Impregnation Isotherms of Linalool on *Radiata Pine* Wood from Supercritical Carbon Dioxide

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Abstract

Supercritical impregnation of *Radiata pine* with linalool using CO_2 as carrier solvent has been studied at lab scale (impregnation vessel = 100 mL). *Radiata pine* is one of the most common wood species that is originally from Australia and is widely grown in Spain and linalool is a biocide substance using as wood preservative with bactericidal and fungicidal effect obtained from natural extracts (herbs, spices, fruits).

In this work, the equilibrium loadings of linalool from supercritical carbon dioxide on *Radiata* pine at different temperatures (35ºC and 45ºC) and pressures (8.2 MPa and 9.1 MPa) are reported. The experimental data were obtained with a dynamic method based on measuring the outlet concentration of linalool (UV absorbance) eluted from the impregnation vessel until the effluent reach the output concentration. Impregnation isotherms of linalool on pine wood have typical shapes and can be modelled by classical two parameter models (Langmuir and Freundlich) or by more complex ones (Redlich-Peterson and Tòth). The fit of impregnation data showed that Freundlich model could correlate the experimental data for linalool satisfactorily (average absolute deviation = 6-13%) and with more simplicity versus other tested models.

INTRODUCTION

The development of green technologies for environmentally sound preservative treatment of wood products is urgently needed [1]. One of the approaches currently attracting scientific and commercial interest is the use of supercritical carbon dioxide (SC-CO_2) carry preservatives as an alternative to conventional liquid carrier solvents [2].

The basic treatability problems associated with the conventional treatment of wood can be overcome by using SCF technology where preservatives are first dissolved in a SCF (usually CO_2) and then passed through the wood structure. Higher diffusion coefficients, lower viscosities, and the absence of surface tension in SCFs enhance mass transfer and lead to deeper preservative penetration. The superior penetration adds durability and workability to the product, while maintaining the natural appearance of the wood [3]. Potentially, a more uniform distribution with less toxic biocides can be achieved with a treatment process designed to efficiently recycle biocide.

In this work, the impregnation isotherms of linalool from supercritical carbon dioxide on *Radiata* pine at different temperatures (35ºC and 45ºC) and pressures (8.2 MPa and 9.1 MPa), corresponding to CO_2-densities in the range 250-650 kg/m^3, were determined.

Radiata Pine was selected as wood material for impregnation due to is one of the most common species in Spain and it is characterized for accepting preservative chemicals very readily due to its permeability and porosity. On the other hand, linalool was the biocide substance using as wood preservative with bactericidal and fungicidal effect obtained from natural extracts (herbs, spices, fruits) [4,5].

EXPERIMENTAL PROCEDURE

Products and Material

Linalool (> 98.5% purity) was purchased from FLUKA. CO_2 (99.95% purity in volume) was supplied by Carburos Metálicos (Valladolid, Spain). Pine wood was purchased in Leroy Merlin (Galician supplier) and is received in long bars (0.02 x 0.02 x 0.475 m) and has a medium density of 526.3 kg/m^3.

Experimental Section

The experimental setup, based on the principles of frontal analysis chromatography, was used to determine the impregnation isotherms of linalool on *Radiata Pine* by supercritical CO_2. In this technique, a step change in the concentration of the solute is imposed at the inlet of the bed (the pressure and temperature were chosen to produce a monophasic system, and the response of this bed to the step change is monitored to obtain the breakthrough curve. Analysis of these curves enables the construction of the impregnation isotherms.

