Effect of the Fractional Distillation on an Increment Patchouli Alcohol Content in Patchouli Oil

Yuliani Aisyah[1,2], Sri Haryani Anwar[1] and Yulia Annisa[1]
[1]*Agricultural Product Technology, Agriculture Faculty, Universitas Syiah Kuala, Banda Aceh, Indonesia, 23111*
[2]*PUI - Atsiri Research Center, Universitas Syiah Kuala, Banda Aceh, Indonesia, 23111*

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Abstract: Indonesia is one of the patchouli oil producers in the world, however, the problem is the quality of patchouli oil, especially patchouli alcohol content that are still below the required standard. One of the methods that can be used to increase the content of patchouli alcohol is fractional distillation method. This research aims to know the influence of the initial concentration of patchouli alcohol and height of column against increment of patchouli alcohol content in patchouli oil. The experimental design which used was Complete Randomized Design (CRD) consist of two factors, first factor namely the initial concentration of patchouli alcohol (C1 = 31,11%, C2 = 32,83%, and C3 = 33,61%) and second factor is height of column (H1 = 25 cm and H2 = 45 cm). Analysis of variance shows that the height of vigreux column has a real influence against the increased levels of patchouli alcohol. The highest levels of patchouli alcohol (83,86%) obtained from the residue fraction of distillation with 31.11 % initial concentration of patchouli alcohol and 45 cm height of column. The higher levels of patchouli alcohol in patchouli oil residue fraction, the higher specific gravity and the refractive index, and solubility in ethanol will be easier. The result shows that this sample have 1.013 specific gravity, clear in ethanol at 1:5 and have 1.5166 refractive index.

1 INTRODUCTION

Patchouli (*Pogostemon cablin* Benth) is one of the plants that produce an essential oil known as the Patchouli oil. Patchouli comes from a family of *Lamiaceae*, the order of *Lamiales* and Class of *Angiospermae*. There are several types of Patchouli in Indonesia, such as *Pogostemon cablin* Benth, or widely known as Aceh Patchouli (Nilam Aceh), which has the oil content of 2.5-5%. Furthermore, the *Pogostemon heyneanus* which is known as Java Patchouli (Nilam Jawa) with the oil content of 0.5-1.5%, and *Pogostemon hortensis* also known as Soap Patchouli with the oil content of 0.5-1.5% (Rukmana, 2003).

According to Aisyah et al. (2008), there are 15 identified chemical constituents of Patchouli oil. The constituents with the highest percentage are patchouli alcohol (32.60%), δ-guaiene (23.07%), α-guaiene (15.91%), seychellene (6.95%) dan α-patchoulene (5.47%). These five components are also similar to the result of Corine and Sellier (2004).

The patchouli alcohol (PA) is one of the quality parameters of patchouli oil. Patchouli alcohol is an oxygenated sesquiterpene that has a boiling point of 140 ºC at 8 mmHg pressure, the molecular weight of 224 and a molecular formula of $C_{15}H_{26}O$ (Bulan et al., 2000). According to the international standard, the best quality of patchouli oil is the one with patchouli alcohol content at least 38% (Essential Oil Association of USA, 1975), and 31% (SNI 06-2385-2006). The patchouli oil produced in Indonesia relatively has a low content of patchouli alcohol which is < 30%. This is because the postharvest handling before distillation is not conducted very well, the distillation process is not optimal (simple method and equipment, and short distillation time), and because of the material source. Therefore, the parameter of patchouli alcohol content needs to be improved to expand the market.

All this time the farmers only capable to produce the oil with patchouli content of 26-28%, while the distillation industry that uses the stainless-steel distillation equipment can produce the oil with patchouli alcohol content up to 31-35% (Sarwono, 1998).

Several types of research have been conducted to improve the patchouli alcohol content in patchouli oil

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by using different method, for instance the fractional distillation (Bulan et al., 2000; Harfizal, 2003; Yanyan et al., 2004), rotary evaporator with fractionation temperature control (Suryatmi, 2008), cellulose acetate membrane (Aisyah et al., 2010), vacuum fractionation distillation (Aisyah et al., 2013; Isaroiny and Mitarlis, 2005), a combination of fermentation, delignification and distillation methods (Muharam et al., 2017). The result showed that the increase of patchouli alcohol content varies depends on the method used.

