Functional substances obtained through biomass pyrolysis

- Functions of acid liquid, bamboo vinegar, etc. -

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## 1. Introduction

Pyrolysis is a procedure for the effective use of biomass resources. Pyrolysis has been known empirically since ancient times. Its principle is simple. Charcoal obtained through mainly wood pyrolysis is widely-used charcoal. Charcoal was once employed as an important domestic solid fuel. Charcoal has recently been used as a soil amendment as well as a fuel, thus heralding a new era. Charcoal materials are thermally decomposed to generate smoke during pyrolysis. The smoke is liquefied by cooling. The liquid is allowed to stand for a while after recovery to produce a peculiar liquid called acid liquid. Acid liquid is generally light red or reddish brown in color. Its distinctive odor is expressed in many ways, such as pungent acid, as well as irritating, chemical, and sweet odors. Most of the functions of acid liquid are empirically known. Acid liquid is used in various ways. Recent studies have demonstrated some functions, such as plant growth inhibitory effects, insect repellent effects, and antimicrobial and antifungal effects. The multiple functions of acid liquid have attracted attention because of an atmosphere of respect for nature. We herein review the properties and functions of acid liquid and bamboo vinegar, which are gradually attracting attention.

## 2. Production of acid liquid and bamboo vinegar

Plant materials, such as woods, are heated and dried. The materials are further heated to thermally decompose the components and generate smoke. The smoke is liquefied by cooling to produce acid liquid and bamboo vinegar.

Thermally-decomposed cellulose, hemicellulose and lignin, the principal components of wood and bamboo are abundant in the smoke. Of these components, hemicellulose is the most unstable to heat and decomposes at around 180°C [1)]. Cellulose is decomposed at around 240°C [2)]. Lignin is decomposed at around 280°C [3, 4)]. These decomposed components are evaporated in smoke. Syn-gas and a liquefaction product (crude acid liquid) generated by cooling are obtained from the smoke. The liquefaction product is separated into two or three layers when left to stand. The upper reddish brown solution is crude acid liquid. The lower black solution is called wood or precipitated tar. When three layers are formed, a thin oily layer is produced on the surface of crude acid liquid. This layer is also a part of wood tar. This layer is called light oil because it is so light as to float on crude acid liquid. On the other hand, precipitated tar is called heavy oil. The acid liquid layer is not completely separated from the wood tar layer. These layers are often gradually dissolved. The crude acid liquid is distilled to generate distillate and residues. The residues are called dissolved tar because they are a part of the wood tar dissolved in the crude acid liquid, thus being distinguished from precipitated tar (Figure 1). The dissolved tar content in the crude acid liquid is employed to assess the quality of acid liquid.

