

Compose

Back Archive Move Delete Spam

- Inbox 1.3K
- Unread
- Starred
- Drafts 5
- Sent
- Archive
- Spam
- Trash
- Less
- Views Hide
- Photos
- Documents
- Emails to myself
- Subscriptions
- Shopping
- Receipts

Article of ChemTech 2 Yahoo/Inbox

ED elvianto daryono <elviantodaryono@yahoo.com> To: submitpaper@rediffmail.com, sphinx_global@rediffmail.com Fri, Nov 20, 2015 at 7:16 AM

Good morning. Here with I send my article. Thank you.

Best regards, Elvianto Dwi Daryono Department of Chemical Engineering Institute Technology of National Malang Indonesia



Article Che... .docx 47.8kB

Navigation icons: back, forward, refresh

Journal sphinx <submitpaper@rediffmail.com> Sun, Nov 29, 2015 at 10:53 AM



Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (*Syzigium aromaticum*) Based on Temperature and Time Process

Elvianto Dwi Daryono

Department of Chemical Engineering, Faculty of Industrial Technology,

Institute Technology of National Malang

Jl. Bendungan Sigura-gura No.2 Malang (65145) Indonesia

e-mail: elviantodaryono@yahoo.com

Abstract: The purpose of this study was to obtain optimum conditions for a reactive extraction process in isolating eugenol from clove essential oil associated with temperature and time process. Research stage begins by inserting a 100 ml clove essential oil and 0.8 N NaOH solution at a ratio of 1:1.1 to the reactor. Turn on the hot plate and set the appropriate reaction temperature variables of the study (30, 40 and 50°C) and set the stirrer speed of 100 rpm. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the reaction product was then separated. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain a pH of 4. Before placing distillation flask, Na-eugenolat that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted condenser and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes. Distillate was eugenol and the residue was NaCl residual reaction products. Eugenol distillate which was then measured its volume and analyzed eugenol concentration by GC. The optimum process conditions obtained in

the reactive extraction temperature of 40°C, reaction time of 30 minutes at a concentration of eugenol of 51.07% and yield of 97.10%.

Keywords: reactive extraction, vacuum distillation, clove essential oil, eugenol, yield

1. Introduction

Essential oil of cloves (*Syzygium aromaticum*) is one of Indonesia's many essential oil demand in the world market from year to year increase. Clove essential oil was produced from the leaves, flowers and stems plant cloves with the extraction process. Potential autumn leaf clovers as raw materials essential oil of approximately 2,368,043 tons/year of 455 393 ha of land area with a yield of 1-4%¹. Based on data from Agricultural Research and Development (2007) exports of Indonesian clove essential oil provides 60% of the world clove oil. Clove oil prices in the world market is US \$ 4.75/kg and the price of eugenol US \$ 7.80/kg. From these data there is a considerable price difference between clove oil and eugenol. Although Indonesia is the largest clove oil exporter in the world, but the fulfillment of eugenol Indonesia still have to import from other countries².

Eugenol is the main component in the essential oil of clove. Clove essential oil (*Syzygium aromaticum* L. *Myrtaceae*) were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (88.58%), β -caryophyllene (1.39%), 2-heptanone (0.93%) , ethyl hexanoate (0.66%), humulenol (0.27%), α -humulene (0.19%), calacorene (0.11%) and calamenene (0.10%)³. Essential oil of clove leaf (*Syzygium caryophyllatum* (L.) Alston) from Bangladesh were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (74.3%), eucalyptol (5.8%), caryophyllene (3.85%) and α -cadinol (2.43%)⁴.

Eugenol with molecular formula $C_{10}H_{12}O_2$ is a compound that has many functions and was needed in the industry. Eugenol serves as an analgesic, anti-inflammatory, antimicrobial, antiviral, antifungal, antiseptic, antispasmodic, antiemetic, a stimulant and a local anesthetic that was widely used in the pharmaceutical world^{5,6}. Eugenol microemulsion with a concentration of 0.6% is able to fight the bacteria *Salmonella Typhi* and *Listeria monocytogenus* compared with clove essential oil at the same concentration⁷. Eugenol microemulsion with a concentration of 61.7% as a more powerful antioxidant than clove essential oil microemulsion⁷. Eugenol which was reacted with a cyclic sulfonic acid ester klorosulfat produce that could inhibit *Escherichia coli* and *Staphylococcus aureus*⁸. Eugenol can be synthesized into 3-(3,4-dimetoksifenil)-propanal as the raw material synthesis of derivatives of antibiotic C-9154⁹. Synthetic vanilla can be made of eugenol, and about 95% of world demand for vanilla flavor filled with synthetic vanilla^{10,11,12}. Vanilla acetate can also be used as a substitute for natural vanilla because of the similarity in nature, and used as food additives¹³.

Vanilla acetate can be made from the oxidation reaction of isoeugenol acetate with $KMnO_4$ with microwave heating¹⁴. A mixture of cloves eugenol from 1.25 to 2.5% with a hydrophobic starch solution can be used as a food packaging¹⁵. Compound eugenol contained in the commercial formulation has a level of stability which varies depending on the concentration. Eugenol with a concentration of 95.26% stable for 24 hours and 100.99% concentration is stable for 20 days¹⁶. Clove bud oil emulsion (CBO) in alkaline solution with the addition of whey protein emulsifier, gum arabic, lecithin or a mixture of all of them is stable for 7 days of storage¹⁷.

Studies on the extraction of essential oil of cloves has been done. Prianto et al.¹⁸ get a yield of 8.6% on a steam distillation process of clove (*Syzygium aromaticum*) for 8 hours with the

physical properties of essential oils that meet SNI 06-4267-1996. In the supercritical CO₂ extraction to get the yield 19.6% and 58.77% eugenol concentration at a pressure of 10 MPa, 50°C for 2 hours¹⁹. Extraction of essential oils clove buds by steam distillation process for 8-10 hours at a yield of 10.1%, hidrodestiasi for 4-6 hours at a yield of 11.5% and soxhlet extraction for 6 hours at a yield of 41.85%¹⁹. On the extraction of essential oil of cloves with *Eugenia caryophyllata* hidrodestilasi method for 150 minutes get a yield of 5.06%, method microwave assisted extraction (MAE) for 10-30 minutes at a yield of 7.42% and microwave steam distillation method (MSD) for 10-30 minutes at a yield of 16.25%²⁰.

Research on the isolation of eugenol from clove oil also has been done. Hidayati²¹ gaining 99.45% eugenol drawn from the oil extraction time of 30 minutes and the volume ratio of oil to the solvent hexane = 1:2. In the isolation of eugenol from clove oil yield of 70.6% gain in the reaction time of 3 hours, stirring speed of 100 rpm, the standing long 19 hours and the ratio of water phase: n-hexane for washing is 1:1, 1:1/2: 1:1/2²². Lutfi et al.²³ get a eugenol content of 90.20% of the initial level of 70% at a concentration of 0.8 N NaOH, the temperature distillation of 195°C, vacuum pressure of $6 \cdot 10^{-2}$ kPa and distillation time of 30 minutes. In the purification eugenol from clove oil, get a yield of 81.3% and eugenol concentration increased from 79.10% to 95.10% by using 1.8 N HNO₃²⁴.

In the study of isolation eugenol from clove oil, there is no data on the reaction temperature used and reaction time used is relatively long. The aim of this study was to obtained optimum process conditions such as temperature and reaction time, and was expected to optimize the isolation of eugenol from clove oil and produce higher yields.

2. Experimental

2.1 Materials and tools

The main research material that clove essential oil purchased from CV. Panadia. Reagents used in the study include HCl (Sigma-Aldrich, 37%), potassium hydrogen phthalate (Sigma-Aldrich, 99%) and NaOH pellets (Riedel-de Haen, 99%). The reaction was performed on a laboratory scale using a three-neck round bottom flask fitted condenser, thermometer and hot plate magnetic stirrer. The reaction temperature was maintained in accordance study variables using water bath and atmospheric pressure. The separation of the reaction products was done by separating funnel. Then proceed purification of the reaction products using a set of distillation apparatus equipped with a vacuum pump.

2.2 Preparation

Clove essential oil that has prepared with analyzed eugenol concentration by GC. Creating 0.8 N NaOH solution, then standardized with potassium hydrogen phthalate. Assembling the reactor as a reaction consisting of a three-neck flask and condenser and to strengthen its position with the buffer and the stand. Then put the reactor on a magnetic stirrer hot plate. Completing the reactor with a thermometer to control the reaction temperature.

