

MATHEMATICAL MODELLING OF HYDRODISTILLATION OF EUCALYPTUS TERETICORNIS OIL

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ABSTRACT

Modelling of hydrodistillation of essential oil of Eucalyptus tereticornis leaf is reported in this paper. Mathematical model was developed based on relative volatility (separation factor) of oil and water. The relative volatility was found to be a function of steam rate used in hydrodistillation and it decreased from 135 to 16 for steam distillation as the steam rate increased from 0.03 to 0.45 kg/h. Similarly, for water distillation the relative volatility decreased from 102 to 11 as the steam rate increased from 0.06 to 0.45 kg/h. The relationship was found to fit a power model with $R^2 = 0.999$. Results obtained from the equilibrium model were found to agree closely with experimental data. The percentage of 1, 8-Cineole in the oil decreased with time of extraction; whereas, of some monoterpenes hydrocarbons namely α -Pinene, β -Pinene, β -Myrecene and γ -Terpenene increased with hydrodistillation time. γ -Terpenene and Fenchol were not detected in the oil extracted in the first 10 minutes of extraction; Fenchol was also not detected in the oil cut obtained between 30 to 40 minutes distillation time.

KEYWORDS: *Eucalyptus tereticornis, Hydrodistillation, 1,8-Cineole, relative volatility, Mathematical Model*

INTRODUCTION

Eucalyptus, like many other plants, contains volatile oils, called essential oils. In eucalyptus, essential oils can occur in many parts of the plant depending on the species, but it is in the leaves that oils are most abundant. Eucalyptus oil is produced and stored in small glands, the leaves of different species containing from 0.1 up to 7 percent of fresh weight of the leaves (Boland *et al.*, 1991). The essential oils of the eucalyptus are readily volatilized, and it is this characteristic that gives crushed eucalyptus leaves their distinctive aromatic odour, and allows easy distillation of the oils (Pearson, 1993).

Zrira *et al.*, (2004), investigated the composition of nine Moroccan eucalyptus species and found that they possessed oils which were rich in 1,8-cineole (>67.5%). *E. smithii* of Madagascan origin was found to possessed only 50% of 1,8-cineole while the same species of Moroccan origin possessed 83.2%. Benyoussef *et al.*, (2005) carried out microscopic observation on spearmint leaf and observed that the majority of the oil was localized in exogenous glands. Cassel *et al.*, (2009) evaluated a diffusion model to predict essential oil recovery by steam distillation of rosemary, basil and lavender. Xavier *et al.*, (2011) and, Sovova and Aleksovski (2006) developed equilibrium models for extraction of essential oil by water distillation, the models were based on the broken and intact cells.

Models governing phenomena taking place and those equations expressing equipment performance are likely to be available in literature for equipment that have been extensively studied as reported by Ahmed, *et al.*, (2007). However, such models describing the mechanism for oil removal from the plant matrix in steam

distillation of eucalyptus oil are insufficient in literature.

Babu and Singh (2009), proposed that the rate of vaporization of oil during hydrodistillation depends on the solubility of its components in steam instead of their relative volatility and used a first order kinetic model for *Eucalyptus cineria* oil, but the model did not fit experimental data. Variables such as steam rate and method of hydrodistillation that may affect the kinetics were not studied. In this work, it is proposed that the mechanism of vaporization of oil in hydrodistillation is a function of the relative volatility of the components and mathematical modelling is performed based on relative volatility of the oil and water.

MATERIALS AND METHODS

Mathematical modelling

The schematic diagram for hydrodistillation shown in Figure 1 consist of distillation still, condenser and essential oil separator. Eucalyptus leaf is immersed in the boiling water in the still. The oil glands are ruptured and released the oil, the flask then contained a mixture of water and the essential oil. Equilibrium is then assumed to exist between the liquid (oil + water) and the vapour (oil + water) phase during the process. The solid part of the leave is assumed not volatile and therefore remained in the flask. Hence, a binary system of oil and water is assumed present. An equilibrium model based on Raleigh equation (equation 3) is proposed to model the mechanism of the extraction. Other assumptions used in the model are: The essential oil is considered to be a pseudo-component and Raoult's law/ Henry's law, hold.