Based on the boiling point, constituents of patchouli oil have boiling point as follows: patchouli alcohol (140°C at 8 mmHg), eugenol (252.66 °C at 760 mmHg), benzaldehyde (178.07 °C at 760 mmHg), cinnamic aldehydes (251.00 °C at 760 mmHg) and cadinene (274 °C at 760 mmHg) (Guenther, 1949). The difference in the boiling point leads the components to be separated by the fractionation distillation process. To provide a thorough result and prevent component damage due to the impact of temperature on ordinary fractionation distillation, the process will be accompanied by vacuum fractionation distillation.

This research aims to optimize the vacuum fractional distillation by considering the factor of initial patchouli alcohol of patchouli oil and factor of fractionational distillation column used in this process. It is assumed that these two factors can produce a higher percentage of final patchouli alcohol than initial patchouli alcohol from patchouli oil.

2 MATERIAL AND METHOD

2.1 Material

The material used in this research is patchouli oil from Meukek, Pasie Raja, and Panjupian Sub-district of Aceh Selatan Regency. The equipment used is a series of vacuum fractionation distillation equipment consisting of 500 ml round neck flasks, vigreux columns, thermometers, condensers, 3 heart-shaped flasks, vacuum pumps, pans, and hot plates. Quality analysis is using Gas chromatography-mass spectrometry Shimadzu GCMS-QP 2010S, GC-QP 2010S, pycnometer, analytical scale, test tubes, drop pipettes and Abbe refractometers.

2.2 Method

Vacuum Fractional Distillation Process (Modified by Aisyah, 2008). The fractional distillation process of patchouli oil is using a series of vacuum fractionation distillation equipment which is accompanied by a vacuum pump. The patchouli oil used is 300 ml. The distillation was done at ±2 KPa (± 15.001 mmHg) pressure and temperature of 30-190 °C. The distillation was conducted until there are no more distillate drops on the heart-shaped flask. The sample of patchouli oil is analyzed by using GC-MS before fractionation. The residue from the fractional distillation then was analyzed to determine the final patchouli alcohol content. Furthermore, the residue with the highest content of patchouli alcohol was analyzed for refractive index and solubility in water.

3 RESULT AND DISCUSSION

3.1 Chemical Constituent of Patchouli Alcohol

The Chromatogram (Figure 1) represents the analysis result of chemical constituent using GC-MS on three patchouli oil before fractionation, and the chemical constituent components in patchouli oil that is above 1% can be seen in Table 1.

Table 1: Chemical constituent of Patchouli Oil

Chemical constituent	Meukek	Pasie Raja	Panju pian
β-Patchoulene	1,62	1,76	1,73
2,4-Diisopropenyl-1-methyl-1-vinyl-cyclohexane	1,00	1.02	1,20
β-Caryophyllene	2,87	2,77	3,06
α-Guaiene	17,39	16,61	18,10
Seychellene	4,68	4,27	4,67
α-Patchoulene	6,89	6,46	6,65
Alloaromadendrene	2,82	2,81	3,32
Δ -Guaiene	21,45	20,23	20,08
1H-Cycloprop[e]azulen-4-ol, decahydro-1,1,4,7-tetramethyl	4,03	5,35	
Patchouli alcohol	31,11	32,83	33,61
2H-Pyran-2,4(3H)-dione, 3-acetyl-6-methyl	1,12		