2.3 Reactive Extraction

Incorporating 100 ml clove essential oil and 0.8 N NaOH solution which has been standardized by a ratio of 1:1.1 to the reactor²³. Turn on the hot plate and set the temperature at the reaction temperature rotation corresponding research variable (30, 40 and 50°C) and set the lap button magnetic stirrer at a speed of 100 rpm²². Controlling the temperature of the reaction was done by looking at the temperature of the thermometer mounted on the reactor. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the

reaction product was then inserted separating funnel and allowed to stand for 24 hours to form two layers. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Separating the two layers and measuring the volume of the aqueous layer.

2.4 Vacuum Distillation

Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain pH 4²¹. Before placing Na-eugenolat distillation flask that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted behind the cooler and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes²³. Distillate was eugenol and the residue was residual NaCl reaction products.

2.5 Analysis

Eugenol distillate which was then measured and analyzed of volume concentration of eugenol using gas chromatography (GC).

3. Results and Discussion

The raw material was the essential oil of cloves eugenol its concentration was analyzed by GC and found concentrations of 25.261%. Yield of eugenol was calculated using the following equation:

$$\text{Yield (\%)} = \frac{[\text{Volume of distillate x concentration of eugenol}]_{\text{end}}}{[\text{Volume of oil x concentration of eugenol}]_{\text{initial}}} \times 100$$

3.1 Effect of Temperature and Reaction Time to Volume Aqueous Layer (Na-eugenolat)

The bottom layer with the separation of the aqueous layer separating funnel which was Na-eugenolat reaction products between eugenol and NaOH. The aqueous layer volume

measurements performed for each variable temperature and reaction time. From Table 1 it can be seen that the temperature and reaction time influence on the volume of aqueous layer obtained. The higher the temperature and reaction time, the greater the volume of aqueous layer to obtain optimum conditions.

Table 1. Volume aqueous layer (Na-eugenolat) at various temperatures and reaction time

Temperature (°C)	Time of Reaction (mnt)	Volume <i>aqueous layer</i> (mL)
30	15	86
	30	87
	45	89
	60	90
	75	91
40	15	96
	30	97
	45	91
	60	89
	75	89
50	15	88
	30	93
	45	96
	60	89
	75	87

The best conditions of each of the different variables. At 30°C temperature variables, the best conditions obtained in a reaction time of 75 minutes with a volume of 91 mL of aqueous layer. In the variable temperature of 50°C, the best conditions obtained on reaction time 45 minutes with a volume of 96 mL of aqueous layer. The variable 40°C, the best conditions obtained in a reaction time of 30 minutes with a volume of 97 mL of aqueous layer and this results in an optimum condition. Theoretically it was known that the higher the reaction temperature the greater the reaction speed, which means the formation of more and more products, but this condition was limited to the optimum condition is reached. NaOH function in this process there are two, namely as a solvent in the extraction process that removes eugenol from kariofilin phase to the aqueous phase. Subsequently NaOH serves as a reactant that will react with eugenol.

3.2 Effect of Temperature and Time Reactions to concentration of eugenol (%)

Distillate distilled namely the isolated compound eugenol, concentration analyzed by GC. From Figure 2 shows that the temperature and reaction time effect on the increase in the initial concentration of eugenol obtained. The highest increase occurred in all variables reaction temperature with a reaction time of 15 minutes, where the concentration of eugenol increased from 25.261% to \pm 51%. After a reaction time of 15 minutes were relatively small increase in the concentration of eugenol and almost evenly on all the variables of temperature and reaction time. The reaction between eugenol and NaOH was a fast reaction reaches equilibrium.

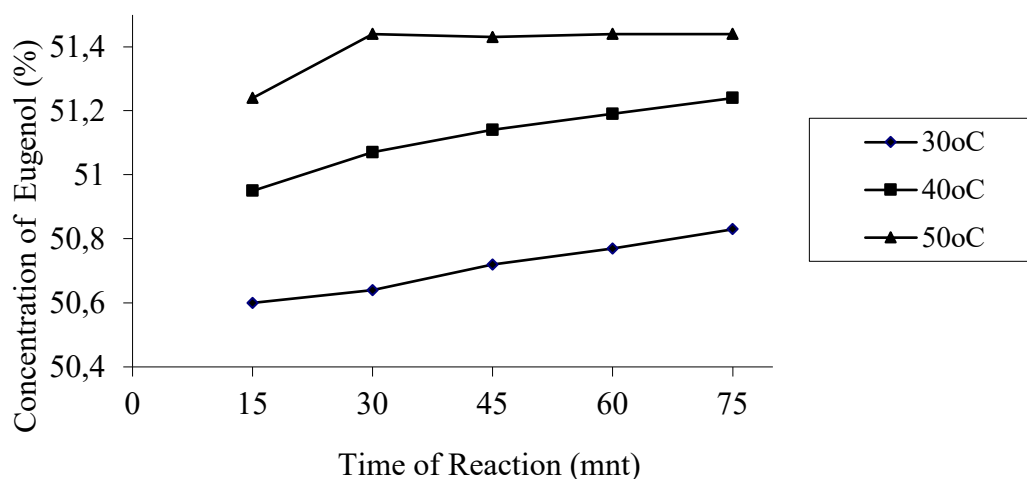


Figure 1. Effect of temperature and reaction time to the concentration of eugenol (%)

Eugenol highest concentrations obtained at 50°C with a reaction time of 75 minutes which is 51.444%. An increase of 26.183% of the initial concentration of eugenol 25.261% to 51.444%. This result was better than the results Lutfi et al.²³ get a 20.20% increase in the concentration of eugenol. As well as research results Haryani et al.²⁴ get a 16% increase in the concentration of eugenol.

3.3 Effect of Temperature and Time Reactions to Yield of Eugenol (%)

For the calculation of yield of eugenol measurable results isolation volume. From Figure 2 shows that the temperature and reaction time affect yield eugenol obtained. Visible optimum conditions were different in each study variable. At a reaction temperature of 30°C variable has not been achieved the optimum conditions because the yield eugenol still increase with the highest yield at the reaction time of 75 minutes was 92.56%. At variable reaction temperature reached 40°C optimum conditions on reaction time 40 minutes at a yield of 97.10%. At variable

reaction temperature 50°C was reached optimum conditions on reaction time 45 minutes at a yield of 97.73%, the difference was only 0.63% compared to the optimum conditions at 40°C. Yield of eugenol obtained from the results of this study were relatively better when compared to previous studies. Fitri and Kawira²² get 70.6% yield with a reaction time of 3 hours. Research Haryani et al.²⁴ get a yield of eugenol 81.3%. Results of this research differs from research Hidayati²¹ to get 99.45% yield with a reaction time of 30 minutes, whereas in the study did not take into account the yield calculation of the concentration of eugenol obtained.

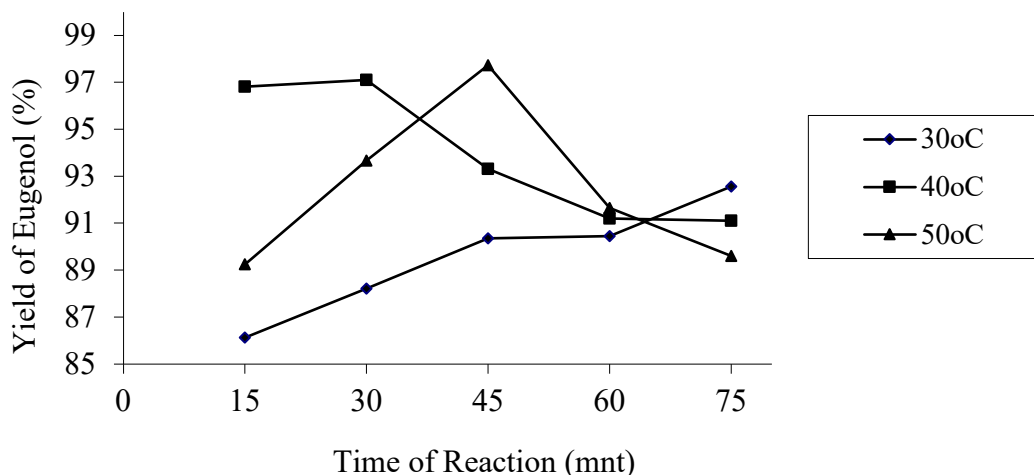


Figure 2. Effect of temperature and reaction time to yield eugenol (%)

