

Optimization and Kinetic Study of Gaharu Oil Extraction

Muhammad Hazwan H., Azlina M.F., Hasfalina C.M., Zurina Z.A., and Hishamuddin J.

Abstract—Gaharu that produced by *Aquilaria* spp. is classified as one of the most valuable forest products traded internationally as it is very resinous, fragrant and highly valuable heartwood. Gaharu has been widely used in aromatherapy, medicine, perfume and religious practices. This work aimed to determine the factors affecting solid liquid extraction of gaharu oil using hexane as solvent under experimental condition. The kinetics of extraction was assumed and verified based on a second-order mechanism. The effect of three main factors, which were temperature, reaction time and solvent to solid ratio were investigated to achieve maximum oil yield. The optimum condition were found at temperature 65°C, 9 hours reaction time and solvent to solid ratio of 12:1 with 14.5% oil yield. The kinetics experimental data agrees and well fitted with the second order extraction model. The initial extraction rate (h) was 0.0115 $\text{gmL}^{-1}\text{min}^{-1}$; the extraction capacity (C_s) was 1.282 gmL^{-1} ; the second order extraction constant (k) was 0.007 $\text{mLg}^{-1}\text{min}^{-1}$ and coefficient of determination, R^2 was 0.945.

Keywords—Gaharu, solid liquid extraction, optimization, kinetics.

I. INTRODUCTION

IN Malaysia, gaharu oil is a very highly valuable product. Gaharu or Agarwood is the resin-impregnated and fragrant heartwood that belongs to the *Aquilaria* genus and *Thymelaeaceae* family [1]. Pathological wounding processes or the response to fungal infection resulted to the wood resinous. When gaharu tree infected with a parasitic mold, it will start to produce an aromatic resin. The fragrant wood that derived from diseased timber forms a dark, brownish patches or streaks in the tree. Among the different species of gaharu, *Aquilaria malaccensis* is the main species lying beneath in the Malaysia's forest [2].

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These days, the gaharu is widely used not only in the cosmetics, medicine, perfume, and aromatherapy industries but also for the religious ritual. In the medicine field, it is reported that Malaysians used gaharu mixed with coconut oil as a liniment, and also in a boiled concoction to treat rheumatism and other body pain [3]. Moreover, gaharu is also prescribed for dropsy, as carminative, a stimulant, for heart palpitations, and also as a tonic taken particularly during pregnancy, after childbirth and for diseases of female genital organs [4].

Various extraction methods can be used to produce essential oils. Currently, hydro distillation, steam distillation, water distillation and solvent extraction are commonly used to extract essential oil from plants [5]. Few studies have been conducted regarding gaharu oil extraction such as using microwave assisted extraction [6], spinning band distillation [7], hydrodistillation [8], ultrasonic assisted steam distillation [9], and ultrasonic assisted hydro distillation [10].

In this study, solid liquid extraction was used as method of gaharu extraction. Soxhlet extraction is an example of solvent extraction solid sample, which is commonly known as solid-liquid extraction. In physicochemical terminology, it is referred as leaching and is one of the oldest ways of solid sample pretreatment [11]. Soluble fraction will transfer from a solid material to a liquid solvent. The soluble fraction that is the solute or leachate will diffuse from the solid into the surrounding solvent.

Various studies have been conducted to describe the kinetics and mechanism of the extraction process. Solid liquid extraction usually fitted the second order mechanism model [12]-[15]. Second-order mechanism model means that the extraction occurs in two simultaneous processes. The first part is when the solute gets extracted quickly caused by driving force of fresh solvent. Meanwhile, the extraction gets much slower in the second stage as the remainder solute will diffuse into the solution [16].

