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Physicochemistry and Utilization of Wood Vinegar from Carbonization of Tropical Biomass Waste

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Abstract

Pyroligneous acid also called wood vinegar is an aqueous liquid produced from pyrolysis of lignocellulose waste and biomass. In general, the pyrolysis types are classified base on heating rate mainly either fast or slow pyrolysis. The characteristic and properties of wood vinegar are primarily influenced by the type of carbonaceous feedstocks as well as the production techniques. Wood vinegar is a complex mixture of polar and non-polar chemicals with various molecular weights and compositions. Its major constituent is water (80–90%). Some physical properties; such as pH, specific gravity, dissolved tar content are, respectively, within the range of 2–4, 1.005–1.016 g/mL, 0.23–0.89% wt, and color, odor and transparency have been reported. In addition, the degree of °Brix was ranged between 1.7 and 6.6. Besides water, the chemical compositions of wood vinegars consisted of acetic acid with the largest component (30.45–70.60 mg.mL⁻¹). A high number of phenol derivatives have been found and those in higher concentrations were 4-propyl-2-methoxyphenol (5–11 mg.mL⁻¹) followed by 2-methylphenol (2–4 mg.mL⁻¹). Wood vinegar has been regarded as a natural product, which claimed to be capable in several fields of application. In agriculture, wood vinegar has been used in vegetable cropping in order to combat disease, pest control, improve growth and fruit quality, seed germination accelerator as well as herbicide. In pharmaceutical and medical applications, it is used for the preparation of detoxification pad while in veterinary and animal production, incorporation of the wood vinegar in feed could promote acidity in large intestine to inhibit growth of enteropathogenic microbes. In food processing, wood vinegar has a characteristic smoke flavor, and also exhibits microbial growth inhibition. In addition, several investigators reported that bio-oil and wood vinegar obtained from fast pyrolysis and carbonization showed a high potential on organic wood preservative. In summary, the wood vinegar prepared from the tropical wood and/or biomass waste is widely beneficial. The chapter attempts to provide essential knowledge relevant to physicochemical characteristics of wood vinegar and its applications.

Keywords: wood vinegar, carbonization, physicochemistry, tropical biomass, utilization

1. Introduction

Pyroligneous acid also called wood vinegar is an aqueous liquid produced from pyrolysis of lignocellulose waste and biomass. They are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, lignin and other constituents of biomass. Those biopolymers were broken into smaller molecule with high temperature under air less atmospheres. The crude condensate smoke during pyrolysis was so called bio-oil. In order to prepare wood vinegar, this liquid is stand in a closed container for at least 3 months and decanted from sedimentation tar of bio-oil. The transparent solution in upper phase is practical wood vinegar. It has a special smoky odor and color is light yellow to brown depending on feedstock properties and pyrolysis system used for preparing it. The wood vinegar was very complex solution; the major proportion was water (80–90%) and minor proportion was more than 200 species of organic compounds. Recently, wood vinegar has been widely applied for various proposes such as medicinal, smoky aroma, food and platelet aggregation and anti-dermatophyte activity in pharmaceuticals [1, 2]. In particular, in organic agriculture, a great number of toxic-chemicals were replaced by wood vinegar, a natural product, which has been used to combat disease and pests, stimulate plant growth, improve the quality of fruit, accelerate the speed of plant seed germination and serve as herbicides [3]. However, the physicochemistry and biological activity of wood vinegar are affected by many factors such as chemical composition of biomass, pyrolysis system and refining method.

2. Definition of wood vinegar

The crude liquid obtained by condensation of an output, gas phase and smoke, during charcoal production process is called bio-oil. After standing the crude liquid in a closed container at ambient temperature for about 3 months, it will be separated into 2 phases. A clear solution of upper phase is wood vinegar or pyroligneous acid, while the lower phase is tar sediment. The acid has smoky odor, and color may vary from light yellow to dark brown (**Figure 1**).

3. Factors influencing properties of wood vinegar

Wood vinegar is a complex mixture of polar and non-polar compounds that varies widely in their property among samples that may be observed. These are primarily influenced by the type of carbonaceous feedstocks as well as production techniques.

3.1. Feedstock

In general, cellulose (42–45%), hemicellulose (28–35%), and lignin (16–33%) are major constituents of the plant cell wall, which are primary components of wood, while water-soluble and organic-soluble compounds are the minor compounds [4]. The biopolymers and minor compounds are arranged in a complex structure as illustrated in **Figure 2**. It should be noted that

