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Application of High-Pressure and High-Temperature Reactor for Extraction of Essential Oil from Kaffir Lime Peel

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Abstract: *This study applied a high-pressure and high-temperature system using water as solvent, to extract the essential oil from kaffir lime peel. In this work, it aimed to determine the effect of temperature and gas such as N_2 and CO_2, on the yield of essential oils extracted from kaffir lime peel and volatile compounds in the extracted essential oils. The essential oils from kaffir lime peel were extracted using 300 g of sample combined with 300 ml of distilled water at a pressure of 5 bar for gas N_2 and 3.4 bar for gas CO_2, and applied temperatures of 100 ºC and 110 ºC for both gases. The results in this work revealed that temperature and type of gases using in the pressurization affected the extraction of essential oil in terms of both yield and volatile compounds in the extracted oil. At extraction temperature of 110 ºC and gas CO_2 provided a yield of essential oil of 1.33 % which is higher than the yield of essential oil using gas N_2 (0.86 %). The extraction parameter including temperature and type of pressurized gases, affected the volatile compounds in the essential oil in terms of the numbers of compounds and the level of concentration. Both essential oil of kaffir lime peel obtained from using N_2 and CO_2 gases contained D-limonene as the major volatile compound. In addition, -Terpineol (13.41 %), Isoborneol (12.41 %), and Terpinen-4-Ol (11.77 %) were found as a majority compound in the essential oil of kaffir lime peel obtained from using N2 gas at temperature 100 ºC. Whereas, using CO_2 gas at the same temperature, β-Pinene (14.44 %) was the majority compound in the essential oil. Thus, the use of a high temperature and high-pressure water system for EO extraction provides a high yield of essential oils and recovery of valuable compounds from kaffir lime peel. Moreover, it is regarded as one of the potential alternatives for improving the extraction efficiency of kaffir lime peel to the growing demand for end-use product manufacturing.*

Keywords: High-pressure reactor; Extraction; Essential oil; kaffir lime

1. INTRODUCTION[1]

Kaffir lime is a spice that has been used in Asian nations such as Laos, Indonesia, Malaysia, Vietnam, and Thailand [1]. This fruit is used in traditional medicine to treat headaches, inflammation, illness, fever, sore throat, bad breath, and digestive issues, hypertension, stomach pain, diarrhea in newborns, flavoring, and reducing body odor [2]. The essential oil obtained from kaffir lime is widely used in the food, beverage, pharmaceutical, flavor, perfume, dye, and other sectors [3]. Numerous studies have revealed that the plant origin and extraction method have an impact on both yield and the main components of essential oils [4]. Due to their low capital cost and simplicity of operation, essential oils are often extracted using classic techniques such as steam distillation and hydro distillation [5]. The high expense of organic solvents, increasingly stringent environmental restrictions, and new medical and food industry needs for ultra-pure and high added value products have intensified the demand for the development of new and clean food processing methods [6]. Therefore, in recent years there has been an extraction technology with the development of new and simpler sample preparation methods such as Subcritical water extraction (SWE), microwave-assisted extraction (MAE) and pressurized hot water extraction (PHWE), which have been described in several previous studies [7].

Subcritical water extraction also referred to as hot water extraction or pressurized (hot) water extraction, is a relatively new extraction technique that has been popular in these recent years, especially in the extraction essential oils and bioactive compounds from natural products. Since, it can extract a large number of compounds quickly while consuming the least amount of energy [8]. Extraction essential oils using solvent like water have been considered as a non-hazardous solvent which is safety to applied in food, pharmaceutical and