4. Conclusions

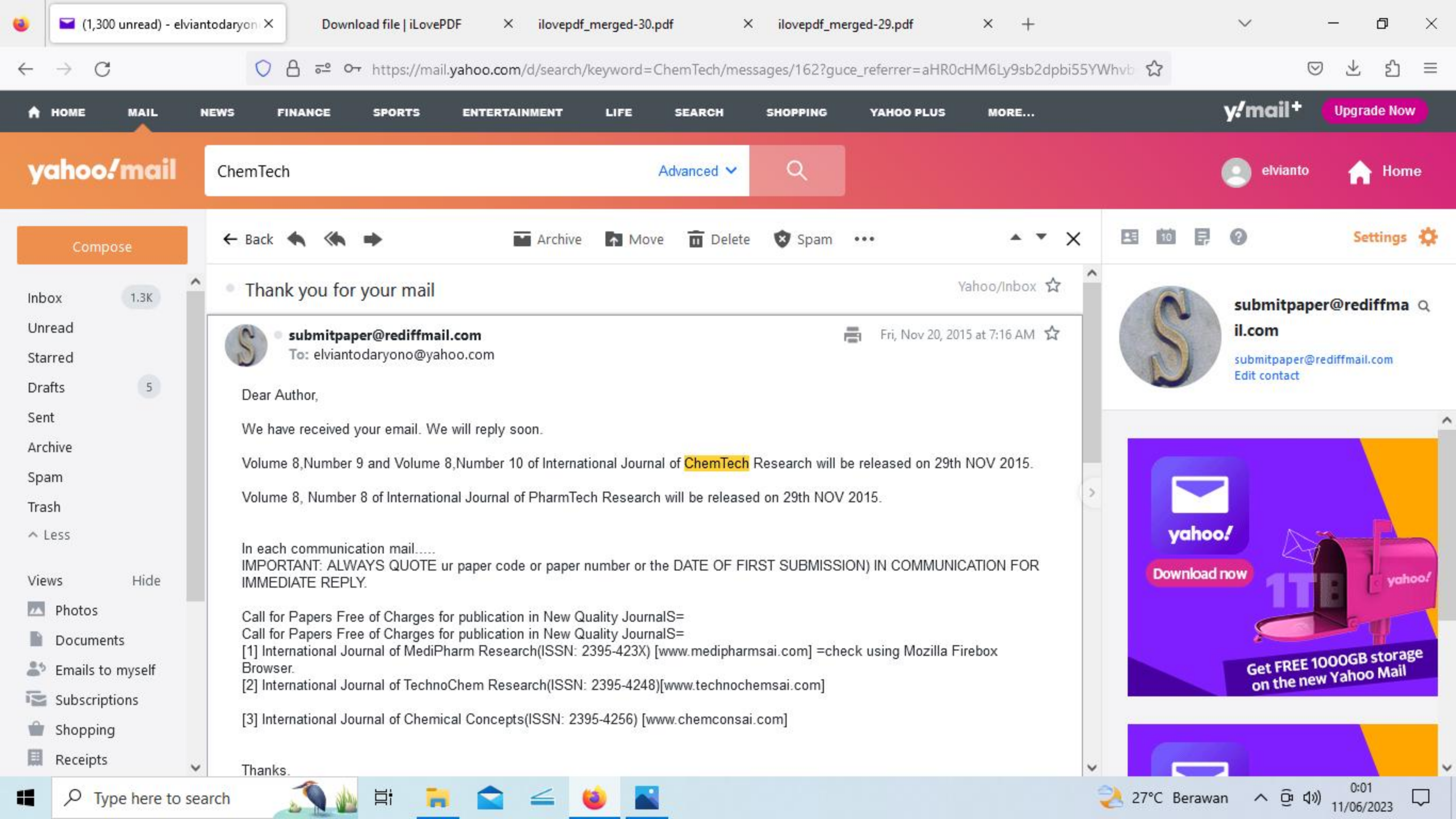
The optimum conditions of temperature extraction reactive process that was 40°C, reaction time of 30 minutes, 0.8 N NaOH concentration, the volume ratio of oil:NaOH was 1:1.1, stirring speed of 100 rpm, separation using 5 N HCl to pH 4, purification eugenol with vacuum distillation at a temperature of 195°C for 30 minutes with a pressure of 6.10^{-2} kPa. In these conditions the concentration of eugenol obtained 51.07% and yield of eugenol 97.10%.

References

1. Bustaman S. 2011. Potensi pengembangan minyak daun cengkeh sebagai komoditas ekspor Maluku. *Jurnal Litbang Pertanian*, 2011, 30: 132-139.
2. Towaha J. The Benefits of Cloves Eugenol in Various Industries in Indonesia. *Perspektif*, 2012, 11: 79-90.
3. Chaieb K, Hajlaoui H, Zmantar T, Kahla-Nakbi AB, Rouabhia M, Mahdouani K, Bakhrouf A. The chemical composition and biological activity of clove essential oil, *Eugenia caryophyllata* (*Syzygium aromaticum* L. Myrtaceae): A short review. *Phyther. Res.*, 2007, 21: 501-507.
4. Bhuiyan MNI, Begum J, Nandi NC, Akter F. Constituents of the essential oil from leaves and buds of clove (*Syzygium caryophyllatum* (L). Alston. *Afr. J. Plant Sci.*, 2010, 4: 451-454.
5. Pramod K, Ansari SH, Ali J. Eugenol: a natural compound with versatile pharmacological actions. *Natural Product Communications*, 2010, 5: 1999-2006.
6. Jirovetz L. Medicinal value of clove. University of Vienna, Department Pharmacy and Diagnostics, Austria, 2010.
7. Hamed SF, Sadek Z, Edris A. Antioxidant and antimicrobial activities of clove bud essential oil and eugenol nanoparticles in alcohol – free microemulsion. *J. Oleo Sci.*, 2012, 61: 641-648.
8. Sudarma IM, Yuanita E, Suana IW. Markovnikov addition of chlorosulfuric acid to eugenol isolated from clove oil. *Indo. J. Chem.*, 2013, 13: 181-184.

9. Ngadiwiyana, Ismiyanto, Jumino, Anwar C. Sintesis 3-(3,4-dimetoksifenil)-propanal sebagai senyawa antara dalam pembuatan turunan antibiotik C-9154 dari minyak daun cengkeh. *JSKA*, 2008, 11.
10. Medicinal Spices Exhibit. Vanilla. 2010.
11. Bilton P. Vanilla : history, extract, essence, syntetic vanilla and vanillism. 2011.
12. Free Press Release. Vanilla bean-artificial vanilla bean extracts. 2012.
13. Rasasti D. Oksidasi eugenol asetat dan uji aktivitas antioksidan senyawa turunannya.. Bandung: UPI. 2006.
14. Kadarohman AH, Siti H, Fareza MS. Konversi dan karakterisasi isoeugenol asetat menjadi vanillin asetat. *Jurnal Sains dan Teknologi Kimia*, 2010, 1: 177-181.
15. Vanit S, Suppakul P, Jinkarn T. Antimicrobial effects of coating solution containing clove oil and hydrophobic starch for coating paper board. *Asian Journal of Food and Agro-Industry*, 2010, 3: 201-212.
16. Saran S, Menon S, Shailajan S, Pokharna P. Validated RP-HPLC method to estimate eugenol from commercial formulations like *Caturjata Churna*, *Lavangadi Vati*, *Jatiphaladi Churna*, *Sitopaladi Churna* and clove oil. *Journal of Pharmacy Research*, 2013, 6: 53-60.
17. Luo Y, Zhang Y, Pan K, Critzer F, Davidson PM, Zhong Q. Self – emulsification of alkaline – dissolved clove bud oil by whey protein, gum arabic, lecithin, and their combinations. *J. Agric. Food Chem.*, 2014, 62: 4417-4424.
18. Prianto HH, Retnowati R, Juswono UP. Isolasi dan karakterisasi dari minyak bunga cengkeh (*Syzigium aromaticum*) kering hasil distilasi uap. *Kimia Student Journal*, 2013, 1: 269-275.