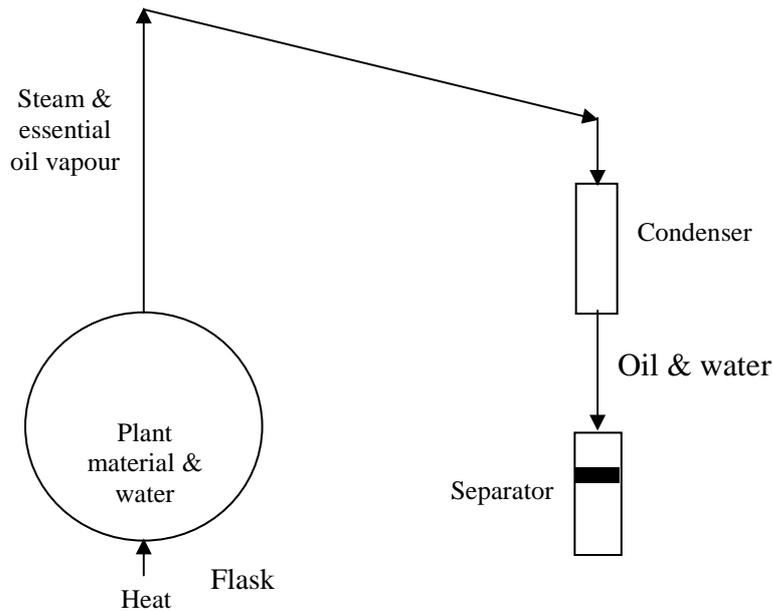


Figure 1: Schematic diagram of hydrodistillation set up

Total material balance

$$(F + S) = D + (W + S)$$

Where:

F = mass of liquid charge of composition x_F (oil/water)

S = solid matter

D = distillate

W = mass of liquid residue of composition x_W (oil/water)

Component A = Oil

Component B = Water

At any time t there are L moles of liquid in the still of composition x mole of A and an amount dD is vaporized.

Table 1: Mass balance

	Total material	Component A
Moles in	0	0
Moles out	dD	y^*dD
Moles accumulated	dL	$d(Lx) = Ldx + xdL$
In-out= acc	$0 - dD = dL$ (1)	$0 - y^*dD = Ldx + xdL$ (2)

Combining equations (1) and (2)

$$(y^* - x)dL = Ldx$$

$$\int_W^F \frac{dL}{L} = \int_{x_W}^{x_F} \frac{dx}{(y^* - x)}$$

$$\ln\left(\frac{F}{W}\right) = \int_{x_W}^{x_F} \frac{dx}{(y^* - x)} \text{----- (3)}$$

Equation (3) is known as Raleigh equation (Treybal, 1981)

where: x_F = Fraction of essential oil initially present in the liquid charge

x_W = Fraction of essential oil that is lost in the final waste

If the relative volatility, which is a measure of separability, $\alpha = \frac{y^*(1-x)}{x(1-y^*)}$ (Treybal, 1981)

$$y^* = \frac{\alpha x}{1 + \alpha x - x}$$

Substituting for y^* in equation (3) and solve using partial fraction gives

$$\ln\left(\frac{F}{W}\right) = \frac{1}{(\alpha - 1)} \left[\ln\left(\frac{x_F}{x_W}\right) + \alpha \ln\left(\frac{1 - x_W}{1 - x_F}\right) \right] \text{-----(4)}$$

Equation (4) is the solution of equation (3), It is an equilibrium model relating relative volatility and other parameters as earlier defined. The relative volatility was evaluated from equation (4), using Microsoft Excel Solver programme.

Isolation and analysis of *E. tereticorns* oil

The essential oil was extracted using modified Clevenger type apparatus, from dried leaf of *E. tereticornis* grown in Ahmadu Bello University Zaria, Nigeria (Latitude 11° 05' N, Longitude 7° 43' E). Dried leaves of *E. tereticornis* (200 g) were fed into a 2 litres round bottom flask connected to a condenser. Water distillation was conducted for 2 hours and cooling water was available at 20°C and 10 cm³/s flow rate. Steam distillation was also conducted using a modified Clevenger apparatus. Sample of 200 g *E. tereticornis* leaves were charged into a 5 liters flask and also steam distilled for 2 hours. The oil collected in each case was dried with sodium sulphate and stored as described by Kaur et al., (2011).

The oil obtained was analyzed using GC-MS QP 2010 PLUS (Shimadzu, Japan) equipment following the method described by Babu and Singh (2009); Hill and Johnson (2002); and Kaur, et al., (2011). The analysis revealed that ten components were identified in the oil.

RESULTS AND DISCUSSION

Figure 2 presents variation of relative volatility with steam rate for two hydrodistillation techniques (steam distillation and water distillation). The larger the value of relative volatility above unity, the greater the degree of

separability (Treybal, 1981). It can be seen that the relative volatility decreased from 135 to 16 for steam distillation as the steam rate increased from 0.03 to 0.45 kg/h. Also for water distillation the relative volatility decreased from 102 to 11 as the steam rate increased from 0.06 to 0.45 kg/h. The gradient is steep for lower steam rates and becomes gentle as the steam rates increase. Relationship between the relative volatility and the steam rate was modelled, and the following power models were obtained:

$$y = 4.749x^{-1.04} \text{-----5}$$

$$y = 3.335x^{-1.07} \text{-----6}$$

where: y = relative volatility and x = steam rate

Equations (5) and (6) applies respectively to steam distillation and water distillation techniques, with $R^2 = 0.999$ for both. Thus, relative volatility is a function of steam rate in hydrodistillation of essential oil.