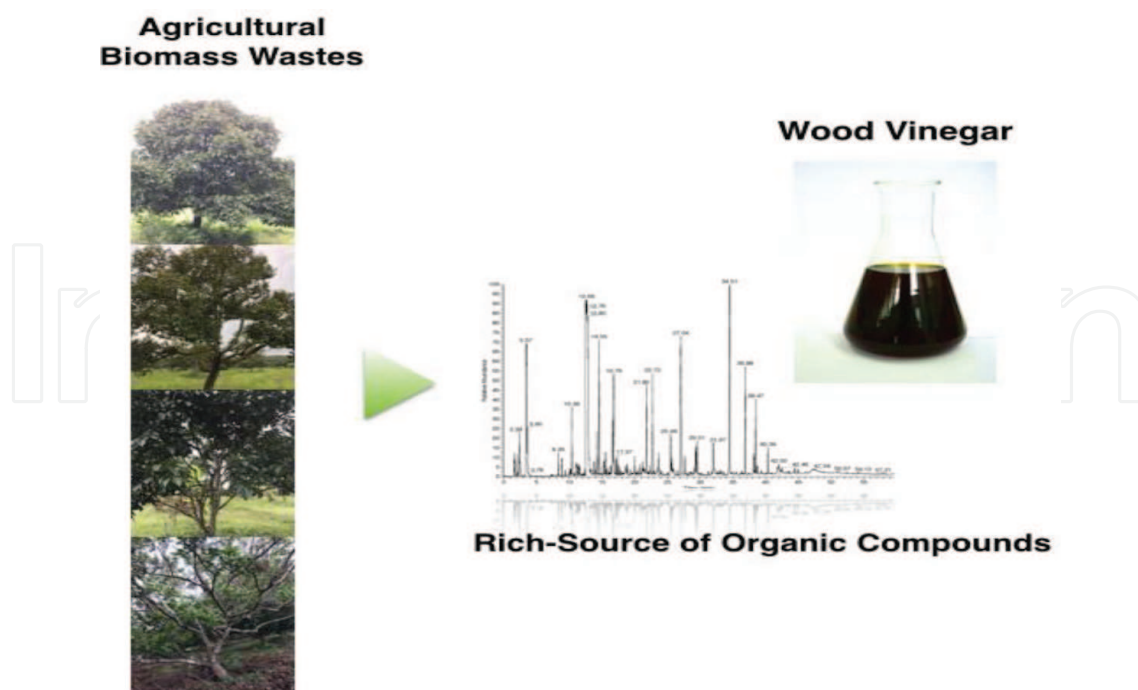


Figure 1. Wood vinegar from agricultural biomass waste.

variations in proportion of the constituents are not only depends on the plant species, but are also influenced by other factors such as habitat, age, part of the tree, etc. Hence, it could be deduced that variations in composition of feedstock used for the preparation of wood vinegar might give rise to different properties of the product.

Cellulose is a long-chain linear polymer of glucose that contains crystalline arrangements with smaller amorphous regions. There are arranged as micro-fibril which contributes to the structural component of the cell wall. In general, a similar content at approximately 43% wt is found in both hardwood and softwood [6].

Hemicellulose is shorter or branched amorphous polymer of five-or six-carbon sugars which naturally are associated with cellulose and lignin to form the matrix. The sub-units of hemicellulose in hardwoods and herbaceous plants such as wheat straw, cornstover and switch grass consist mainly of D-xylose, whereas D-mannose, D-xylose and D-galactose are the principal constituents in softwood [7].

Lignin, the third cell wall component, is a three-dimensional polymer formed from phenyl propane units with many different types of linkages between the building blocks. The main building blocks in the biosynthesis of hardwood and softwood lignin are different in structure. In softwoods, guaiacyl lignin is predominantly found resulting from polymerization of a higher fraction of conifer phenyl propane units. In hardwood, guaiacyl-syringyl lignin is present. It is a copolymer between coniferyl and sinapyl phenyl propane units where sinapyl unit fraction is higher than that in softwood lignin [8].

The water-soluble and organic-soluble compounds may be extracted from the lignocellulose biomass. For instance, the organic-soluble compounds in wood include terpenes, fats, waxes, phenolic compounds, hydrocarbons and sugars, while the water-soluble compounds are