19. Wenqiang G, Shufen L, Ruixiang Y, Shaokun T, Can Q. Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods. *Food Chemistry*, 2007, 101: 1558-1564.
20. Kennouche A, Bencaki-Ali F, Scholi G, Eppe G. Chemical composition and antimicrobial of the essential oil of *Eugenia caryophyllata* Cloves extracted by conventional and microwave techniques. *Journal of Biologically Active Products from Nature (TBAP)*, 2015, 5: 1-11.
21. Hidayati N. Ekstraksi eugenol dari minyak daun cengkeh. *Jurnal Teknik Gelagar*, 2003, 14: 108-114.
22. Fitri N, Kawira JA. Perbandingan variabel pada isolasi dan pemurnian eugenol dari minyak daun cengkeh. *Media Litbang Kesehatan*, 2006, 16: 16-21.
23. Lutfi M, Jati W, Purbasari A. Peningkatan kadar eugenol pada minyak atsiri cengkeh dengan metode saponifikasi – distilasi vakum. *Jurnal Teknologi Kimia dan Industri*, 2013, 2: 198-203.
24. Haryani HW, Hidayat N, Rahmah NL. Pemurnian eugenol dari minyak daun cengkeh dengan reaktan asam monoprotik. *Kajian jenis dan konsentrasi asam. Jurnal Industria*, 2014, 3.



yahoo!mail

ChemTech

Advanced



elvianto

Home

Compose

- Inbox 1.3K
- Unread
- Starred
- Drafts 5
- Sent
- Archive
- Spam
- Trash
- Less
- Views Hide
- Photos
- Documents
- Emails to myself
- Subscriptions
- Shopping
- Receipts

Back Archive Move Delete Spam

Thank you for your mail

Yahoo/Inbox



submitpaper@rediffmail.com
To: elviantodaryono@yahoo.com

Fri, Nov 20, 2015 at 7:16 AM

Dear Author,

We have received your email. We will reply soon.

Volume 8, Number 9 and Volume 8, Number 10 of International Journal of ChemTech Research will be released on 29th NOV 2015.

Volume 8, Number 8 of International Journal of PharmTech Research will be released on 29th NOV 2015.

In each communication mail.....

IMPORTANT: ALWAYS QUOTE ur paper code or paper number or the DATE OF FIRST SUBMISSION) IN COMMUNICATION FOR IMMEDIATE REPLY.

Call for Papers Free of Charges for publication in New Quality Journals=

Call for Papers Free of Charges for publication in New Quality Journals=

[1] International Journal of MediPharm Research(ISSN: 2395-423X) [www.medipharmsai.com] =check using Mozilla Firebox Browser.

[2] International Journal of TechnoChem Research(ISSN: 2395-4248)[www.technochemsai.com]

[3] International Journal of Chemical Concepts(ISSN: 2395-4256) [www.chemconsai.com]

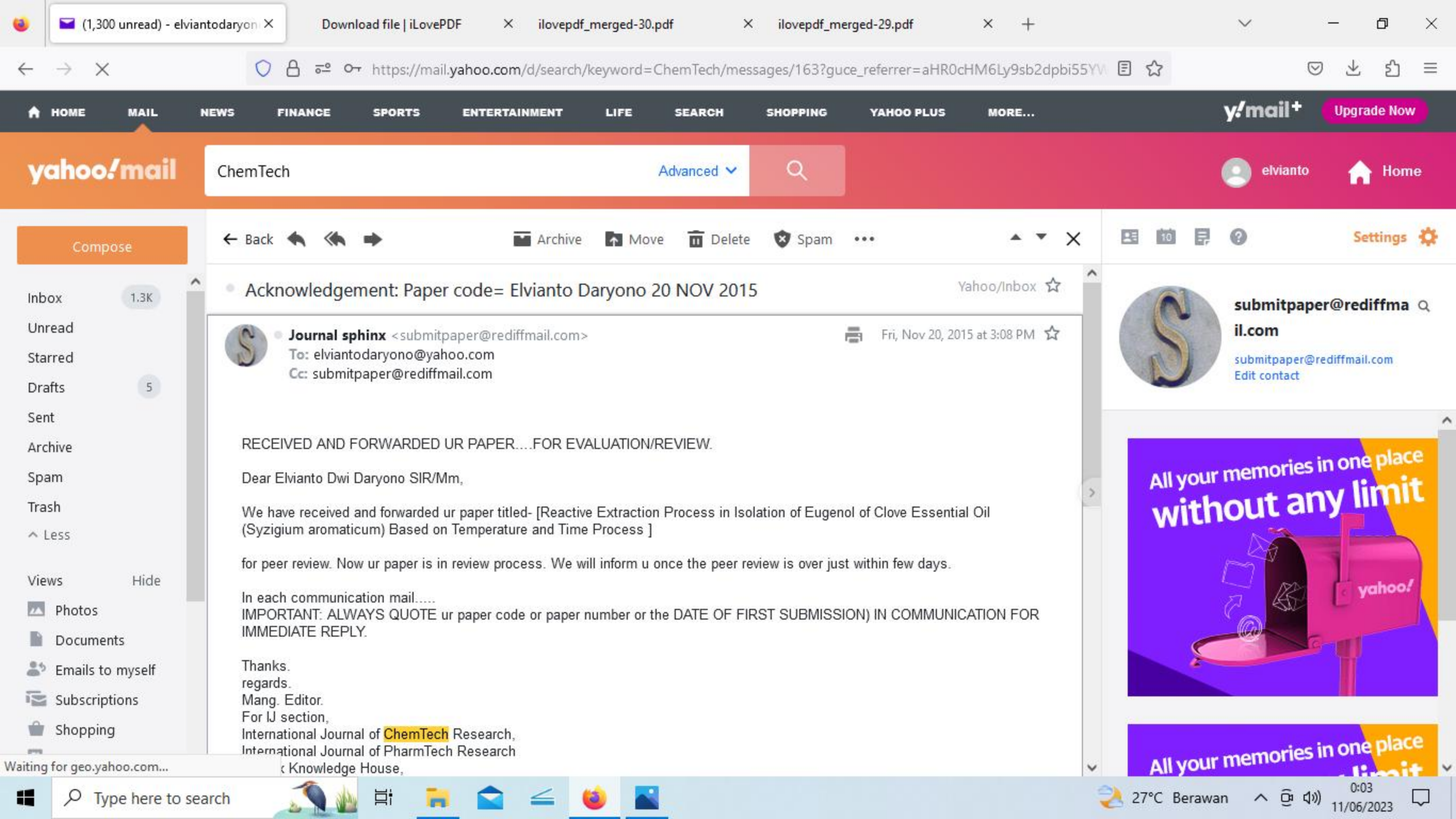
Thanks.



submitpaper@rediffmail.com
il.com
submitpaper@rediffmail.com
Edit contact

yahoo! Download now

Get FREE 1000GB storage on the new Yahoo! Mail



yahoo!mail

ChemTech

Advanced



elvianto

Home

Compose

Inbox 1.3K

Unread

Starred

Drafts 5

Sent

Archive

Spam

Trash

Less

Views Hide

Photos

Documents

Emails to myself

Subscriptions

Shopping

Back Archive Move Delete Spam

Acknowledgement: Paper code= Elvianto Daryono 20 NOV 2015

Yahoo/Inbox

Journal sphinx <submitpaper@rediffmail.com> To: elviantodaryono@yahoo.com Cc: submitpaper@rediffmail.com

Fri, Nov 20, 2015 at 3:08 PM

RECEIVED AND FORWARDED UR PAPER....FOR EVALUATION/REVIEW.

Dear Elvianto Dwi Daryono SIR/Mm,

We have received and forwarded ur paper titled- [Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (Syzigium aromaticum) Based on Temperature and Time Process]

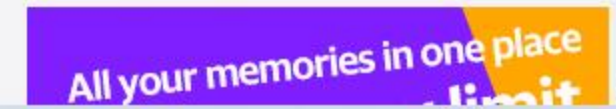
for peer review. Now ur paper is in review process. We will inform u once the peer review is over just within few days.

In each communication mail..... IMPORTANT: ALWAYS QUOTE ur paper code or paper number or the DATE OF FIRST SUBMISSION) IN COMMUNICATION FOR IMMEDIATE REPLY.