The second order mechanism model is as follows. The rate of dissolution for the oil contained in the solid to solution can be described by (1):

$$dC_t/dt = k(C_s - C_t)^2 \quad (1)$$

where:

k = The second-order extraction rate constant ($\text{mLg}^{-1}\text{min}^{-1}$)

C_s = The concentration of oil at saturation (gmL^{-1})

C_t = The concentration of oil in the solution at any time (gmL^{-1}), t (min)

The integrated rate for a second-order extraction was obtained by considering the boundary condition $t = 0$ to t and $C_t = 0$ to C_t :

$$C_t = C_s^2 kt / (1 + C_s kt) \quad (2)$$

Linear form of the (2) becomes:

$$t/C_t = (1/kC_s^2) + (t/C_s) \quad (3)$$

The extraction rate can be written as the following:

$$C_t/t = 1/[1/kC_s^2 + (t/C_s)] \quad (4)$$

The initial extraction rate, h , when t approaches 0 can be written as:

$$h = kC_s^2 \quad (5)$$

Rearranging (4), the concentration of oil at any time can be obtained as:

$$C_t = t / [(1/h) + (t/C_s)] \quad (6)$$

By plotting t/C_t versus t , the initial extraction rate, h , the extraction capacity, C_s and the second order extraction constant, k , can be calculated experimentally.

The objective of the present study were to determine the factors affecting solid liquid extraction of gaharu oil using hexane as solvent under experimental condition and to study the kinetics and mechanism of solid liquid extraction of gaharu based on a second order model.

II. MATERIALS AND METHODS

A. Raw Material Preparation

Gaharu chips were grounded by Wood Chipper Model Pallman PH 12X430. It is dried in for overnight in 104°C to reduce the moisture content. After the drying process, the gaharu chip is made into powdered form by Ring Knife Flaker Model Pallman TZ8.

B. Oil Extraction from Gaharu Powder

The effect of three main factors, which are temperature, reaction time and solvent to solid ratio were investigated to get the optimum parameters for achieving maximum yield. Approximately 20g of gaharu powders were used for oil extraction using hexane as solvent. The extraction temperature was investigated at 45°C, 55°C and 65°C (near boiling point of hexane). The reaction time was varied from 6 to 9 hours. The solvent to solid ratio was fixed of 10:1, 11:1, 12:1 and 13:1. The experiment was conducted by varying one variable at a time method by Soxhlet extractor. At the end of extraction, the powder was filtered by a vacuum filtration (Millipore glass base and funnel) using Advantec filter paper to remove suspended solids. Then, the solvent was separated from the oil by using rotary evaporator R215 and was gathered

in the receiving flask. The oil meanwhile remained in the sample flask was weighed. The percentage of extracted oil was calculated by dividing the amount of obtained oil by amount of gaharu powders multiply by 100. All experiments were repeated twice.

C. Kinetic Study

Considering the optimum parameters achieved from the optimization process, the rate of extraction of gaharu was determined at temperature of 65°C that is around boiling point of hexane. Extraction was carried out between 30 minutes to 9 hour with 30 minutes intervals for first hour and one hour intervals until the end of the extraction. Each extraction interval time was repeated twice.

III. RESULTS AND DISCUSSIONS

A. Effect of Temperature

Fig. 1 shows the total amount of extracted oil from gaharu powder at different temperature. Extraction at 65°C (near boiling point of hexane) gave about 13% of oil which was the highest yield obtained. Volatility effect is very crucial for oil extraction. At higher temperatures, the oil becomes more volatile, which allows more oil to be extracted [17]. However, if the extraction is done higher than the boiling point of solvent, the percentage of extracted oil decrease as it tends to vaporize. Nevertheless, the extraction improved as the diffusion coefficient and solubility of oil in solvent are increased when increasing the extraction temperature approaching to the boiling point of solvent [18].

