Hot compressed water extraction of essential oil from cinnamon barks

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Abstract

Cinnamon oil extract is rich in antibacterial substances, and hence hot compressed water extraction was applied for extraction essential oil from cinnamon (*Cinnamomum zeylanicum*) barks as it is an environmentally friendly technique. In this research, study on the essential oil extract from cinnamon by hot compressed water with 1:30 (g/mL) solid to liquid ratio loading. The optimum condition for extraction was studied including temperature (120, 140, 180 and 200°C), pressure (5, 7.5 and 10 bar), and extraction time (45 and 60 min) to evaluate yield percentage from the ratio of the extracted essential oil to sample weight prior an extraction. Using hot compressed water extraction, cinnamon bark oils approximately range of 14 to 30% were obtained. The results showed that the temperature of 120°C under the pressure of 7.5 bar for 60 min provided the highest yield as 29.8%. Additionally, the results demonstrated individual parameters influenced on extraction efficiency relating to improve mass transfer, lead to essential oil yield.

Keywords: Hot compressed water extraction, cinnamon bark, essential oil

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บทคัดย่อ

สารสกัดจากน้ำมันอบเชยอุดมไปด้วยสารยับยั้งการเจริญเติบโตของแบคทีเรีย ด้วยเหตุนี้การสกัดด้วยน้ำร้อนอัดความดันจึงถูกนำมาประยุกต์ใช้ในการสกัดน้ำมันหอมระเหยจากเปลือกของอบเชย เนื่องจากถือเป็นเทคนิคที่เป็นมิตรต่อสิ่งแวดล้อม ในงานวิจัยนี้ศึกษาการสกัดน้ำมันหอมระเหยจากอบเชยด้วยน้ำร้อนอัดความดันที่อัตราส่วนของแข็งต่อของเหลว 1:30 (กรัมต่อมิลลิลิตร) โดยศึกษาสภาวะที่เหมาะสมในการสกัดน้ำมันหอมระเหย ได้แก่อุณหภูมิ (120, 140, 180 และ 200 องศาเซลเซียส) ความดัน (5, 7.5 และ 10 บาร์) และเวลาที่ใช้ในการสกัด (45 และ 60 นาที) เพื่อหาร้อยละผลได้จากอัตราส่วนปริมาณน้ำมันหอมระเหยที่สกัดได้ต่อน้ำหนักของของแข็งก่อนทำการสกัด การใช้การสกัดด้วยน้ำร้อนอัดความดันทำให้ได้ผลได้ของน้ำมันหอมระเหยจากเปลือกอบเชยประมาณ 14 ถึง 30% จากการทดลองพบว่าที่สภาวะอุณหภูมิ 120 องศาเซลเซียส ภายใต้ความดัน 7.5 บาร์เป็นเวลา 60 นาทีได้ผลได้สูงสุดเป็น 29.8% นอกจากนี้ผลที่ได้ยังแสดงให้เห็นถึงพารามิเตอร์แต่ละตัวที่ส่งผลต่อประสิทธิภาพในการสกัดเกี่ยวข้องกับการถ่ายเทมวล ซึ่งนำไปสู่ผลผลิตของน้ำมันหอมระเหย

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Nitinan Suksom

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Nomenclature

ABTS	2,2-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid
B	Boltmann constant
C	Solute concentration at any location in particle
CE	Catechin equivalent
D	Diffusion coefficient or diffusivity
DPPH	2,2-Diphenyl-1-picrylhydrazyl
DW	Distilled water
FRAP	Ferric reducing antioxidant power
GAE	Gallic acid equivalent
HCWE	Hot compressed water extraction
IS	Internal standard peak area ratio for gas chromatography
L	Liquid volume
R	Average particle size
T	Temperature
T_{bc}	Temperature before it was cooled
T_i	Initial temperature
TE	Trolox equivalent
TPC	Total phenolic contents
S	Solid mass
$SCCO_2$	Supercritical carbon dioxide extraction
SWE	Subcritical water extraction
m	Mass
v	Volume
w	Weight
t	Extraction time
t_h	Time to heat up to a desired temperature
t_c	Time to cool down to a temperature of 50°C
x	Distance
ε	Dielectric constant
μ	Solvent viscosity

CHAPTER I
INTRODUCTION

1.1 Background

Human society nowadays places health as a primary concern as the environment is full of pathogens that contributes to disease. Bacteria are one of the factors to inflammation and infection that causes the pathogenesis. Several researchers attempted to find natural ingredients that may be an anti-inflammation and inhibit pathogenic bacteria leading to the production of highly effective anti-inflammatory drugs [1]. Therefore, the appropriate extraction methods are important to obtain the better quantify of biological ingredients for pharmaceutical industries.

Many researchers have been studying the extraction of bioactive compound for long times. Jayawardena et al. [2] indicated superheated water extraction of cinnamon leaves yielded an oil containing over 98% of eugenol and Lis-Balchin et al. [3] manifested that the increasing valuable as essential oils rich in eugenol, like in cinnamon leaf oil demonstrated a high activity of biological activity. Subcritical water and superheated CO_2, have gained much interest as methods for extracting compounds, especially phenolic compounds and essential oils in the last decade [4]. Therefore, subcritical water extraction (SWE) or supercritical CO_2 extraction ($SCCO_2$) is clearly preferred green technology to obtain various bioactive compounds from herbal material, avoiding the waste of organic solvent. However, the drawback of supercritical CO_2 is condemned causing oxidation due to a higher operated temperature (over 750°C) and limitation of low polarity of CO_2 has been successfully overcome by the use of modifier to improve the extraction efficiency [5]. Moreover, $SCCO_2$ is likely to be expensive due to its operation with specific appliance. Meanwhile, SWE is preferred interested, mainly including the reduction time, simplicity, less expensive operation, higher efficiency of the extracts [6].

In this regard, SWE uses the unique properties with high temperature (between 100 to 374°C) and pressure which enough maintain liquid state below the critical pressure of 22.1 MPa which generally use the temperature and pressure in range of (100–250 °C) and (1–8 MPa), respectively [7]. Under such condition, its dielectric constant will decrease steadily with elevated temperature resulting in possibility of tuning its polarity, thus interpreting solute-solvent interactions. Conversely, the diffusivity characteristics are improved caused greater mass transfer through diffusion.

Whereas the elevated pressure can assist in the extraction by forcing water to penetrate into matrix. As mentioned above, the knowledge of changes in water with pressure and temperature is critical to understanding to applied in hot compressed water extraction (HCWE), which is a promising alternative application to organic compound extraction.

Based on these, the objectives of this study were to extract essential oil from cinnamon barks by HCWE. It was particularly of interest to determine if this extraction method would give a higher quantity essential oil and avoid the problem of organic solvent waste. Besides, to study the main parameters influencing the cinnamon essential oil extract by HCWE.

1.2 Objectives

1.2.1 To extract essential oil from cinnamon barks by hot compressed water method.

1.2.2 To study the main parameters influencing the essential oil extracts from cinnamon barks with hot compressed water extraction.