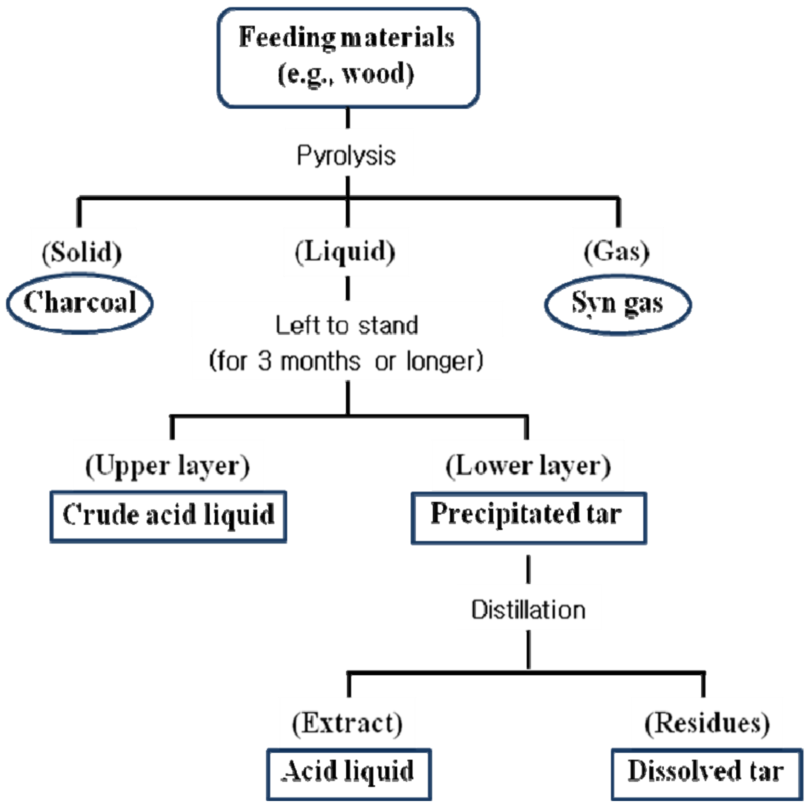


Figure 1. Components obtained through the pyrolysis of woods, etc.

3. Components of acid liquid and bamboo vinegar

The yields and components of acid liquid and bamboo vinegar vary with pyrolysis procedures, water contents of feeding materials, kinds of feeding materials, storage conditions, etc. The components of the acid liquid and bamboo vinegar produced in a charcoal kiln are organic compounds (10-20%) and water (80-90%). The components of the organic compounds include acidic substances, alcohols, phenols, neutral substances (e.g., aldehydes and esters) and basic substances. The principal components of acid liquid and bamboo vinegar are listed in Table 1 [5, 6, 7]. The principal components are acidic substances. Of these substances, acetic acid is the most abundant, after which acid liquid and bamboo vinegar are named. Of the alcohols, methanol is the most abundant. Phenols tend to determine the properties of the components of charcoal materials. Charcoal materials are classified into broad- and needle-leaved trees and bamboo. Generally, guaiacyl compounds are abundant in needle-leaved trees, while syringyl compounds are abundant in broad-leaved trees and bamboo [8]. Guaiacol and cresols are the important components of wood creosote [9].

Table 1. Principal components of acid liquid and bamboo vinegar

| Kinds | Compounds |
|---|---|
| Acidic substances | Acetic acid, propionic acid, butyric acid, cis-crotonic acid, trans-crotonic acid, 2-pentenoic acid, valeric acid, isovaleric acid, 2-butyric acid, formic acid, a butyrate, isobutyrate, etc. |
| Alcohols | Methanol, cyclotene, acetoin, 2-methyl-4-oxo-pentane-2-ol, acetoin propylene glycol, 2-acetoxy ethanol, furfuryl alcohol, maltol, 1-butanol, 2-methyl-2-heptanol, tetrahydro 2-methyl-2-furanol, etc. |
| Phenols | Guaiacol, syringol, 2-methoxy-4-cresol, 4-ethylguaiacol, ethylphenol, o-cresol, m-cresol, p-cresol, 4-methyl-syringol, 4-ethyl-syringol, vanillin, apocynin, 4-allyl-syringol, phenol, 4-propylphenol, 2,4-xylenol, 3,5-xylenol, 3,4-xylenol, etc. |
| Neutral substances (including carbonyls) | Acetone, methyl acetate, 2-cyclopentenone, 3-octyl propionate, furfural, hexane-2,5-dione, 3-methyl-2-cyclopentenone, 5-methyl furfural, pentane-4-olide, butane-4-olide, 2-butene-4-olide, 3,5-dimethylcyclopentane-1,2-dione, pentane-5-olide, 2,6,10-trimethyl-5,9-undecadienal, nonane-4-olide, formaldehyde, acetaldehyde, propionaldehyde, valeraldehyde, butyraldehyde, methyl butyl ketone, methyl isopropyl ketone, methyl ethyl ketone, acrolein, etc. |

Of the components of acid liquid and bamboo vinegar, organic acids (e.g., acetic and propionic acids), alcohols (e.g., methanol, acetoin, and cyclotene), and neutral substances (e.g., acetone and furfural) are generated mainly from hemicellulose and cellulose [10]. Phenol components (e.g., phenol and cresol) are generated mainly through the decomposition of lignin [11]. Acetic acid, the principal component of acid liquid, is generated through the decomposition of the acetyl group of hemicellulose and the carboxyl group of uronic acid in wood. Methanol is generated mainly from the methoxyl groups of components [1, 2, 12, 13].