Mole fractions of essential oil in feed evaluated from equation (4) were compared with that obtained from experimental data. This is presented in Figures 3 and 4 for various steam rates. It can be seen from the Figures that values obtained from experimental data agree closely with those from the model.

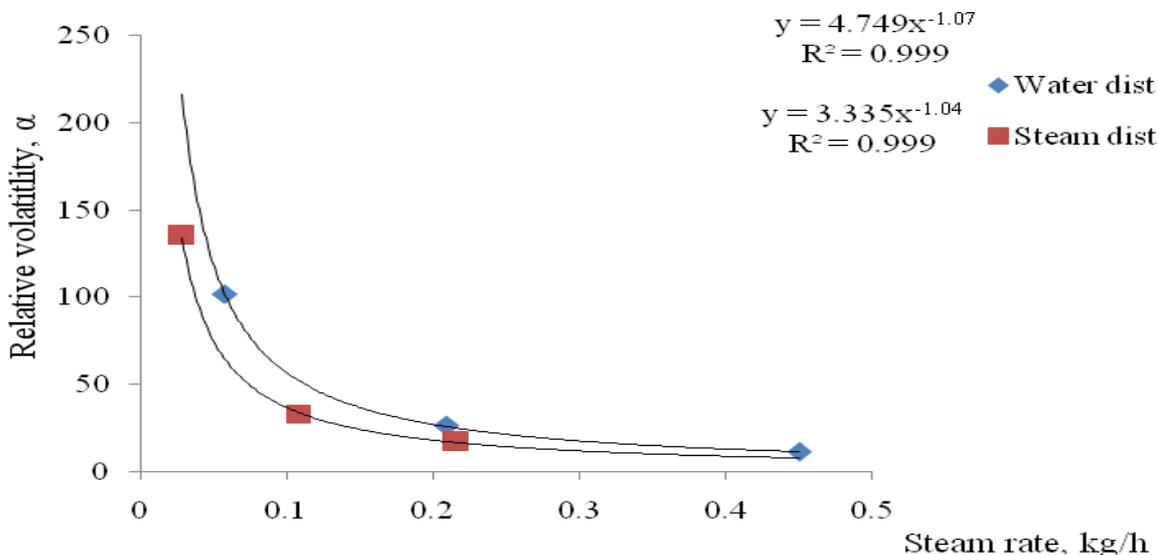


Figure x: Relative volatility versus steam rate

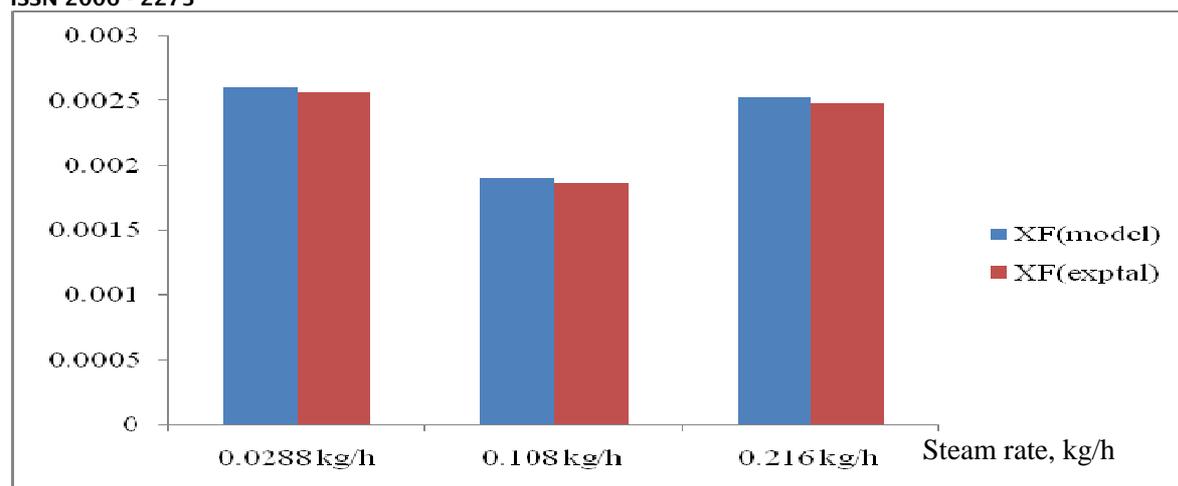


Figure 3: Mole fraction from experimental data and prediction from model (steam distillation)