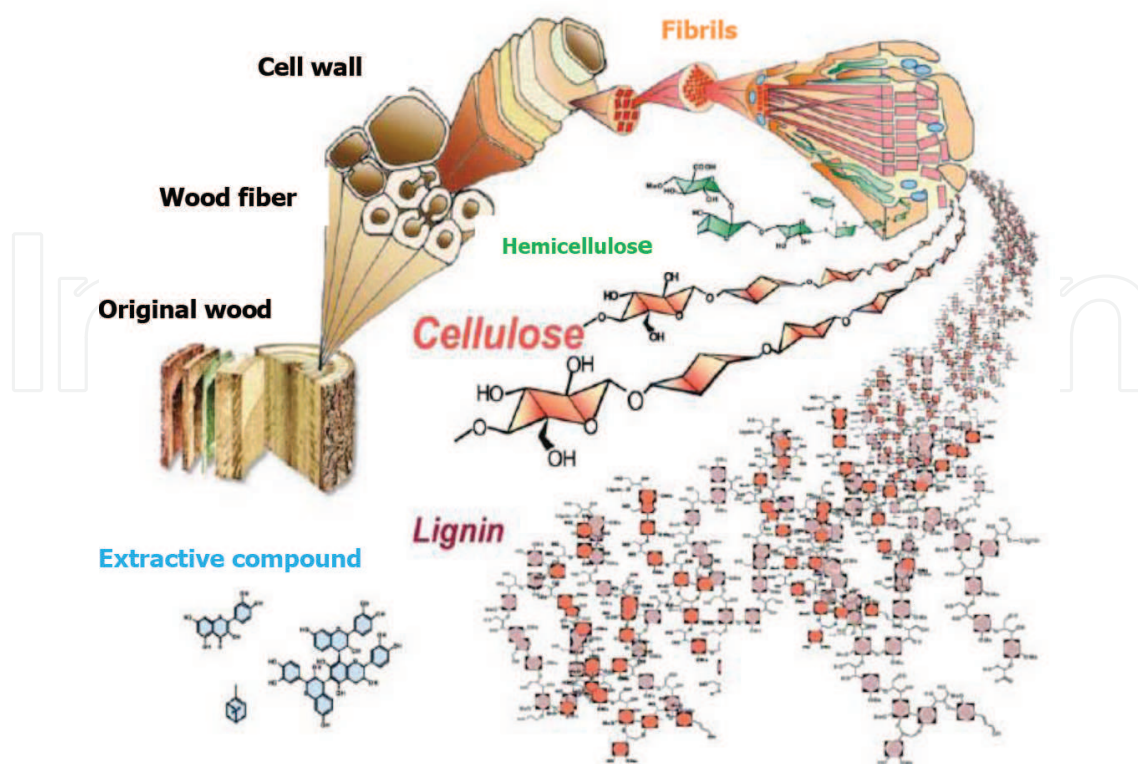


Figure 2. Composition of wood, illustrating the structure of lignocellulosic biomass [5].

sodium and potassium salts. In general, herbaceous biomass typically contains significant amounts of inorganic salts and organic-soluble compounds which may be found at approximately 15 and 20%wt, respectively. In contrast, in common woods, there are usually lower content which the inorganic salts and organic-soluble compounds may be found at approximately 0.3–0.4%wt and 2–3%wt, respectively [9].

3.2. Pyrolysis processes and preparation of wood vinegars

Pyrolysis is mainly technology used to produce wood vinegar with thermal degradation of organic material. According to this system, the larger molecules were transformed to smaller with high temperature and air less condition. Pyrolysis technology has been continuously developed to support various purposes. In general, the pyrolysis types were classified based on heating rate mainly fast and slow pyrolysis.

Fast pyrolysis is an advance process in which biomass is rapidly heated to moderate temperature of around 500°C and short residence time of typically less than 2 seconds. Fast pyrolysis kinetic of wood constituents determined the rate of thermal breakdown as presented in **Figure 3**. Hemicelluloses are fast decomposed in temperature range from 200 to 300°C and cellulose is the least stable polymer decomposed from 300 to 400°C. Lignin exhibits intermediate thermal degradation behavior from 250 to 500°C. Thermal decomposition studies on separated lignin will not necessarily match the pyrolysis behavior of this component when it is present in the original biomass [10]. Typical product yields, dry wood basis, consisted of

liquid, char and gas at 75, 12 and 13% respectively [11]. The main objective of developing fast pyrolysis is to generate an enhanced fuel for generating heat and power. Fast pyrolysis technology has long been developed as a thermochemical conversion technology to produce high yields of bio-oil from biomass [4].

Slow pyrolysis is a simple technology that has been practiced by the ancient Chinese. It has long been known as carbonization. The reaction is a thermal conversion process where wood or other biomass material is slowly heated in the absence of air or oxygen up to final temperature of about 500°C. In slow pyrolysis, hemicelluloses are degraded in temperature range from 200 to 260°C, cellulose at 240–350°C and lignin at 280–500°C [12]. Charcoal is most important product with about 30% of wood slow pyrolysis. It has long been used for heating, cooking, and industrial purposes. Bio-oil content was about 30% and gas content was about 35%.

In Asia, slow pyrolysis was used to prepare charcoal. With the current increasing concern in regard to environment issues, the smoke from charcoal making could be called a pollutant. The wood vinegar produced by smoke from charcoal making has many benefits such as stimulating vegetables and plant growth, anti-harmful microorganisms [10]. Today, however, there is much diversity of charcoal wood including thinned wood, sawdust and backboard dust produced by sawmills, bark, windfall trees, dead trees, waste wood from agriculture and demolished buildings, bamboo, straw and rice husks. Different charcoal wood requires a different carbonization kiln but the principle of charcoal-making, i.e. baking charcoal wood by regulating the airflow, remains the same for all types of kilns. Similarly, the principle of recovering bio-oil has remained unchanged. To recover bio-oil, the chimney is placed above the smoke outlet of the charcoal kiln while a container is placed in the lower end of the chimney to collect the dripping, condensed liquid.

The color of the smoke produced in the carbonization of wood changes depending on the progress of this process. These are used as an impotent indicator to recover bio-oil. When carbonization starts, the white smoke first appears. This is wet smoke because the water

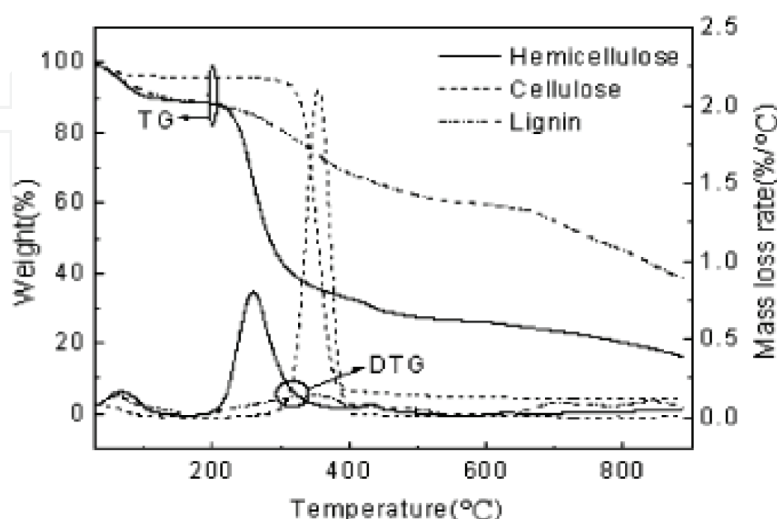


Figure 3. Fast pyrolysis kinetics of hemicellulose, cellulose, and lignin: TG = thermogravimetry; DTG = differential thermogravimetry [10].