1.3 Scopes of Work

1.3.1 Extraction of essential oil from cinnamon barks by hot compressed water method

1.3.2 Study variables

1.3.2.1 Independent variables

- Extraction time (45 and 60 min)
- Operating temperature (120, 140, 180 and 200°C)
- Operating pressure (5, 7.5 and 10 bar)

1.3.2.2 Dependent variable

- Yield percentage of essential oil

1.3.2.3 Controlled variables

- Solid to liquid ratio of 1:30 w/v
- 0.075 to 0.425 mm in particle size of samples
- Rotating speed of 88 rpm in extraction
- Water used as an extraction solvent
- Type of cinnamon barks (*Cinnamomum zeylanicum*)
- Cinnamon barks achieved from Thailand

1.4 Expected Outputs

1.4.1 Understand the effect of parameters to successfully achieve essential oil from cinnamon barks by hot compressed water extraction.

1.4.2 Understand the principle and mechanism of hot compressed water method applying in various material along with advantages of hot compressed water extraction.

1.4.3 Obtain the biological ingredients from cinnamon barks by hot compressed water extraction.

CHAPTER II
LITERATURE REVIEW

This chapter has described in detail the constituents present in essential oil, cinnamon barks selected in order to extract essential oil, biological activities, general information of subcritical water extraction instance, principles, mechanism and influencing parameters of subcritical water extraction. This relevant information obtained from several studies is briefly described to pinpoint an appropriate research methodology for this work.

2.1 Essential oil

Essential oils are aromatic oily liquid found at the different parts of plant for instance, leaves, barks, seeds, flowers and peels. Essential oils can be isolated by various extraction method such as steam distillation, solvent extraction, supercritical carbon dioxide extraction, subcritical water extraction and so on. The several studies have been confirmed the biological activities obtained from plant oils including antibacterial, antiviral, anti-inflammatory, antifungal, and antioxidant. Thereby, the essential oils play an active role in natural additive for food. Likewise, has been used for a medicinal and health purposes.

In general, the constituents in essential oils are divided into two major groups which are terpene hydrocarbons and oxygenated compounds.

2.1.1 Terpene hydrocarbons

Terpene hydrocarbons are the molecules containing C and H atoms arranged in chains which are the repetitive molecules of isoprene (C_5H_8) unit jointed in head-to-tail manner. Terpenes mainly found in essential oil are monoterpenes, sesquiterpene and diterpenes. The hydrocarbon skeleton of these terpenes could be rearranged into acyclic, cyclic, or aromatic [8].

2.1.2 Oxygenated compounds

Tongnuanchan and Benjakul[8] described the oxygenated compounds are combination of C, H and O molecules which are the most common type of functional group in essential oils. Terpenes containing oxygen are called terpenoids are mainly esters, aldehydes, ketones, alcohols and phenols. As Macwan et al.[9] said that geraniol, menthol, linalool, citronellol, carvone, thymol, carvacrol, geranyl acetate, eugenyl acetate, geranial, neral and 1,8-cineole are well-known terpenoids in essential oils. The dominant of oxygenated compounds is highly odoriferous [9].

Additionally, phenylpropenes are aromatic compounds as are an important group to flavor and fragrance industry. Phenylpropenes constitute a subfamily of phenylpropanoids for example, cinnamaldehyde, cinnamyl alcohol, chavicol, eugenol, methyl eugenols and methyl cinnamate.

2.2 Information of Cinnamon

Figure 2.1 Cinnamon bark (*Cinnamomum zeylanicum*) [10]

Generally, over 250 species of cinnamon have been discovered worldwide among the cinnamon genus, belongs to Lauraceae family. The evergreen tree of cinnamon is approximately 10 to 15 m tall and is considered a small tree. A study, *Cinnamomum zeylanicum,* also named true cinnamon or Ceylon cinnamon and distributed in south-east Asia, China and Australia [11]. The barks of cinnamon were used in traditional (used as a spice and flavoring agent) and medicines due to its important constituents are cinnamaldehyde and trans-cinnamaldehyde which are present in the essential oil [12]. Likewise, the essential oil has long been used as an ingredient in food and pharmaceutical industries.

Jayaprakasha et al. [13] reported detailed main compounds present in cinnamon essential oil, namely cinnamaldehyde, camphor, cinnamyl-acetate, caryophyllene, *trans* α-bergamotene, caryophillene oxide, linalool, geraniol, bornyl acetate, α-cubebene, γ-elemene, α-copaene, guaiol, and eugenol, among others. The essential oil may be obtained from either the outer bark or its leaves of cinnamon.

For trade, cinnamon oil is often obtained from *Cinnamomum zeylanicum*, *Cinnamomum cassia*, and *Cinnamomum camphora*[11]. However, the cinnamon essential oil composition varies according to its geographical provenance and the parts of the plant used. Similarly, Vangalapati et al. [14] investigated in following Table 2.2, a variety of chemical constituents present in different parts of cinnamon.

Table 2.1 Chemical constituents of different parts of cinnamon [14]

Part of the plant	**Compound**
Leaves	Cinnamaldehyde: 1 to 5% Eugenol: 70 to 95%
Bark	Cinnamaldehyde: 65 to 80% Eugenol: 5 to 10%
Root bark	Camphor: 60%
Fruit	*trans*-Cinnamyl acetate: 42 to 54% caryophyllene: 9 to 14%
C. zeylanicum buds	Terpene hydrocarbons: 78% *alpha*-Bergamotene: 27.38% *alpha*-Copaene: 23.05% Oxygenated terpenoids: 9%
C. zeylanicum flowers	(E)-Cinnamyl acetate: 41.98% *trans-alpha*-Bergamotene: 7.97% Caryophyllene oxide: 7.2%

2.2.1 Antibacterial activities

Throughout history, the essential oils from herbs have been used for antibacterial purposes in food science field [11]. Bouhdid et al. [15] tested the presence of cinnamaldehyde as the most abundant compound in cinnamon essential oil and as its main bactericidal compound. A study of activity in inhibiting the growth of micro-organisms from Hili et al. [16] indicated that cinnamon oils have potential action against various bacteria, including *P. aeruginosa*, *S. aureus*, and *E. coli*. The tested antimicrobial potential by Mello et al. [17] revealed the presence of cinnamon essential oil with MIC and MBC values of 0.075 and 1.25 mg/mL could against *Y. enterocolitica* which was the most sensitive bacteria followed by followed by *L. monocytogenes* and *B. cereus.* However, these antibacterial activities were due to presence of oxygenated compounds such as linalool, 1,8-cineole, neral, and geranial in cinnamon oil.

Similarly, Al-fekaiki et al. [18] showed that cinnamaldehyde as main component in essential oil of cinnamon (*Cinnamomum zeylanicum*) extracted using hydro-distillation method. The inhibition test *Listeria monocytogenes*, *Escherichia coli*, *Enterobacter aerogenes*, *Pseudomonas erogenous* and *Staphylococcus aureus* indicated that the essential oil from cinnamon has the antibacterial activity against both Gram-positive and Gram-negative bacteria.

2.3 Subcritical water extraction

2.3.1 Principle of subcritical water

Subcritical water extraction is also called pressurized hot water extraction which is an eco-friendly method used the unique properties of subcritical water that is hot water above boiling point to high temperature-pressure conditions just below its critical point (374 °C, 220 bar) to maintain the liquid state illustrating in Figure 2.5.

In generally, the pressures elevated from 1 to 10 MPa at extraction temperatures ranging from 100 to 300°C are used in subcritical water condition.

