CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106191

Comparison of Hydrodistillation for the Extraction of Essential Oils from Fruit Peels with Other Methods

Chao Ma[a], Lih J. Yu[a,*], Cik S. Hassan[a], Natarajan Elango[a], Wah Y. Tey[a], Gavin N.Y. Lai[b], Ruey S. Chen[c], Moaa'th A. Tarawneh[d]

[a]Faculty of Engineering, Technology & Built Environment, UCSI University, 56000 Cheras, W.P Kuala Lumpur, Malaysia
[b]Faculty of Science and Engineering, University of Nottingham Ningbo China, 199 Taikang East Road Ningbo, 315100 China
[c]Department of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[d]Department of Physics, College of Science, Al-Hussein Bin Talal University, P.O. Box 20, Ma'an, Jordan
yulj@ucsiuniversity.edu.my

There are many essential oil extraction methods developed and emphasize yield production efficiency. However, there is lack of comparative study among these methods. In this study, reassessment of conventional hydro-distillation of essential oils extraction of California navel orange was conducted, focusing on optimization of hydro-Distillation Extraction conditions. The Response surface methodology (RSM) predicted results were validated via experiments to determine optimize process parameters, aim to achieve maximum yield. Three process parameters studied were the ratio of water to orange peel (2:1 to 8:1 mL/g), extraction time (60 to 120 min) and extraction temperature (60 to 100 °C). Both experimental and RSM results showed a maximum essential oil yield of 3.2—3.4 %, when the optimum process conditions were achieved: with a water to raw material ratio of 4.68:1 (mL/g), an extraction time of 91.28 min and an extraction temperature of 82.50 °C. The optimization study of limonene extraction was then compared with existing studies and the results showed that hydro-distillation extraction of essential oil achieving comparable essential oil yield percentage, while ensuring relatively low energy consumption and maintaining its economy value.

1. Introduction

In recent years, due to increased global health awareness, there has been a focus on the health services sector and a shift towards the use of natural products as medicines, food and consumer products (Wang et al., 2016). Many studies have also shown that natural compounds in plants have an important role in improving human health (Yang et al., 2017), for example, it has shown significant chemopreventive and therapeutic effects against chemocarcinogen-induced cancers of the breast, lung, stomach, liver and skin in rodents. The mechanism of action may be due to the inhibition of isoprenylation of small molecule G proteins associated with cell growth and increased production and activity of the potential growth inhibitor TGFβ (Jessica et al., 2011). Limonene has been shown to have significant chemopreventive and therapeutic effects against cancer, in addition it has also been found to have strong antibacterial activity against many fungi and bacteria (Abubakar et al., 2020). d-Limonene has been found by many researchers to have strong antibacterial activity against many bacteria and fungi and has also been shown to be effective in inhibiting the growth of food spoilage bacteria such as Aspergillus niger, Bacillus subtilis and Staphylococcus aureus (Auta et al., 2018). Based on these properties, limonene is often used in food processing, daily chemical production and many other applications. Limonene can be obtained from the extraction of essential oil from citrus fruits, such as orange, grapefruits, pomelo and so on.

As the demand for essential oils increases, the production of essential oils should cope with the demand. The production industry is looking for improvement opportunities for high yield, energy efficient and economic methods. There are new extraction methods been developed, such as organic solvent extraction (Miyazawa et

Paper Received: 19 March 2023; Revised: 18 July 2023; Accepted: 30 September 2023
Please cite this article as: Ma C., Yu L.J., Hassan C.S., Elango N., Tey W.Y., Lai G.N., Chen R.S., Tarawneh M.A., 2023, Comparison of Hydrodistillation for the Extraction of Essential Oils from Fruit Peels with Other Methods, Chemical Engineering Transactions, 106, 1141-1146 DOI:10.3303/CET23106191

al., 2013), supercritical carbon dioxide extraction (Ibrahim and Sarbatly, 2012) and ultrasonic assisted extraction (Jokić et al., 2022). However, these methods compromise the investment cost with production yield. Therefore, in this study, reassessment of Respond Surface Methodology optimization was conducted on the extraction of limonene essential oil from orange peel, via conventional hydro-distillation method, focus on the hydro-distillation extraction optimization condition. An extensive review was conducted in comparison of obtained experimental results, with available extraction methods in aspect of temperature, time and yield. The aim is to re-evaluate the productivity value of hydro-distillation method, as compared to other methods, when the hydro-distillation extraction condition is optimized.