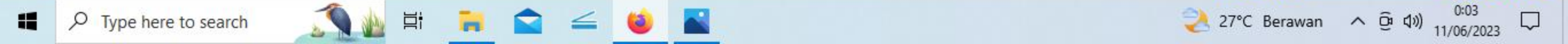
Thanks. regards. Mang. Editor. For IJ section, International Journal of ChemTech Research, International Journal of PharmTech Research Knowledge House,

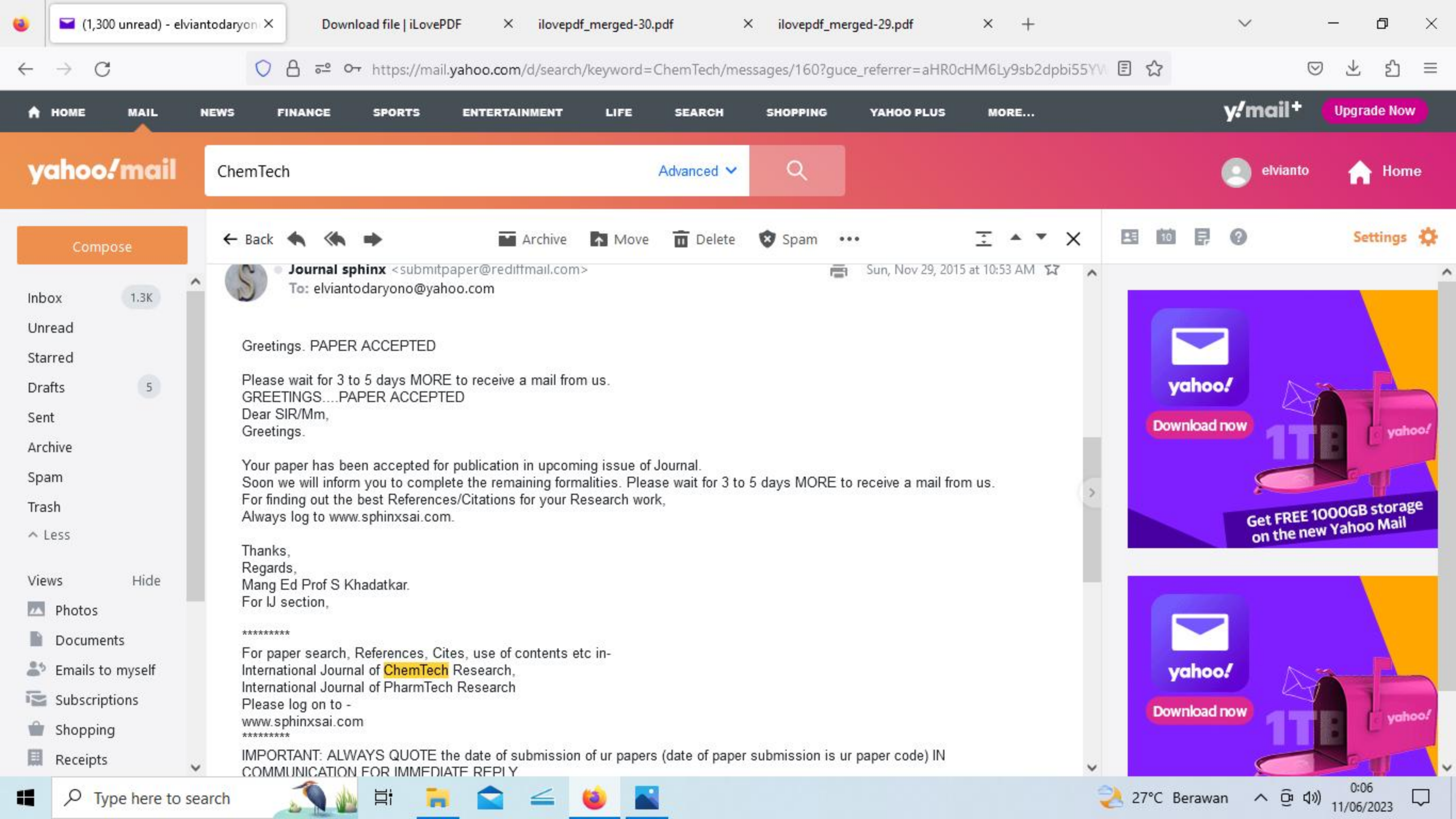


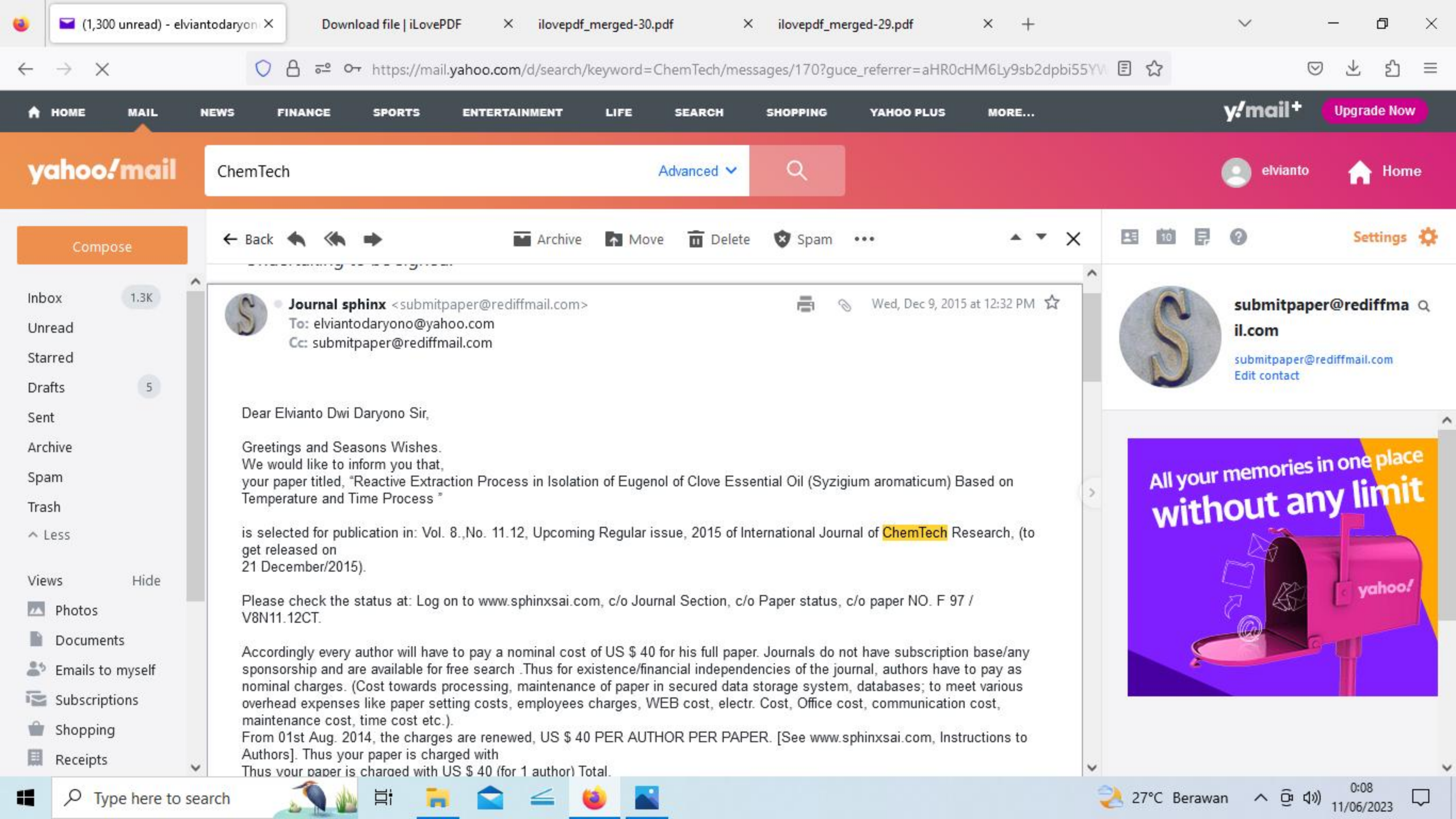
submitpaper@rediffmail.com il.com submitpaper@rediffmail.com Edit contact



Waiting for geo.yahoo.com...







yahoo!mail

ChemTech

Advanced

Upgrade Now

elvianto Home

Compose

- Inbox 1.3K
- Unread
- Starred
- Drafts 5
- Sent
- Archive
- Spam
- Trash
- Less
- Views Hide
- Photos
- Documents
- Emails to myself
- Subscriptions
- Shopping
- Receipts

Back Archive Move Delete Spam

Journal sphinx <submitpaper@rediffmail.com>
 To: elviantodaryono@yahoo.com
 Cc: submitpaper@rediffmail.com
 Wed, Dec 9, 2015 at 12:32 PM

Dear Elvianto Dwi Daryono Sir,

Greetings and Seasons Wishes.
 We would like to inform you that,
 your paper titled, "Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (Syzygium aromaticum) Based on Temperature and Time Process "

is selected for publication in: Vol. 8., No. 11.12, Upcoming Regular issue, 2015 of International Journal of **ChemTech** Research, (to get released on 21 December/2015).

Please check the status at: Log on to www.sphinx sai.com, c/o Journal Section, c/o Paper status, c/o paper NO. F 97 / V8N11.12CT.