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nutraceutical products. The limitation of highly polar water for non-polar EO extraction can be overcome by using subcritical water extraction (SWE), an emerging extraction technology. Water is used as a solvent in the SWE extraction method at temperatures over its ambient boiling point (100 ºC) but below its critical point (374 ºC), with pressures high enough to maintain the water's liquid condition [9]. Water is in a subcritical phase in this condition, which has tunable physicochemical characteristics that can enhance water's capacity to dissolve less polar compounds [10]. So, while temperature has a significant impact on solvation capacity due to its effects on water's physicochemical properties and polarity, it is not the only factor that can affect essential oil extraction. Pressure acting on heated water maintains the liquid phase and contributes to the subcritical properties of water. Pressure, on the other hand, has a minor effect on essential oil yield [11]. Furthermore, the efficacy of SWE in essential oil extraction has been demonstrated in a number of studies, including the extraction of essential oil from Aquilaria malaccensis leaves that provided the yield at 3.8 µl at temperature of 156 ºC and time of 25 min [12] and extract essential oil from woods at temperature of 225 ºC and time 17 min which provided the yield of 16 µl [13]. In addition, extraction by using SWE with nitrogen gas from Trachyspermum ammi seeds gave the yield of 2.58% was extract at the condition of (150 ºC, 150 mins and pressure 20 bar) [14] and for Zataria multiflora Boiss. leaves provided the yield of 12% at condition of pressure gas 2 MPa and temperature of 175 ºC [15], and also from others samples such as Coriandrum sativum L. leaves [16] and Foeniculum vulgare seeds [17]. Thus, the application of a high-temperature and high-pressure system for EO extraction is perceived as one of the potential alternatives to improve the extraction efficiency of kaffir lime peel. However, research on Cambodian kaffir lime peel essential oils with modern technology, such as a high-temperature and high-pressure systems is still limited.

Therefore, the purpose in this work aimed to determine the effect of temperature and the effect of different gases nitrogen (N_2) and gas carbon dioxide (CO_2) on the essential oil yield and essential oil accumulation rate from kaffir lime peel by using a high-pressure system. Moreover, gas chromatography mass spectrometry (GC-MS) was also performed to identify the volatile compositions of kaffir lime peel essential oil.

2. METHODOLOGY

2.1 Sample collection and preparation

Fresh kaffir lime used in this study was bought from Siem Reap province in the northern region of Cambodia. Fresh kaffir lime was cleaned and chopped into (0.5×1) ± 0.2 cm of average size. The chopped kaffir lime peel was frozen at -20 ºC before being used as the sample for the extraction of essential oil.

2.2. High-pressure and high-temperature extraction of essential oil

Fig. 1 gives the experimental setup for a high-pressure and high-temperature system for the extraction of essential oil from kaffir lime peel. In this work, 300 g of frozen kaffir lime peel was mixed with 300 ml of distilled water, the mixture was placed into the reactor tank (1). Gas N_2 or CO_2 was delivered into the system from the gas tank (2), then the pressure of the system was adjusted to 5 bar for N_2 and 3.4 bar for CO_2 systems. The temperature of the system was set to 100 and 110 ºC for both extractions using gas N_2 and CO_2. The essential oil was collected at the outlet (3) and its accumulation rate was recorded in every 15 min until it remained constant, and then the extraction was completed. The essential oil yield was calculated using the following equation (Eq.1) where messential oil (g) and msample (g) are mass of essential oil and kaffir lime peel, respectively.

$$Essential\ oil\ yield\ (\%w/w) = \frac{m_{essential\ oils}}{m_{sample}} \times 100 \quad \text{Eq.1}$$

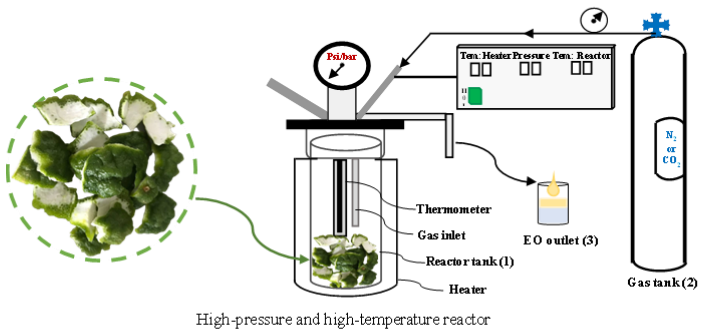

Fig. 1. Experimental setup for high-pressure and high-temperature system for essential oil

2.3. Characterization of essential oils

The essential oil extracted from the kaffir lime peel was identified the volatile compounds using gas chromatography mass spectrometry (GC-MS). The condition of GC-MS was adopted by Mohamed Hanaa [18]. Firstly, 10 mg of essentials was mixed with 1 ml of n-hexane and the mixture was used to inject into the GC-MS system. The GC-MS system consists of an HP5-MS column with a head column pressure of 9.3 psi, a flow rate of 1 ml/min, and a split ratio of 1:20. After holding the oven temperature at 50 °C for two minutes, it was raised to 240 °C at a rate of 8 °C/min. The temperature of the flame ionization detector (FID) was 280 °C, and the temperature of the injector was 240 °C, helium was used as the carrier gas, with a linear velocity of 30 ml/min. The identification of volatile compounds was done by comparing the mass molecular weight to the NIST database.