2. Methodology

2.1 Material

California navel orange peel was dried and ground into small 0.5 cm sized pellets to be used as a raw material for the extraction of limonene. After dry treatment of the orange peel pellets, 100 g of grinded orange peel powder was prepared as the raw material for each experimental run.

2.2 Extraction

In this experiment, limonene essential oil was extracted from orange peel by hydro-distillation method. The essential oil was collected and weighed through a condenser tube. Response surface analysis was chosen to consider the effects of multiple factors and the interactions between the factors. To facilitate the RSM procedure, design-expert 8.0 software, Box-Behnken Design (BBD) were used for the experiments of experiment. The control variables were heating temperature (60 °C, 80 °C, 100 °C), heating time (60 min, 90 min, 120 min), solid-liquid ratio (1:2, 1:4, 1:8) and central replicate group (80 °C, 90 min, 1:4) replicated 3 times for a total of 15 times. Two hundred grams of pretreated peels were weighed and placed in a three-neck flask, and a quantitative amount of pure water was added according to the solid-liquid ratio of the experimental group. The three-neck flask was placed in a heating mantle and the time was calculated when the temperature in the three-neck flask reached the desired level. The essential oil vapor will come out of the condenser tube attached to the outlet of the three-neck flask. Essential oil in liquid form shall be collected upon condensation.
Yield percentage in Eq (1) was used to determine the collected essential oils, where: v_2 is the mass of the essential oil after preparation (after standing to remove the water), v_1 is the mass of the dispensing funnel and v_0 is the mass of the navel orange peel weighed before the start of each group's experiment.

$$Essential\ oil\ yield(\%) = \frac{v_1 - v_2}{v_0} \times 100\% \quad (1)$$

3. Result and discussion

3.1 Experimental results

Table 1 shows the results of experiment runs as suggested by BBD methods, the group with the highest yield results (3.4 %) was obtained at temperature of 80 °C, an extraction time of 90 min and a solid-liquid ratio of 1:4, while the group with the lowest yield (1.4 %) had a temperature of 60 °C, an extraction time of 60 min and a solid-liquid ratio of 1:4. Comparing the results of the highest and lowest yield groups, it can be seen that the yield significant impacted by the changes of temperature and time. This means yield depending on the combination of temperature and time condition. The RSM optimization predicted that the best yield at 3.23794 %, which is very close to the best yield of this experiment (3.4 %). In addition, the deviation table in Table 2 shows a standard deviation of 0.128564, reflecting the close distribution of the data to the mean. Furthermore, the results for essential oil yields were all within the 95% confidence interval (2.86766 to 3.60822), indicating the high reliability of the experimental data obtained.

Table 1: Experiment results

Number	Temperature (A)	Time (B)	Ratio (C)	Yield
1	60	120	5	1.9
2	100	60	5	2.03
3	100	90	8	2.05
4	80	120	2	2.25
5	80	120	8	1.98
6	80	60	8	1.87
7	60	60	5	1.4

Table 1: Experiment results (cont'd)

Number	Temperature (A)	Time (B)	Ratio (C)	Yield
8	100	90	2	2
9	100	120	5	2.05
10	80	90	5	3.3
11	80	60	2	2.35
12	60	90	8	1.96
13	80	90	5	3.4
14	80	90	5	3.27
15	60	90	2	1.69

Table 2: Results of optimization

Two-sided		Confidence=95%			n=1	
Factor	Name	Level	Low Level	High Level	Std.Dev.	Coding
A	Temperature	81.30	60.00	100.00	0.000	Actual
B	Time	81.68	60.00	120.00	0.000	Actual
C	Ratio	3.97	2.00	8.00	0.000	Actual
Response	Prediction	Std.Dev	SE(n=1)	95 %PI low	95% PI high	
Yield	3.23794	0.128564	0.144045	2.86766	3.60822	

3.2 Response surface methodology analysis

The analysis of variance for the model created by the RSM shows that the model has an *F*-value of 43.79 which means that the model is highly significant with only a 0.03 % probability of being caused by noise. The model has a *p*-value of 0.0003, which is highly significant. The data obtained an insignificant under-fit value of 0.1684. Based on this, the model is proposing its validity in its description and that the model is highly compatible with the actual experiment. The model also had a high R^2 (0.9875) indicating a good fit of the parameters to the responses. The p-values for A, C, AC, A^2 , B^2 , C^2 are all less than 0.05, indicating that they are significant model terms. A, B, C are temperature, time, and solid-liquid ratio, and AB, AC, BC, A^2, B^2, C^2 are quadratic model terms that affect the yield of the essential oil in a two-by-two interaction between the A, B, C model terms. The low lack of fit *P*-value of 0.1684, indicating the data are in high accuracy of the A, B, C interaction.