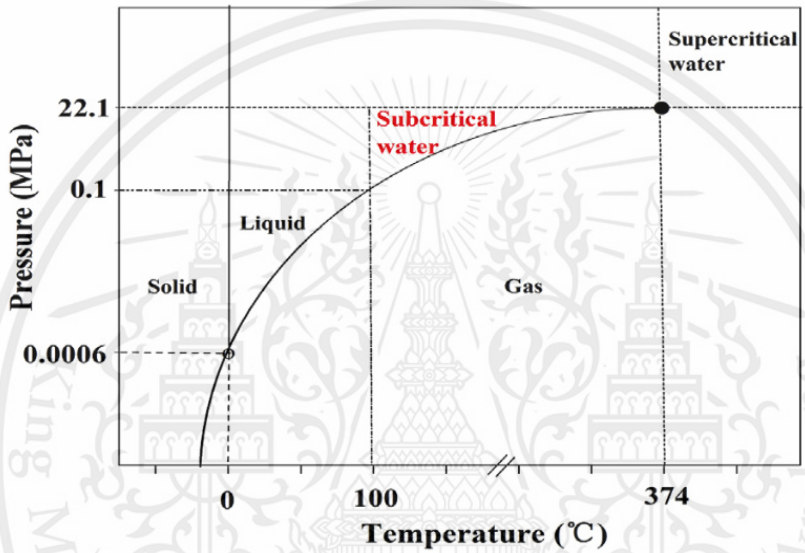

Figure 2.2 Physical state of water at different temperature and pressure [19]

Zhang et al. [19] reported the elevated temperature influences the decreasing of dielectric constant, viscosity and surface tension. While the diffusivity characteristics are improved. The dielectric constant of water at 25 °C is 80. When the temperature is raised to 250 °C and the pressure is 25 bar, the dielectric constant drops to 25, which falls between those of methanol (ε = 33) and ethanol (ε = 24) at 25 °C. Under such conditions, some properties of water are similar to organic solvents which reduces to values similar to organic solvent under subcritical conditions.

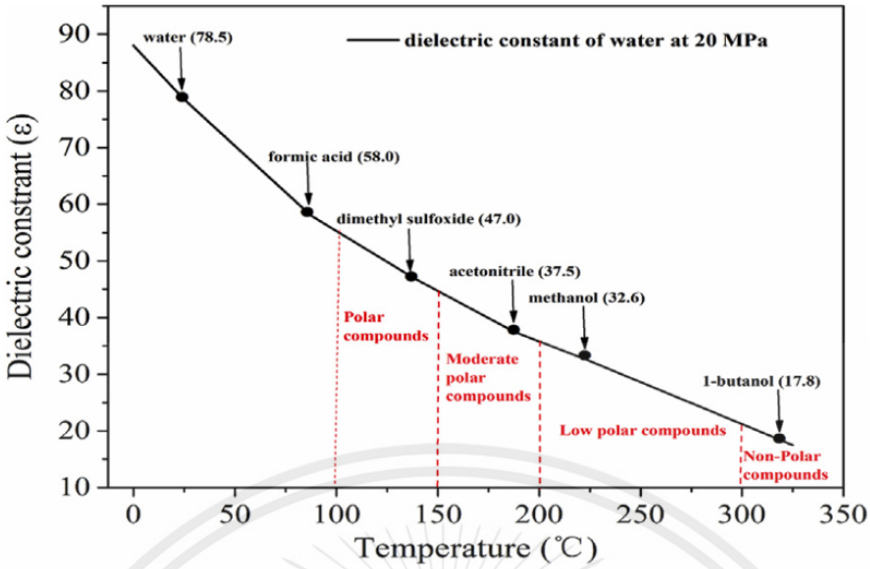

Figure 2.3 The dielectric constant values of water equivalents to some common organic solvents at room temperature and constant pressure (25°C and 0.1 MPa) [19]

2.3.2 Extraction mechanism

The extraction mechanism relates a transfer of solutes from matrix active sites to the solvent by diffusion, partitioning equilibrium and convection [7]. Haghighi et al. [20] reported the mechanism of subcritical water extraction involves six sequential steps (1) solvent diffusion through film layer to matrix active sites (2) desorption of solutes from matrix active sites (3) diffusion of solutes through organic materials; (4) diffusion of solutes through static fluid in porous materials; (5) diffusion of solutes through layer of stagnant fluid outside particles and (6) elution of solutes by the flowing bulk of fluid.

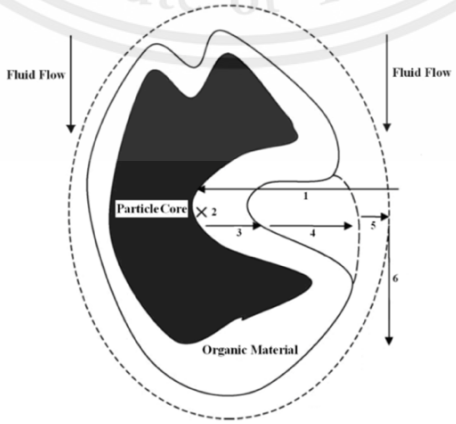

Figure 2.4 Proposed schematic presentation of the extraction steps [20]

Chan et al. [21] reported that the extraction mechanism comprises of a fast diffusion step taking place when solute diffuses from the external surface of the solid to the bulk fluid, and a slow extraction step which solute diffuses from interior of solid matrix and diffuses in solvent to surface. The extraction rate is limited by the slowest step, hence the diffusion of solutes to solid surface is rate-limiting mechanism for extraction.

2.3.3 Influencing parameters of subcritical water extraction

The main process parameters are temperature, pressure, solid to liquid ratio, particle size, and extraction time.

2.3.3.1 Temperature

Extraction temperature is one of the most important factors affecting subcritical water extraction efficiency and selectivity. An increased temperature enhances the solubility of the compounds, solute-matrix interactions are more easily broken and a higher diffusion rate is achieved following the Einstein equation [22].

$$D = \frac{BT}{6\pi\mu R} \qquad 2\text{-}2$$

Where B is the Boltzmann constant, T is the temperature, μ is the solvent viscosity and R the average particle size. Also, causes the decreasing in permittivity, viscosity and surface tension, facilitating the extraction.

Under high temperature condition, the nature of subcritical water has changed, the property of the water changes from polar to non-polar as the temperature increasing which promotes the dissolution of less polar compounds in water [19]. Temperature strongly influences to subcritical water extraction. Accordingly, a lot of research widely discussing the effect of temperature on extraction. On the studied of the amount of linalool from *C. sativum* under the temperature range of 100 to 175°C at 20 bar for 45 min. Eikani et al. [23] revealed the highest amount of linalool from *C. sativum* extracting was at 125°C. An extract with burning smell was produced resulting of degradation of some constituents under higher temperature.

Similar to the extraction temperature for potato peels was optimized in order to maximize the phenolic extraction yield as key components. Its influence was studied between 100 and 240°C at pressure of 6 MPa and extraction time of 60 min. It had obviously seen the high phenolic compound recoveries at 180°C. Whereas the

degradation of phenolic compound occurred above temperature of 180°C [24]. Besides, He et al. [6] was found the highest total phenolic compound from pomegranate seeds extracting under temperature of 220°C at 6 MPa for 30 min which the studied temperatures were between 80 to 240°C. A large number of compounds in pomegranate seeds could be hydrolyzed by subcritical water at high temperature, and much more free phenolics were extracted from the matrix. Clearly, the pomegranate seed phenolics were more soluble in subcritical water at relative higher temperature.

In the same way, the amount of phenolics did not increase beyond 220°C as a result of degradation of phenolics at the higher temperature. Therefore, the appropriate extraction temperature is an important factor to extract the various compounds with subcritical water.