Accordingly every author will have to pay a nominal cost of US \$ 40 for his full paper. Journals do not have subscription base/any sponsorship and are available for free search. Thus for existence/financial independencies of the journal, authors have to pay as nominal charges. (Cost towards processing, maintenance of paper in secured data storage system, databases; to meet various overhead expenses like paper setting costs, employees charges, WEB cost, electr. Cost, Office cost, communication cost, maintenance cost, time cost etc.).
 From 01st Aug. 2014, the charges are renewed, US \$ 40 PER AUTHOR PER PAPER. [See www.sphinx sai.com, Instructions to Authors]. Thus your paper is charged with
 Thus your paper is charged with US \$ 40 (for 1 author) Total.

submitpaper@rediffmail.com
 il.com
 submitpaper@rediffmail.com
 Edit contact

All your memories in one place
 without any limit

yahoo!



www.sphinxsai.com

PharmTech

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290

International Journal of PharmTech Research
CODEN (USA): IJPRIF ISSN: 0974-4304

INVOICE

09 December 2015

Dear Elvianto Dwi Daryono Sir,

Greetings and Seasons Wishes.

We would like to inform you that,

your paper titled, "Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (*Syzigium aromaticum*) Based on Temperature and Time Process "

is selected for publication in: Vol. 8.,No. 11.12, Upcoming Regular issue, 2015 of International Journal of ChemTech Research, (to get released on 21 December/2015).

Please check the status at: Log on to www.sphinxsai.com, c/o Journal Section, c/o Paper status, c/o paper NO. F 97 / V8N11.12CT.

Accordingly every author will have to pay a nominal cost of US \$ 40 for his full paper. Journals do not have subscription base/any sponsorship and are available for free search .Thus for existence/financial independencies of the journal, authors have to pay as nominal charges. (Cost towards processing, maintenance of paper in secured data storage system, databases; to meet various overhead expenses like paper setting costs, employees charges, WEB cost, electr. Cost, Office cost, communication cost, maintenance cost, time cost etc.).

From 01st Aug. 2014, the charges are renewed, US \$ 40 PER AUTHOR PER PAPER. [See www.sphinxsai.com, Instructions to Authors]. Thus your paper is charged with

Thus your paper is charged with US \$ 40 (for 1 author) Total.

We request you to make the payment of US \$ 40 at earliest, on or before BEFORE 18th December 2015, by the following mode and inform us by email with accuracy. :

Send the charges ONLY AND ONLY by ---

* **BANK TRNSFER/ WIRE TRANSFER** to the Bank Account Number given below
[using the information given below],

Or by

***Western Union.**

***1] For sending the charges by BANK TRNSFER/ WIRE TRANSFER use the following details --**

Send the charges US \$ 40 to the bank account number details given below...

Details for DEPOSITING DIRECTLY INTO A BANK ACCOUNT.

Name of bank: State Bank of India,

**Address of Bank= Kaulkhed, Akola, Dist: Akola, Maharashtra
State, Pin: 444004, INDIA.**

Branch Code: 012015

Name of (Beneficiary) Account holder : SPHINX KNOWLEDGE HOUSE,

Address of Account holder : AKOLA, M.S., India.

SBI Bank Account Number = 307 805 14763.

Type of bank account = Current

Swift Code for Funds transfer = SBIN INBB 533.

IFSC Code : SBIN0012015

MICR Code: 444002546

[Payment by any other mode will not be accepted].You can send it from any Country.

***2. For sending the charges by “WESTERN UNION MONEY TRANSFER” USE the following details ONLY -**

Name of Receiver: Sagar Shivdas Suratane.

Gender: Male

[sending the charges to any other name will not be accepted]

**Address of Receiver = Kasod Shivpur, Akot, District: Akola,
M.H., INDIA 444101.**

[sending the charges to any other name will not be accepted]

On transfer of Fees, please inform us the details as....Name of sender, Country from which money transferred, Date of transfer, amount sent and the **SCANNED SLIP/DOCUMENT AS A PROOF OF TRANSFER only** to -
saiee_sevak@rediffmail.com AND, submitpaper@rediffmail.com

***2.** Download the attached Undertaking, sign it (by the main author) and send its scanned copy only to saiee_sevak@rediffmail.com and submitpaper@rediffmail.com
Without this signed undertaking your paper will not get displayed.

Thanks,

ALWAYS QUOTE YOUR PAPER NUMBER IN COMMUNICATION.

+Note: Without the receipt of payment/charges AND signed undertaking, paper will not be selected for publication (and will not get published). Please take care of making the payment before due date. (Papers from Editorial members and referees only are published free of cost other papers are nominally, reasonably charged.)

Thanks,

Expecting a reply at your earliest for further processing of your paper.

Regards,

Prof S S Khadatkar.

Managing Editor, International Journal Section,

Sphinx Knowledge House,

www.sphinxsai.com

.....

Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (*Syzygium aromaticum*) Based on Temperature and Time Process

Elvianto Dwi Daryono

Department of Chemical Engineering, Faculty of Industrial Technology,
Institute Technology of National MalangJI. Bendungan Sigura-gura No.2
Malang (65145) Indonesia

Abstract: The purpose of this study was to obtain optimum conditions for a reactive extraction process in isolation of eugenol from clove essential oil associated with temperature and time process. Research stage begins by inserting a 100 ml clove essential oil and 0.8 N NaOH solution at a ratio of 1:1.1 to the reactor. Turn on the hot plate and set the appropriate reaction temperature variables of the study (30, 40 and 50°C) and set the stirrer speed of 100 rpm. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the reaction product was then separated. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain a pH of 4. Before placing distillation flask, Na-eugenolat that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted condenser and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes. Distillate was eugenol and the residue was NaCl residual reaction products. Eugenol distillate which was then measured its volume and analyzed eugenol concentration by GC. The optimum process conditions obtained in the reactive extraction temperature of 40°C, reaction time of 30 minutes at a concentration of eugenol of 51.07% and yield of 97.10%.

Keywords: reactive extraction, vacuum distillation, clove essential oil, eugenol, yield.

1. Introduction

Essential oil of cloves (*Syzygium aromaticum*) is one of Indonesia's many essential oil demand in the world market from year to year increase. Clove essential oil was produced from the leaves, flowers and stems plant cloves with the extraction process. Potential autumn leaf clovers as raw materials essential oil of approximately 2,368,043 tons/year of 455 393 ha of land area with a yield of 1-4%¹. Based on data from Agricultural Research and Development (2007) exports of Indonesian clove essential oil provides 60% of the world clove oil. Clove oil prices in the world market is US \$ 4.75/kg and the price of eugenol US \$ 7.80/kg. From these data there is a considerable price difference between clove oil and eugenol. Although Indonesia is the largest clove oil exporter in the world, but the fulfillment of eugenol Indonesia still have to import from other countries².

Eugenol is the main component in the essential oil of clove. Clove essential oil (*Syzygium aromaticum* L. Myrtaceae) were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (88.58%), β -caryophyllene (1.39%), 2-heptanone (0.93%), ethyl hexanoate (0.66%), humulene

(0.27%), α -humulene (0.19%), calacorene (0.11%) and calamenene (0.10%)³. Essential oil of clove leaf (*Syzigium caryophyllatum* (L.) Alston) from Bangladesh were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (74.3%), eucalyptol (5.8%), caryophyllene (3.85%) and α -cadinol (2.43%)⁴.

Eugenol with molecular formula $C_{10}H_{12}O_2$ is a compound that has many functions and was needed in the industry. Eugenol serves as an analgesic, anti-inflammatory, antimicrobial, antiviral, antifungal, antiseptic, antispasmodic, antiemetic, a stimulant and a local anesthetic that was widely used in the pharmaceutical world^{5,6}. Eugenol microemulsion with a concentration of 0.6% is able to fight the bacteria *Salmonella Typhi* and *Listeria monocytogenus* compared with clove essential oil at the same concentration⁷. Eugenol microemulsion with a concentration of 61.7% as a more powerful antioxidant than clove essential oil microemulsion⁷. Eugenol which was reacted with a cyclic sulfonic acid ester klorosulfat produce that could inhibit *Escherichia coli* and *Staphylococcus aureus*⁸. Eugenol can be synthesized into 3-(3,4-dimetoksifenil)-propanal as the raw material synthesis of derivatives of antibiotic C-9154⁹. Synthetic vanilla can be made of eugenol, and about 95% of world demand for vanilla flavor filled with synthetic vanilla^{10,11,12}. Vanilla acetate can also be used as a substitute for natural vanilla because of the similarity in nature, and used as food additives¹³.