3.3 Yield equation

The proposed function describes the influence of the process parameters and the interactions on the achieved oil yield. In other words, the reaction receives the effects of first order and second-order variables, including temperature (A), time (B), solid-to-liquid ratio (C) and their interaction terms.
Final equation is:

$$\text{Yield} = 3.32 + 0.26A + 0.066B - 0.17C - 0.12AB + 0.17AC + 0.052BC - 0.95A^2 - 0.53B^2 - 0.68C^2 \quad (2)$$

$$\text{Yield} = -19.48699 + 0.39535A + 0.12163B + 0.4163C - 2(E{-}0.04AB) + 2.875\,(E{-}0.03AC) + 5.9333(E{-}0.04BC) - 2.36667 - 0.03A^2 - 0.04B^2 - 0.075463C^2 \quad (3)$$

The results from the main term of the equation, with an exponent of 1, show that the value of A does not correlate well with yield (the importance of A needs to be re-judged). Figure 1(a) shows a line plot of predicted versus actual values, where the scatter distribution of the data where the actual and predicted values intersect is close to the best fit of a straight line, which indicates the high accuracy of the results and shows that the human errors in the experiment (weighing, errors in measurement) are negligible and generally fit the experimental arithmetic design in general.
In addition, Figure 1(b) shows the residuals of the experimental attempts, which are randomly distributed and irregular, indicating that the model developed has the potential to accurately predict yield. Therefore, the model is meaningful, and the results of the model and the experimental results are both trustworthy.

3.4 Model adequacy checks

Figure 2(a) shows the normal probability plot of the residuals, and the normal assumption is consistent with the residual plot, which is shown along a straight line. Figure 2(b) below shows the comparison of the predicted response with the residuals. The residuals are found to be randomly distributed within a certain confidence level, which implies that the variance Y of the original survey is constant at all values. Therefore, we believe that the empirical model can describe the extraction rate of limonene essential oil from RSM.

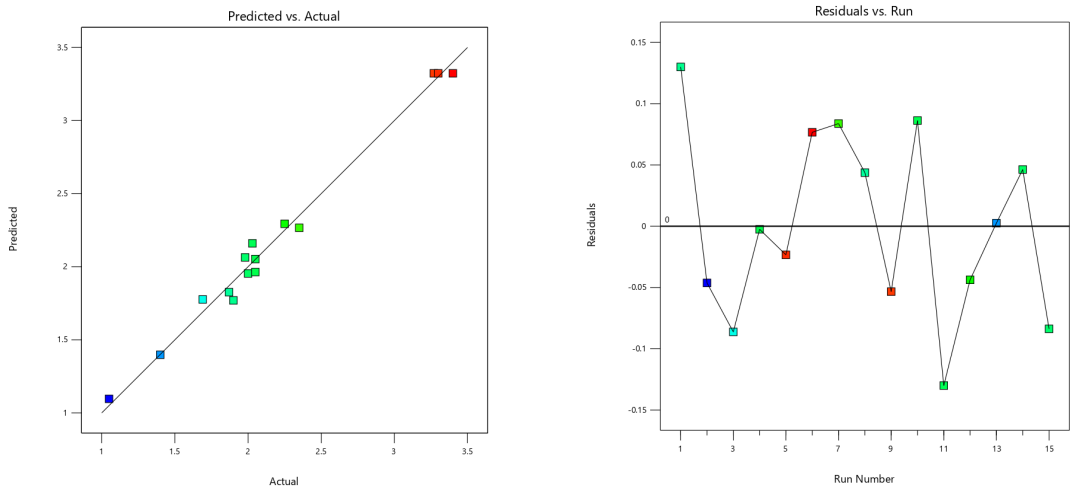

Figure 1: (a) The predicted versus actual values; (b) The residuals versus run number