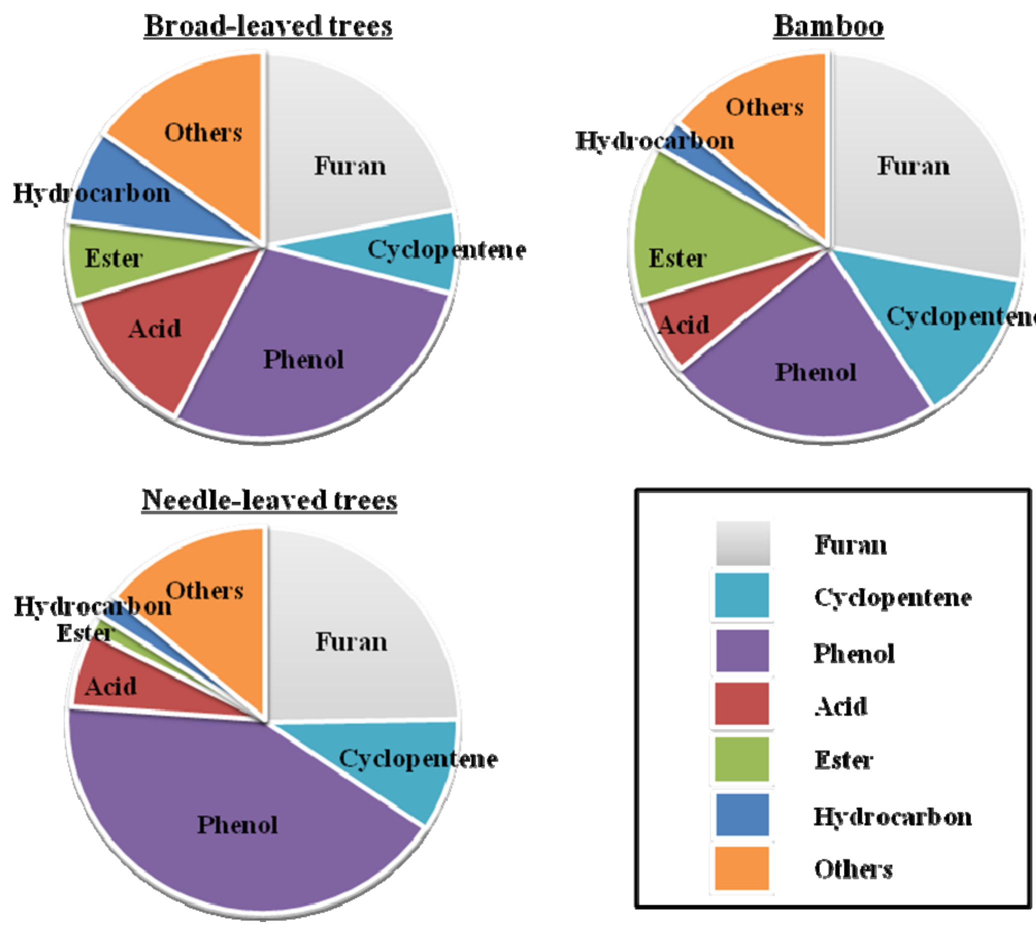


Figure 2. Odor components of acid liquid and bamboo vinegar

4. Odors of acid liquid and bamboo vinegar

The smoke generated during the thermal decomposition of woods or bamboos in a charcoal kiln has peculiar odors. The acid liquid and bamboo vinegar generated by cooling the smoke has the same odors. The thermal decomposition products of woods or bamboos have empyreumatic and fumigant odors, a complex odor of multiple components [14].

