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Preliminary Study: Kinetics of Oil Extraction from Sandalwood by Microwave-assisted Hydrodistillation

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Sandalwood and its oil, is one of the oldest known perfume materials and has a long history (more than 4000 years) of use as mentioned in Sanskrit manuscripts. Sandalwood oil plays an important role as an export commodity in many countries and its widely used in the food, perfumery and pharmaceuticals industries. The aim of this study is to know and verify the kinetics and mechanism of microwave-assisted hydrodistillation of sandalwood based on a second-order model. In this study, microwave-assisted hydrodistillation is used to extract essential oils from sandalwood. The extraction was carried out in ten extraction cycles of 15 min to 2.5 hours. The initial extraction rate, the extraction capacity and the second-order extraction rate constant were calculated using the model. Kinetics of oil extraction from sandalwood by microwave-assisted hydrodistillation proved that the extraction process was based on the second-order extraction model as the experimentally done in three different steps. The initial extraction rate, h, was 0.0232 g L^{-1} min^{-1}, the extraction capacity, C_S, was 0.6015 g L^{-1}, the second-order extraction rate constant, k, was 0.0642 L g^{-1} min^{-1} and coefficient of determination, R^2, was 0.9597.

Keywords : sandalwood oil; microwave-assisted hydrodistillation; extraction; kinetic study

INTRODUCTION

Sandalwood and its oil, is one of the oldest known perfume materials and has a long history (more than 4000 years) of use as mentioned in Sanskrit manuscripts. Sandalwood is still used in religious rituals in India and is also used as a medium from which to carve deities and temples. The ancient Egyptians imported the wood and used it in medicine, embalming and ritual burning to venerate the gods. The oil has been in public use since the early 1800s (Arctander, 1960). Sandalwood has developed into a commercial timber crop over the past 10-15 years, with substantial sandalwood plantations established in India, China and Australia, and more modest plantings being established in Indonesia, Fiji, Vanuatu, Hawaii and Sri Lanka (Hettiarachchi et al., 2010).

Sandalwood oil plays an important role as an export commodity in many countries and its widely used in the food, perfumery and pharmaceuticals industries. Sandalwood oil is used as a flavor

component in many food products, including alcoholic and non-alcoholic beverages, frozen dairy desserts, candy, baked goods and gelatin and puddings at use levels generally below 0.001% (10 ppm) except in hard candy. The highest maximum use level for sandalwood oil in food products is approximately 90 ppm. Sandalwood oil is generally used as a natural flavoring substance or in conjunction with other flavor ingredients (Burdock and Carabin, 2008).

In perfumery, sandalwood oil is used extensively. It blends well with rose, violet, tuberose, clove, lavender, oakmoss and labdanum products. It is also commonly used in woody, wood-floral and Oriental-floral bases. The oil is also used as a base for co-distillation of other essential oils. It blends well with other chemicals such as ionones and methylionones. Because of the scarcity of sandalwood oil, the search for efficient synthetic substitutes has been conducted extensively to investigate the structure odor relationship of sandalwood constituents (Shvets and Dimoglo, 1998; Bajgrowicz and Frater, 2000). Several investigators have extensively studied and attempted to synthesize santalol derivatives with comparable olfactory activity (Buchbauer et al., 1992, 1997, 2001). Opdyke (1974) reported the use of sandalwood oil in fragrances in the USA to be approximately 48,000 lb/year.

Sandalwood oil is used medicinally for common colds, bronchitis, fever, infection of the urinary tract, inflammation of the mouth and pharynx, liver and gallbladder complaints and other maladies (PDR Herbal, 2004). In the Indian system of medicine (Ayurvedic), sandalwood oil is largely used as a demulcent, diuretic and mild stimulant (Pande, 1977). The daily recommended dosage of sandalwood oil per the German Commission E review is 1–1.5 g for not more than six weeks (Anonymous, 1998). Imdorf et al. (1999) reported that sandalwood oil acts as a repellent of the pest *Varroa jacobsoni* Oud., in honey bee colonies and has been used as an acaricide. Choi et al. (2006) reported modest activity against *Lycoriella mali* (the mushroom fly).