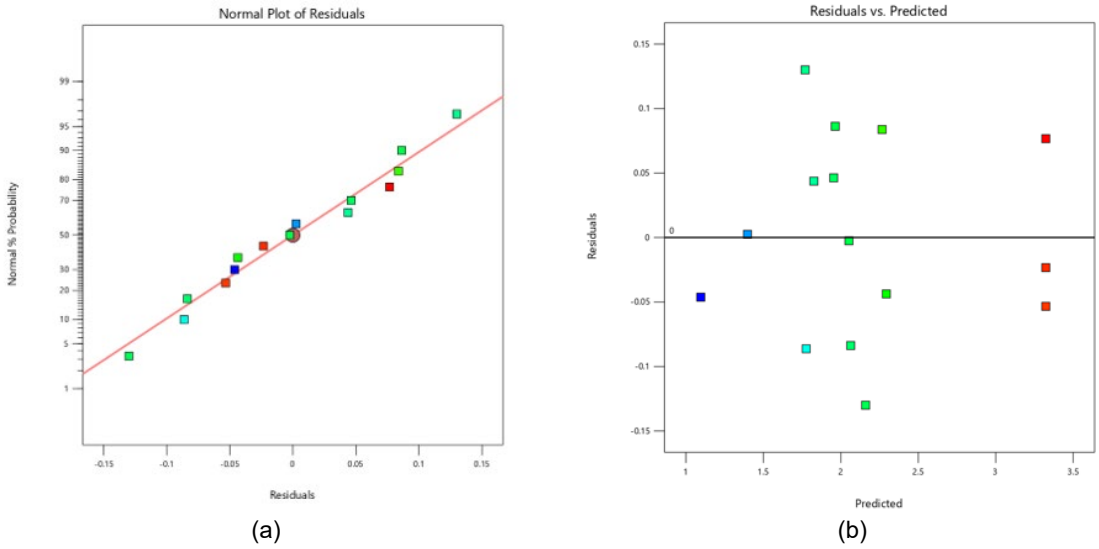

Figure 2: (a) Normal probability plot of the residuals; (b) Predicted response with the residuals

3.5 Comparison of methods

A high temperature and high-pressure extraction method were proposed by Lopresto et al. (2014), showing that the yields obtained 3.56 % at an optimal process of 30 min, 150 °C and a solid to liquid ratio of 1:15. In addition, high temperature and high-pressure extraction methods proved to be superior to hydro-distillation extraction in terms of energy savings and the reduced extraction time. The success of Lopresto's experiments was due to the high temperature and pressure conditions, but also depending on the raw material condition. Lopresto et al. (2014) dried the peel and controlled the peel size (125 μm -1 mm), which effectively increased the reaction time and contact surface. However, with Lopresto's experimental approach, the high temperature and pressure conditions were consuming greater energy and demanding a higher control requirement of the water-vapor pressure control. Qinenki et al. (2018) also used hydro-distillation extraction as an extractant and anhydrous sodium sulphate as a drying agent to further separate the water and impurities from the essential oils, with significantly improved results averaging yield of 2.33 %.

Chen and Gu (2008) using organic solvent extraction was concerned with the emerging issue of additive selection and conducted a comparative experiment using four additives, ammonium chloride, sodium chloride, sodium sulphate and calcium carbonate, with a fixed orange peel fraction of 200 g and a solid to liquid ratio of 1:2, resulting in the yield percentage of: sodium chloride (2.4 %), ammonium chloride (2.6 %), sodium sulphate

(2.1 %), calcium carbonate (2.2 %) and no additives (1.8 %). Therefore, additives were used to increase the extraction rate of the essential oil and ammonium chloride was the best organic solvent extractant. The addition of the organic solvent reduced the overall temperature of the product and effectively reduced the thermal decomposition of limonene, but the extraction time of the organic solvent was too long and inefficient. However, the usage of additives may not be preferable in the production industry as it increases the overall manufacturing cost with additives and there is a need for waste treatment procedures at the end of production for the additives. Yang et al. (2017) performed GC-MS analysis of the fresh fruit peel of Ouguang by solvent extraction, and found that the content of limonene in the peel extract of Ouguang was 86.39% when the peel was pounded and determined by meteorological chromatography at 50 °C. Hiroaki et al. (2015) applied the extraction method by immersion to extract aromatic substances from the peel of Galimundia orange grown in the Philippines, using n-hexane as the solvent, and obtained The content of limonene in the volatile components was 58.2%. However, this method has a long extraction time, low productivity, residual organic solvents and environmental pollution, and organic solvents are more hazardous to the operator. The extract also requires further refinement due to the high content of impurities, resulting in increased costs and economic unreasonableness. Therefore, the method will not be used in the production of industrial grade and so on.