The odor of acid liquid varies with feeding materials. The odor components of acid liquid and bamboo vinegar produced from charcoal materials, i.e., broad-leaved trees (quercus and oak), needle-leaved trees (cedar and cypress), and bamboo (moso bamboo), are summarized in Figure 2 [15]. Principal odor components include acidic and neutral substances, such as phenols, cyclopentene, and furfural. Phenols, furans, and cyclopentenes are relatively abundant, accounting for 60% of all components. Representative compounds and their odor characteristics are summarized in Table 2. Phenols are more abundant in needle-leaved than in broad-leaved trees. Acids and acid esters are scarce in needle-leaved as compared with broad-leaved trees. Furans are most abundant in bamboos, followed by phenols and acids and acid esters. The principal components of the materials are similar. However, the kinds and composition ratios of these components and trace substances differ, thereby generating the different odors of acid liquid and bamboo vinegar.

Table 2. Odor components and characteristics of acid liquid and bamboo vinegar

| | Representative compounds | Odor characteristics |
|---|---|---|
| Acids and acid esters | Acetic acid methyl ester, propionic acid methyl ester, butanoic acid methyl ester, acetic acid, butanoic acid, etc. | Pungent acid smell Irritating odor |
| Phenols | Phenol, cresol, xylenol, etc. | Phenol and cresol odors |
| | Guaiacol, 2,6-dimethoxy phenol, etc. | Fumigant phenol odor |
| | 4-methyl-guaiacol, 4-methyl-2,6-dimethoxy phenol, etc. | Fumigant sweet odor |
| | 1,2-dimethoxy-benzene, 4-methyl-1,2-dimethoxybenzene, etc. | Vanilla odor |
| Cyclopentenes | 2-cyclopentenes (2,3-substitution product), etc. | Bitter odor |
| | 2-cyclopentenes (others), etc. | Grassy potato odor |
| Furans | Furfural, 2-acetylfuran, 5-methylfurfural, 2-methyl-3-pentanone, etc. | Sweet odor |

5. Functions and applications of acid liquid and bamboo vinegar

Acid liquid has various functions. These functions have been applied in many ways. Sales according to the applications of acid liquid are shown in Table 3 [16]. Acid liquid is mainly used for agriculture, livestock, and feedstuff. Table 4 shows recent investigations on the applications of acid liquid and bamboo vinegar [17-30]. The antibacterial properties of acid liquid and bamboo vinegar have been known empirically and investigated for a long time. We have investigated the antibacterial properties and functions of acid liquid and bamboo vinegar. Our investigations will be discussed below.

Table 3. Sales according to the applications of acid liquid in 2000

| Applications | Sales (ton) | % |
|---|---|---|
| Agriculture | 5,232.3 | 65.1 |
| Golf course | 7.7 | 0.1 |
| Livestock | 412.1 | 5.2 |
| Feedstuff additive | 530.8 | 6.6 |
| Repellent | 66.1 | 0.8 |
| Food industry | 1,128.7 | 14.1 |
| Deodorant | 264.6 | 3.3 |
| Bath | 349.3 | 4.3 |
| Disinfectant | 3.7 | 0.0 |
| Greening and gardening | 1.3 | 0.0 |
| Others | 41.5 | 0.5 |
| Total | 8,038.1 | 100.0 |

*: Prepared based on surveys by the Japan Charcoal and Fuel Association.