2.3.3.2 Pressure

The water phase has changed when the pressure is adjusted. While the general purpose of pressure adjusting in order to maintain the liquid state of water [19]. Pressures elevated from 1 to 10 MPa at extraction temperatures ranging from 100 to 300°C are generally used to maintain water in the liquid state during subcritical water extraction. Unlike temperature, Krieger et al. [25] reported that the pressure has no significant effect or minor effect on increasing the efficiency from the natural products during the process of subcritical water extraction. Similarly, the essential oil in *Acorus Tatarinowii Schott.* was investigated by Deng et al. [26] which revealed that the varying pressures had mild effect on recoveries.

2.3.3.3 Solid to liquid ratio

The solid to liquid ratio is an important parameter to consider the subcritical water extraction in static extraction mode. The lower in solid to liquid ratio increases the concentration gradient of the solutes allowing for a higher extraction rate [7]. Pomegranate seed residue was investigated by He et al.[6] for production the phenolic compounds by SWE. The solid to liquid ratio (1:10 to 1:50 m/v) was determined at 140°C over 30 min. They found the solid to water ratio of 1:40 caused the highest yield of total phenolic compounds (40.86 mg GAE/g). An optimum solid to liquid ratio maintains just the right concentration gradient between the sample matrix and the solvent during extraction. The used lower water in extracting resulting the low extraction efficiencies due to water limiting and powder was just immersed in subcritical water [27].

2.3.3.4 Particle size

The comparison seed particles (0.25, 0.50 and 1 mm) of C. *sativum* in the subcritical water extraction at 125 °C temperature, 2 ml/min flow rate, 20 bar and 120 min extraction time was revealed that the extraction yield for small particle sizes is relatively high, while the larger particle sizes is low which the extraction time needs to be extended [23]. The particle size influences the diffusion distance of the natural compound in the matrix. Therefore, the particle size has an important impact on the reducing the extraction time and increasing the extraction efficiency.

2.3.3.5 Extraction time

The extraction time is identified that as a time for water contacting with matrix under desired temperature and pressure. Subcritical water extraction could be performed in static mode and dynamic mode. The static extraction is defined by equilibrium between solutes and water phase which the solutes are already solubilized. The limited volume of water used in static mode as result of incomplete extraction [28]. However, the extraction time needed to fully extract a particular matrix will depend on the solutes, matrix and number of cycles [29]. The investigation in essential oil extracts obtained from *Thymbra spicata* by Ozel et al. [30] manifested the recoveries of some compounds in various time. The experiment was carried out at 150°C and a flowrate of 2 ml/min. The increased extraction time from 0 to 20 min caused higher extraction efficiencies, which had obviously seen the highest recoveries of main components as Carvacrol and Thymol took 20 min. However, the extraction efficiencies of individual components were showed in difference extraction times.

Correspondingly, the study of Gong et al. [27] revealed that sea buckthorn seed residues phenolics increased when extraction time increased from the time interval of 15 to 45 min under 120°C, 6 MPa and water to solid ratio of 20. Nonetheless, the phenolics decreased when the time reached 45 min since the equilibrium state and phenolics couldn’t be dissolved in the water.

2.3.4 Solid diffusion

Diffusion in a solid matrix is more complex because, although the active compound may appear to be diffusing within the solid matrix, it may actually be diffusing through liquid contained within that matrix or through the gas phase in a porous solid. Therefore, diffusion in solid is classified into two types.

2.3.4.1 Structure-insensitive diffusion

The diffusion takes place when the solute is actually dissolved in the solid to form a more or less homogenous solution, with diffusion is normally based on concentration gradients within the solution. In solid-liquid extraction, this diffusion usually relates to marc (insoluble solids). It suggests that diffusivity is significantly lower with a greater resistance.

However, diffusion process is normally based in terms of the solute concentration in the solid. Therefore, Fick's law may be used for determining the diffusivity. The diffusion coefficient or diffusivity (D) is an important property for characterization the mass transfer phenomena [31].

Mass transfer can be defined as the transport of a substance under the influence of a concentration gradient in order to reach chemical equilibrium. Fick derived a general conservation equation for one-dimensional non-steady state diffusion when the concentration within the diffusion changes with respect to time, known as Fick's second law [20].

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad 2\text{-}1$$

Where C is the solute concentration at any location in the particle, D is the diffusion coefficient or diffusivity assuming that D is constant with the concentration, t is extraction time and x is the distance.

2.3.4.2 Structure-sensitive diffusion

A situation which refers to diffusion in porous solids.

Table 2.2 Extraction of bioactive compounds by subcritical water extraction

Sample		SWE condition	Yield		References
Pomegranate seed residues	seeds	220°C, S/L ratio=1:40w/v, 6 MPa		TPC=4854.7mg/100g DW	He et al. [6]
Cinnamomum zeylanicum (L.)	leaves	100°C, 20 bar, 30 min, 2 g sample	Eugenol 98.2±0.2%		Khuwijitjaru et al. [4]
		150°C, 20 bar, 30 min	Eugenol 98.7±0.12%		
		200°C, 20 bar, 30 min	Eugenol 98.7±0.25%		
	barks	100°C, 20 bar, 30 min	Cinnamaldehyde 83.7±2.56%		
		150°C, 20 bar, 30 min	Cinnamaldehyde 79.9±0.46%		
		200°C, 20 bar, 30 min	Cinnamaldehyde 79.3±3.26%		
Acanthophyllum glandulosum		121°C, 1.5 atm, 10 g sample, pH of solution=4,		Antioxidant activity=90.5±0.1%	Tabrizi et al. [32]
Cinnamomum zeylanicum		200°C, 6 MPa, fine powder=1g (<500um), 25 min	Cinnamaldehyde 56%		Jayawardena et al. [2]
Peppermint		130°C, 10.3 MPa, 10 min, S/L ratio =1:3w/w		56.38±3.56 mg GAE/g sample	Cam et al. [33]
Thymbra spicata	leaves	150°C, 60 bar, flow rate=2ml/min, 30 min, 1.5 g sample	3.4g essential oil/100g dried leaves		Ozel et al. [30]

Table 2.3 Extraction of bioactive compounds by subcritical water extraction (continued)

Curculigo latifolia	roots	180°C, 30 min, 100 bar, S/L ratio=1:10w/v, flow rate=0.5 ml/min	36.50%	TPC = 92.55 mg GAE/g Antioxidant activities = 66.8mg trolox equivalent/g sample	Zabidi et al. [34]
Rosemary	leaves	150°C, 60 bar, flow rate=1ml/min		Antioxidant activity=11.4µm/ml	Ibanez et al. [35]
***Coriandrum sativum* L.**	seeds	125°C, 20 bar, flow rate=2 ml/min, particle size=0.5mm			Eikani et al. [23]
Potato	peels	180°C, 60 min, 6 MPa, flow rate=2ml/min	Total essential oil=14.1		Singh et al. [24]
Laurel	leaves	150°C, 50 bar, flow rate=2ml/min, 3 g, static extraction time=30min, dynamic extraction time=25 min		Cumulative area ratio = 3.71 (1,8-Cineole/IS)	Virgina et al. [36]
Pseuderanthemum palatiferum* (Nees) *Radlk.	leaves	110-270°C, 80 bar, 15 min, S/L ratio =1:70(g/mL), 2g samples, particle size= <710 µm	Yield=0.59 ± 0.01 (270°C)	TPC=33.68±0.29 (mg CE/g) (190°C) DPPH, FRAP, ABTS assay= 102.53±12.4, 185.83±2.23, 306.4±21.7 µM TE/g (230°C)	Ho et al. [37]

CHAPTER III
RESEARCH METHDOLOGY

In this chapter, the hot compressed water extraction using autoclave and an analytical method for determining the yield of essential oil obtaining from cinnamon extracts were described as following.