Zareen et al. (2012) used polarity modifiers to change the polarity of supercritical carbon dioxide to increase the polarity of neroli oil, but from the results, the essential oil yield was not satisfactory, only 0.5-2.0 %. Zareen (2012) then started to investigate the effect of different polarity modifiers. At high temperature and pressure (45 °C, 12 MPa), the concentration of limonene increased significantly with the addition of methanol, while the addition of n-heptane showed little change. The content of alcohols (linalool and pineol) in the essential oil increased significantly with the addition of n-heptane. However, the issue of toxicity carried by organic solvents and disposal of used organic solvents may pose potential problems if not managed properly. Wang et al. (2016) also used supercritical carbon dioxide extraction with molecular distillation by increasing the temperature (46 °C) and pressure (25 MPa) and the flow rate of carbon dioxide to 20 l/h. As a result, the yield of orange peel oil reached 1.973 % with the least number of organic solvents used. The disadvantage of this method is the need to resort to ultrasonic assisted apparatus, which is not only expensive and technically difficult to operate, requiring the entire extraction experiment to be completed in ultrasonic shaking, in addition to the yield of essential oil as a result of this experiment remained unimproved. Compared to the results of Zhang (2014) (1.973 % yield), the significance of using the hydrodistillation method is favorable because of the high yield (3.4 %) and low equipment investment costs.

Song (2016) employed ultrasonic assisted system in essential oil extraction, obtained a yield of 16.8 %. In contrast, Wang et al. (2016) used the ultrasonic assisted method only obtained 2.43 % yield, which was lower than the essential oil yield of the work demonstrated in this experiment (3.4 % yield). The optimization of ultrasonic assisted technique needs to improve, and more studies are needed to investigate the essential oil yield consistency in respond to ultrasonic assisted system. Dong et al. (2019) explored five different types of orange peels in 2019 with yields varying greatly from 0.05 to 0.9 %, all peels were treated in the same way and their results showed that Sichuan honey orange (0.05 %), sugar orange (0 %), grapefruit (0.35 %), navel orange (0.6 %) and ice sugar orange (0.9 %). Dong et al. (2019) verified the effect of peel type on essential oil yield by comparing essential oil yields from five different peels, although the ultrasonic extraction method was effective in increasing essential oil yields and improving the lengthy extraction time by reducing it to less than 30 min (90 min for hydrodistillation). However, the extremely high price of the ultrasonic assisted apparatus remains the most prominent feature of the method.

The optimum conditions for this experiment were a water to orange peel ratio of 5:1 (mL/g), an extraction time of 91 min, an extraction temperature of 80 °C and a maximum yield of 3.4 %. In a laboratory setting, firstly in terms of hydro-distillation extraction equipment, going to compare supercritical carbon dioxide extraction with ultrasonic extraction, the Hydro-distillation extraction method is cheaper. Secondly, there is the issue of safety. The hydro-distillation extraction method fundamentally avoids the hazards of organic solvents to humans and the environment, and the hydro-distillation extraction method does not produce dangerous conditions such as high temperatures and pressures. In addition, the heating extraction time range for hydro-distillation extraction (45-180 min) is longer than that for ultrasonic extraction, but within reasonable limits. The hydro-distillation extraction method does not require specialist technicians, saving laboratory costs. Most importantly, even without the help of organic solvent extraction or ultrasound, the same high quality essential oil yields can be obtained by finding exactly the best conditions for essential oil yields with the help of RSM. Hydro-distillation extraction therefore solves many of the problems that new essential oil extraction methods cannot improve, while protecting the environment, reducing costs and ensuring the yield and quality of essential oils.