Vanilla acetate can be made from the oxidation reaction of isoeugenol acetate with $KMnO_4$ with microwave heating¹⁴. A mixture of cloves eugenol from 1.25 to 2.5% with a hydrophobic starch solution can be used as a food packaging¹⁵. Compound eugenol contained in the commercial formulation has a level of stability which varies depending on the concentration. Eugenol with a concentration of 95.26% stable for 24 hours and 100.99% concentration is stable for 20 days¹⁶. Clove bud oil emulsion (CBO) in alkaline solution with the addition of whey protein emulsifier, gum arabic, lecithin or a mixture of all of them is stable for 7 days of storage¹⁷.

Studies on the extraction of essential oil of cloves has been done. Prianto et al.¹⁸ get a yield of 8.6% on a steam distillation process of clove (*Syzigium aromaticum*) for 8 hours with the physical properties of essential oils that meet SNI 06-4267-1996. In the supercritical CO_2 extraction to get the yield 19.6% and 58.77% eugenol concentration at a pressure of 10 MPa, 50°C for 2 hours¹⁹. Extraction of essential oils clove buds by steam distillation process for 8-10 hours at a yield of 10.1%, hidrodestilasi for 4-6 hours at a yield of 11.5% and soxhlet extraction for 6 hours at a yield of 41.85%¹⁹. On the extraction of essential oil of cloves with *Eugenia caryophyllata* hidrodestilasi method for 150 minutes get a yield of 5.06%, method microwave assisted extraction (MAE) for 10-30 minutes at a yield of 7.42% and microwave steam distillation method (MSD) for 10-30 minutes at a yield of 16.25%²⁰.

Research on the isolation of eugenol from clove oil also has been done. Hidayati²¹ gaining 99.45% eugenol drawn from the oil extraction time of 30 minutes and the volume ratio of oil to the solvent hexane = 1:2. In the isolation of eugenol from clove oil yield of 70.6% gain in the reaction time of 3 hours, stirring speed of 100 rpm, the standing long 19 hours and the ratio of water phase: n-hexane for washing is 1:1, 1:1/2: 1:1/2²². Lutfi et al.²³ get a eugenol content of 90.20% of the initial level of 70% at a concentration of 0.8 N NaOH, the temperature distillation of 195°C, vacuum pressure of 6.10^{-2} kPa and distillation time of 30 minutes. In the purification eugenol from clove oil, get a yield of 81.3% and eugenol concentration increased from 79.10% to 95.10% by using 1.8 N HNO_3 ²⁴.

In the study of isolation eugenol from clove oil, there is no data on the reaction temperature used and reaction time used is relatively long. The aim of this study was to obtained optimum process conditions such as temperature and reaction time, and was expected to optimize the isolation of eugenol from clove oil and produce higher yields.

2. Experimental

2.1 Materials and tools

The main research material that clove essential oil purchased from CV. Panadia. Reagents used in the study include HCl (Sigma-Aldrich, 37%), potassium hydrogen ptalat (Sigma-Aldrich, 99%) and NaOH pellets (Riedel-de Haen, 99%). The reaction was performed on a laboratory scale using a three-neck round bottom

flask fitted condenser, thermometer and hot plate magnetic stirrer. The reaction temperature was maintained in accordance study variables using water bath and atmospheric pressure. The separation of the reaction products was done by separating funnel. Then proceed purification of the reaction products using a set of distillation apparatus equipped with a vacuum pump.

2.2 Preparation

Clove essential oil that has prepared with analyzed eugenol concentration by GC. Creating 0.8 N NaOH solution, then standardized with potassium hydrogen ptalat. Assembling the reactor as a reaction consisting of a three-neck flask and condenser and to strengthen its position with the buffer and the stand. Then put the reactor on a magnetic stirrer hot plate. Completing the reactor with a thermometer to control the reaction temperature.

2.3 Reactive Extraction

Incorporating 100 ml clove essential oil and 0.8 N NaOH solution which has been standardized by a ratio of 1:1.1 to the reactor²³. Turn on the hot plate and set the temperature at the reaction temperature rotation corresponding research variable (30, 40 and 50°C) and set the lap button magnetic stirrer at a speed of 100 rpm²². Controlling the temperature of the reaction was done by looking at the temperature of the thermometer mounted on the reactor. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the reaction product was then inserted separating funnel and allowed to stand for 24 hours to form two layers. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Separating the two layers and measuring the volume of the aqueous layer.

2.4 Vacuum Distillation

Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain pH 4²¹. Before placing Na-eugenolat distillation flask that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted behind the cooler and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes²³. Distillate was eugenol and the residue was residual NaCl reaction products.

2.5 Analysis

Eugenol distillate which was then measured and analyzed of volume concentration of eugenol using gas chromatography (GC).

3. Results and Discussion

The raw material was the essential oil of cloves eugenol its concentration was analyzed by GC and found concentrations of 25.261%. Yield of eugenol was calculated using the following equation:

$$\text{Yield (\%)} = \frac{[\text{Volume of distillate} \times \text{concentration of eugenol}]_{\text{end}}}{[\text{Volume of oil} \times \text{concentration of eugenol}]_{\text{initial}}} \times 100$$

3.1 Effect of Temperature and Reaction Time to Volume Aqueous Layer (Na-eugenolat)

The bottom layer with the separation of the aqueous layer separating funnel which was Na-eugenolat reaction products between eugenol and NaOH. The aqueous layer volume measurements performed for each variable temperature and reaction time. From Table 1 it can be seen that the temperature and reaction time influence on the volume of aqueous layer obtained. The higher the temperature and reaction time, the greater the volume of aqueous layer to obtain optimum conditions.

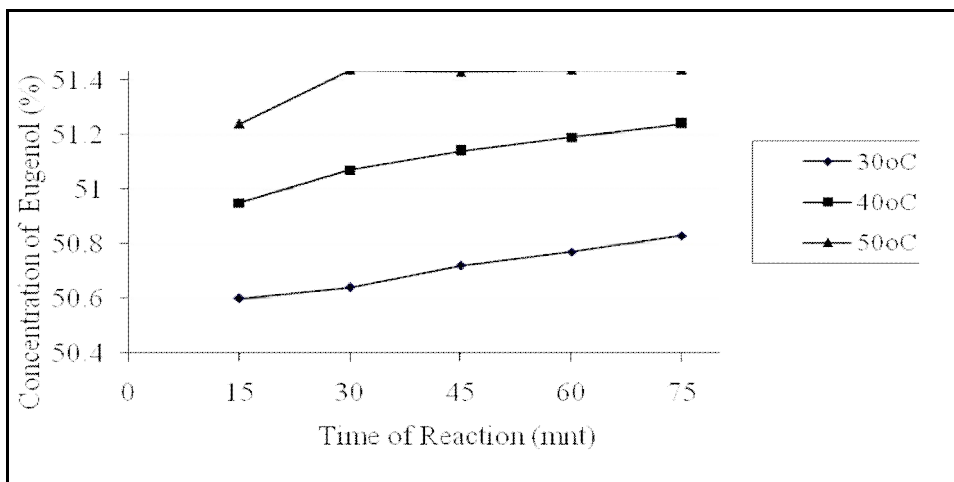
Table 1. Volume aqueous layer (Na-eugenolat) at various temperatures and reaction time

Temperature (°C)	Time of Reaction (mnt)	Volume <i>aqueous layer</i> (mL)
30	15	86
	30	87
	45	89
	60	90
	75	91
40	15	96
	30	97
	45	91
	60	89
	75	89
50	15	88
	30	93
	45	96
	60	89
	75	87

The best conditions of each of the different variables- At 30°C temperature variables, the best conditions obtained in a reaction time of 75 minutes with a volume of 91 mL of aqueous layer. In the variable temperature of 50°C, the best conditions obtained on reaction time 45 minutes with a volume of 96 mL of aqueous layer. The variable 40°C, the best conditions obtained in a reaction time of 30 minutes with a volume of 97 mL of aqueous layer and this results in an optimum condition. Theoretically it was known that the higher the reaction temperature the greater the reaction speed, which means the formation of more and more products, but this condition was limited to the optimum condition is reached. NaOH function in this process there are two, namely as a solvent in the extraction process that removes eugenol from kariofilin phase to the aqueous phase. Subsequently NaOH serves as a reactant that will react with eugenol.

3.2 Effect of Temperature and Time Reactions to concentration of eugenol (%)

Distillate distilled namely the isolated compound eugenol, concentration analyzed by GC. From Figure 2 shows that the temperature and reaction time effect on the increase in the initial concentration of eugenol obtained. The highest increase occurred in all variables reaction temperature with a reaction time of 15 minutes, where the concentration of eugenol increased from 25.261% to ± 51%. After a reaction time of 15 minutes were relatively small increase in the concentration of eugenol and almost evenly on all the variables of temperature and reaction time. The reaction between eugenol and NaOH was a fast reaction reaches equilibrium.