The main methods to obtain essential oils from the plant materials are hydrodistillation, steam distillation, solvent extraction, supercritical fluid extraction (SC-CO_2) and liquid CO_2 extraction have been used to obtain the volatile oil from sandalwood (Moretta et al. 1998; Marongiu et al. 2006). Among these method, hydrodistillation has been the most common approach to extract the essential oils from the medicine herbs and plants (Chinese Pharmacopoeia Committee, 2010). Alternative methods, employing microwaves, have been developed in order to shorten extraction time, improve the extraction yield, and reduce the operational costs. Microwave-assisted procedures for isolating essential oils have become attractive for use in laboratories and industry. The advantages of using microwave energy for oil extraction are more effective heating, fast energy transfer, faster response to process heating control, faster start-up, increased production, and elimination of some process steps.

However, to the best of authors' knowledge no work has been published on the extraction of essential oil from

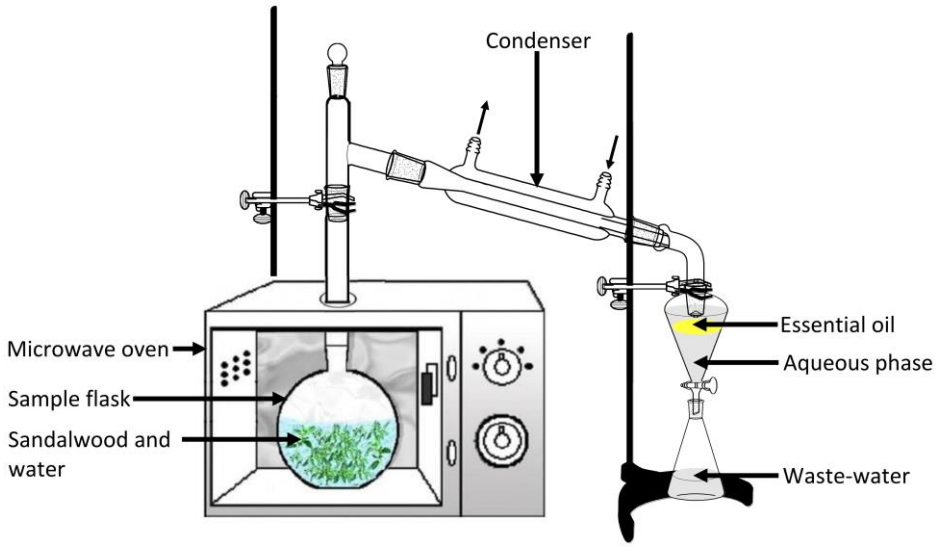

Fig. 1: Schematic representation of the microwave-assisted extraction apparatus used in this study

Santalum species using microwave ovens for heating. Therefore, the objective of this study were to investigate the potential of microwave-assisted hydrodistillation for the extraction of essential oils from sandalwood. In this study, the author also attempted to know and verify the kinetics and mechanism of microwave-assisted hydrodistillation of sandalwood based on a second-order model.

MATERIALS AND METHODS

Raw Materials

The main raw material used in this study is sandalwood that comes from the Kupang, East Nusa Tenggara, Indonesia in powder form. All other chemicals and solvents used were of analytical grade.