4. Conclusion

RSM optimization and experimental results confirmed that the highest essential oil yield of 3.4% was achieved under the treatment conditions of holding time (91 min), temperature (80 °C) and solid-liquid ratio (1:5). The obtained results were compared with organic solvent extraction, supercritical CO2 extraction, additive-assisted and ultrasonic-assisted methods. In conclusion, the hydrodistillation method can be highly recommended for the feasibility of large-scale production due to its high yield, simple operation, low investment cost and low environmental impact. Meanwhile, the use of RSM optimization can help us to quickly determine and verify the optimal process conditions for the hydrodistillation method. According to the RSM optimization of hydrodistillation conditions and without using any dangerous organic solvents with high temperature and pressure and other conditions, the optimal extraction conditions of this experiment resulted in a yield of 3.4% with the use of only a relatively inexpensive thermostatic heater, so the productivity value of the hydrodistillation method is still not negligible.

Acknowledgments

The project was funded by Ministry of Higher Education Malaysia, Fundamental Research Grant Scheme (FRGS/1/2022/UCSI/02/01), and UCSI University (REIG-FETBE-2021-014).

References

Abubakar E., Theodor P.C., Scruton N., 2020, Extraction of limonene from orange peel, Malaysian Journal of Basic and Applied Sciences, 8(2), 115–120.

Auta U., Musa.D.G., Tsado A.A., Faruq A.G., Isah S., Raji C., Nwanisobi C., 2018, Optimization of citrus peels D-limonene extraction using solvent-free microwave green technology, Chemical Engineering Communications, 46(2), 17–33.

Chen J., Gu X., 2008, Process study on the extraction of d-limonene from waste citrus peel, Chemical Industry Times, 22(5), 46–47.

Dong Y., Chen W., Yang S., Li C., Wu C., Chen Z., Deng H., Chen L., 2019, Experimental study on limonene extraction, Asia-Pacific Traditional Medicine, 12(5), 91–94.

Jessica A.M., Patricia A.T., Iman A.H., Chow H.H.S., Thomson C.A., 2011, d-Limonene: A bioactive food component from citrus and evidence for a potential role in breast cancer prevention and treatment, Oncology Reviews, 5, 31–42.

Jokić S., Molnar M., Cikoš A.M., Jakovljević M., Šafranko S., Jerković I., 2022, Separation of selected bioactive compounds from orange peel using the sequence of supercritical CO_2 extraction and ultrasound solvent extraction: Optimization of limonene and hesperidin content, Separation Science and Technology, 55(15), 2799–2811.

Hiroaki T., Yoshihitou U., Masayoshi G., 2015, Volatile Comstituents of Calamondin Peel and Juice (Citrus madurensis Lour) Cultivated in the Philippines, Biotechnology Techniques, 13(5), 23-26.

Ibrahim A., Sarbatly R., 2012, Effects of modifier polarity on extraction of limonene from Citrus Sinensis L. Osbeck using supercritical carbon dioxide, Malaysian Journal of Fundamentals and Applications, 8(2), 115–120.

Lopresto C.G., Petrillob F., Casazzac A.A., Aliakbarianc B., Peregoc P., Calabròb V., 2014, A non-conventional method to extract d-limonene from waste lemon peels and comparison with traditional soxhlet extraction, Separation and Purification Technology, 137, 13-20.

Miyazawa N., Fujita A., Kubota K., 2013, Optimization of solvent extraction process of essential oil from lemon peel, Bioscience, Journal of Agricultural Chemistry, 74(4), 835-842.

Qinenki B.B., Yuqin L., Siabong L., Li S., 2018, Optimization of the extraction process of lemon essential oil optimization and its GC-MS analysis, Food and Machinery, 28(1), 186-189.

Song Q., 2016, Optimization of lemon essential oil extraction process, Guangdong Chemical Industry, 9(37), 175–176.

Yang S.F., Quip P.H., Li Y., 2017, GC - MS analysis of petroleum ether extract of Ouguan, Analytical Laboratory, 26(1), 85–87.

Wang B.M., Gao J., Wei S., 2016, Process study on the extraction of essential oil from lemon peel by ultrasonic assisted method, Guangzhou Chemical Industry, 44(12), 102–104

Zareen A., Rosaria C., Monica L.R., Carà P.D., Lopez-Sanchez J.A., Pagliaro M., 2012, Limonene: A versatile chemical of bioeconomy, Chemical Communications Cambridge, 17(4), 41-44.