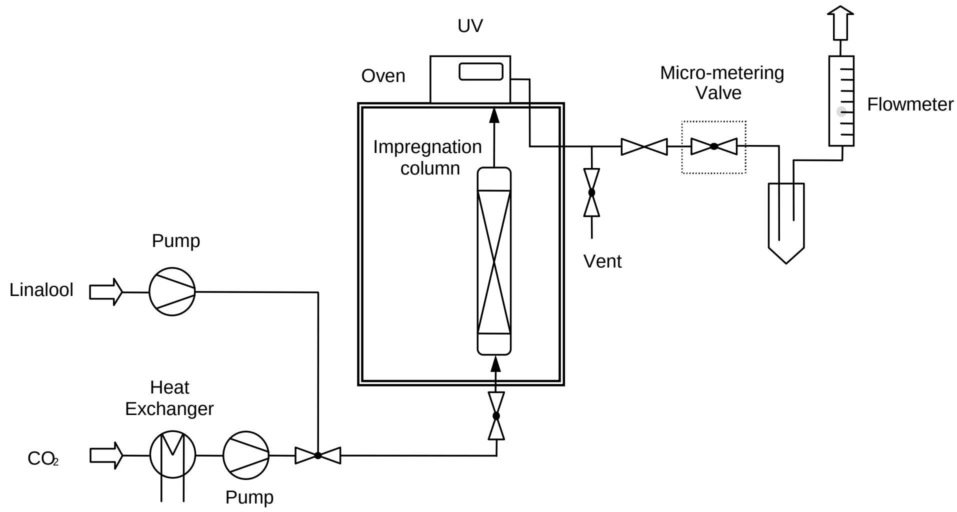


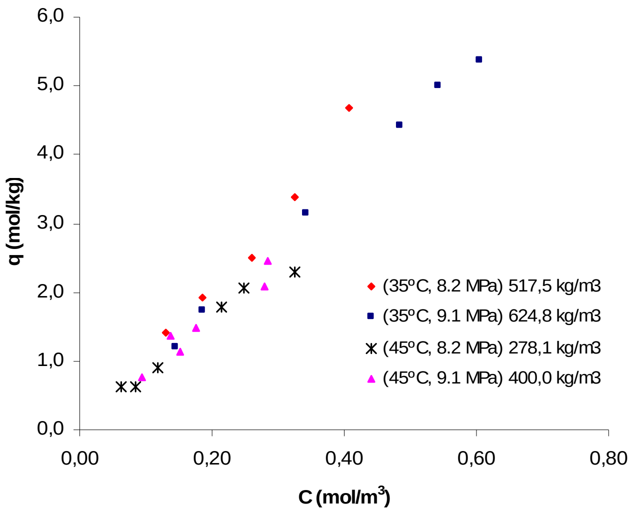
Figure 1. Schematic diagram of the experimental apparatus for impregnation measurements.

The flow sheet of the experimental setup is presented in **Figure 1**. The wood is received in long bars with a height and width of 0.02 m and a length of 2 m. In order to adjust the wood sample to dimensions of the impregnation vessel the wood bars are cut in small pieces of 0.02 x 0.02 x 0.475 m. After the treatment vessel has been charged with wood packages, the vessel is pressurized using CO_2 up to desired pressure and heated by a heat exchanger made of a coil immersed in stirred temperature-controlled bath (jacketed impregnation vessel). Purified CO_2 (99.95%) was sent to the impregnation vessel using a diaphragm pump. A secondary high pressure pump was used to pump the fungicide into the treatment vessel. The operating conditions were fixed to ensure the fungicide was completely dissolved in supercritical CO_2.

The effluent concentration was obtained on-line with a UV-detector (HP 1100) and the measured absorbance was monitored by an integrator/recorder. The response of the UV cell as a function of linalool concentration was examined and found to obey Beer´s law. The micro-.metering valves were used to control the flow and to release the pressure of supercritical CO_2 to collect the solute samples under atmospheric pressure. A complete description of impregnation procedure can be found in a previous work [6].

RESULTS AND DISCUSSION

The impregnation isotherms of linalool on *Radiata Pine* in supercritical carbon dioxide at temperatures of 35 and 45ºC, and pressures of 8.2 and 9.1 MPa, corresponding to CO_2-densities in the range 250-650 kg/m^3, are presented in **Figure 2**.



	CO_2 Densities (kg/m^3)	
	P = 8.2 MPa	P = 9.1 MPa
T = 35.0ºC	517.5	624.8
T = 45.0ºC	278.1	400.0

Figure 2. Adsorption isotherms of linalool on *Radiata Pine* from SC-CO_2.

These adsorption isotherm data indicate that the equilibrium loading of linalool on *Radiata Pine*, for a fixed temperature, decreases when the pressure increases. This indicates that at higher pressure (or higher density), the interaction forces between the solute and the carbon dioxide molecules increases as compared to the bonding forces between the solute and the pine wood surface. These results are consistent with the results from the literature [7,8]. On the other hand, for a fixed pressure, the impregnation loadings decrease when temperature increases. This fact can be attributed to the narrowing in the pore width when temperature goes up [9]. In every case, the linalool concentration in wood increases with fluid phase concentration (favourable isotherm).

Modelling of Adsorptiom Isotherms

In order to describe mathematically the adsorption isotherms at fixed densities, some well-known relationships, Langmuir, Freundlich, Redlich-Peterson and Tóth isotherms, were tested.

The adsorption isotherm models, commonly found in the literature and their parameters are listed in *Table 2*. The modelled isotherms are shown in **Figure 3**.

Table 2: Langmuir, Freundlich, Redlich-Peterson and Tóth adsorption equilibrium constants.

		ISOT. 1	ISOT. 2	ISOT. 3	ISOT. 4
		(35°C, 8.2MPa)	(35°C, 9.1MPa)	(45°C,8.2MPa)	(45°C, 9.1MPa)
		517.5 kg/m^3	624.8 kg/m^3	278.1 kg/m^3	400.0 kg/m^3
LANGMUIR	q_s (mol/kg)	10.36	10.23	8.04	8.97
	k (m^3/mol)	1.226	1.570	1.319	1.300
	A.A.D.	0.341	0.395	0.096	0.128
FREUNLICH	K (mol/kg)/(mol/m^3)$^{1/n}$	10.58	9.01	7.41	9.29
	n	0.987	1.017	1.014	0.942
	D.A.M.	0.139	0.060	0.112	0.073
REDLICH-PETERSON	A (mol/kg)	10.22	9.52	8.85	9.06
	B (m^3/mol)^M	0.980	1.032	0.985	0.980
	M	11.88	6.28	1.60	1.37
	D.A.M.	0.143	0.040	0.098	0.124
TÓTH	q_m (mol/kg)	10.50	9.306	7.77	8.76
	K_1 (m^3/mol)^m	0.941	0.850	0.860	0.740
	m	8.52	8.50	8.459	8.49
	D.A.M.	0.143	0.064	0.113	0.117