Table 4. Investigations on the applications of acid liquid and bamboo vinegar

| Kinds | Investigations on the applications of acid liquid and bamboo vinegar |
|---|---|
| Acid liquid and amboo vinegar | Deodorant [17], Smoke liquid (flavor, etc.) [17]<br>Compost manufacturing [6], Dyeing (dyeing of wood, etc.) [17]<br>Feedstuff additive [18], etc. |

| | |
|---|---|
| | Antibacterial and antifungal properties<br>(soil bacteria [19], damping-off pathogens of needle-leaved trees [20], soil-borne wheat mosaic virus [21], Trichophyton [22], etc.)<br>Nematocide [23], Deodorant [24], Antioxidant [8, 17]<br>Feedstuff additive (egg production, etc.) [25]<br>Insect repellent and insecticide (stink bug [26], fly [27], etc.)<br>Plant growth regulator [28, 29]<br>Mushroom fruit-body formation stimulant [30], etc. |

### 5-1. Antioxidative properties of acid liquid

Besides bacterial decomposition, the oxidization of dietary lipid (oil) is a major cause of food deterioration. Lipid oxidation generates various oxidized products. The oxidized products may cause sour odors and toxicities [31]. Antioxidants play an important role in preventing these. Smoke liquid and odor have traditionally been used for foods mainly because of their antioxidative activities. Tilgner reported the antioxidative activities of smoke. The antioxidative activities are mainly caused by phenolic compounds [32]. Acid liquid may contain similar components. Thus, the antioxidative activities of acid liquid were investigated [8]. Figure 3 shows the antioxidative activities determined by the iron thiocyanate method. Bamboo vinegar and quercus acid liquid had higher antioxidative activities than those of α-tocopherol, a well-known natural antioxidant. Larch acid liquid had high antioxidative activities, although lower than those of α-tocopherol. Antioxidative activities vary with measurement methods. However, the antioxidative activities of acid liquid were comparable between iron thiocyanate and other methods. Of acid liquid components, syringyl phenolic compounds had markedly high antioxidative activities. These substances were relatively abundant in acid liquid made from broad-leaved trees (e.g., quercus) and bamboo vinegar, but were scarce in needle-leaved trees (e.g., larch). These results suggest the usefulness of acid liquid made from broad-leaved trees and bamboo vinegar as antioxidants.

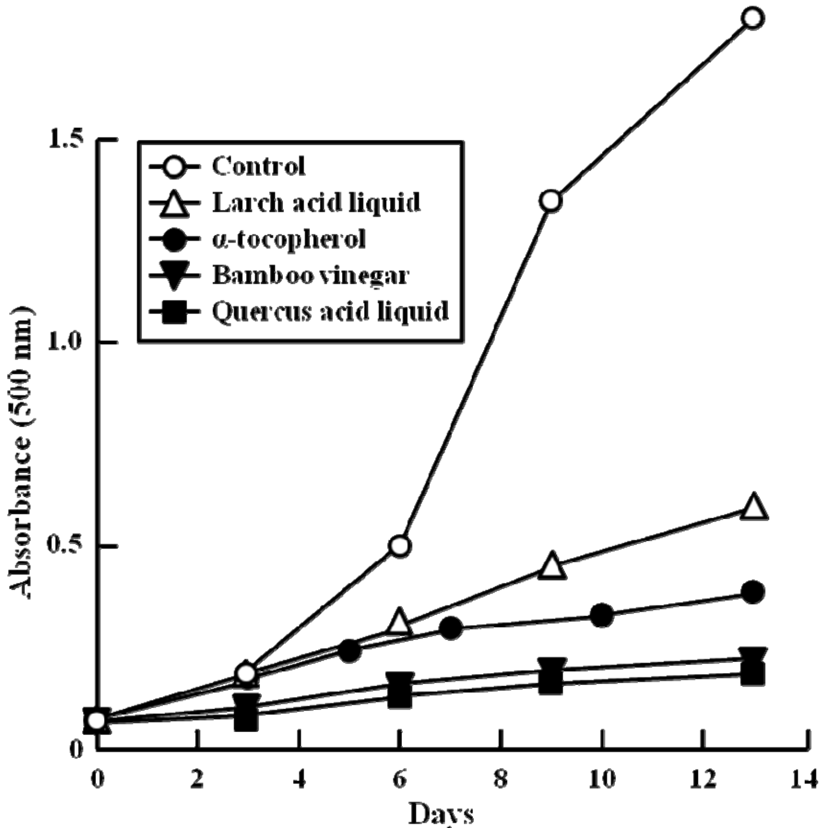


Figure 3. Antioxidative activity of acid liquid extracted with benzene, determined by the iron thiocyanate method.

