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Conversion of Limonene into More Valuable Aroma under Hydrothermal Conditions

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Abstract The aromatic components in citrus essential oils are monoterpenes, sesquiterpenes, and some oxygenated compounds. It is known that monoterpenes, such as limonene, take a little part of the aroma and are sometimes removed by deterpenation processes. In this study, a novel technology through a wet oxidation process using hydrogen peroxide was investigated for the conversion of limonene. Experiments were conducted using a batch type reactor to study the effects of temperature and reaction time on the conversion of limonene under the following conditions: temperature range of 150 to 200°C at reaction time of 10-80 min. After each run, samples consisting of 2 layers (oil and water phases) were collected. The oil layer was qualitatively analyzed of its composition using a gas chromatography-mass spectrometry (GC-MS) apparatus, while the organic carbon content in water layer was analyzed using a total organic carbon (TOC) analyzer. Results obtained under these conditions indicated highly selective conversion of limonene especially into its isomers.

Keywords: *limonene, subcritical water, hydrothermal, oxidation*

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1. Introduction

Recent developments in transportation infrastructures has increased citrus production and processing in countries with a suitable climate for its cultivation [1]. As a result, there is an urgent need for dealing with the increasing volume of juice processing residues, which are normally disposed despite the presence of valuable compounds. The peel, for example, contains valuable organic compounds such as essential oils. These oils have been recognized as valuable in food and beverage flavorings, perfumery, and chemical industry. The aromatic components in citrus essential oils are monoterpenes, sesquiterpenes, and its oxygenated compounds. The characteristic of citrus flavor is mostly dependent on oxygenated terpene derivatives, alcohols, aldehydes, esters, and ketones [2]. It is known that the monoterpenes, such as limonene, take a little part of the aroma despite its presence in highest concentration. Thus, deterpenation processes have been developed to remove the limonene and convert it into valuable components until now. For example, Fan et al. [3] tried to remove monoterpenes including limonene by the combined conventional vacuum distillation and supercritical CO_2 extraction. Our group has succeeded in effectively removing limonene from the essential oil using supercritical CO_2 technology. However, our present concern is to devise new usage for this enormous citrus by-product.

As an example, Nakano et al. [4] succeeded in converting optically inactive compound to optically active compound without catalysts by the addition of limonene and alcohol. This method was suggested as an effective approach for the utilization of limonene.

Another approach is to convert limonene to more valuable terpenic compounds. Some oxygenated derivates of limonene such as limonene oxide, carvone and carveol are important materials for the pharmaceutical industry for fragrant concoctions to use for foods, perfumes and cosmetic industry. Recently, various techniques to convert monoterpene to terpene oxides have also been investigated. These techniques utilize metal catalyzed oxidation using an organic solvent. However, these techniques require the use of expensive catalysts and organic solvents in large quantities in order to improve reaction efficiency. As a result, there comes the problem of cost and environmental impact accompanying the use of organic solvents. In recent study, Nunes et al. [5] succeeded in converting limonene to its oxidation product by using supercritical CO_2 .

In this study, we tried to convert limonene to valuable compounds efficiently under hydrothermal condition by using subcritical water. Subcritical water has unique properties. The dielectric constant and the ion product of water (Kw) could be dramatically changed by manipulating the temperature and pressure [6,7]. Due to these properties, it is expected that non-catalytic hydrolysis and dissolution of hydrophobic substance in subcritical water can be controlled by adjusting the pressure and temperature. In addition, to facilitate high conversion and for obtaining various oxygen functionalized compounds effectively, hydrogen peroxide was used as oxidizing agent. Hydrogen peroxide is non-toxic, and is safe to use in food applications. Thus, in this work, partial oxidation or isomerization of limonene was investigated to convert it to new fragrance by hydrothermal wet oxidation process with hydrogen peroxide serving as oxidant without using any metal catalysts.

2. Experiment

Hydrothermal treatment and wet oxidation treatment with hydrogen peroxide (Wako Pure Chemicals Industries Ltd., Osaka, Japan) was carried out using batch type reactor (AKICO Co., Japan) as shown in Figure 1. Limonene (Wako Pure Chemicals Industries Ltd., Osaka, Japan) and each solvent were charged into the batch reactor with stainless steel balls. The reactor was then shaken to mix the reactants inside the reactor. The effects of temperature and reaction time on the conversion of limonene were studied under the following conditions: reaction times of 10-80 min, temperatures of 150 and 200°C. After each run, samples consisting of 2 layers (oil and water phases) were collected. After separation of these two layers, component compositions of the oil phase were qualitatively analyzed using gas chromatography-mass spectrometry (GC-MS) (Hewlett-Packard Inc., Japan), while the organic carbon content in the water phase was analyzed by total organic carbon (TOC) analyzer (Shimadzu Co. Ltd., Japan).