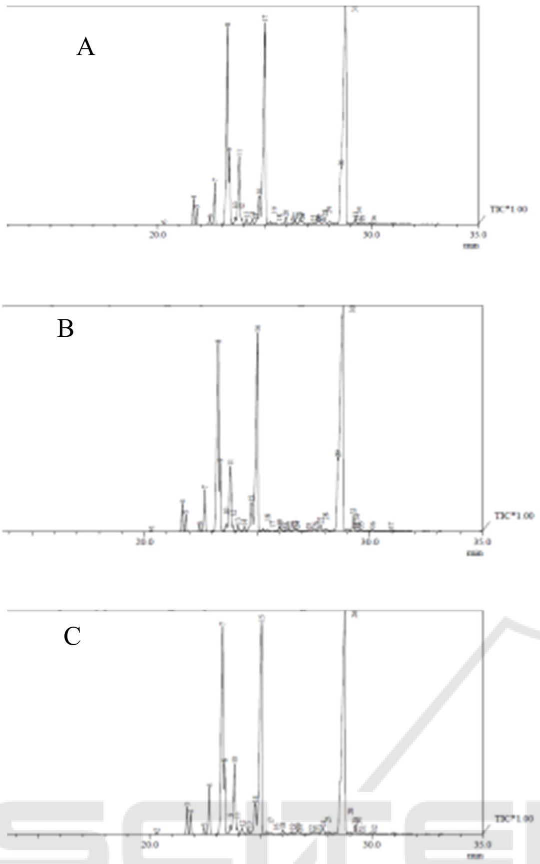

Figure 1: Chromatogram of GC-MS result of Patchouli Oil: (a) Meukek Patchouli Oil, (b) Pasie Raja Patchouli Oil, (c) Panjupian Patchouli Oil

Based on Figure 1, it shows that each oil has the same chromatogram pattern but has different peak heights, which means that each patchouli oil has different percentage of each of the different chemical constituent components. The five highest constituents are *patchouli alcohol*, *Δ-guaiene, α-guaiene, α-patchoulene, seychellene, and β-carryophyllene*, with a different percentage in each patchouli oil (Table 1).

The difference in the percentage of each oil caused by some factors, namely genetic (type), cultivation, environment, postharvest and postharvest handling (Irawan, 2010). It is assumed that the most influencing factor from all of the mentioned factors is the factor of the distillation process that leads to the difference in the chemical constituent of patchouli oil before the fractionation. It has been mentioned before that the oils come from three different distillation location. Thus, the distillation was conducted differently.

The result from GC-MS analysis on Table 1 is slightly different from the research by Corine and Sellier (2004), who identified 4 new constituents which are *γ-gurjunene, germacrene D, aciphyllene* and *7-epi-α-selinene.* Whereas in this research, the result from analysis on oil before fractionation found the component of *γ-gurjunene* and *germacrene A*. Besides the factors mentioned above, it is assumed that this difference is due to the method used in analyzing using GC-MC is also different.

3.2 Patchouli Alcohol Content

Vacuum fractional distillation which was conducted at ±2 KPa pressure can produce an average of 3 fractions, which are 2 distillates and 1 residue. Each fraction was produced from a different temperature. Based on the research of Aisyah (2008) we know that the residue fraction from fractional distillation as a higher content of patchouli alcohol than the other fraction. Therefore, this research is analyzing the patchouli alcohol using GC on residue fraction.

The result from GC analysis shows that the patchouli alcohol ranged from 31.98% to 83.86% with the average of 55.17%. The result from analysis of variance shows that the height of Vigreux column has a significant effect ($P \leq 0,01$) on the increase of patchouli alcohol content in patchouli oil. Meanwhile, the initial content of patchouli alcohol and interaction between two factors has no significant effect ($P>0,05$) on the increase of patchouli alcohol content in patchouli oil. The influence of Vigreux column height on the increase of patchouli alcohol content can be seen in Figure 2.

$LSD_{0.05}$ test result shows that the 45 cm column can increase the patchouli alcohol content in patchouli oil and higher than the use of a 25 cm column. Based on Figure 2, the increase of patchouli alcohol content on the 45 cm column is different significantly with the 25 cm column.

The column is used to separate the vapor from liquid compound which has a similar boiling point (<20°C). The barrier (tray/plate) in the fractionation column causes vapors with the same boiling point will both evaporate or compounds with low boiling points that will continue to rise until finally condenses and descends as a distillate. Meanwhile, if the compounds with higher boiling points have not reached the boiling point value, they will drip back into the distillation flask, which eventually will reach the boiling point value if the heating continues. The compound will evaporate, condense and drop/drip as a distillate.

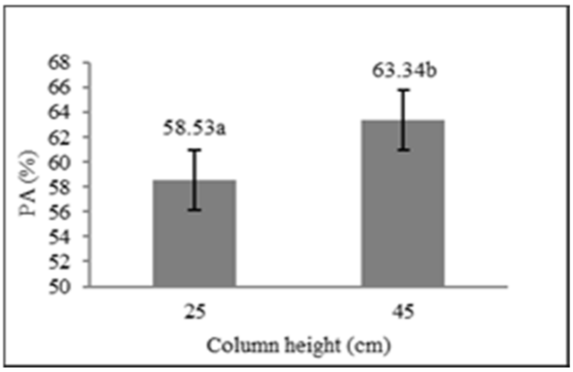

Figure 2: The effect of vigreux column height on the increase of patchouli alcohol (PA) content in residue fraction ($LSD_{0.05}$ = 4,06, CV = 20,18%, values that followed by the same letter show no significant difference).