contained in charcoal wood comes out as steam. At this stage, temperature inside kiln and the smoke out of the chimney are about 300 and 80°C, respectively. After that the color of the smoke changes to a mixture of white and yellowish brown with an irritating burning smell then the color changes back to white within a short time. The white smoke reappears and the smell changes to a sweet smell. The temperature inside kiln and the smoke out of the chimney is lower than 300°C and range from 80 to 150°C. This stage recommends as the optimal condition to recover bio-oil [13].

On wood vinegar preparation, the crude bio-oil solution is kept in a closed container and stands at ambient temperature for about 3 months. The solution then will be separated into 2 phases; the clear upper phase that is wood vinegar is drained off, while the lower phase is called tar sediment.

4. Physicochemical properties of wood vinegars

Wood vinegar is a complex mixture of polar and non-polar chemicals with varying molecular weights and compositions, which depends upon feedstock and processing condition. Some physical properties such as pH, specific gravity, color, odor, dissolved tar content, ignition residue and transparency have been reported. Due to the presence of organic acids such as acetic acid, formic acid and propionic acid, the acidity of wood vinegar is often in the range of pH 2–4. Total soluble tar contents were found within a range of 0.23–0.89% wt. The specific gravity and °Brix was reported within a range of 1.005–1.016 g/mL and 1.7–6.6, respectively [3, 14].

The major proportion in wood vinegar is water (80–90%) that is a result of feedstock dehydration. Water is usually miscible with the oligomeric lignin-derivative components because of the solubilizing effect of other polar hydrophilic compounds, low-molecular-weight acids,

Sample	Physical and chemical parameters								
	pH	SG (g.mL ⁻¹)	TAC ^b (% by weight)	pKa	Total soluble tar (% by weight)	Degree Brix	$\lambda_{\max}$ (nm)	A _{max}	Water content (% by weight)
<i>L. leucocephala</i> 1	3.40	1.006 ± 0.000	4.47 ± 0.01	4.70	0.37 ± 0.02	3.80 ± 0.10	274.50	154.00 ± 5.00	91.13 ± 0.27
<i>L. leucocephala</i> 2	3.10	1.007 ± 0.000	4.61 ± 0.02	4.70	0.57 ± 0.01	4.60 ± 0.10	270.80	375.50 ± 6.20	84.54 ± 0.02
<i>A. indica</i> 1	3.40	1.004 ± 0.000	3.28 ± 0.03	4.70	0.37 ± 0.02	3.00 ± 0.10	273.40	150.50 ± 5.00	91.50 ± 0.06
<i>A. indica</i> 2	3.20	1.005 ± 0.000	3.16 ± 0.04	4.70	0.58 ± 0.03	3.40 ± 0.10	271.00	298.00 ± 6.50	93.48 ± 0.15
<i>E. camaldulensis</i> 1	3.10	1.006 ± 0.000	4.62 ± 0.04	4.70	0.57 ± 0.02	4.60 ± 0.10	272.60	221.00 ± 5.00	89.44 ± 0.25
<i>E. camaldulensis</i> 2	3.50	1.008 ± 0.000	3.62 ± 0.03	4.70	0.49 ± 0.02	3.40 ± 0.10	270.80	393.00 ± 8.00	90.37 ± 0.20
<i>H. brasiliensis</i>	2.90	1.012 ± 0.000	4.92 ± 0.02	4.70	0.96 ± 0.03	6.00 ± 0.20	268.00	467.00 ± 7.00	85.30 ± 0.50
<i>D. asper</i>	2.90	1.010 ± 0.000	4.92 ± 0.02	4.70	0.71 ± 0.01	5.60 ± 0.20	269.20	470.00 ± 6.00	81.44 ± 0.26

Table 1. Physicochemical property of eight wood vinegars from five wood species [15].

