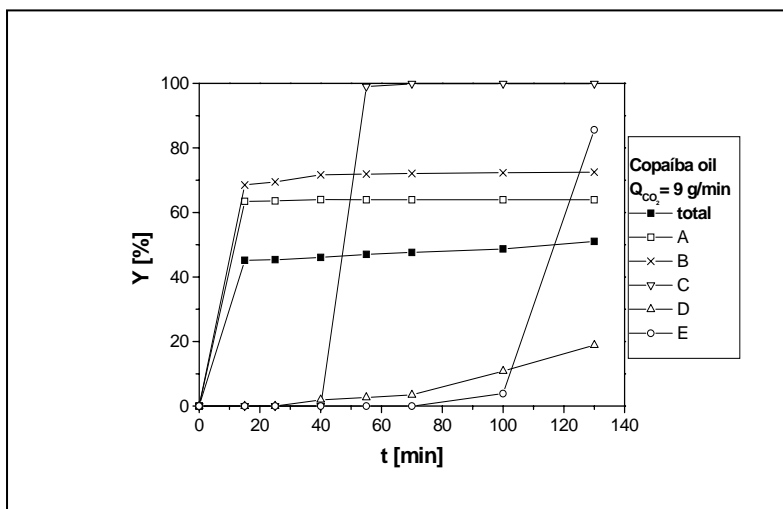


Figure 4: Yield of Copaiba oil and some selected components at 323 ($q = 0.09 \text{ g}_{\text{Oil}}/\text{g}_{\text{Adsorbent}}$).

[1] França, L. F., Machado, N. T., Corrêa, N. C. F., Zetzl, C., Brunner, G. Measurement of adsorption isotherms of oleic acid in supercritical CO_2 using γ -alumina as adsorbent. In: Anais VII SLACA, 2007, Campinas-São Paulo, Brazil.
 [2] Raiol, I.A.S.; Araújo, M.E.; Franca, L.F.; Neves, R.F.; Machado, N.T.: *Supercritical CO_2 Recovery of Carotenoids from Activated Alumina*, Proceedings of the 5th International Symposium on Supercritical Fluids, Atlanta, 2000.

column coated with $0.25 \mu\text{m}$ (5%-Phenyl Methylpolysiloxane, J&W Scientific, Model: DB-05). Nitrogen was used as the carrier gas, and the following temperature program was used: Oven temperature 373 K; Injection temperature 553 K, and detector temperature of 593 K. The temperature rate was [3 K/min] in the interval 373-433 K, as shown in Figure 3, which shows the fractions obtained during the respective time slices, characterized by specific peaks on the chromatogram. The yield is depicted together with the calculated yield of some characteristic fraction components (A-E) in Figure 4.

The yield of the major compounds was calculated through the obtained total mass of a fraction, multiplied with the area percentage of the respective chromatogram. Figure 4 exhibits a good demonstration of a selective supercritical desorption by a stepwise pressure increase. The compounds A and B are volatile components recovered at low pressure with a yield of 60 to 70 [wt.%].

The low yield of the volatile compounds may be caused by high mass losses in the separator due to aerosol formation. Component C was released at a higher pressure of 15 MPa with a yield of more than 99 [wt.%]. Component E was observed in the last fraction at a pressure of 40 MPa. The compound D in contrast was released within a great pressure spectrum and was not selectively desorbed. This method seems to be an alternative to fractionation of real liquid mixtures.