Characterization of essential oil from baby java orange (*Citrus sinensis*) solid waste

I A Dewi, A M Prastyo, S Wijana, and A Ihwah

Department of Agroindustrial Technology, Faculty of Agricultural Technology, Universitas Brawijaya, Malang, Indonesia

E-mail: ikaatsaridewi@ub.ac.id

**Abstract.** Baby Java orange (*Citrus sinensis*) is a varietal orange juice developed in Malang Regency East Java Province. The area of baby Java cultivation in Malang Regency reaches 1000 hectare with the production rate about 24,500 annually. The orange solid waste which were thrown away were distilled to get valuable volatile oil. The research method used was randomized block design with distillation time-delay process factor for 2, 4, 6, and 8 days. Determination of the best treatment is done by performing calculations with multiple comparisons method based on refractive index response. The best treatment result was characterised using GC-MS and then compared to control volatile agent. Specific gravity was also measured for all treatments. The results of ANOVA refractive index showed that all treatments had significant difference to time-delay process. Tukey test obtained showed that the best treatment was distillation time-delay for 6 and 8 days. The highest response of refractive index was 72.60% brix, and the specific gravity for the best treatment was 0.84 g/cm³. Limonene produced from the best treatment received 100% value while from the control treatment was 96.42%. The value of limonene produced from the best treatment was 100%, while from the control treatment was 96.42%.

1. **Introduction**

Citrus plants are one of the plants widely cultivated in Indonesia. Malang Regency is one of the most productive areas for citrus cultivation, particularly baby Java orange [1]. The sweet taste of the orange makes it widely used as fruit juice. Yet, other potential valorisation are also possible. Solid waste from the fruit juice processing such as mesocarp, exocarp, seed, and wall of the orange are often disposed without being processed, although it contains volatile substances that can be used as a source of essential oils [2]. Dewi [3] reported that using the steam and water distillation method with 8 days distillation treatment can produce essential oil by 0.63% with 24.21% moisture content.

The purpose of time-delay process is to prolong the storage of any raw material to be distilled which does not meet production capacity. The handling of the selected material is by placing the material in a room that is protected from direct sunlight exposure but the process of air drying can still take place. The treatment is chosen so it will not cause excessive heat which can cause the evaporation of water and large volatile substances. Another advantage of wind drying is low cost [4].

The control treatment was carried out on baby java orange waste in fresh condition. Good characteristics of essential oils can be assessed from the refractive index value [5].
2. Materials and Methods
2.1. Materials
The main raw material used in this study is baby Java orange solid waste resulting from the orange juice extraction taken from the citrus plantation in Dau District, Malang Regency. The additional material needed in this water and steam distillation is clean water.

2.2. Experimental design
The research method used is a completely randomized design using 1 factor of drying time with 4 levels (i.e. 2, 4, 6, and 8 days) and 5 repetitions in each level. Each treatment of the dried waste is calculated using the refractive index and specific gravity. The best treatment is obtained from the refractive index response value based on ANOVA test and Tukey Test using IBM SPSS 17.0 software. The best treatment results and control treatments were tested for volatile substances with GC-MS according to Pavia et al. [6].

2.3. Essential oil production
The production of essential oil was started by preparing organic solid waste from baby java orange. As many as 2.5 kg of baby Java orange waste were air-dried for 2, 4, 6 and 8 days. After this time-delay process pre-treatment, the waste were chopped into smaller pieces with maximum area of 4 cm². Before the process of distillation, moisture content of each treatment was measured.

Distillation process was started by filling 2.5 L of water into the kettle (distillatory cylinder), then heated up to 100-115°C. The dried waste was distilled for 4 hours. Remaining water and waste after distillation were measured, as well as the essential oil obtained.

2.4. Analysis
Determination of the refractive index is done by a Bellingham & Stanley Limited refractometer at a temperature of 30°C. Refractive index at a temperature of 25°C is calculated using the formula [7]:

\[ R = R' + k (T' - T) \]  

Where: \( R \) is refractive index at temperature (°C), \( R' \) is refractive index reading at temperature (°C), \( T \) is expected temperature (standard temperature), \( T' \) is temperature reading, and \( k \) = correction factor = 0.00045.

The specific gravity analysis was measured using pycnometer following AOAC procedure [7].