3.1 Hot compressed water extraction

3.1.1 Materials and chemicals

Dried cinnamon barks (*Cinnamomum zeylanicum*) provided from a local traditional market (Bangkok, Thailand) were grinded and sieved to obtain fine powders with particle sizes in range of 75 to 425 μm. The samples were kept inside airtight bags. Distilled water was used as a solvent.

3.1.2 Apparatus

1) Autoclave (AMAR 250 mL)
2) Analytical balance
3) Glassware
   - Beaker
   - Glass cylinder
4) Vacuum filter
5) Filter paper (11 μm)
6) Aluminum foil paper
7) Rotary vacuum evaporator
8) Hot air oven

3.1.3 Experiment procedures

The extraction condition was determined for evaluating the effect of independent variables on hot compressed water extraction. The variables affecting the yield of extracts consisted of three variables: extraction time (45 and 60 min), temperature (120,140,180 and 200°C) and pressure (5, 7.5 and 10 bar).

Table 3.1 The experimental conditions for studying the effect of extraction time on essential oil yield

Time (min)	Temperature (°C)	Pressure (bar)
45	120	10
60	120	10

Table 3.2 The experimental conditions for studying the effect of extraction temperature on essential oil yield

Time (min)	Temperature (°C)	Pressure (bar)
60	120	10
60	140	10
60	180	10
60	200	10

Table 3.3 The experimental conditions for studying the effect of extraction pressure on essential oil yield

Time (min)	Temperature (°C)	Pressure (bar)
60	120	5
60	120	7.5
60	120	10

3.1.3.1 Hot compressed water extraction

The whole experiments were performed in the static mode at varying parameter conditions affecting the yield of essential oils according to Table 3.1, 3.2 and 3.3.

1) The hot compressed water extraction was carried out using an autoclave as following procedure (Figure 3.1).

Figure 3.1 The autoclave assembly

1. Weigh 5 g of cinnamon powder and put into 250-ml beaker. Cinnamon powder mixed with 150 ml distilled water is placed inside the extraction vessel.
2. Install the impeller and adjust the motor speed to obtain rotating speed of 88 rpm.
3. In this manner, nitrogen gas is used for inert gas. The pressure of system is controlled by a pressure control valve at the specified pressure. Turn off pressure control valve at the position of gas inlet to maintain the desired pressure in the system.
4. Heat up to the desired temperature. Start the extraction time when reach to the desired temperature. When the specified time is over, turn off the heater.
5. The eluted extract in the extraction vessel is cooled down by cooling water to preclude the degradation at approximately temperature of 50°C. Also, gradually release gas out to the atmosphere.
6. Afterwards, the extract is inserted in the 250-ml beaker according to seal by aluminum foil paper.

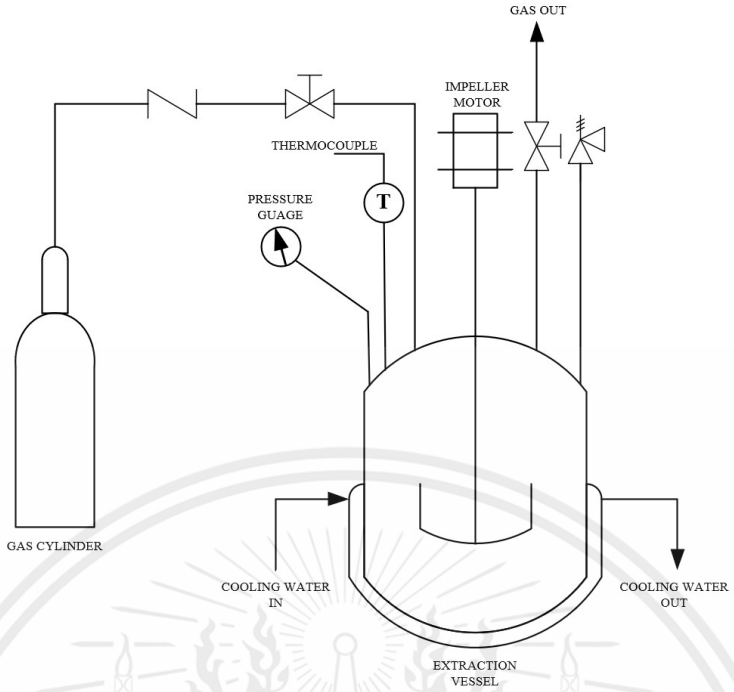

Figure 3.2 Schematic diagram of autoclave

2) After completion of extraction procedure, filtrate the mixture obtaining from extraction vessel (step 1) in order to separate extract from solid particles by vacuum filter.
3) In the extract, it consists of water phase and oil phase. Remove the water phase by using rotary vacuum evaporator to maintain water a small and equal amount of water in each extract to prevent attaching to the container.

Table 3.4 The condition to evaporate water using rotary vacuum evaporator

Temperature	**55°C**
Rotary	50 rpm
Time	45 min
Pressure pump	90 mbar
Cooling water	25°C

4) Residue water is evaporated again by using hot air oven at 80°C for 15 hr, eventually obtain only essential oil.
5) Calculate the extraction yield of essential oil as a data for further studying the varying parameter conditions affecting the yield of essential oils.

3.2 Analytical procedure

3.2.1 Quantification of received essential oil in cinnamon barks

In a specific case of amount of essential oil extracted from the cinnamon barks, the yield percentage of essential oil was calculated by using the following formula:

$$\text{Yield percentage of essential oil} = \frac{\text{Essential oil weight}}{\text{Sample weight}} \times 100 \qquad 3\text{-}1$$

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the independent variables affecting the essential oil extraction from cinnamon barks by hot compressed water was investigated. The obtained results were discussed to determine more significant extraction variables. The three main parameters including (4.1) extraction time (min), (4.2) extraction temperature (°C), and (4.3) extraction pressure (bar) were investigated the impact on extraction yield of essential oils under the hot compressed water extraction. The sample particle size was studied in the range of 0.075 to 0.450 mm. The solid to liquid ratio 1:30 (w/v) loading was used for performing the effects of different extraction parameters.

