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## **ACCEPTED MANUSCRIPT**

Supercritical fluid extraction of *Eucalyptus globulus* leaves. Experimental and modelling studies of the influence of operating conditions and biomass pretreatment upon yields and kinetics

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#### **Abstract**

Supercritical fluid extraction of *Eucalyptus globulus* leaves was accomplished using carbon dioxide at different pressures (200, 250 and 300 bar) and ethanol contents (0.0, 2.5 and 5.0 wt.%), with and without biomass pretreatment (grinding or dewaxing), with the objective to study total ( $\eta_{Total}$ ) and triterpenic acids ( $\eta_{TTA}$ ) extraction yields. A factorial design of experiments and response surface methodology was performed to assess and optimize the impact of both operating conditions at 40 °C and 12 g<sub>CO2</sub> min<sup>-1</sup>. The best results were obtained for 250 bar and 5.0 wt.% ethanol, for which  $\eta_{Total}$  = 3.95 % and  $\eta_{TTA}$ = 0.67 %. Three kinetic extraction curves were measured and modeled, in order to quantify the influence of both biomass pretreatments, being concluded that grinding favors the total extraction yield while dewaxing enhances the TTAs concentration in the extract. The Broken plus Intact Cells model disclosed kinetic and structural differences between the three biomass samples (natural, ground and dewaxed leaves), being able to explain the distinct trends of the various removal curves.

**Keywords:** Cosolvent; Design of Experiments; *Eucalyptus globulus* leaves; Response Surface Methodology; Supercritical CO<sub>2</sub> extraction; Triterpenic acids

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