Compound	Concentration (mg.mL ⁻¹)							
	<i>L. leucocephala</i> 1	<i>L. leucocephala</i> 2	<i>A. indica</i> 1	<i>A. indica</i> 2	<i>E. camaldulensis</i> 1	<i>E. camaldulensis</i> 2	<i>D. asper</i>	<i>H. brasiliensis</i>
Organic acidic								
Acetic acid	40.26 ± 1.02	55.98 ± 1.22	37.38 ± 0.04	35.26 ± 0.15	65.29 ± 0.02	32.49 ± 0.08	69.34 ± 0.17	70.60 ± 0.20
Alcohol derivatives								
Methanol	3.92 ± 0.04	8.12 ± 0.27	3.85 ± 0.66	3.80 ± 0.07	3.62 ± 0.03	6.13 ± 0.14	4.43 ± 0.09	4.52 ± 0.05
n-Propanol	ND	ND	ND	ND	ND	0.02 ± 0.00	ND	ND
n-Butanol	ND	ND	ND	ND	ND	ND	ND	ND
Σ Alcohol derivatives	3.92	8.12	3.85	3.80	3.62	6.15	4.43	4.52
Furfural and furan derivatives								
2-Furfuraldehyde	0.45 ± 0.00	3.06 ± 0.01	0.60 ± 0.02	4.06 ± 0.02	2.24 ± 0.01	5.23 ± 0.01	2.69 ± 0.03	0.67 ± 0.01
Methyl-2-furoate	0.18 ± 0.01	0.74 ± 0.01	0.08 ± 0.00	0.37 ± 0.01	0.41 ± 0.01	0.87 ± 0.01	0.62 ± 0.02	0.13 ± 0.01
2-Methylfuran	0.23 ± 0.01	0.54 ± 0.01	0.27 ± 0.00	0.31 ± 0.01	0.39 ± 0.01	0.34 ± 0.00	0.79 ± 0.02	0.55 ± 0.03
Σ Furfural and furan derivatives	0.86	4.34	0.95	4.74	3.04	6.44	4.10	1.35
Phenol derivative								
Phenol	0.94 ± 0.01	0.95 ± 0.01	0.75 ± 0.01	0.54 ± 0.02	0.45 ± 0.01	1.01 ± 0.01	0.67 ± 0.01	0.46 ± 0.02
2-Methylphenol	3.82 ± 0.02	2.85 ± 0.01	2.76 ± 0.01	1.57 ± 0.01	2.07 ± 0.01	3.17 ± 0.01	2.16 ± 0.11	4.06 ± 0.06
3-Methylphenol	1.67 ± 0.01	0.78 ± 0.68	0.68 ± 0.00	0.69 ± 0.01	0.61 ± 0.00	1.28 ± 0.05	0.05 ± 0.00	0.32 ± 0.0
4-Methylphenol	0.11 ± 0.00	0.19 ± 0.01	0.07 ± 0.00	0.13 ± 0.01	0.04 ± 0.00	0.16 ± 0.00	0.09 ± 0.00	0.04 ± 0.00
2-Ethylphenol	0.03 ± 0.00	0.03 ± 0.00	ND	0.02 ± 0.00	ND	0.03 ± 0.00	0.06 ± 0.00	0.03 ± 0.00
2,6-Dimethylphenol	ND	0.03 ± 0.00	ND	ND	ND	0.05 ± 0.00	0.42 ± 0.00	ND
2,5-Dimethylphenol	0.29 ± 0.01	0.10 ± 0.00	0.17 ± 0.01	0.07 ± 0.00	0.13 ± 0.01	0.24 ± 0.00	0.20 ± 0.00	0.12 ± 0.00
2,4-Dimethylphenol	ND	0.26 ± 0.22	ND	0.21 ± 0.01	ND	ND	ND	ND
2,3-Dimethylphenol	0.06 ± 0.00	0.04 ± 0.00	ND	0.03 ± 0.00	ND	0.04 ± 0.00	0.05 ± 0.00	ND
Σ Phenol derivatives	6.92	5.23	4.43	3.26	3.30	5.98	3.70	5.03
Methoxyphenol derivatives								

Compound	Concentration (mg.mL ⁻¹)							
	<i>L. leucocephala</i> 1	<i>L. leucocephala</i> 2	<i>A. indica</i> 1	<i>A. indica</i> 2	<i>E. camaldulensis</i> 1	<i>E. camaldulensis</i> 2	<i>D. asper</i>	<i>H. brasiliensis</i>
4-Propyl-2-methoxyphenol	6.90 ± 0.05	8.92 ± 0.03	5.88 ± 0.03	6.43 ± 0.03	5.54 ± 0.02	5.54 ± 0.02	11.56 ± 0.04	9.56 ± 0.01
4-Methyl-2-methoxyphenol	1.51 ± 0.01	3.09 ± 0.01	0.24 ± 0.00	1.51 ± 0.02	0.89 ± 0.01	1.27 ± 0.01	2.59 ± 0.06	2.23 ± 0.01
4-Ethyl-2-methoxyphenol	1.46 ± 0.02	3.10 ± 0.02	0.20 ± 0.01	1.85 ± 0.01	0.91 ± 0.01	1.34 ± 0.02	2.81 ± 0.02	2.33 ± 0.01
Guaiacol	0.40 ± 0.00	0.42 ± 0.00	0.66 ± 0.01	1.17 ± 0.01	0.51 ± 0.01	0.36 ± 0.01	1.33 ± 0.04	4.28 ± 0.02
Eugenol	0.27 ± 0.01	0.21 ± 0.02	ND	2.41 ± 0.02	0.06 ± 0.00	0.21 ± 0.01	5.23 ± 0.02	2.16 ± 0.02
Syringol	1.20 ± 0.02	2.01 ± 0.01	0.93 ± 0.01	3.15 ± 0.02	2.62 ± 0.02	3.88 ± 0.01	3.57 ± 0.02	0.06 ± 0.00
Acetovanillone	ND	ND	ND	ND	ND	ND	0.18 ± 0.00	ND
Σ Methoxyphenol derivatives	11.74	17.75	7.91	16.22	10.53	12.60	27.27	20.62
Σ Total phenol derivatives	18.66	22.98	12.34	19.48	13.83	18.58	30.97	25.65
1,2 Dihydroxybenzene	ND	ND	ND	ND	0.18 ± 0.00	ND	0.18 ± 0.01	ND

Table 2. Chemical compositions of eight wood vinegars from five wood species [15].

alcohols, hydroxyaldehydes, and ketones, mostly originating from the decomposition of carbohydrates.