Microwave Extraction of Sandalwood Oil

A domestic microwave oven (EMM-2007X, Electrolux, 20 L, 800 W; variable in 200 W increments, 2.45 GHz) was modified for microwave-assisted hydrodistillation operation. The dimensions of the PTFE-coated cavity of the microwave oven were 46.1 cm x 28.0 cm x 37.3 cm. Twenty grams of sandalwood powder samples were placed in a 1 l flask containing deionized water (400 mL). The flask was setup within the microwave oven cavity and a condenser was used on the top (outside the oven) to collect the extracted essential oils (Fig. 1). The microwave oven was operated at 600 W power level for a period of 2.5 h. This period was sufficient to extract all the essential oils from the sample. The extraction was carried out in ten extraction cycles of 15 min to 2.5 hours. To remove water, the extracted essential oils were then dried over anhydrous sodium sulfate, weighed and stored in amber vials at 4 °C until they were used for analysis. The yield of sandalwood oil was found by the following equation

$$y = \frac{v}{w} \text{ X } 100 \quad (1)$$

where y is the sandalwood oil yield (%, w/w), V is the weight or mass of extracted sandalwood oil (g) and W is the weight or mass of sandalwood powder (g).

Kinetic Model

Second-order mechanism model means that the extraction occurs in two simultaneous processes. The amount of extracted oil increases rapidly with time at the beginning and then decreases slowly with the time until the end of extraction process [Ho et.al., 2005; Rabesiaka et.al., 2007; Uhm et.al., 2011; Meizane and Kadi, 2008]. The rate of dissolution for the essential oil contained in the solid to solution can be described by Equation (2)

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = k(C_S - C_t)^2 \quad (2)$$

where k is the second-order extraction rate constant (L g^{-1} min^{-1}), C_S the extraction capacity (concentration of essential oil at saturation in g L^{-1}) and C_t is the concentration of sandalwood oil at any time t (min).

By considering the initial and boundary conditions, t = 0 to t and C_t = 0 to C_t, the integrated rate law for a second-order extraction was obtained:

$$C_t = \frac{C_S^2 kt}{1 + C_S kt} \quad (3)$$

By transforming Eq. (3), a linear form shown in Eq. (4) can be obtained and the extraction rate can be written as Eq. (5):

$$\frac{t}{C_t} = \frac{1}{kC_S^2} + \frac{t}{C_S} \quad (4)$$

$$\frac{C_t}{t} = \frac{1}{(1/kC_S^2) + (t/C_S)} \quad (5)$$

The initial extraction rate, h, as Ct/t when t approaches 0, can be defined as:

$$h = kC_S^2 \quad (6)$$

and, the concentration of essential oil at any time can be expressed after rearrangement as:

$$C_t = \frac{t}{(1/h) + (t/C_S)} \quad (7)$$

The initial extraction rate, h, the extraction capacity, C_S, and the second-order extraction rate constant, k, can be determined experimentally from the slope and intercept by plotting t/C_t versus t.

RESULTS AND DISCUSSION

As shown in Fig. 2, the rate of extraction was increased as the time of extraction increase until it reached plateau or constant after 120 min of extraction. 0.93% extractable oil was obtained in the 1.5 hours of extraction until it became plateau (1.02%). The experimental result was analyzed using second-order model by plotting t/C_t versus time as shown in Fig 3.

According to Fig. 2, the rate of extraction was fast at the beginning and slow until the end of the extraction process. The extraction process takes place in three different steps: an equilibrium phase where the phenomena of solubilization and partition intervene, in which the substrate is removed from the outer surface of the particle at an