5-2 Functions of acid liquid odors

Distinctive acid liquid odors may have effects on various organisms. Study examples are given below.

5-2-1 Acid liquid odors as plant growth regulators

The effects of acid liquid and bamboo vinegar odors, generated at around room temperature, on plant growth, etc., are shown in Figure 4 [15)]. Acid liquid and bamboo vinegar markedly suppress plant growth. The suppressive activity was enhanced by increasing the test liquid, suggesting the involvement of odor components. Major odor substances were investigated to explore substances involved in the suppressive activity. The results are shown in Figure 5. All the odor substances suppressed plant growth. Of these substances, acetic acid, acetic acid methyl ester, and furfural had marked suppressive activities. The suppressive activities remained high even if the amounts were reduced to one-tenth. Acid liquid odors can transiently, but not completely suppress plant budding and growth depending on their amounts. Thus, a acid liquid solution is not sprayed on leaves, but acid liquid odor is diffused into the atmosphere. For example, acid liquid should be used to adjust the shipping time of crops grown in greenhouses and control plant growth in nurseries.

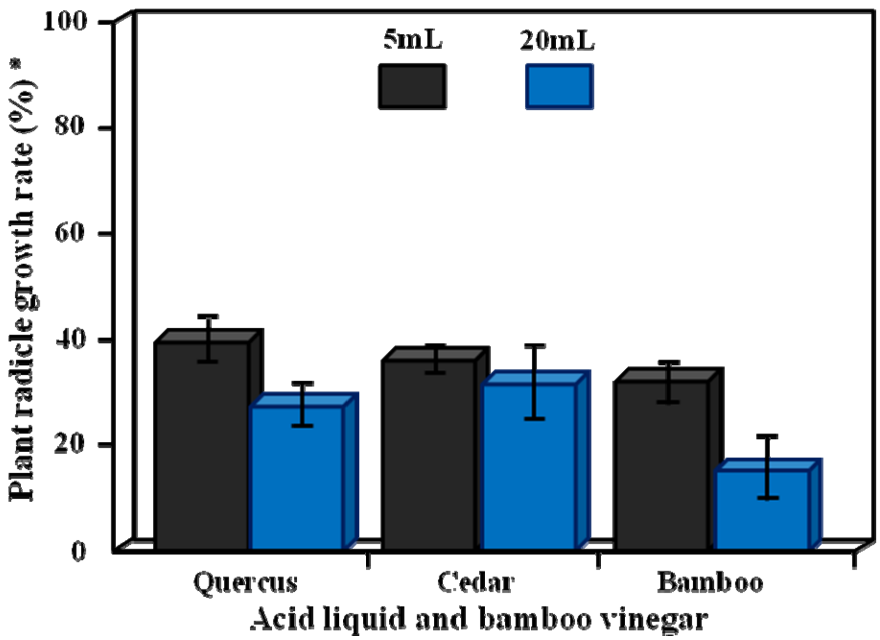


Figure 4. Effects of acid liquid and bamboo vinegar odors on plant growth

*: Percentages of the control value (%)