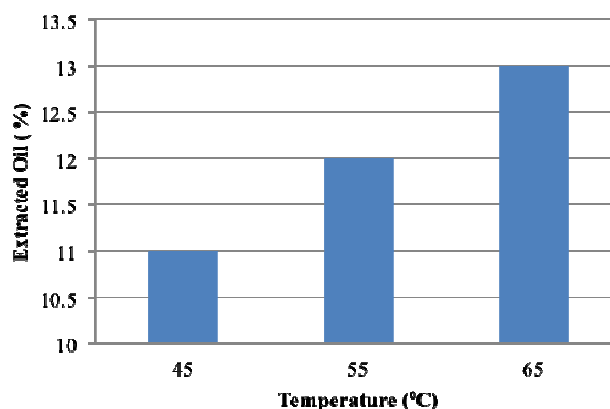


Fig. 1 Effect of temperature on amount of extracted oil of 7 hour reaction time and solvent to solid ratio 13:1

B. Effect of Reaction Time

The effect of reaction time on amount of extracted oil is showed in Fig. 2, which showed that the longest reaction time (9 hour) gave more oil yield. Based on findings, the oil yield for 6 hour, 7 hour, 8 hour and 9 hour reaction time were 12%, 13, 13.5%, and 14.5% respectively. This findings supported by Wang et al. who reported that the extractability (percent ratio of extracted lipid yield to the total lipid content in the grains sorghum) increased with the increased of reaction time [19].

Moreover, 9 hour reaction time had reported as the best reaction time of gaharu extraction as it produced the highest yield [9]-[10].

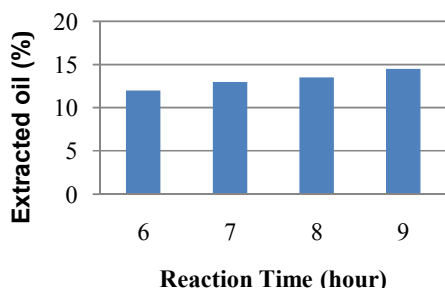


Fig. 2 Effect of reaction time on amount of extracted oil at temperature 65°C and solvent to solid ratio 13:1

C. Effect of Solvent to Solid Ratio

Fig. 3 shows the amount of extracted oil at four different solvent to solid ratios. An increasing trend was observed whereby the oil yields increased as the solvent to solid ratio increased. There was no increment of extracted oil can be obtained by increasing the solvent to solid ratio up to 13:1. The effect of solvent to solid ratio is very essential consideration to exploit maximum extractability while scaling up or down the sample preparation method [20]. The procedures become more complex when larger solvent volumes were used. In addition, if smaller solvent volumes were used, it can make the target extraction incomplete [21]. Equilibrium of the process is a condition where the solute concentration in both the solid and the solvent phases are equal [22]. When the solvent to solid ratio is sufficient to cater the solubility of solute, solution adhering to the solids will have the same concentration as liquid or solvent phase. Therefore within the contact or extraction time investigated, adequate amount of solvent to solid ratio need to be identified for the extraction process. By increasing solvent to solid ratio up to a specific limit, the oil yield increase [16]. This is resulted by the concentration gradient between the solid and the liquid phase becomes greater that enhance good mass transfer.

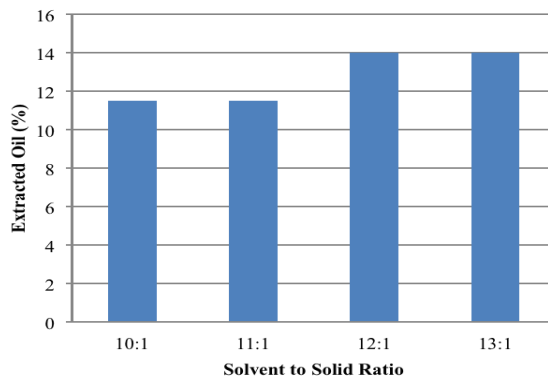


Fig. 3 Effect of solvent to solid ratio on amount of extracted oil at temperature 65°C and 9 hours extraction time

D. Kinetic Study

In kinetic study, Fig. 4 shows that the extraction rate fast at the beginning and slow until the end of the extraction process. Changes of solute concentration in the liquid phase affected the mass transfer of extraction process [23]. At the first stage, the gaharu oil concentration was low. Thus, oil diffuses rapidly from solute to liquid phase. Besides, the free gaharu oil on the surface of gaharu powder was solubilised when the solute was exposed to fresh solvent [16]. Diffusion rate decreased as the time of extraction increased due to the high solute concentration in liquid at thesecond stage. The straight line curve as shown in Fig. 4 proved and verified the assumptions that solid liquid extraction of gaharu oil takes place in two subsequent stages.