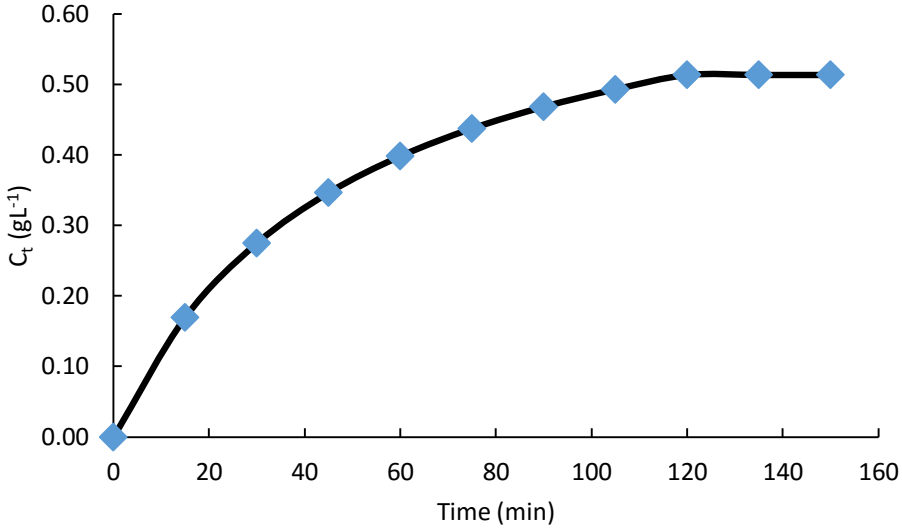

Fig. 2: The concentration of sandalwood oil in the solution at any time, C_t (g L^{-1}) versus time (min)

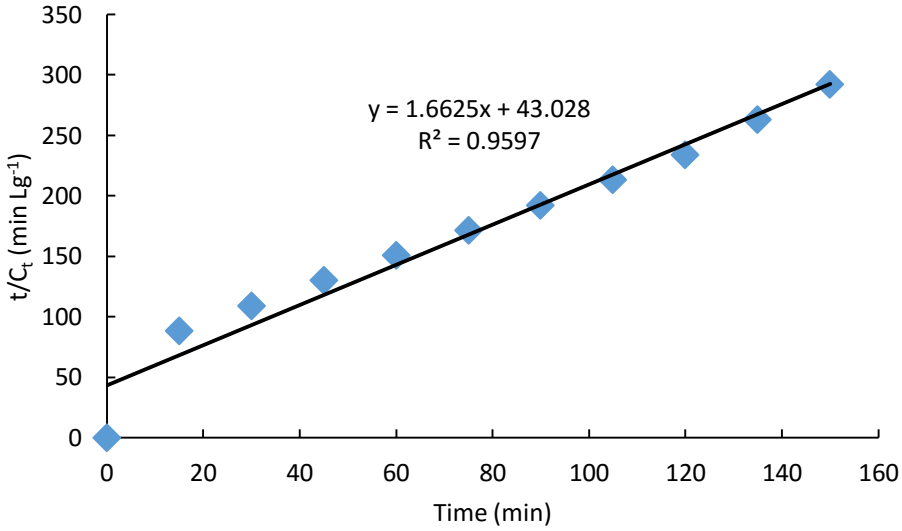

Fig. 3: Second-order extraction kinetics of sandalwood

approximately constant velocity. Then, this stage is followed by an intermediary transition phase to diffusion. The resistance to mass transfer begins to appear in the solid–liquid interface; in this period the mass transfer by convection and diffusion prevails. In the last phase, the solute must overcome the interactions that bind it to the matrix and diffuse into the extracting solvent. The extraction rate in this period is low, characterized by the removal of the extract through the diffusion mechanism. This point is an irreversible step of the extraction process; it is often regarded as the limiting step of the process [Raynie, 2000]. Diffusion rate decreased as the time of extraction incressed due to the high solute