3. Results and Discussion
3.1. Refractive index analysis
The criteria in determining the purity quality of the baby java orange essential oils waste by steam and water distillation method can be done by looking at the value of the refractive index. Refractive index is the ratio between the speed of light in the air and in an oil substance. Refractive index value of essential oil is influenced by the components within. The more long chain components such as sesquiterpene or oxygen-clustered-components are distilled, the higher the density of essential oils will be. In consequence, the coming light will be harder to refract. This factor can cause a larger oil refractive index. According to Armando [8], the higher the refractive index value of essential oil, the oil will be purer or better and the lower the refractive index value, the oil will get worse. Refractive index average data and the ANOVA test result is represented in Table 1. ANOVA test results on the refractive index response data state that there are significant differences between treatments since p-value < 0.05.
Table 1. Refractive index data.

| Delay Process Time (Days) | Replication (Brix) | Average | Differences | Notation |
|--------------------------|-------------------|---------|-------------|----------|
|                          | 1                 | 2       | 3           | 4        | 5       |
| P2                       | 71.23             | 71.37   | 71.20       | 71.45    | 71.47   | 71.34   | 71.71 | a        |
| P4                       | 72.37             | 72.07   | 71.62       | 71.95    | 71.17   | 71.84   | 72.21 | b        |
| P6                       | 72.47             | 72.42   | 72.07       | 72.40    | 72.30   | 72.34   | 72.70 | c        |
| P8                       | 72.90             | 72.62   | 72.62       | 72.52    | 72.30   | 72.60   | -     | c        |

Furthermore, multiple comparisons are calculated using the Tukey test to determine the real difference in delay time for each refractive index response. In addition, the Tukey test is also used to determine the optimum value of the refractive index response based on the maximum value. The results of the Tukey test show that all treatments are significantly different, except that P6 is not significantly different from P8. Both P6 and P8 can be selected as the best treatment.

The trend of the refractive index is shown in Figure 1. In the figure, the trend of the refractive index formed is increasing in proportion to the length of the refining time delay. The longer the refining process is delayed, the higher the refractive index value. Delay time is directly proportional to the number of material cell walls that will open, so that the components of the active compound in distillation process can potentially come out to maximum quantity. Chemical components in oil such as volatile substances will increase oil density, so the incoming light will be refracted. Marlon [9] states that wilting is carried out to a certain moisture content, that is, until the leaves are damaged. Withering is executed to open the cell wall so it will be easier for water vapor to penetrate. In consequence, volatile substances in it will be more easily lifted together with hot steam.

The rupture of oil cells in materials can optimize the process of removing the volatile substances contained in the material by moisture. Reduced water contained in the ingredients causes the oil produced will be purer. The maximum removal of volatile substances contained in the ingredients will increase the value of the refractive index [10].

![Refractive index of the essential oil of baby Java orange solid waste with the delayed distillation pretreatment (Replication=5).](image)

According to Sumarsono [11], the length of delay process influence the content of essential oils produced. Where, the longest delay time produce more essential oils as indicated by a high refractive index. Furthermore, higher refractive index also represent its lower water content, which contribute to
a better mixing with other substances [12]. Delay time in distillation process affect both specific gravity and the component in the essential oils [13]. As can be seen in Table 4 that essential oil from each treatment has different specific gravity.

The specific gravity of essential oils is often associated with the components within. High density will affect the content in it, and vice versa if essential oils have a low specific gravity, the content in them will be less [13]. The specific gravity of pure essential oil will be lower than the specific gravity of the essential oil that has been mixed by the solvent. The larger or smaller the weight fraction in it will affect the specific gravity [12].

The specific gravity data of Baby Java Orange is shown in Table 2. According to Ejeziofor [14] the value of the refractive index of essential oils derived from sweet oranges is 0.843 g/cm³. The results of the study when compared with Ejeziofor [14] have the difference in the nearest value is in the delayed distillation treatment for 2 days with a difference in the value of 0.0001 g/cm³.

Decreased values can result from the volatile substances in the essential oil. Guenter [15] states that the major and minor components contained in essential oils can affect the weight value of essential oils. The main components that should be contained in essential oils of sweet oranges are limonene.

### Table 2. Specific gravity data.

| Time-delay Process (Days) | Replication (g/cm³) | Average |
|--------------------------|---------------------|---------|
|                          | 1       | 2       | 3       | 4       | 5       |         |
| P₂                       | 0.843   | 0.843   | 0.843   | 0.843   | 0.843   | 0.843   |
| P₄                       | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   |
| P₆                       | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   |
| P₈                       | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   | 0.842   |

3.2. Test results of volatile substances (GC-MS)

Although 6 and 8 days of time-delay process were considered as the best treatment, but to find out the longer time-delay process treatment volatile substances, P₈ was chosen to be analysed using GC-MS. This is also as an anticipation if implemented in production scale, and the raw material is excessive, so the longer time-delay process is needed. GC-MS testing is carried out on two samples, including control treatment (without preliminary treatment before distillation) and the results of the best treatment calculation in P₈ treatment (8 days of time-delay process). The test results of volatile substances in essential oils of orange baby Java waste can be seen in Table 3.