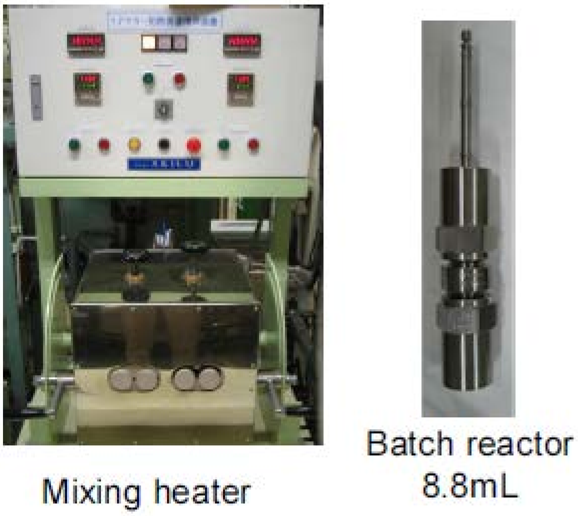


Figure 1. Batch type reaction apparatus

3. Result and Discussion

Limonene conversion experiments were carried out under hydrothermal wet conditions with or without oxidants. In the presence of an oxidant, conversion rate was high. Figure 2 and Table 1 shows the limonene derivatives in the presence of oxidants. Isomers and oxygenated compounds were detected in the products derived from limonene. For example, at a temperature of 200°C, with 2.0 M hydrogen peroxide, and reaction time of 50 min, 24 different types of products were detected. A few of them have fragrances which contribute to the distinct aroma of citrus such as terpinolene and Y-terpinene.

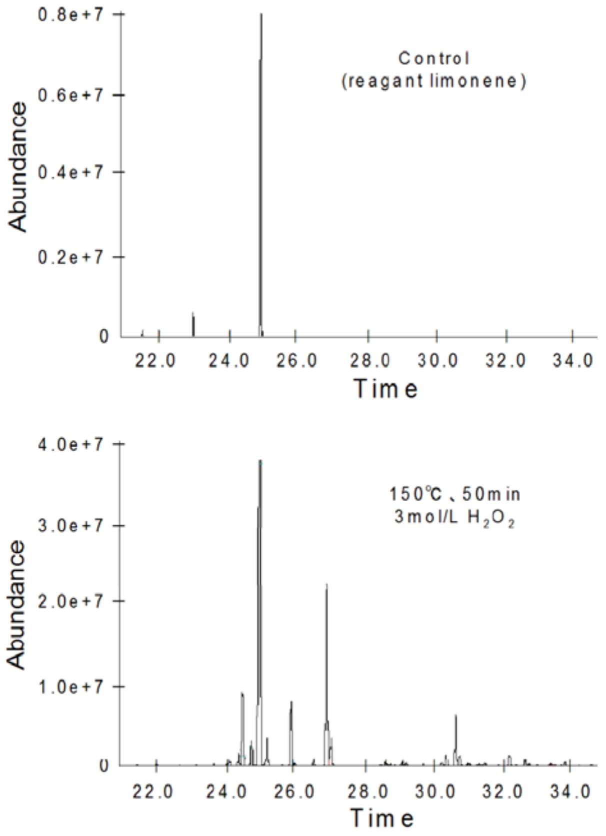


Figure 2. GC-MS chromatogram of limonene derivatives in the oil phase

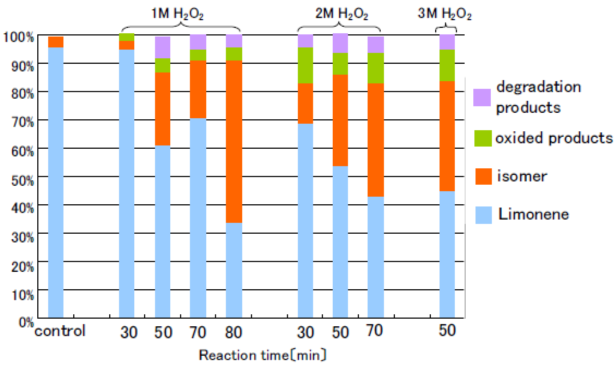


Figure 3. Effect of concentration of oxidant and reaction time on the composition of the oil layer obtained at 150°C

At a temperature of 200°C, it was observed that isomers with high selectivity were detected in the oil layer after reaction. In particular, approximately 100%

of limonene raw material was converted into its isomers at hydrogen peroxide concentration of 2.0 M and reaction time of 50 min. On the contrary, oxygenated compounds were also detected in the products obtained at 150°C. Figure 3 shows the effect of reaction conditions on the generation behavior of the limonene conversion products at 150°C.