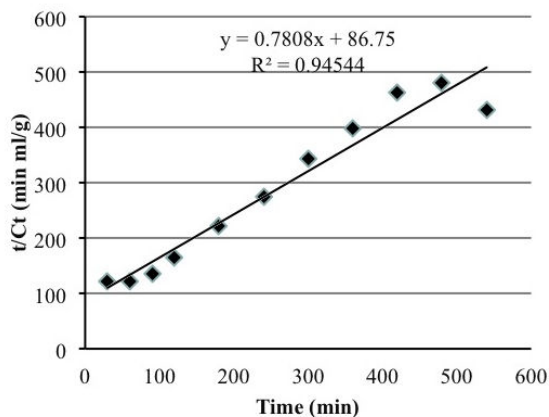


Fig. 4 Second order extraction kinetics of gaharu oil extraction

The initial extraction rate (h), the extraction capacity (Cs), the second order extraction constant (k) and coefficient of determination (R²) were calculated experimentally by referring to the linear plot in Fig. 4. From graph t/Ct versus time, the slope is equal to 1/Cs and intercept is equal to 1/kCs². The data is showed in Table I.

TABLE I
LINEARIZATION OF SECOND ORDER KINETIC MODEL OF SOLID LIQUID
EXTRACTION OF GAHARU

C_s (gmL ⁻¹)	k (mLg ⁻¹ min ⁻¹)	h (gmL ⁻¹ min ⁻¹)	R ²
1.282	0.007	0.0115	0.945

IV. CONCLUSION

In general, it can be concluded that the optimum condition for solid liquid extraction of gaharu oil at 9 hour reaction time, solvent to solid ratio 12:1 and temperature 65°C with 14.5% oil yield. The kinetics experimental data agrees and well fitted with the second order extraction model. The initial extraction rate (h) was 0.0115 gmL⁻¹min⁻¹; the extraction capacity (C_s) was 1.282gmL⁻¹; the second order extraction constant (k) was 0.007 mLg⁻¹min⁻¹ and coefficient of determination, R² was 0.945.