### Table 3. Components of volatile substances for essential oils of baby Java orange solid waste.

| Components of Volatile Substances | P₀ (%) | P₈ (%) |
|----------------------------------|--------|--------|
| Limonene                         | 96.42  | 100    |
| Tetrasiloxane                    | 3.58   | -      |
| Total                            | 100    | 100    |

Note: P₀ = control treatment, P₈ = 8 days delayed distillation

The table shows the components of volatile substances contained in two different samples. The first sample is the control treatment sample (P₀), where in this control treatment there are two components that are read from the GC-MS test which are limonene and tetrasiloxane. Limonene obtained amounted to 96.42% area, and tetrasiloxane obtained amounted to 3.58% area. In contrast to the results of volatile substances obtained from the treatment of refining delays for 8 days. The volatile substances obtained from the distillation for 8 days are only limonene with 100% of the area detected.
by GC-MS. Orange peels contain different compounds, depending on varieties, so the aroma is different. According to Siburian [16], the more abundant component found in sweet orange essential oil is limonene. Limonene content is differed for each orange variety with the values can be more than 70% [17]. The results from this study was in accordance to previous study which reported that the largest component of citrus essential oil is limonene. For example, according to Muhtadin et al. [18], that the quality of orange peel oil obtained has increased along with the pre-treatment with withering.

4. Conclusion
ANOVA test result showed that distillation time-delay process had significant effect on refractive index value. However, the refractive index of 6 and 8 days of time-delay process were not significantly different and they were considered as the best treatment. The refractive index values were 72.35 and 72.60 brix. Volatile substances obtained from essential oils resulting from the treatment of distillation delay for 8 days get the best limonene content with a percentage of 100%. It can be concluded that the value of volatile substances is influenced by the pretreatment of the delayed distillation.

References

[1] Artarlina S S, Noor 2006 The quality of tangerines in tidal fields, in monograf of siamese oranges in tidal land, Its Management and Development Center for Agricultural Land Resources Research and Development of Swampland Research Centre Banjarbaru, Indonesia. [In Indonesian]

[2] Kurniawan E 2015 Sweet orange fruit sorting system design based on skin color difference Teknik Industri Heuristic 12 2 93-99.

[3] Dewi I A 2018 Extraction of essential oil from baby orange (Citrus sinensis) solid waste using water and steam distillation IOP Conf. Series: Earth Environ. Sci. 131 1-4.

[4] Pramono S 2006 Post-harvest management and its influence towards natural drug therapy effect Proceedings of the National Seminar on Indonesian Medicinal Plants XXVIII Bogor PP 1-6. Indonesia. [In Indonesian]

[5] Kurniawan D 2011 Effect of distillation duration against the yield of citrus hystrix oil using vacuum distillation Undergraduate Thesis Chemical Engineering Department Universitas Diponegoro Semarang Indonesia. [In Indonesian]

[6] Pavia D L, Lampman G M, Kritz G S, Engel R G 2006 Introduction to Organic Laboratory Techniques Thomson Brooks Publishing New York USA.

[7] AOAC 2018 (online) Official Methods of analysis retrieved from http://www.ema.aoac.org/methods/info.asp?ID=199 [Accessed on December 13th 2018].

[8] Armando R 2009 Producing Qualified Essential Oil Penebar Swadaya Jakarta Indonesia. [In Indonesian]

[9] Marlon L 2012 The basic commodity treatment and refining water-stem application towards the rendement and organoleptik characteristic of essential oil Ekosains 1(1)1-7.

[10] Kristian J, Zain S, Nurjanah S, Widyasanti A, Putri S H 2016 The effect of duration of extraction to yield and quality of jasmine oil by using solvent extraction method Jurnal Teknotan 10 2 34-43. [In Indonesian]

[11] Sumarsono 2005 Change in water content of patchouli leaves during drying process with different air stream velocities and tray dryer rotation Ilmu-ilmu Pertanian Indonesia 71 59-67. [In Indonesian]

[12] Sastrohamidjojo 2004 (online) Determination of patchouli oil quality standards retrieved from http://repository.usu.ac.id/bitstream/handle/123456789/16961/Chapter%20II.pdf?sequence=3 [Accessed on June 3rd 2017]. [In Indonesian]

[13] Hikmah N 2017 Yield and quality of essential oil from ginger (Zingiber officinale Rose) HutanTropis Borneo 8 20 8-16. [In Indonesian]
[14] Ejeziofor T N, Eki N V, Okechukwu R I, Nwoguikpe R N, Duru M 2011 Waste to wealth: industrial raw materials potential of peels of Nigerian sweet orange (Citrus sinensis) Afr. J. Biotechnol. 10 33 1-8.
[15] Guenter E 1990 Essential Oil 4th Ed. Universitas Indonesia Press Jakarta Indonesia. [In Indonesian]
[16] Siburian R 2008 Isolation and identification of essential oil main components from Citrus sinensis L. originated from Timor, East Nusa Tenggara Natur Indonesia 11 1 8-13. [In Indonesian]
[17] Research and Development 2008 Orange essential oil: the opportunity to develop orange peel economic value Warta Penelitian dan Pengembangan Pertanian 30 (6) 7-8. [In Indonesian]
[18] Muhtadin A F, Wijaya R, Mahfud 2013 Retrieving essential oil from fresh and dry orange skin using steam distillation method Jurnal Teknik ITS 2 1 98-101. [In Indonesian]