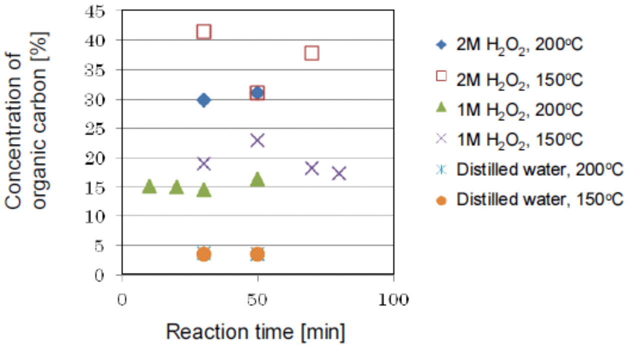


Figure 4. Organic carbon content of the aqueous layer of reaction products

The oxygenated compounds derived from limonene tend to increase with the concentration of oxidant. The amount of the isomers derived from limonene was found to increase with increasing reaction time.

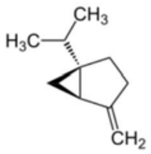
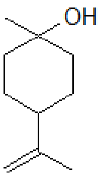
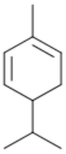
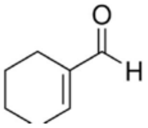
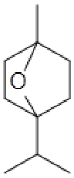
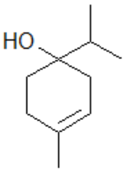
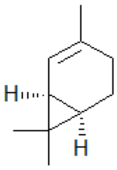
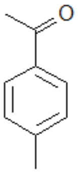
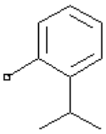
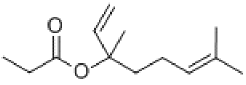
From the results in Figure 2, compounds having some hydroxyl groups such as 4-methylene-phenol and 4-methyl-4-(1-methylethenyl)-cyclohexanol were observed.

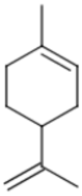
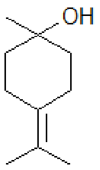
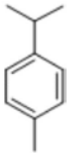
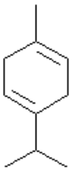
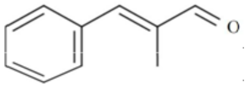
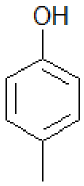
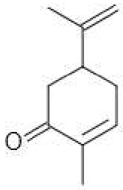
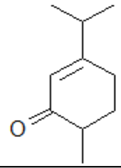
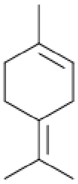
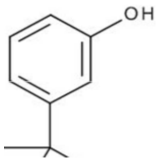
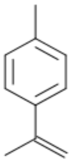
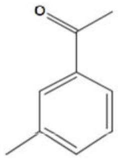
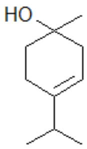
Figure 4 shows the amount of water soluble compounds containing hydroxyl group obtained by TOC analysis. The organic carbon content of the aqueous layer tend to increase with the increase in hydrogen peroxide concentration. The aqueous layer also possesses citrus fragrance. The fragrance was in negligible level prior to conversion reaction (data not shown). In the future, it is necessary to analyze what components were present in the aqueous layer in order to further identify water-soluble limonene derivatives if there should be any.

4. Conclusion

We have succeeded in converting limonene into its isomers and oxygenated compounds with higher aroma and fragrance without using any catalyst. Reaction selectivities into isomers and oxygenated compounds can be manipulated by changing reaction conditions. Especially, the concentration of oxidizing agent has significant effect on the production of oxygenated compounds. It was also observed that some conversion products were present not only in the oil phase but also in the aqueous layer. Applications of the obtain products to food and cosmetic industries are foreseen in the near future.

Table 1. Compounds corresponding to the peaks indicated in Figure 2

time	compound name	structure	time	compound name	structure
21.95	Sabinene		28.94	β-Terpineol	
24.03	α-phellandrene		29.06	Cyclohexene carbaldehyde	
24.28	P=Menthane		30.08	p-Menth-1-en-4-ol	
24.39	(+)-2-carene 6.77		30.19	Acetophenone	
24.66	o-Cymene		30.46	Linalyl propanoate	

24.88	Limonene		30.59	γ-Terpineol	
25.10	Eucalyptol		30.81	p-Cymene	
25.79	γ-Terpinene		31.92	α-Methylcinnamic aldehyde	
25.88	p-Cresol		32.00	Carvone	
26.42	5.5-Dimethylcyclopentaduene		32.45	Piperitone	
26.80	Terpinolene		33.17	3-tert-Butylphenol	
26.92	p-Cymenene		33.58	1-m-tolyl-ethanone	
28.46	1-Terpineol		31.92		

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