3. RESULT AND DISCUSSION

3.1. Yield of essential oils

The yield of essential oil extracted from kaffir lime using a high-pressure and high-temperature system under various conditions was given in Table 1. The essential oil yield obtained from a high-pressure and high-temperature system was 3.9 ml or 1.33 % v/w using CO_2 as pressurized gas and a temperature of 110 °C. Extraction kaffir lime peel using a high pressure system at high temperature performed with carbon dioxide gas provided a higher yield than using a conventional method such as hydro distillation (0.8 % ± 0.01) [19] and steam distillation method [20] and with a shorter extraction time of 120 min to only 60 min of extraction.

However, at the extraction temperature of around 100 °C the yield of essential oil was slightly different between the conventional methods and high-pressure and high-temperature system. This indicated that different extraction methods provided different yields of essential oil [21]. At the extraction temperature 100 °C with nitrogen gas resulted in the lowest yield of essential oil at 0.9 ml (0.69 %), while the highest yield of essential oil at 3.9 ml (1.33 %) resulted in at the condition of temperature at 110 °C with gas carbon dioxide. It expressed that gas and temperature had a significant impact on the accumulation rate or yield of essential oil.

Table 1 Yield of essential oil obtained from various extraction methods

Methods	Extraction condition		Yield (%v/w)
	Gas	Temperature (°C)	
High-pressure and High-temperature (This study)	N_2	100	0.69
		110	0.86
	CO_2	100	0.72
		110	1.33
Hydro-distillation [19]			0.8
Steam distillation [20]			0.64

In general, as shown in Figs. 2a and 2b., the gas CO2 is quite soluble in water in which more than 99 % exists as the dissolved gas and less than 1 % as carbonic acid (H_2CO_3), which partly dissociates to give H^+, HCO^{-3}, and CO_2^{-3}. Carbon dioxide reacts with water is facilitating hydrolysis which can release essential oil better than before. Then, both carbon dioxide and water are carried more essential oil from the acidic phase to the vapor phase. More importantly, carbon dioxide has polar connections between carbon and oxygen, even though the molecule is not considered polar due to its symmetry. Because oxygen is less electronegative than carbon, it has a partial negative charge. This is also true for the hydrogen-oxygen bonds in water, so the partial charges of water and carbon dioxide interact more than the partial charges of other gases with water. Moreover, carbon dioxide is a gas in its normal state and can become liquid by pressurizing carbon dioxide. The acidic condition facilitates the extraction through enhancing the hydrolysis of the structure. However, nitrogen has a lower viscosity and poor solubility in oil and requires a much higher pressure to generate or develop miscibility [22]. In addition, nitrogen and water does not have any reaction in the non-acidic phase, in which have only water can carry out essential oil to vapor phase. Thus, after extraction carbon dioxide is the non-polar compound that can carry more essential oil better than vapor water alone and water with nitrogen. So, the essential oil yield by using carbon dioxide gas provides a better yield than nitrogen gas.

3.2. Effect of gas and temperature on accumulation rate of essential oils

Effect of gas and extraction temperature on the essential oil accumulation rate is showed in Figs. 3 and 4. It is found that using either N_2 or CO_2 gases required the extraction time of about 50 min to reach the equilibrium state. However, there is a largely different of accumulation rate of essential oils extracting at different extraction temperature (100 °C and 110 °C) using either N_2 or CO_2 as the pressurized gases. The accumulation rate of essential oil extracting using CO_2 as the pressurized gas is higher than that of N_2. This is because nitrogen dissolves poorly in oil and has a reduced viscosity, miscibility cannot form or develop without a significant increase in pressure when compared with carbon dioxide [23]. While, carbon dioxide dissolves in water much better than other gases. When carbon dioxide reacts with water, carbonic acid is formed, from which hydrogen ions dissociate, increasing the acidity of the system which can carry out more essential oil during the extraction.

