Kinetic Study of Hydrodistillation of Citrus Sinensis and Quality of the Oil

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Abstract-- *Citrus sinensis* is widely grown fruit crop in the world and exhibits a lot of valuable properties such as antioxidant, anti-inflammatory and anti-tumour. The peels of *Citrus sinensis* consist high amount of essential oil, which can be used as an ingredient in perfume, cosmetic products and food. There are various extraction techniques used to extract the essential oil from *Citrus sinensis*, such as solvent extraction, hot water extraction and supercritical fluid extraction. In this study, a simple and economic hydrodistillation technique is used to extract essential oil from *Citrus sinensis* peel at different steam rate. Kinetic study was done to determine the kinetic parameters of hydrodistillation of orange oil while GCMS and FTIR analysis was done to determine the quality of the essential oil. FESEM was also done to observe the structure of the peels before and after extraction. The highest oil yield was found as 5.73 wt% at steam flow rate 2.43ml/min. The value for concentration of oil at saturation ($C_s$), the extraction rate ($k$) and initial extraction rate ($h$) was increased when the steam rate increased. Limonene was found as the most abundant constituent in the essential oil.

Index Term – *Citrus sinensis*, hydrodistillation, kinetics, GCMS, FTIR, FESEM

I. INTRODUCTION

*Orange* or *Citrus sinensis* is one of the citrus fruit belonging to Rutaceae family. The essential oil of orange is contains in its peel and it has a lot of valuable properties such as antioxidant, anti-microbial and anti-inflammatory.

Therefore, it is often used as the main ingredient in perfume, cosmetic products, medication, especially to cure constipation and mouth ulcers, domestic household products and pharmaceutical formulations [1-2]. In food industry, *Citrus sinensis* oil is used to give orange aroma and flavour enhancer in carbonated drinks and ice-cream. The unique properties of *Citrus sinensis* have attracted the interest of researchers and efforts had been done to extract and recover this valuable oil, especially from the orange peels.

Over the past decade, a lot of extraction methods and techniques have been introduced and investigated to extract *Citrus sinensis* oil. The techniques involved conventional techniques such as solvent extraction (liquid–liquid and solid–liquid extraction) by assistance of external factors (e.g. mechanical agitation, pressing, or heating systems). Besides, modern and automated methods including supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE) and ultrasound assisted extraction (UAE) have also been used [3]. The modern methods usually costly and laborious as compared to the conventional techniques. Hydrodistillation is one of the conventional methods often used to extract essential oil. It provides good quality essential oil, operated in a relatively simple and safe manner and environmentally friendly since it used water as solvent. There are some studies which compare the efficiency between conventional and modern method [3-5]. In comparison between conventional and modern methods, it was observed that each methods has its own effects on extraction yield and bioactive compounds extracted.

With regards to the attraction of essential oil, it is useful to develop, improve and optimize the process of extraction. The study of kinetic modelling is essential to design an efficient extraction process for recovery of bioactive compound. Besides, this study can predict the behavior of extraction process and useful for scaling up the process. There are a lot of kinetic studies have been reported which include Fick’s Law [6, 7], unsteady diffusion [8] and empirical equations [9]. Therefore, a suitable proposed model can be selected based on operating conditions of the process.

The objective of this study is to determine the quantity and quality of orange essential oil, which is extracted from orange peel via hydrodistillation, in terms of the oil yield and chemical constituents. Besides, the kinetic models at different steam flow rate of the hydrodistillation process will also be investigated.

II. MATERIALS AND METHODS

2.1 Plant Material

The orange fruits were obtained from local market and were cut into pieces. The orange peels then were dried in an
oven at 60°C for 24 hours. The dried peels was then blended and sieved.

2.2 Hydrodistillation

About 30 g of orange peel powder was mixed with 300 ml of water and agitated at 150 rpm in the reaction vessel. The steam flow rate was adjusted by controlling the heating mode of the heating mantle. Samples were collected every 5 minutes. The amount of yield, which is the orange essential oil, is measured by comparing the initial weight of orange peel and final weight of the oil.

2.3 Kinetic Model

This study was done to determine the kinetics parameter which is important to predict the extraction process. The second order kinetic model is a plausible method for hydrodistillation and can be written as [10]:

\[ \frac{dC_t}{dt} = k(C_e - C_t)^2 \]  

(1)

where \( k \) is the second-order extraction rate constant (mL/g min), \( C_e \) is the equilibrium concentration of oil in the liquid extract (g/mL), and \( C_t \) is the total concentration of oil in the liquid extract at a given extraction time \( t \) (g/mL).