The minor proportions of 10–20% wt are water-soluble organic compounds. These comprise of acids, alcohols, aldehydes, ketones and sugars. It appears that acetic acid is the highest proportion [14] in this fraction. The other components are also found, for instance, phenols and monolignols (guaiacol and syringol) which are degradation products from lignin. Levoglucosan, levoglucosenone, furfural, substituted furan, are derived from cellulose. The simpler organic molecules are converted from fats, mucilage, wax, alkaloids, and terpenoids. For inorganic salts and metallic complex are commonly reduced to ash.

The physicochemical characteristics of eight wood vinegars from the carbonization of five wood species—*Leucaena leucocephala* (Katin), *Azadirachta indica* (Sadao), *Eucalyptus camaldulensis*, *Hevea brasiliensis* (rubber wood) and *Dendrocalamus asper* (bamboo), which were produced by heating wood samples up to 400°C in a Thai-Iwate kiln showed the pH of 2.9–3.5, total soluble tar of 0.325–0.963% by weight and total soluble tar not more than 3%. The values of the specific gravity of only two products, from rubber wood (1.012 g mL⁻¹) and bamboo (1.010 g mL⁻¹) were within the acceptance criteria of quality assessments of Japan's standards, **Table 1** [15]. Chemical compositions of wood vinegars consisted of acetic acid as the largest component (30.45–70.60 mg mL⁻¹). A high number of phenol derivatives (16 compounds) were found and those in higher concentrations were 4-propyl-2-methoxyphenol (5–11 mg mL⁻¹) followed by 2-methylphenol (2–4 mg mL⁻¹), **Table 2**.

However, it has been showed that wood vinegar is unstable during prolong storage or aging process. The viscosity of the mixture gradually increases and phase separation is slowly occurs. Apart from sedimentation of a high-density particle and colloidal matter, this might be a result from the series of chemical reaction such as an aldol condensation reaction between aldehydes and alcohols, and self-aggregation of aldehydes with those of reactive oligomers. In addition, the metallic components may also play important role as reaction catalysis [16].

5. Quality of wood vinegars

As mentioned earlier, there are wide variations in the property of wood vinegar due to its mixture of many compounds with different concentrations. However, Japan Pyroligneous Liquor Association, an industrial body for pyroligneous liquor trader sets 7 parameters in order to standardize a good quality of the product. These are included pH value of around 3.0, standard specific gravity around 1.010–1.050, color should be a pale yellow, bright brown or reddish brown, has a marked smoky odor, the dissolved tar content should not more than 3%, ignition residue should not more than 0.2%, and exhibit transparency without suspended solid matter [13]. However, Fagernäs et al. [12] stated that the commercialized wood vinegar in European Unions (EU) has not been accepted because quality is widely varies. Accordingly, attention should be paid to obtain knowledge base on the preparation processes and quality control using a practical and cheap procedure.

The quality assessments of wood vinegars in Thailand were determined according to criteria from the Japan standard with slightly modification. Eight wood vinegars from the carbonization of five wood species—*Leucaena leucocephala* (Katin), *Azadirachta indica* (Sadao), *Eucalyptus camaldulensis*, *Hevea brasiliensis* (rubber wood) and *Dendrocalamus asper* (bamboo) grown in Thailand, which produced by heating wood samples up to 400°C in a Thai-Iwate kiln showed that all wood vinegar samples appeared to be good quality in terms of odor, color and transparency. An acetic acid concentration from the eight samples whose presence was indicated by pKa at 4.7 (**Table 1**) was mainly responsible for the pH values as shown in the good correlations of plots between pH and acetic acid concentrations (Correlation coefficient, $R = 0.92$). The specific gravity showed good correlations with total soluble tar and degree Brix ($R = 0.87$ for both); in turn the degree Brix showed good correlation with the total soluble tar ($R = 0.87$). Thus, the degree Brix which was easy to determine could be used as a general indicator of total soluble tar. The amount of total soluble tar signified the presence of phenolic compounds, of which previous studies suggested antifungal activity and usefulness as wood preservatives. In addition, phenolic compounds were also confirmed by the ultraviolet absorption maximum (λ_{max}) at 268–274 nm, [15].

6. Semi-purification of wood vinegars

The crude wood vinegar, bio-oil, is very complex solution contained with at least 200 constituents. Some of those components can be prone to such complex reaction as oxidization and polymerization. Physicochemical characteristics of wood vinegar produced from different sources even between producing batch in the same source have very high variability. It will bring to the inconsistency on the utilization efficiency. Therefore, if wood vinegar is to be a future source of natural chemicals production with consistence activity, an effective separation method must be developed to generate semi-purified bioactive components. Several methods such as standing, filtering, distillation and solvent extraction have been developed for semi-purified and classified components. In order to obtain more specific and consistent property of product, the wood vinegar may be fractionated into semi-purified product. These could be achieved by several techniques such as sedimentation, filtration, chromatography, distillation and solvent extraction.