4.1 Effect of extraction time on the essential oil yield

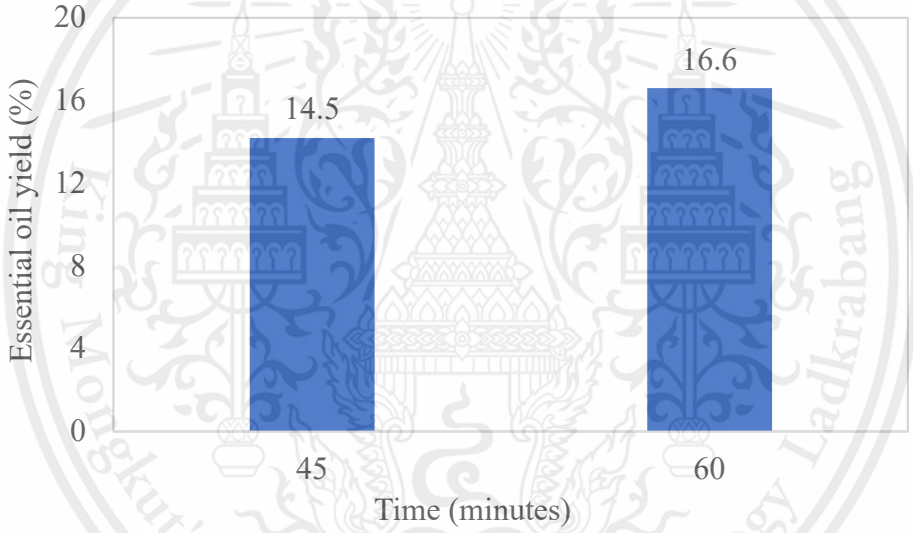

Figure 4.1 Effects of different times on the extraction yield of essential oils under hot compressed water extraction

The effect of extraction time on the essential oil extraction yield was shown in Figure 4.2 at a fixed temperature of 120°C with a constant pressure of 10 bar. The extraction times of 45 and 60 min were investigated to obtain optimal time on hot compressed water extraction. The essential oil yield was 14.5% in 45 min and increased to 16.6% in 60 min. The results showed that the extraction yield was obtained slightly changed after the extension of time, then the highest essential oils (16.6%) was observed at 60 min. In this study, the result cannot indicate optimum time under hot compressed water extraction due to too little data. However, it could be roughly

described as the static extraction is defined by equilibrium concentration during the extraction, and hence the essential oil yield increased until reached equilibrium. Therefore, the extraction time is also controlled by the limited volume of hot compressed water.

The longer extraction time provided the higher essential oil yield which was consistent with the report of Khuwijitjaru et al. [4], the total phenolic content increased rapidly for the early stage due to its more concentration differences and free oil attached at particle surface (external mass transfer). However, it still gradually increased until reached equilibrium at a later time but decreased the extraction rate. Therefore, increasing time leads to reduced diffusivity (D) to following Fick's second law equation.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Solute concentration in water increases with increasing time so a decrease in the rate of diffusion could take place. It was a result of higher essential oil yield in small quantities with increased time. Hence, the extraction time facilitates reducing the volume of solvent needed and excess extraction time has no impact on efficiency extraction [38]. In this study, 60 min was selected as the optimum extraction time.

4.2 Effect of extraction temperature on the essential oil yield

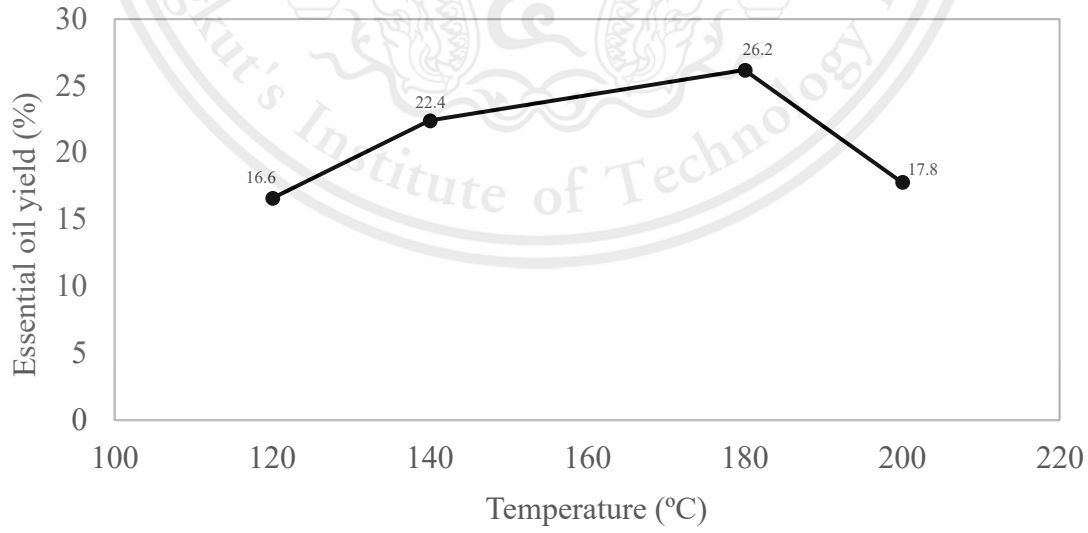

Figure 4.2 Effects of different temperatures on the extraction yield of essential oils under hot compressed water extraction

The effect of temperature on the essential oil extraction yield was shown in Figure 4.2 at the pressure of 10 bar and 60 min extraction time. Regarding extraction of essential oils, the extraction temperature was carried out at 120, 140, 160, and 180°C. As seen in Figure 4.1, the essential oil extraction yield increased evidently with an increase in temperature from 120 to 180°C, and hence it became the yielded highest essential oil at a temperature condition of 180°C as 26.2%.

The elevated temperature showed a significant difference in extraction yield. This could be explained by the elevated temperature that increases the diffusivity (D), thermal energy disturbed solute-solute and solute-matrix interactions by decreasing activation energy required for desorption according to Einstein equation [22].

$$D = \frac{BT}{6\pi\mu R}$$

In addition, the decreased dielectric constant of hot compressed water at higher temperature enhances the solubility in non-polar compounds which could be explained that hot compressed water favors the solubility of polyphenols and other molecules with similar characteristics led to improve mass transfer and extraction rate increases, consequently the optimal temperature for essential oil extraction yield was found in temperature of 180°C. The higher temperature also causes a decrease in surface tension and viscosity provided better contact of the solutes with the hot compressed water and penetration of solute into the matrix, eventually affecting the yield of extracts[38]. However, the temperature influences working pressure which enhances the extraction efficiency as well.

From 180 to 200 °C, it decreased the essential oil yield to 17.8% although still higher than that found in 120°C. Because the extract with a burning smell were produced due to further degradation of some components after being liberated from the matrix at such high temperature [23]. Also, chemical reactions may occur such as hydrolysis and oxidation.

Since cinnamaldehyde is widely found in cinnamon bark extracts. Jayawardena and M. Smith [2] reported the highest yield of oil rich in cinnamaldehyde from cinnamon barks at the temperature of 150°C and decreased to 200°C. Therefore, it is supported that cinnamaldehyde may decompose at such high temperatures corresponding to decreasing essential oil yield in this study, and hence an appearance

of extracts in higher temperature may be caused by the Maillard reaction between amino acids and reducing sugars that gives highly browned product melanoidins.

As reported by Chan et al. [21], it showed that extraction with elevated temperature for thermal sensitive compounds exerting a negative effect on extraction yield by decreasing stability, hence the criteria of suitable extraction temperature was considered crucial to nature compound to achieve extraction efficiency.