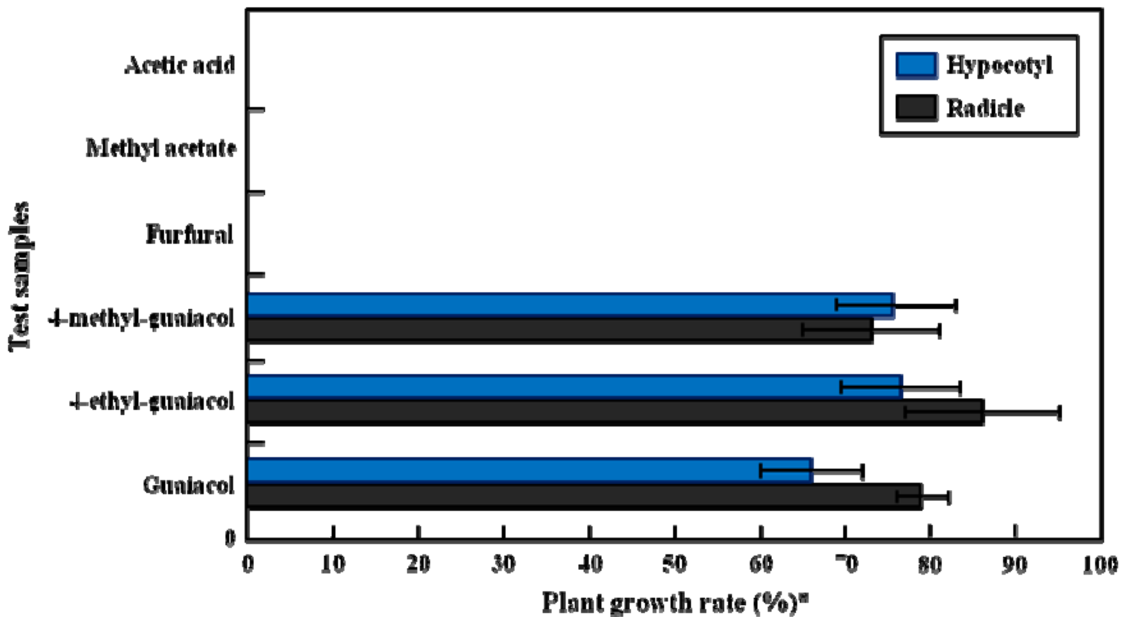


Figure 5. Effects of the principal odor components of acid liquid and bamboo vinegar on plant (radish) growth

*: Percentages of the control value, Mean ± SD (N=10)

5-2-2 Acid liquid odors as bacterial growth suppressors

The effects of acid liquid odors on bacteria have also been investigated. Terashita et al. [33] investigated the effects of volatile acid liquid on bacteria. As a result, the mycelial growth of plant disease pathogens (*Fusarium oxysporum*, *Rhizoctonia solani*, and *Rosellinia necatrix*) was inhibited (Figure 6). Additionally, components other than acid liquid odor components did not inhibit mycelial growth, suggesting the antibacterial effects of the odor components. Furthermore, Terashita et al. [33] investigated acetic acid, a major odor component, to identify an antibacterial substance, and demonstrated that acetic acid completely inhibited mycelial growth at the same concentration as the acetic acid contained in acid liquid.

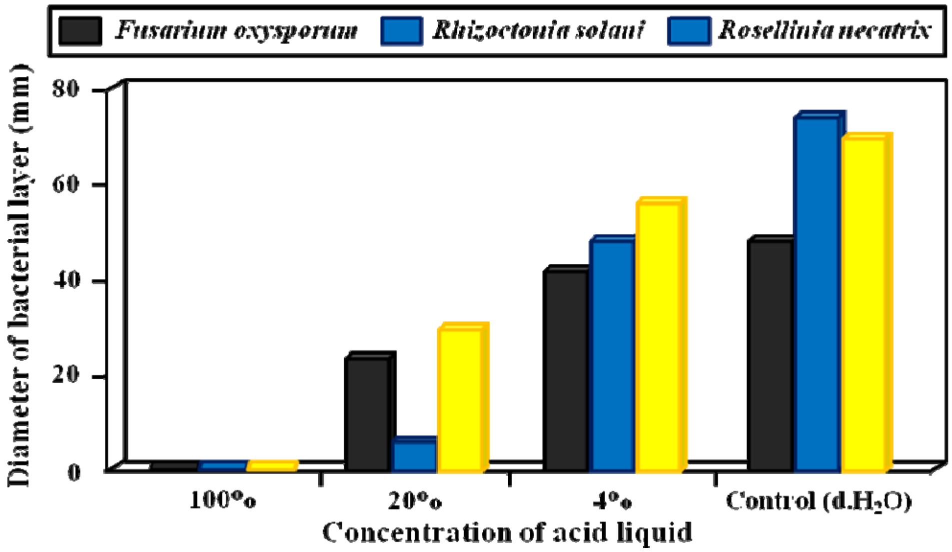


Figure 6. Effects of volatile quercus acid liquid on the mycelial growth of plant disease pathogens