6.1. Standing method

This is used to prepare wood vinegar from crude bio-oil. It is simplest and most highly efficient method that keep crude bio-oil standing in a container. When left standing, the unstable constituents in raw wood vinegar are oxidized or polymerized to precipitate, suspend or adhere to the inner wall of the container. The thin oily film on the surface of the liquid and transparent wood vinegar separate on the middle phase must be discarded and the suspended as well as precipitated matters are filtered to produce transparent wood vinegar. When the standing and filtering processes are repeated several times, stable, transparent wood vinegar is obtained. While the standing method requires a long time, it is easy and inexpensive compared to other methods and good results are assured. In practice, wood vinegar is easily separated

from whole bio-oil and a viscous oligomeric lignin-containing fractions setting at the bottom by standing at least 3 months [12].

6.2. Filtration

Filter like filter paper is used to remove the precipitated as well as suspended matters. The filtering of freshly recovered bio-oil cannot fully remove unwanted constituents, causing the appearance rely on filtering method. To obtain transparent wood vinegar, combining the filtering with the standing method is necessary. In the filtering process, the oil and suspended matters in wood vinegar gradually clog the filter paper or filter, lengthening the filtering time. In order to prevent this, frequent changes of the filter paper or filter are necessary. The appearance of suspended matter in transparent wood vinegar after future standing means that unstable constituent remains requiring further filtering.

6.3. Column chromatography

The principle of column chromatography is that substances are separate based on their different adsorption capabilities on stationary phase. Large polar compounds are contained in wood vinegar. In general, highly polar molecules are easily adsorbed in the stationary phase, while weak polar molecules are not. Thus, the process of column chromatography involves adsorption, desorption, re-adsorption, and re-desorption. Silica gel is commonly used as the stationary phase, and an eluent is selected based on the polarity of compounds from wood vinegar. Paraffin eluents, such as hexane and pentene, are used to separate aliphatic compounds. Aromatic compounds are usually eluted with benzene or toluene. Some other polar compounds are obtained by elution with methanol or other polar solvent [17–19].

6.4. Distillation

Distillation is a common separation technology in the chemical industry. This method separates the components successively according to their different volatilities, and it is essential for the separation of liquid mixtures. In general, there are two distillation systems i.e. the normal pressure and reduced pressure distillation. In both systems, compounds are separated by mean of the deference boiling points

The carbonizing wood vinegar has water content of as high as 80–90% with a rather small difference in boiling point between the remaining 10% of organic matters. Therefore, the boiling of wood vinegar starts below 100°C under atmospheric pressure, and then the distillation continues up to 250–280°C, whereupon 35–50% of residue is left [20].

Distillation method is quite effective to concentrate wood vinegar and also to remove substance with particularly low and high boiling points. However the distillation process cannot entirely remove unwanted polymer. It is more practical to use this method after unwanted polymer in crude vinegar removed by standing method., However, it should be carefully because the heating to boil sample may be induce the oxidation and polymerization in which bring to losing bioactivity of any components.

6.5. Solvent extraction

Liquid–liquid extraction method so called solvent extraction, involves the selective transfer of a substance from one liquid phase to another. Usually, an aqueous solution of the sample is extracted with an immiscible organic solvent. Thus the solute A distributed between an aqueous and an organic solvent:

$$K_D = \frac{[A]_{\text{solvent}}}{[A]_{\text{aqueous}}}$$

where square bracket denote concentration and K_D is known as the equilibrium distribution of partition coefficient which is independent of total solute concentration. It should be note that constant temperature and pressure are assumed and that A must exist in exactly the same form in both phases. Equilibrium is established when the chemical potentials (free energies) of the solute in the two phase are equal and is usually achieve within a few minutes by vigorous shaking. The value of K_D is a reflection of the relative solubility of the solute in the two phases [21].

Solvent extraction or liquid–liquid extraction has been introduced for semi-purification active compounds from wood vinegar mixture. This technique is used for the separation of compounds with different partition or relative solubility between the 2 solvent phases. Commonly, an aqueous solution of the sample is extracted with an immiscible organic solvent. By selecting appropriate polarity of the solvents for extraction, such as hexane, diethyl ether, ethyl acetate, acetone, water etc., the desired products may be obtained. In order to obtain the higher purity of bioactive compounds from wood vinegar, Oasmaa et al. [22] suggested that step-by-step extraction on the basis of polarity order may be employed. Some reports showed that phenolic compounds and organic acids were extracted from wood vinegar using ethers and dichloromethane [12, 23, 22]. However, they found that a considerable amount of the high polarity and volatile compounds have been lost because of co-evaporation of the compounds at solvent drying step.

In another phenomenon, synergistic function was characterized to be the mode of action of wood vinegar. The most researchers have long suggested that phenolic and organic acid were active component. However, the new report in 2011 presented other unidentified components has high possibility to be active compounds [24]. The highly classified efficiency method to identified components is very necessary. It will bring to the right answer about what is important bioactive compound of wood vinegar and then it might be used as biochemical markers to quantify wood vinegar quality.