Similarly, the accumulation rate of essential oil obtained at extraction temperature of 110 °C is much increased. It shows that at a higher temperature, it offered accumulation rate of the essential oil higher than that at low temperature, using both CO_2 and N_2 as the pressurized gases (see Figs. 3 and 4). At low temperature, the solubility of non-polar essential oil compounds is limited due to the high polarity of water. Moreover, at elevated temperatures under a subcritical condition, the dielectric constant of water decreases and water behaves like certain organic solvents that are able to dissolve a wide range of compounds from medium to low polarity [11]. Thus, an increment in essential oil accumulation rate was observed at 110 °C, which might be due to the improvement of solubilization capacity. In addition, when temperature is high, it also increased the solubility of sample into the solvent, then increasing water diffusivity as well as mass transfer rate [22].

This mechanism will lead to increase the extraction yield [7].

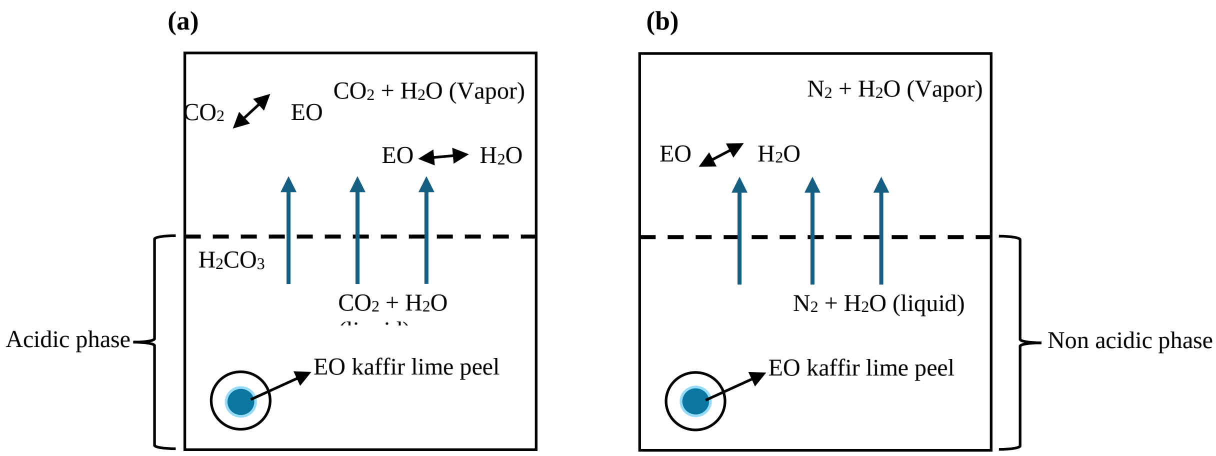

Fig. 2. Extraction mechanism for essential oil, water, and gas system: (a) water and CO_2 system and (b) water and N_2 system