**Figure 1. Effect of temperature and reaction time to the concentration of eugenol (%)**

Eugenol highest concentrations obtained at 50°C with a reaction time of 75 minutes which is 51.444%. An increase of 26.183% of the initial concentration of eugenol 25.261% to 51.444%. This result was better than the results Lutfi et al.²³ get a 20.20% increase in the concentration of eugenol. As well as research results Haryani et al.²⁴ get a 16% increase in the concentration of eugenol.

3.3 Effect of Temperature and Time Reactions to Yield of Eugenol (%)

For the calculation of yield of eugenol measurable results isolation volume. From Figure 2 shows that the temperature and reaction time affect yield eugenol obtained. Visible optimum conditions were different in each study variable. At a reaction temperature of 30°C variable has not been achieved the optimum conditions because the yield eugenol still increase with the highest yield at the reaction time of 75 minutes was 92.56%. At variable reaction temperature reached 40°C optimum conditions on reaction time 40 minutes at a yield of 97.10%. At variable reaction temperature 50°C was reached optimum conditions on reaction time 45 minutes at a yield of 97.73%, the difference was only 0.63% compared to the optimum conditions at 40°C. Yield of eugenol obtained from the results of this study were relatively better when compared to previous studies. Fitri and Kawira²² get 70.6% yield with a reaction time of 3 hours. Research Haryani et al.²⁴ get a yield of eugenol 81.3%. Results of this research differs from research Hidayati²¹ to get 99.45% yield with a reaction time of 30 minutes, whereas in the study did not take into account the yield calculation of the concentration of eugenol obtained.

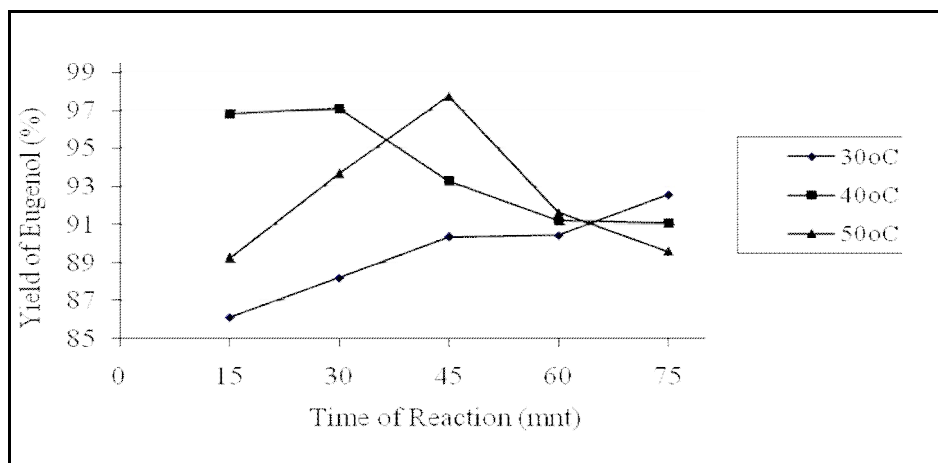


Figure 2. Effect of temperature and reaction time to yield eugenol (%)

4. Conclusions

The optimum conditions of temperature extraction reactive process that was 40°C, reaction time of 30 minutes, 0.8 N NaOH concentration, the volume ratio of oil:NaOH was 1:1.1, stirring speed of 100 rpm, separation using 5 N HCl to pH 4, purification eugenol with vacuum distillation at a temperature of 195°C for 30 minutes with a pressure of 6.10^{-2} kPa. In these conditions the concentration of eugenol obtained 51.07% and yield of eugenol 97.10%.

References

- Bustaman S. 2011. Potensi pengembangan minyak daun cengkeh sebagai komoditas ekspor Maluku. Jurnal Litbang Pertanian, 2011, 30: 132-139.
- Towaha J. The Benefits of Cloves Eugenol in Various Industries in Indonesia. Perspektif, 2012, 11: 79-90.
- Chaieb K, Hajlaoui H, Zmantar T, Kahla-Nakbi AB, Rouabhia M, Mahdouani K, Bakhrouf A. The chemical composition and biological activity of clove essential oil, *Eugenia caryophyllata* (*Syzigium aromaticum* L. Myrtaceae): A short review. Phytoter. Res., 2007, 21: 501-507.

4. Bhuiyan MNI, Begum J, Nandi NC, Akter F. Constituents of the essential oil from leaves and buds of clove (*Syzigium caryophyllatum* (L). Alston. Afr. J. Plant Sci., 2010, 4: 451-454.
5. Pramod K, Ansari SH, Ali J. Eugenol: a natural compound with versatile pharmacological actions. Natural Product Communications, 2010, 5: 1999-2006.
6. Jirovetz L. Medicinal value of clove. University of Vienna, Department Pharmacy and Diagnostics, Austria, 2010.
7. Hamed SF, Sadek Z, Edris A. Antioxidant and antimicrobial activities of clove bud essential oil and eugenol nanoparticles in alcohol – free microemulsion. J. Oleo Sci., 2012, 61: 641-648.
8. Sudarma IM, Yuanita E, Suana IW. Markovnikov addition of chlorosulfuric acid to eugenol isolated from clove oil. Indo. J. Chem., 2013, 13: 181-184.
9. Ngadiwiyana, Ismiyanto, Jumino, Anwar C. Sintesis 3-(3,4-dimetoksifenil)-propanal sebagai senyawa antara dalam pembuatan turunan antibiotik C-9154 dari minyak daun cengkeh. *JSKA*, 2008, 11.
10. Medicinal Spices Exhibit. Vanilla. 2010.
11. Bilton P. Vanilla : history, extract, essence, syntetic vanilla and vanillism. 2011.
12. Free Press Release. Vanilla bean-artificial vanilla bean extracts. 2012.
13. Rasasti D. Oksidasi eugenol asetat dan uji aktivitas antioksidan senyawa turunannya.. Bandung: UPI. 2006.
14. Kadarohman AH, Siti H, Fareza MS. Konversi dan karakterisasi isoeugenol asetat menjadi vanillin asetat. Jurnal Sains dan Teknologi Kimia, 2010, 1: 177-181.
15. Vanit S, Suppakul P, Jinkarn T. Antimicrobial effects of coating solution containing clove oil and hydrophobic starch for coating paper board. Asian Journal of Food and Agro-Industry, 2010, 3: 201-212.
16. Saran S, Menon S, Shailajan S, Pokharna P. Validated RP-HPLC method to estimate eugenol from commercial formulations like *Caturjata Churna*, *Lavangadi Vati*, *Jatiphaladi Churna*, *Sitopaladi Churna* and clove oil. Journal of Pharmacy Research, 2013, 6: 53-60.
17. Luo Y, Zhang Y, Pan K, Critzer F, Davidson PM, Zhong Q. Self – emulsification of alkaline – dissolved clove bud oil by whey protein, gum arabic, lecithin, and their combinations. J. Agric. Food Chem., 2014, 62: 4417-4424.
18. Prianto HH, Retnowati R, Juswono UP. Isolasi dan karakterisasi dari minyak bunga cengkeh (*Syzigium aromaticum*) kering hasil distilasi uap. Kimia Student Journal, 2013, 1: 269-275.
19. Wenqiang G, Shufen L, Ruixiang Y, Shaokun T, Can Q. Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods. Food Chemistry, 2007, 101: 1558-1564.
20. Kennouche A, Bencaki-Ali F, Scholi G, Eppe G. Chemical composition and antimicrobial of the essential oil of *Eugenia caryophyllata* Cloves extracted by conventional and microwave techniques. Journal of Biologically Active Products from Nature (TBAP), 2015, 5: 1-11.
21. Hidayati N. Ekstraksi eugenol dari minyak daun cengkeh. Jurnal Teknik Gelagar, 2003, 14: 108-114.
22. Fitri N, Kawira JA. Perbandingan variabel pada isolasi dan pemurnian eugenol dari minyak daun cengkeh. Media Litbang Kesehatan, 2006, 16: 16-21.
23. Lutfi M, Jati W, Purbasari A. Peningkatan kadar eugenol pada minyak atsiri cengkeh dengan metode saponifikasi – distilasi vakum. Jurnal Teknologi Kimia dan Industri, 2013, 2: 198-203.
24. Haryani HW, Hidayat N, Rahmah NL. Pemurnian eugenol dari minyak daun cengkeh dengan reaktan asam monoprotik. Kajian jenis dan konsentrasi asam. Jurnal Industria, 2014, 3.