The integrated equation can be obtained by taking the initial and boundary conditions as \( t = 0 \) and \( c = 0 \) to \( c \). The equation can be written as:

\[ C_t = \frac{C_e^2kt}{1+kC_e \cdot t} \]  

(2)

The linear form of Eq. (2) can be written as:

\[ \frac{t}{C_t} = \frac{1}{kC_e^2} + \frac{t}{C_e} \]  

(3)

When extraction time approaches zero, initial extraction rate which can be denoted by \( h \), can be defined by Eq. (4).

\[ h = kC_e^2 \]  

(4)

Eq. (5) can be obtained after rearranging eq. (4) and can be written as:

\[ C_t = \frac{t}{(k/h)+(t/C_e)} \]  

(5)

By plotting \( t/C_t \) against \( t \), the value of \( C_e, h \) and \( k \) were determined experimentally from the slope and intercept of the graph.

2.4 Gas Chromatography Mass Spectrometry

The chemical composition of the essential oil is determined by using Gas Chromatography Mass Spectrometry (GCMS). The analysis was done using an Agilent 6890 device equipped with a split/splitless injector (250°C, split ratio 275:1) using an Agilent HP-5MS column (30 m x 0.25 mm, film thickness, 0.25 µm). The temperature program started at 35°C and rose to maximum temperature at 250°C. Helium was used as the carrier gas at a flow rate of 1ml/min. The volume of the injected sample is 1 µL.

2.5 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done on the collected essential oil to compare and analyze the differences of the compound. It was performed by using FTIR analyser (Perkin Elmer) over the range of 900 – 4000 cm⁻¹. Spectral data obtained was plotted on a graph of absorbance versus wavenumber (cm⁻¹).

2.6 Field Emission Scanning Electron Microscope

Field-emission scanning electron microscopy (FESEM) images were obtained using the Hitachi SU8010 electron microscope at an accelerating voltage of 5 kV. The analysis was done for Citrus sinensis peels before and after the hydrodistillation process.

III. RESULTS AND DISCUSSION

3.1 Extraction yield

Fig. 1 shows the percentage of extraction yield of orange oil at different steam flow rate. From the figure, it can be seen that the highest oil yield is at 2.43 ml/min steam flow rate which is 5.73%. Meanwhile, the lowest percentage of oil yield is at 0.99 ml/min which is 1.23%. The yield obtained in this study is higher as compared to findings from Manila et al [11] which used the same hydrodistillation method. The mechanism of the extraction comprised of two stages which are washing stage and diffusion stage [12]. During the washing stage, the oil yield increased rapidly as the solvent starts to penetrate into the matrices of orange peel. This caused the cytoplasm layer of the cell to be exposed directly to the

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solvent and the oil is easier to dissolve into the solvent [13]. The latter stage is the diffusion stage where the extraction rate is slow and almost constant. In this stage, the oil is diffused from the internal matrices of orange peel and dissolved into the solvent.

3.2 Kinetic Study

Fig. 2 shows the values of t/Ct were plotted against time for three average steam rate using second-order model approach. The values for concentration of oil at equilibrium ($C_e$), second order extraction rate constant ($k$) and initial extraction rate ($h$) were calculated from the linear plot in Fig. 2. From the graph, the slope is equal to $1/C_e$ and the intercept is equal to $1/kC_e^2$. This straight line shows a good agreement with the second order extraction model. The values for $C_e$, $h$ and $k$ at different steam flow rate are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Steam flow rate (ml/min)</th>
<th>Concentration of oil at saturation, $C_e$ (g/ml)</th>
<th>Second-order extraction rate constant, $k$ (ml/g.min)</th>
<th>Initial extraction rate, $h$ (g/ml.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99</td>
<td>0.0202</td>
<td>3.120</td>
<td>0.0013</td>
</tr>
<tr>
<td>2.35</td>
<td>0.0499</td>
<td>3.4994</td>
<td>0.0087</td>
</tr>
<tr>
<td>2.43</td>
<td>0.0713</td>
<td>16.6992</td>
<td>0.0850</td>
</tr>
</tbody>
</table>

From Table I, it can be observed that the value of $C_e$, $k$ and $h$ increased with the increase of steam flow rate. It was due to the increased of heating modes and thus would increase the flow rate of the steam. The speed of the reaction was improved and thus the reaction proceeds faster. Hence, the initial extraction rate ($h$) follows theoretically where it is proportional to the extraction rate constant ($k$) and the concentration of oil. The rate constant ($k$) and the initial extraction rate ($h$) are significant to measure the speed of chemical reaction [14]. The rate constant is specific for a given reaction at a given temperature, therefore it is largely affected by the change of temperature.