4.3 Effect of extraction pressure on the essential oil yield

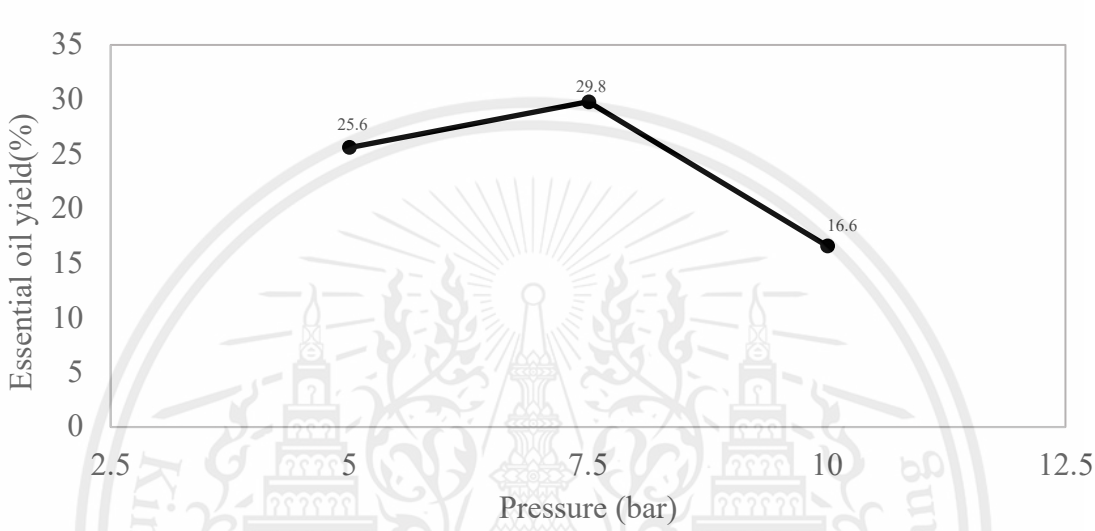

Figure 4.3 Effects of different pressures on the extraction yield of essential oils under hot compressed water extraction

Figure 4.3 showed the study of different pressures influencing the essential oil yield. The extraction pressure was carried out at 5, 7.5, and 10 bar with a fixed temperature of 120°C for 60 min. The resulted curves showed that essential oil yield increased from 5 to 7.5 bar, the highest yield was found at 7.5 bar (29.8%) and intensively decreased in pressure of 10 bar (16.6%). This was the result of rapture speed of cell wall accelerating with pressure rising and hence improved the extraction efficiency. Increasing pressure also facilities the penetration of hot compressed water into the porosity of sample matrix that was unreachable at ambient temperature, and consequently better contacts with oil possibility.

On the other hand, excessively high pressure would result in negligible extraction of essential oils trapped in pores of matrix and hence the became lower extraction yield (16.6%) at the operating pressure of 10 bar. Besides, the structural compound may be damaged at high pressure and air bubble occurring at such high

pressure may intercept in oil extraction. Therefore, concluded that no additional pressure is needed.

To optimize the operating pressure of hot compressed water extraction from cinnamon barks; 7.5 bar at 120°C was selected which provided the highest yield of essential oil as 29.8%. It could roughly specify that the major components found in low temperature at such pressure be slightly insoluble.

CHAPTER V
CONCLUSION

5.1 Conclusion

In this work, hot compressed water extraction was applied to extract essential oil from cinnamon barks. Three main parameters including extraction time, temperature and pressure were studied to explain a result of independent parameters influencing the obtained extracts. The study of the extraction mechanism was of great importance in determining the optimal parameters for the extraction of essential oils from the cinnamon barks.

The study on effect of extraction time demonstrated that a suitable time on HCWE was 60 min (at 120°C,10 bar) to obtain highest essential oil as 16.6%. Even if the studied extraction times weren't enough for considering the optimal time for static extraction, but it could roughly explain that static extraction is defined by equilibrium concentration. While the obtained results of temperature showed that the essential oil yield increased as a result of the solubility of nonpolar components such as cinnamaldehyde into hot compressed water with elevated temperature. In addition, other factors including surface tension solute-matrix interaction were reduced to improve mass transfer and hence observed the highest yield (26.2%) of essential oil extracts at 180°C with pressure of 10 bar for 60 min. Above 180°C, degradation of some compounds occurred observing from its burning smell. For the effect of pressure on yield of essential oils, 7.5 bar at 120°C with 60 min extraction time was selected for optimal condition (29.8%). That could be explained the penetration of hot compressed water into matrix to enhance mass transfer. The rapture speed of cell wall accelerated with pressure rising and hence improved the extraction efficiency.

In conclude, the parameters influencing on yield of essential oils could be considered due to its various components existing in cinnamon barks. Therefore, the nature sample was also a crucial to more study to determine optimum condition.

5.2 Suggestion

5.2.1 Purify the essential oil by eliminating carbohydrate and sugar possible occurring during extraction by solvent such as ethyl acetate.

5.2.2 Mass balance calculation to ensure the presence of essential oil in dried cinnamon.

5.2.3 Study on the independent variables influencing the essential oil extracts and optimal condition for hot compressed water extraction by using Minitab Software.

5.2.4 Study on the characteristic of essential oil by using analytical method to identify the individual components influencing the antibacterial activities.

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APPENDIX

APPENDIX A
RESULTS OF HOT COMPRESSED WATER EXTRACTION AT DIFFERENCE PARAMETER

1. Calculation of essential oil yield

The amount of essential oil extracted from cinnamon barks (*Cinnamomum zeylanicum*) in form of yield percentage (%) was calculated according to this formula

$$\text{Yield percentage of essential oil} = \frac{\text{Essential oil weight (g)}}{\text{Sample weight (g)}} \text{ x } 100$$

Table A1 Obtained results of essential oil yield (%) from hot compressed water extraction with three independent variables including extraction time (min), temperature (°C) and pressure (bar) with solid to liquid ratio of 1:30 (g/mL)

Time (min)	Temperature (°C)	Pressure (bar)	Essential oil yield (%)
45	120	10	14.5
60	120	10	16.6
60	140	10	22.4
60	180	10	26.2
60	200	10	17.8
60	120	5	25.6
60	120	7.5	29.8

Table A2 Time for heating and cooling at given condition

Condition	T_i (°C)	t_h (min)				t (min)	T_{bc} (°C)	t_c (min)
		120°C	140°C	180°C	200°C			
120°C, 10 bar	27.3	33	-	-	-	45	119	33
120°C, 10 bar	27.5	32	-	-	-	60	119.5	34
140°C, 10 bar	32.2	29	30	-	-	60	139.9	44
180°C, 10 bar	28.5	34	28	27	-	60	181.2	40
200°C, 10 bar	25.6	36	32	20	20	60	199.3	39
120°C, 5 bar	24.8	35	-	-	-	60	119.7	33
120°C, 7.5 bar	26.0	34	-	-	-	60	119.4	36

Where T_i is the initial temperature
T_{bc} is the temperature before it was cooled
t_h is the time to heat up to a desired temperature
t is the extraction time
t_c is the time to cool down to a temperature of 50°C.