The components of a substance undergoing the fractionation distillation process will experience direct contact in the column. The fractionation column (vigreux column) contains a tray that serves as a component selection media. During the distillation process, the components in the oil will evaporate according to the boiling point of each component and pass through the trays in the column. The farther the tray is from the heat source, the lower the temperature of the tray.

It is assumed that the components that can rise to the top of the 45 cm column and becomes distillate are only those who have boiling point lower than patchouli alcohol. This is due to the low temperature of the tray at the top of the column. Hence, only the components with a low boiling point that can maintain the form of gas after hitting the tray. Whereas the temperature difference between base and top of 25 cm column is not too far away that makes the components with a similar boiling point with patchouli alcohol also evaporate and becomes distillate.

According to Geankoplis (1983), condensation or the process of gas turn into liquid occurs when saturated gas touches the solid that has a temperature below gas temperature. This conversion makes the components that have a low boiling point fall back down to the base of the column.

Geankoplis (1983) also stated that if the component is in liquid form when passing through the tray, then the components will fall to the previous tray. Meanwhile, the components in the gas form will keep drove off to the next tray where the components will be having more contact with the liquid that coming down from the tray above it. Under these conditions, the concentration of the component with a low boiling point will increase in the vapor and decrease in the liquid which descends towards the bottom of the fractionation column. This statement implies that the fractionation column, especially the tray in the column, can affect the chemical composition of the distillate fraction and the residue from the fractionation distillation.

According to Ma'mun and Maryadhi (2008), patchouli alcohol has a relatively higher boiling point than other components in patchouli oil. The content that was obtained in this research is lower than the content of patchouli alcohol from the research of Ma'mun and Maryadhi (2008) which is about 91.5%. This is due to the difference of pressure used by those researchers with the pressure used in this research. This research is using the pressure of ± 2 KPa because it was the minimal pressure that can be reached by the vacuum pump. Meanwhile, Ma'mun and Maryadhi (2008) used the pressure of 0 cmHg (similar with 0 KPa) that caused the boiling point of those components can be reduced further and the separation occurs more easily without having to experience overheating which allows decomposition.

The result of the research is also contrary to the research from Aisyah et al. (2008). It is assumed that the difference was due to the same cause which is the difference in the condition of the vacuum fractional distillation process. The comparison of results from several types of research about vacuum fractional distillation of patchouli alcohol can be found in Table 2.

Table 2: The comparison of research result of vacuum fractional distillation of patchouli oil

Condition	Aisyah (2008)	Ma'mun (2008)	This research
Pressure	4 mmHg	0 mmHg	2 KPa (15 mmHg)
Temperature	90-135 ºC	150-180 ºC	140-190 ºC
Highest patchouli alcohol content	87.36 %	91.5 %	83.86 %

3.3 Physical Properties of Residue Fraction of Patchouli Oil

Analysis of physical properties was performed on specific gravity, solubility in ethanol and refractive index. The sample is residue fraction from treatment which has initial content of 31.11% with 3 different columns. The chosen sample is the sample from the treatment that produced a residue fraction with a patchouli alcohol content higher than other samples.

3.4 Specific Gravity

Specific gravity is the result of the ratio comparison between oil weight and water weight at the same volume and temperature (SNI, 2006). According to Gunther (1949), this parameter is essential in finding the foreign matter in a liquid or the shifts that may be affecting the quality of the oil. The result from the analysis of specific gravity (Table 3) shows that the specific gravity of the sample goes beyond the standard that has been determined by the Indonesian National Standard (SNI) which is about 0.950-0.975. This suggests that the residue fraction of patchouli oil from the treatment of 25 cm and 45 cm column cannot be sell as crude oil. However, the residue fraction can be applied as a material in derivative products from patchouli oil.