3.3 GCMS Analysis

The identification of chemical constituents in orange essential oil was done using GCMS. The constituents are listed in Table II and divided by steam flow rate used.

Fig. 3. The effect of different steam flow rates on the chemical bonding of *Citrus sinensis*, a)0.99 ml/min, b)2.35ml/min, c)2.43ml/min
Table II
Chemical constituents of orange essential oil at different steam flow rate

<table>
<thead>
<tr>
<th>Chemical Constituents</th>
<th>GCMS Peak Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Steam flow rate (ml/min) :</td>
</tr>
<tr>
<td>α-pinene</td>
<td>0.425</td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>0.549</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>1.231</td>
</tr>
<tr>
<td>D-Limonene</td>
<td>97.136</td>
</tr>
<tr>
<td>β-Myrcene</td>
<td>0.15</td>
</tr>
<tr>
<td>Decanal</td>
<td>0.236</td>
</tr>
<tr>
<td>Spathulenol</td>
<td>0.128</td>
</tr>
<tr>
<td>Valencene</td>
<td>0.144</td>
</tr>
<tr>
<td>Sabinene</td>
<td>0.204</td>
</tr>
<tr>
<td>3-Carene</td>
<td>0.357</td>
</tr>
<tr>
<td>trans alpha-bergamotene</td>
<td>0.071</td>
</tr>
</tbody>
</table>

From Table 2, the most abundant constituents were D-Limonene, α-pinene, β-Pinene, β-Phellandrene and 3-carene. Prior studies have also reported that these constituents are contained in orange essential oil [1, 14]. D-Limonene is the most abundant constituent present in all steam flow rate. It can be concluded that monoterpene hydrocarbons which consist of D-Limonene, α-pinene, β-Phellandrene, β-Pinene, β-Myrcene, Sabinene and 3-Carene has higher amounts in the essential oil extracted. Meanwhile, oxygenated compounds such as spathulenol shows lower amounts as compared with the monoterpene hydrocarbons. In terms of fragrance contribution of the essential oil, oxygenated compounds are highly valuable [15]. This is due to the highly odoriferous of the oxygenated compounds than monoterpene compounds, hence make it more valuable.

3.4 **Fourier Transform Infrared Spectroscopy Analysis**

In order to confirm the identity of functional groups of the chemical compounds, the samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra of different steam flow rates are presented in Fig. 3. The spectra are in consistent with the work done by Galvao et al., 2015 [16], where C-H stretching vibration are observed at 2965 and 2919 cm⁻¹, C=C stretching at region 1650-1500 cm⁻¹, asymmetric CH₃ deformation vibration at 1436 cm⁻¹ and symmetric CH₃ deformation vibration at 1376 cm⁻¹. Signature spectra of carbohydrate are also observed at wavelength 950-1200 cm⁻¹, where C-O stretching and C-H deformation are found at 1160-1000 cm⁻¹ and 960-730 cm⁻¹ respectively [17]. It shows the presence of pectin which is a complex mixture of polysaccharides often found in orange peel [18]. In addition, D-Limonene was also observed in this sample at C-H stretching spectra at around 2919 cm⁻¹. This is in agreement with other study where D-Limonene was also found around 2900 cm⁻¹ [19].

3.5 **FESEM**

Fig. 4 and 5 shows the FESEM images of orange powder before and after the hydrodistillation experiment. The essential oil glands in the fresh orange powder are closed and thus a dense structure is observed in Fig. 4. This is because the essential oil glands are located inside the orange powder [20]. After the hydrodistillation process, open porous structure is found in the samples as shown in Fig. 5. This shows the opening of the glands and hence the essential oil is extracted during the hydrodistillation. Contrary finding was reported by Allaf et al. 2013 [21] where the glands of the essential oil in the orange peel were shrunk and collapsed after the hydrodistillation. This may due to the inconsistent heat transfer in the orange peel. Comparatively, this study uses orange powder in steads of orange peel, heat transfer on smaller particle is more uniform and thus more open and structured glands can be found.
Fig. 5. FESEM image for orange powder before after hydrodistillation

IV. CONCLUSION

Hydrodistillation is one of the conventional method for extraction of bioproducts. From this study, the highest oil yield was found at the highest steam flow rate. Kinetic study done shows that all the kinetic parameters increased with the increased of steam flow rate. The essential oil content was rich with D-Limonene at every steam flow rate and in consistent with literature studies reported. Open structure was found after extraction. Further research on optimization of hydrodistillation and modelling on mass transfer is recommended to determine an efficient extraction process behavior.

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