6. Properties of acid liquid made from the waste materials of construction and forest lands

Recently, various waste materials are being carbonized for resource recycling. The properties of charcoal and thermal decomposition liquid obtained through wood pyrolysis have been investigated. Study examples on the waste materials of construction and forest lands are described below.

6-1 Acid liquid made from medium-density fiberboard

Medium-density fiberboard (MDF) is a main wood material used for construction and furniture. Pyrolysis has attracted attention as a procedure for resource recycling. Acid liquid obtained by carbonizing the material may be contaminated with the thermal decomposition products of adhesive besides natural wood. Thus, the acid liquid may have a distinctive odor. Table 5 shows the analytical results of acid liquid made from MDF with urea resin applied as an adhesive. Nitrogen-containing compounds were extracted from detected substances [34]. Twenty substances were detected and identified, suggesting that various nitrogen-containing compounds were contained. These substances were barely detectable in acid liquid made from wood, suggesting that they were generated through the reaction of urea resin or reaction between urea resin and wood. Some of these substances may be hazardous. Thus, acid liquid should be used with caution for safety reasons. No conclusion can be drawn for all materials from this study on MDF. However, caution should be exercised when using acid liquid made from materials containing artificial substances.

Table 5. Components of acid liquid made from MDF

| Carbonized samples | Nitrogen-containing compounds in acid liquid |
|---|---|
| MDF | Triethlamine, pyridine, pyrazine, 2-Methy-pyridine, N-Methyl-formamide, N, N-Dimethyl-formamide, Methyl-pyradine, Methyl-pyrimidine, N, N-Dimethyl-acetamide, N-Methyl-propanamide, Methyl-1H-imidazole, Acetamide, Propanamide, 2-Pyrimidinamine, Butanamide, 2-Amino-4-methylpyrimidine, N, N-Dimethyl-urea, Trimethyl-isocyanurate, Methyl-1H-pyrazole, 3-Pyridinol |
| Urea resin | Acetnitrile, N, N-Dimethyl-formamide, 2-Pyrimidinamine, N-Methyl-formamide |

6-2 Acid liquid made from the waste materials of forest lands (needle-like leaves of cedar)

Cedar, a representative forest tree in Japan, is frequently used for construction. However, needle-like leaves produced in large amounts during tree trimming and pruning are barely used. Their efficient use for resource recycling is desired. In the present study, the pyrolysis of needle-like leaves of cedar was investigated to find some interesting properties of pyrolysis products. Needle-like leaves air-dried for about 1 hour (dried leaves) were processed in a simple pyrolysis furnace to generate a thermal decomposition liquid like acid liquid. This acid liquid-like liquid was compared with acid liquid to demonstrate that this liquid contained terpenes in small amounts, phenols at the same percentages as those of acid liquid, and furans and cyclopentanes at lower percentages than those of acid liquid. Fatty acids contained at high percentages included acetic, hexadecanoic, 14-pentadecenoic, propanoic, pentadecanoic, octanoic, and butanoic acids. The terpenes included monoterpenes (α-pinene, sabinene, limonene, etc.) and diterpenes (16-kaurene, ferrugino, etc.), which are contained in essential oils at high percentages [35]. Thus, the thermal decomposition liquid obtained from dried cedar leaves contained known biological substances in large amounts, suggesting various potential functions.

## 7. Conclusions

Pyrolysis is a promising recycling procedure for biomass. More beneficial pyrolysis products will be effectively utilized. More efficient pyrolysis procedures should be developed to recycle biomass resources generated in large amounts.

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