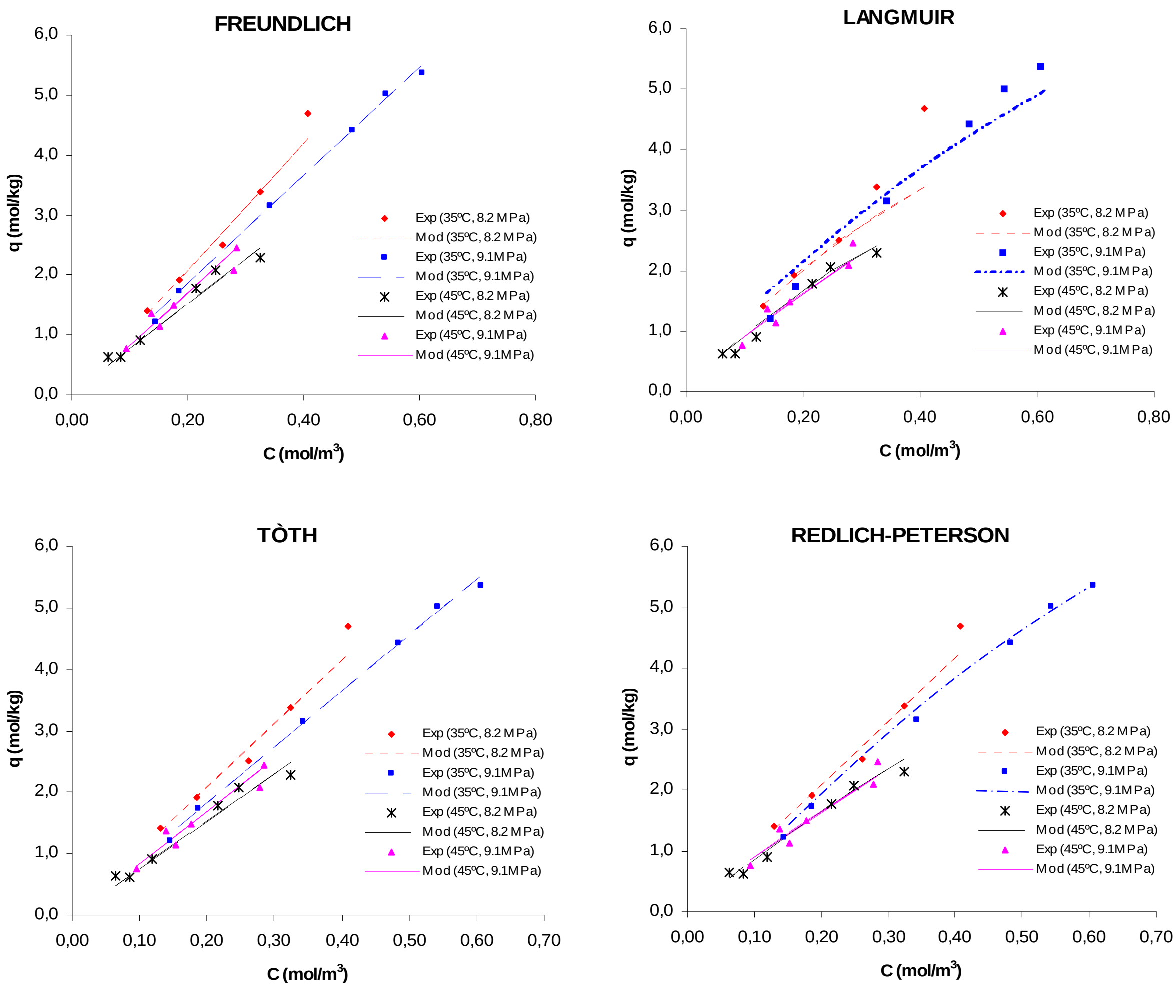


Figure 3. Correlation of the experimentally determined impregnation isotherms.

From the analysis of **Table 2** and **Figure 3**, it can be concluded that all models give good fits of the experimental impregnation data of linalool on *Radiata Pine* in supercritical conditions, but the Freundlich model, a simple two-parameter correlation, provides the best fit with an average absolute deviation of 6-13%.

CONCLUSIONS

Continuous measurements using the apparatus shown in **Figure 1** were conducted to provide the equilibrium loadings of linalool on Radiata Pine wood from supercritical carbon dioxide. The data obtained were correlated with four models described in the literature (Langmuir, Freundlich, Redlich-Peterson and Tòth). From this study, it can be concluded that Freundlich model leads to a precise correlation of the data. The equilibrium data showed that, when the temperature increased at fixed pressure, the amount of biocide in wood was reduced. The same effect was observed when the pressure was increased at fixed temperature. The solvent power increase with pressure and the narrowing in the pore width when temperature goes up, corroborated both facts.

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