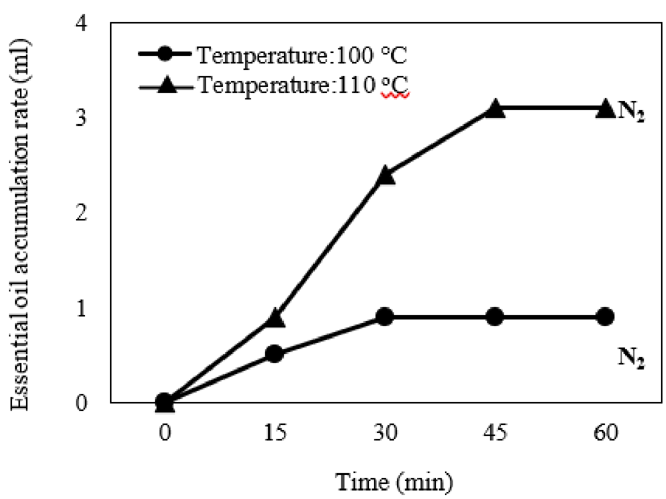

Fig. 3. Effect of gas N2 on essential oil accumulation rate

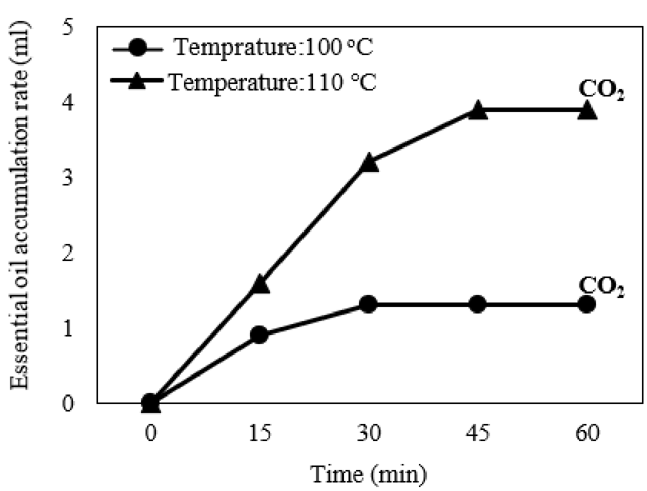

Fig. 4. Effect of gas CO2 on essential oil accumulation rate

3.3. Volatile compounds in essential oils

The chemical compositions of the essential oil extracted from kaffir lime peel were determined using a GC-MS analysis. The compositions of kaffir lime peel essential oil obtained at each studied temperature of the subcritical water extraction 100 oC and 110 oC were analyzed. According to the obtained results in Table 2, there was 20 volatile compounds that present in kaffir lime peel essential oils. Based on the results, monoterpene compounds such as D-limonene, β-Pinene and Terpinen-4-Ol were still found as a majority volatile compound present in kaffir lime peel under a high temperature system and hydro-distillation methods [19] but in the different of concentration level. Moreover, the number of volatile compounds presented in different temperatures and gases were similar whereas the major difference in volatile compounds is the concentration of the specific volatile molecules. An extraction temperature 110 oC might result from the loss of volatiles due to compound degradation at high temperature. The absence of monoterpenes at high temperatures at 110 oC could be due to the instability of monoterpenes which have lower molecular weight with extremely high-volatile characteristics. Furthermore, extended contact between analytes and hot water might result in compound degradation and modification, reducing the quantity and quality of the essential oil [23]. Thus, this result means that, the aromatic of essential oil extracted from different method, gases and temperature may provide a difference in quality, number of volatile compounds and the concentration of a specific volatile compound..

Table 1. Effect of extruder condition on cooking qualities of extruded rice vermicelli

Nº	Common name	Peak area%			
		Gas N_2		Gas CO_2	
		100ºC	110ºC	100ºC	110ºC
1	α-Pinene	2.5	-	3.19	-
2	β-Pinene	8.7	9.96	14.44	10.76
3	β-Myrcene	1.6	4.37	2	3.98
4	α-Phellandrene	1.71	3.68	-	3.97
5	(+)-4-Carene	7.1	-	4.71	-
6	D-Limonene	15.83	13.14	18.97	14.68
7	γ-Terpinene	7.26	6.33	6.17	6.76
8	Linalool	5.7	4.82	5.84	6.35
9	2-Carene	8.09	6.78	5.33	6.62
10	dl-Isopulegol	8.5	7.25	3.45	7.93
11	Citronellal	1.18	5.01	5.45	4.85
12	Isoborneol	12.41	-	-	-
13	Terpinen-4-Ol	11.77	8.92	10.25	8.54
14	α-Terpineol	13.41	-	8	7.78
15	Citronellol	2.74	4.78	4.5	4.91
16	β-Phellandrene	-	4.57	6.1	-
17	Δ-Amorphene	-	-	1.6	-
18	α-Terpinene	-	6.39	-	6.56
19	Ethyl 2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-yl carbonate	-	5.48	-	-
20	Caryophyllene	-	-	-	1.72

Different superscript letters in the same row indicate significant differences ($p<0.05$)
ns: not significantly different ($p>0.05$)

4. CONCLUSIONS

In this work, a high-temperature and high-pressure system was applied to extraction essential oil from kaffir lime peel. The effect of gases such as nitrogen gas and carbon dioxide, and the effect of temperature were also investigated. Results indicated that extraction using carbon dioxide (CO2) as the pressurized gas provided the essential oil yield of 1.33 % which is higher than that obtained from using gas nitrogen (N2) (0.86 %) at extraction temperature of 110 oC. Type of pressurized gas and temperature play the important role in extraction of essential oil using high-pressure and high-temperature system. Moreover, the major compound present in kaffir lime peel essential oil is D-limonene with the high concentration of 18.97%. It also can be concluded that high-pressure extraction can be a promised green technique and a powerful alternative method for extracting essential oils since it can offer high yield and take a short extraction time, compared to hydro-distillation.

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