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REFERENCES

- [1] A. Nasima and Z.N. Anantha, *Agarwood Plantation at BRAC Tea Estate: Introduction, Environmental Factors and Financial Analysis*, Bangladesh: Research and Evaluation Division, 2008.
- [2] M.A. Nor Azah, Y.S. Chang, J. Mailina, A. Abu Said, J. Abd. Majid, S. Saidatul Husni, H. Nor Hasnida, H. and Y. Nik Yasmin, "Comparison of chemical profiles of selected gaharu oils from Peninsular Malaysia," *Malaysian Journal of Analytical Sciences*, vol.12, no. 2, pp. 338-340, 2008.
- [3] I. Burkill, *A Dictionary of Economic Products of the Malay Peninsula*, I. Government of Malaysia and Singapore. Kuala Lumpur: The Ministry of Agricultural and Cooperatives, 1966.
- [4] K. Chakrabarty, A. Kumar and V. Menon, V., *Trade in Agarwood*. New Delhi: TRAFFIC India and WWF-India, 1994.
- [5] A. Anees, F.M.A. Abbas, H. Sufia, M.S. Bazlul and W.D. Khoo, "Optimization of soxhlet extraction of herba Leonuri using factorial design of experiment," *International Journal of Chemistry*, vol. 2, no. 1, pp. 198-205, 2010.
- [6] R. Mohd. Rosli, "Extraction of gaharu essential oil using microwave assisted extraction (MAE)," Unpublished degree dissertation, 2006.
- [7] Z. Ahmad Fadzli, "Extraction of gaharu essential oil using spinning band distillation," Unpublished degree dissertation, 2006.
- [8] I. Mohd. Syazami, "Extraction of gaharu essential oil using hydro distillation," Unpublished degree dissertation, 2006.
- [9] J. Ahmad Junaidy, "Extraction of gaharu essential oil using ultrasonic assisted steam distillation," Unpublished degree dissertation, 2008.
- [10] M. I. Zubair, M., "Extraction of gaharu essential oil using ultrasonic assisted hydro distillation," Unpublished degree dissertation, 2008.
- [11] M. D. Luque de Castro and L. E. Garcia-Ayuso, "Soxhlet extraction of solid materials: an outdated technique with a promising innovative future," *Analytica Chimica Acta*, vol. 369, no.1-2, pp. 1-10, 1998.
- [12] Y.S. Ho, H. A. H. Oumarou, H. Fauduet and C. Porte, "Kinetics and model building of leaching of water-soluble compounds of Tilia sapwood," *Separation and Purification Technology*, vol. 45, no. 3, pp. 169-173. 2005.
- [13] L. R. Rabesiaka, J. Havet, C. Porte and H. Fauduet, "Solid-liquid extraction of protopine from *Fumaria officinalis* L. - Analysis determination, kinetic reaction and model building," *Separation and Purification Technology*, vol. 54, no. 2, pp. 253-261, 2007.
- [14] S. Meizane and H. Kadi, "Kinetics and thermodynamics of oil extraction from olive cake," *Journal of the American Oil Chemist's Society*, vol. 85, no. 4, pp. 391-396, 2008.
- [15] J.T. Uhm and W.B. Yoon, "Effects of high-pressure process on kinetics of leaching oil from soybean powder using hexane in batch systems," *Journal of Food Science*, vol. 76, no. 6, pp. 444-449, 2011.
- [16] S. Sayyar, Z.Z. Abidin, R. Yunus and A. Muhammad, "Extraction of oil from Jathropa seeds-optimization and kinetics. *American Journal of Applied Sciences*, vol. 6, no. 7, pp. 1390-1395, 2009.
- [17] M. Mamata, *Natural Extracts Using Supercritical Carbon Dioxide*. New York: CRC Press, 2000.
- [18] J. F. Richardson and J. H. Harker, *Coulson and Richardson's Chemical Engineering-Particle Technology and Separation Processes*. Oxford: Butterworth-Heinemann, 2002.
- [19] L. Wang, C. L. Weller and K.T. Hwang, "Extraction of lipids from grain sorghum DDG," *Transactions of the ASAE*, vol. 48, no. 5, pp. 1883-1888, 2005.
- [20] R. L. Shogren, G. F. Fanta and F. C. Felker, "X-ray diffraction study of crystal transformations in spherulitic amylose/lipid complexes from jet-cooked starch, *Carbohydrate Polymers*, vol. 64, no. 3, pp. 444-451, 2006.
- [21] M. Wenyang, L. Yanbin, D. Xiojing, L. Rui, H. Ruilin and P. Yuanjian, "Determination of anti-tumor constitute mollugin from traditional Chinese medicine *Rubia cordifolia*: Comparative study of classical and microwave extraction techniques," *Journal Separation Science and Technology*, vol. 44, no. 4, pp. 995-1006, 2009.
- [22] R. T. Toledo, *Fundamentals of food process engineering 3rd edition*. USA: Springer, 2007.
- [23] K. Y. Pin, L.A. Chuah, A. A. Rashih and M. A. Rasadah, "Solid liquid extraction of betel leaves (*Piper Betel* L.)," *Journal of Food Process Engineering*, vol. 34, no. 3, pp. 549-565, 2011.