Table 3: Specific gravity and refractive index of residue fraction of patchouli oil

Sample	Specific Gravity	Refractive Index
Without fractionation	0.953	1.5070
25 cm column height	1.005	1.5156
45 cm column height	1.013	1.5166

Table 3 shows the increase of the specific gravity of patchouli oil before and after fractionation (control). This increase influenced by the components in the oil. According to Rizal (2010), specific gravity represents the comparison between heavy fractions and light fractions contained in the oil. The heavier fractions contained a higher specific gravity. The heavy fractions are influenced by the length of the molecular chain of a compound contained in the oil.

Patchouli oil is a compound with a molecular formula of $C_{15}H_{26}O$. Hence, this compound has a relatively long molecular chain which caused the oil to dominated by high specific gravity patchouli alcohol components. The result is shown in Table 3. The patchouli oil before fractional distillate only contains 31.11% of patchouli alcohol and a specific gravity of 0.953, while the residue fraction of patchouli oil which has been fractionated by 25 cm column has 75.14% of patchouli alcohol and a specific gravity of 1.005. Furthermore, the residue fraction of patchouli oil which has been fractionated by 45 cm column has 83.86% of patchouli alcohol and a specific gravity of 1.013.

3.5 Refractive Index

The refractive index is the ratio of the velocity of light in air to its *velocity* in the examined substance at a certain temperature (Armando, 2009). According to Guenther (1949), the index of refraction value of patchouli oil or other essential oil can be determined by using Abbe refractometer. The result from the analysis of the refractive index (Table 3) shows the treatment of a 45 cm column with the initial content of 31.11% resulting in the highest refractive index of 1.5166. Guenther (1949) explained that the value of the specific gravity of essential oil will affect the refractive index value. As can be seen at Table 3, Patchouli oil which has not been fractionated and with a patchouli alcohol content of 31.11% with a specific gravity value of 0.953, has a refractive index value of 1.5070, where this value is much lower than after fractionation with a 45 cm column height of 1.5166. This is in accordance with the statement from Armando (2009) who stated that the more components with a long chain-like sesquiterpene or sesquiterpene or oxygen clusters components contained, the density of essential oil medium will increase. Hence, the light will be harder to refract and the refractive index value will be higher.

3.6 Solubility in Ethanol 90%

The solubility of patchouli oil in ethanol is one of the examinations of patchouli oil quality based on physical properties. This test is conducted to determine the purity of essential oil.

Table 4: Residue fraction of patchouli oil solubility in Ethanol 90%

Without fractionation	25 cm column height	45 cm column height
1 : 5 Turbid	1 : 4 Turbid	1:3 Turbid
1 : 6 Turbid	1 : 5 Turbid	1:4 Turbid
1 : 7 Turbid	1 : 6 Turbid	1:5 Soluble
1 : 8 Soluble	1 : 7 Soluble	1:6 Soluble

Based on Table 4, it can be seen that the patchouli oil residue fraction resulting from the K_1T_2 treatment is soluble at a ratio of 1: 5 (1 ml of oil and 5 ml of ethanol). The treatment shows a clear solution at the lowest ratio compared to other treatments, even clearer than the raw material (control) which is soluble at a ratio of 1:8. According to Guenther (1949), the solubility of oil in alcohol is determined by the type of chemical components contained in essential oil. In general, essential oils which contain oxygenated terpene compounds will be more soluble in alcohol compared to essential oils containing non-oxygenated terpene components. This is because of the non-oxygenated terpene compounds which are nonpolar compounds that do not have functional groups. Thus, it is difficult to react with alcohol.

Patchouli alcohol is a component in patchouli oil which is included in an oxygenated terpene compound and has a functional group. Therefore, patchouli oil which has a higher level of patchouli alcohol such as the residual fraction resulting from the K_1T_2 treatment will be more soluble in alcohol compared to other treatment.

4 CONCLUSION

The height of vigreux column used in vacuum fractionation distillation has a significant effect on the increase of patchouli alcohol levels in patchouli oil residue fraction, while the initial patchouli alcohol levels did not affect the increase in patchouli alcohol levels in patchouli oil residue fraction. The value of specific gravity and refractive index from the fraction of residual fractionation result of patchouli oil is higher than patchouli oil before fractionation so that the solubility in ethanol will be easier. The highest alcohol content of patchouli was obtained from fractionation distillation using a column height of 45 cm which was 83.86%.