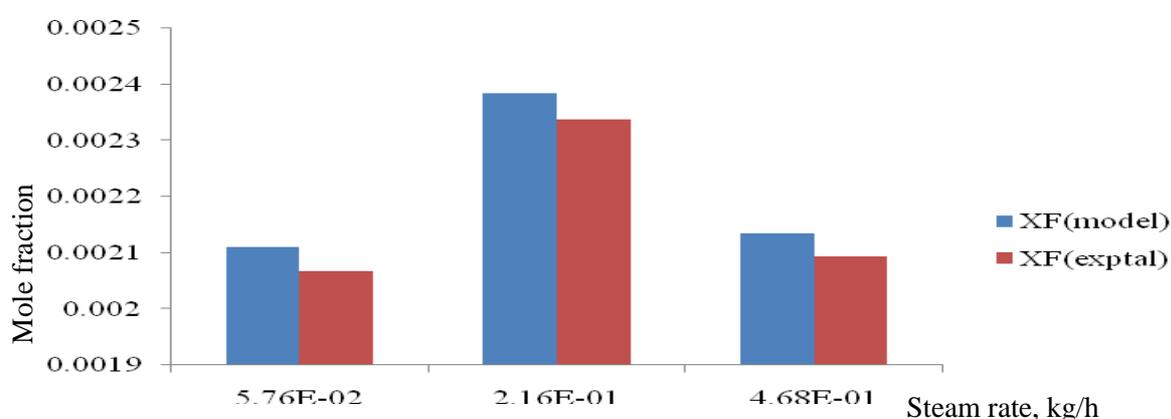


Figure 4: Mole fraction of oil from the model and experimental data (water distillation) data

Composition of essential oil extracted was determined at various intervals of extraction time. The results are presented in Table 1. Ten components were identified, 4 were oxygenated monoterpenes and 6 were monoterpenes hydrocarbons. The main constituents were found to be 1,8-Cineole, α -Pinene and β -Pinene. Kaur *et al.*, (2011) reported that the presence of 1, 8-Cineole and α -Pinene as major constituents of *E. tereticornis* oil were also supported by earlier reports (Coelhode-Souza *et al.*, 2005; Hill and Johnson, 2002). It can be seen from Table 1, that 1, 8-Cineol, one of the components which

determine the application of the oil (Pearson, 1993) decreased from 77.6 % to 65.5 % as extraction time increased from 10 to 40 minutes. Oil extracted at the first 10 minutes had 77 % 1, 8-Cineole while that obtained from 30 to 40 min has 65.5 % 1,8-Cineole. The percentage of monoterpenes hydrocarbons α -Pinene, β -Pinene, β -Myrcene and γ -Terpenene increased as hydrodistillation time increases. γ -Terpenene and Fenchol were not detected in the oil extracted at the first 10 minutes.

Table 2: Chemical composition of *Eucalyptus tereticornis* oil with extraction time

Compound	Percentage			
	0 - 10 min	10 - 20 min	20 - 30 min	30 - 40 min
α -Pinene	16.23	16.86	18.77	20.84
β -Pinene	1.98	2.38	2.58	2.99
β -Myrcene	0.26	0.36	0.41	0.48
1,8-Cineole	77.6	71.57	68.99	65.50
γ -Terpenene	-	0.35	0.43	0.55
Fenchol	-	1.17	1.06	-
2(10)-Pinen-3-ol	1.55	2.74	2.87	3.42
2(10)-Pinen-3-one	0.67	1.10	1.08	1.23
Borneol	0.50	1.10	1.06	1.36
α -Terpeneol	1.21	2.37	2.74	3.62
	100.00	100.00	100.00	100.00

CONCLUSION

Equilibrium models were proposed for hydrodistillation of eucalyptus oil based on relative volatility of oil and water. The relative volatility was found to be a function of the steam rate; its numerical value decreased from 135 to 16 for steam distillation as the steam rate increased from 0.03 to 0.45 kg/h. Also for water distillation the relative volatility decreased from 102 to 11 as the steam rate increased from 0.06 to 0.45 kg/h. Results obtained from the model agree closely with the experimental data. 1, 8-Cineole and α -Pinene were found to be the major

constituents of essential oil of *E. tereticornis* grown in Zaria. The percentage of 1, 8-Cineole in the oil decreased from 77.6 % to 65.5 % within time of extraction of 40 minutes; whereas, that of α -Pinene, β -Pinene, β -Myrcene and γ -Terpinene increased with hydrodistillation time.

Acknowledgements

The authors acknowledged the financial support of the Education Trust Fund TETFUND, Ahmadu Bello University, Zaria.

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