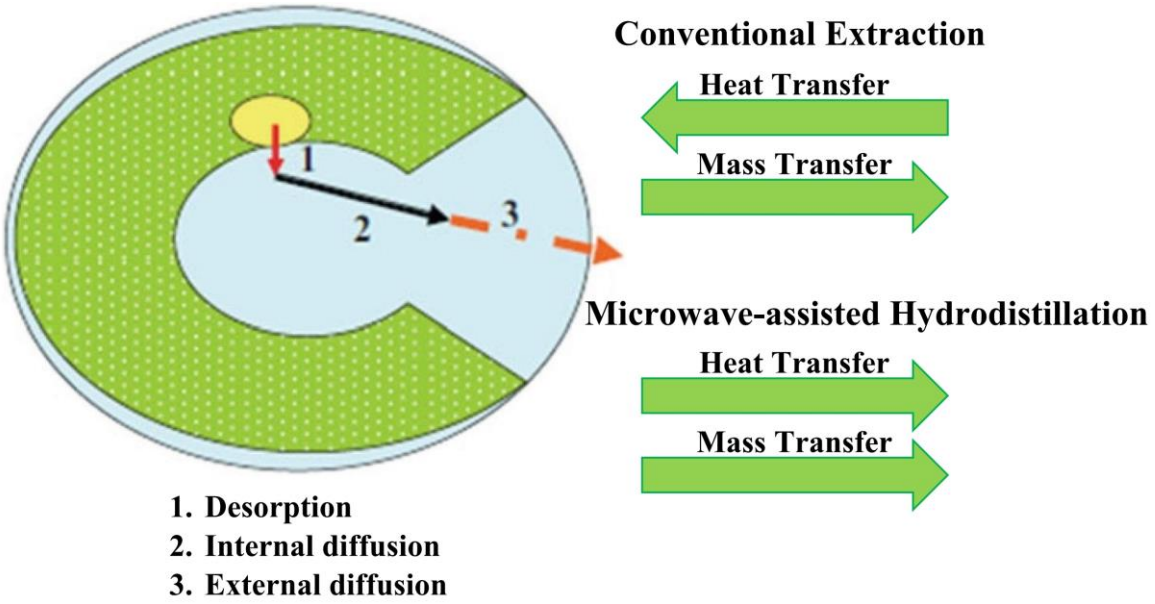

Fig. 4: Heat and mass transfer mechanisms in microwave-assisted hydrodistillation and conventional extraction of sandalwood oil

concentration in liquid at the third stage. Even though the extraction time incressed after the maximum sandalwood oil was extracted, it did not show any changes or significant in amount of oil extracted. The trend of sandalwood oil recovery under extraction time of 60 min (77.58%), 105 min (18.46%) and 150 min (3.96%).

The initial extraction rate, h, the extraction capacity, C_S, the second-order extraction rate constant, k, and coefficient of determination, R^2, were calculated experimentally by referring to the linier curve in Fig 3. From graph t/C_t versus time, slope is equal to $1/C_S$, and intercept is equal to $1/h$. The data showed in Table 1.

Table 1. Linierization of second-order kinetic model of microwave-assisted hydrodistillation of sandalwood

C_S (g L^{-1})	k (L g^{-1} min^{-1})	h (g L^{-1} min^{-1})	R^2
0.6015	0.0642	0.0232	0.9597

For this study, the maximum yield oil extracted by microwave-assisted hydrodistillation is higher compared to conventional hydrodistillation. In the work of Hettiarachchi et al. (2010) it was observed that sandalwood oil yield extracted by conventional hydrodistillation for 9 hours is 0.43%. The fundamentals of the microwave-assisted hydrodistillation process are different from those of conventional methods because the extraction occurs as the result of changes in the cell structure caused by electromagnetic waves. In microwave-assisted hydrodistillation, the process acceleration and high extraction yield may be the result of a synergistic combination of two transport phenomena: heat and mass gradients working in the same direction [Chemat et al., 2009]. On the other hand, in conventional extractions the mass transfer occurs from inside to the outside, although the heat transfer occurs from the outside to the inside of the

substrate (Fig. 4). In addition, although in conventional extraction the heat is transferred from the heating medium to the interior of the sample, in microwave-assisted hydrodistillation the heat is dissipated volumetrically inside the irradiated medium.

CONCLUSIONS

Kinetics of oil extraction from sandalwood by microwave-assisted hydrodistillation proved that the extraction process was based on the second-order extraction model as the experimentally done in three different steps. The initial extraction rate, h, was 0.0232 g L^{-1} min^{-1}, the extraction capacity, C_S, was 0.6015 g L^{-1}, the second-order extraction rate constant, k, was 0.0642 L g^{-1} min^{-1} and coefficient of determination, R^2, was 0.9597.

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