REFERENCES

Aisyah, Y., Hastuti, P., Sastrohamidjojo, H., and Hidayat, C. 2008. Komposisi Kimia dan Sifat Antibakteri Minyak nilam *(Pogostemon cablin). Majalah Farmasi Indonesia,* 19 (3), 151-156.

Aisyah, Y., Hastuti, P., Hidayat, C., and Sastrohamidjojo, H. 2010. Peningkatan Kadar Patchouli Alkohol Minyak Nilam (*Pogostemon cablin* Benth) dengan Menggunakan Membran Selulosa Asetat. *Jurnal Agritech,* 30(3), 184-191.

Aisyah, Y., S.H. Anwar., and Y, Annisa. 2013. Increment of patchouli alcohol in patchouli oil by vacuum distillation fraction method. *Proceedings of The 3rd Annual International Conference Syiah Kuala University (AIC Unsyiah) In conjunction with The 2nd International Conference on Multidisciplinary Research (ICMR).*

Armando, R. 2009. *Memproduksi 15 Jenis Minyak Atsiri Berkualitas*. Penebar Swadaya, Jakarta.

BSN (Badan Standardisasi Nasional). 2006. SNI No. 06-2385-2006. *http://sisni.bsn.go.id* (10 Mei 2012).

Bulan, R. 2004. *Esterifikasi Patchouli Alkohol Hasil Isolasi dari Minyak Daun Nilam (Patchouli Oil***).** Jurusan Kimia Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Sumatera Utara.

Corine, M.B., Sellier, N.M., 2004. Analysis of The Essential Oil of Indonesian Patchouli *(Pogostemon cablin Benth.)* Using GC/MS (EI/CI). *J. Essent. Oil Res.,* 16, 17-19.

Essential Oil Association of USA. 1975. *EOA Spesifications and Standard*. EOA USA. New York.

Geankoplis, G.J. 1983. *Transport Process and Unit Operation***.** Second Edition, Allyn and Bacon, Inc, Boston, London, Sydney, Toronto.

Guenther, E. 1949. *Essential Oils : Volume II.* Van Nostrand Reinhold Company, New York.

Harfizal. 2003. Penerapan teknologi distilasi vakum untuk meningkatkan mutu minyak nilam. *Prosiding Seminar Teknologi untuk Negeri.*

Irawan, B. 2010. *Peningkatan Mutu Minyak Nilam dengan Ekstraksi dan Destilasi Pada Berbagai Komposisi Pelarut.* Tesis. Magister Teknik Kimia Universitas Diponegoro, Semarang.

Isaroiny, R., Mitarlis. 2005. Peningkatan Kadar Patchouli Alkohol pada Minyak Nilam (Pogostemon cablin Benth) dengan Metode Distilasi Fraksinasi Vakum. *Berk. Penel. Hayati*, 10, 123–127.

Ma'mun., Adhi Maryadhi. Isolasi Patchouli Alkohol dari Minyak Nilam untuk Bahan Referensi Pengujian dalam Analisis Mutu. *Bul. Littro,* 19(1), 95 – 99.

Muharam, S., Lela, M. Y., and Iim, S. R. 2017. Peningkatan Kualitas Minyak Nilam (*Pogostemon Cablin* Benth) menggunakan Kombinasi Metode Fermentasi, Delignifikasi dan Destilasi. *Jurnal Kimia Valensi*, 3 (2), 116-121.

Rizal, S. 2010. *Kajian Proses Penyulingan Minyak Nilam Menggunakan Sistem Distilasi Air.* Fakultas Teknologi Pertanian IPB, Bogor.

Rukmana, R. 2003. *Nilam: Prospek Agribisnis dan Teknik Budidaya*. Kanisius. Yogyakarta.

Sarwono, B. 1998. *Budidaya Nilam di Purbalingga*. Trubus 343-Th XXIX-Juni 1998. 77-78.

Suryatmi, R.D. 2008. Fraksinasi minyak nilam. *Prosiding Konferensi Nasional Minyak Atsiri.*

Yanyan, F.N., Zainuddin, A., Sumiarsa, D. 2004. Peningkatan kadar patchouli alkohol dalam minyak nilam (*patchouli oil*) dan usaha derivatisasi komponen minornya. *Jurnal Perkembangan Teknologi TRO,* 16, 72-78.