3. Cinnamon powder as samples

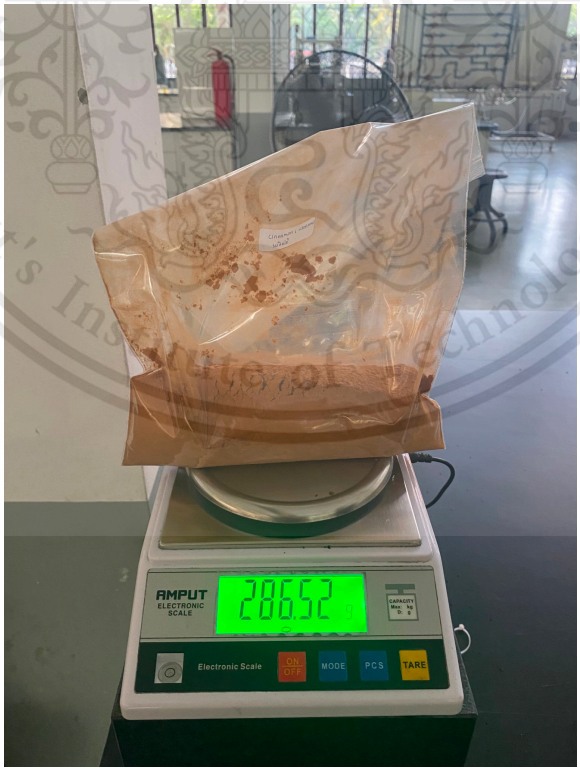


Figure A1 Grinded cinnamon barks as samples

4. Hot compressed water extraction using an autoclave

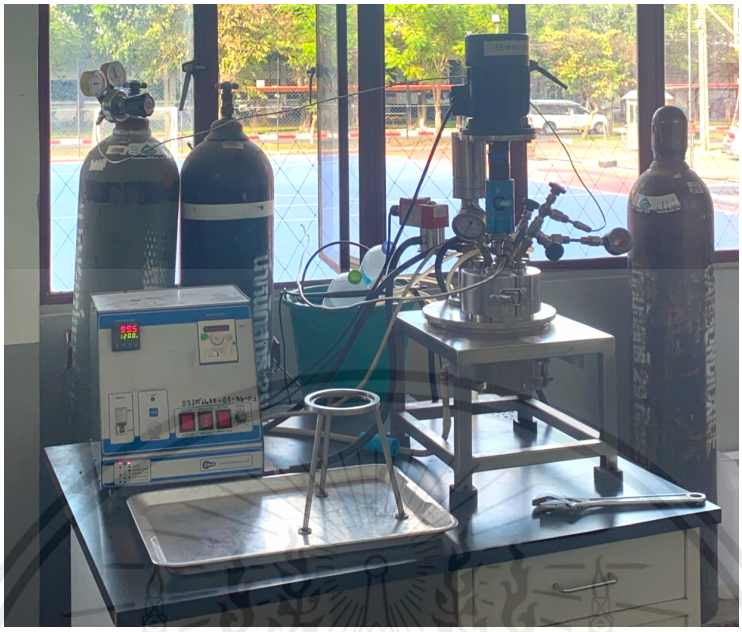


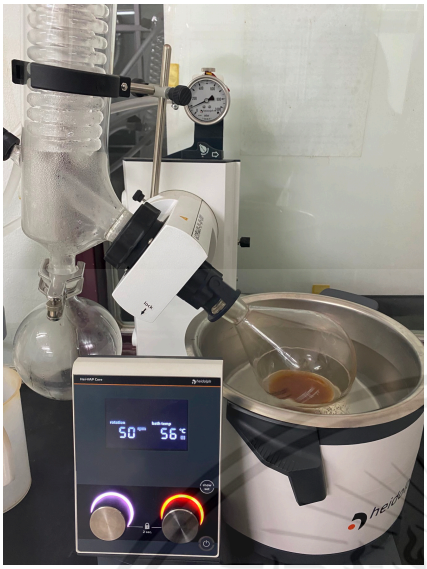
Figure A2 Autoclave reactor for hot compressed water extraction

5. Separating solid residues from extracts using vacuum filter

(a) (b)

Figure A3 Separating solid particles from extracts (a) liquid phase (b) solid phase

6. Separating water phase from extracts

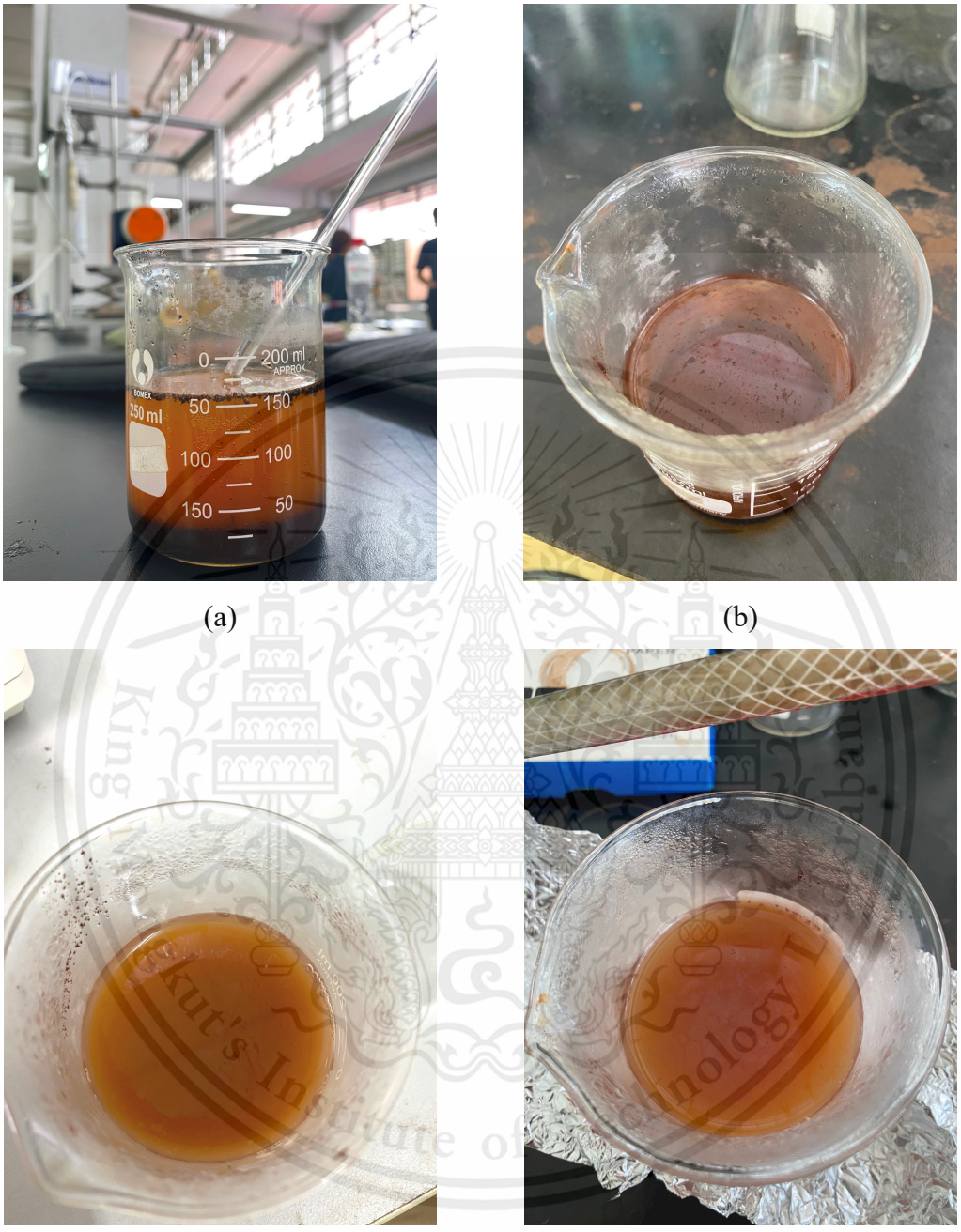


(a)

(b)

Figure A4 Separating water phase from extracts using (a) rotary vacuum evaporator (b) Hot air oven

7. Extracts from hot compressed water extraction in difference conditions



(a) (b)

(c) (d)

Figure A5 Extracts obtaining under pressure of 10 bar for 60 min at different temperatures (a) 200°C (b) 180°C (c) 140°C (d) 120°C

BIBLIOGRAHPY

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