7. Utilization of wood vinegar

7.1. The organic agriculture

Utilizing chemical fertilizers was not only imposing heavy loads and pollution on the environment but also threatening our health. Long-term application of chemical fertilizers exposed the

following problem: exhaustion of soil organics, lower conservation of water and nutrition, deterioration of the soil structure and heavy losses of water and soil. Excessive chemical fertilization not only polluted the soil, water and air but also kept most residues in vegetables, which decreases the quality and security of our food supply. Therefore, it was very important to find and develop natural material for vegetable production. Wood vinegar was highly suitable for use in organic agriculture. Since wood vinegar were naturally organic compounds. A great number of toxic-chemical in agriculture was replaced by wood vinegar, natural product, which has been used to promote growth and yield for field cultivation crops such as rice, *Oriza sativa* [25], sweet potato, *Ipomoea batatas* [26], sugar cane, *Saccharum officinarum* [27], melon, *Cucumis melo* [28]. In addition it also used to improve the quality of fruit, combat disease and pests, accelerate the speed of plant seed germination and serve as herbicides [3, 28, 29].

7.2. Alternative medicine

Wood vinegar was believed to promote equilibrium and greater healing in the body. Toxin could be accumulated in the body from a number of sources such as chemical pesticide and fertilizers from food, polluted air and as a by-product from our metabolism. The result of continued accumulation of toxin was poor health as manifested by weakness, pains and aches, disease and sickness. Common examples of illnesses caused by bodily toxins were gout, arthritis, rheumatism, and back pains. Therefore, regular removal of toxins from our bodies may result in good health. Wood vinegar from carbonization was used in preparation of detoxification pad available in Japan, America, Korea and China. The direction of using detoxification pad is by placing at the bottom of both feet before going to bed. The detoxification pad will directly attach to the reflex points on the feet. It was believed to promote equilibrium and greater healing in the body. The sap sheet was believed to help by cleaning out waste and toxic material that were excreted in the form of the sweat under the feet. However, a clinical study of the effectiveness of using sap sheet or detox pad are under investigation.

Wood vinegar was utilized as prebiotics which are defined as non-digestible food ingredients that beneficially affect the host by selectively stimulating the growth and activity of one or a limited number of bacteria in the colon, and thus improve host health. Consumption of food containing less fiber, more meat and carbohydrate, and toxin may reduce good bacteria in large intestine. Wood vinegar was a source of short chain fatty acids that help to promote acidity in large intestine, resulting in inhibition of the growth of bad bacteria, enteropathogenic bacteria [30], and protozoa, *Cryptosporidium parvum* [31], and stimulate the growth of prebiotics, *Enterococcus faecium* and *Bifidobacterium thermophilum* [32]. In addition, it also reduces the absorption of alkaline carcinogen, enhancing calcium and magnesium absorption and increase blood circulation.

The distilled wood vinegar could inhibit allergic reaction, in particular, Type I allergic reaction by oral administration. This solution was indicated for preventing allergic rhinitis, hay fever, allergic conjunctivitis, atopic dermatitis, allergic asthma, urticarial and food allergy [33].

7.3. Food processing

Foods are subjected to many environmental condition such as temperature changes, oxidation and exposure to microbes, which can change their original composition. Foods also cause

illnesses because of their susceptibility to contamination during production, processing and storage. Food-borne illnesses are under reported and are often a common, and sometimes life-threatening, problems for millions of people around the world [34].

Food additives play a key role in maintaining the food quality and characteristic that consumers demand, keeping food safe. They may be classified by one of six primary functions they serve: preservation, improvement in nutritional value, addition or replacement of color, addition or replacement of flavor, improve texture or processing aids [35]. Recently, synthetic food additive I has been reduced demand worldwide because greater consumer awareness. Therefore, natural food additives have become popular [36]. Many natural additives and preservatives have been widely used in food such as spices, herb, essential plant oils and wood vinegar.

Wood vinegar is food additive obtained from nature to use as additives and preservative functions. It can be used in processed food to prevent microbial growth by phenols and short chain organic acids containing in vinegar [37]. In addition the smoke flavors extracted from Wood vinegar had application to food as a safety product [33]. Moreover, the U.S. Food and Drug Administration (FDA) allows using pyroligneous acid for smoke flavoring and preservation of food such as ham, bacon, sausage, fish and cheese.

7.4. Wood preservative potential of wood vinegar

7.4.1. Economic impact of wood and related industries

As world population is progressively growing, the demand of using wood for several purposes is also increasing. In contrast, due to worldwide concern on forest conservation, the availability of natural timber is limited and/or no longer available. Therefore, the timber from economic plants such as cedar, pine, maple, and rubber (*Hevea brasiliensis*) are an alternative. Among of them, with particular in Thailand, rubber wood has become a major raw material in the furniture industry, wood composites and panel products such as particle board, block board and medium density fiberboard [38].

Rubber plantations (*Hevea brasiliensis* Muell. Arg) are found in more than 30 countries around the world. The total planting area is approximately 9 million hectares with almost 90% are in Asia, and about 75% of this is in Thailand, Indonesia and Malaysia. Rubber trees reach their prime of latex production within 25 years, after which it is no longer of economical to use [38]. Several years ago, the expired rubber trees were simply burnt in the fields, prior to plant a new stock, or used as firewood for making bricks and also for the production of charcoal briquettes.

During the last two decades, however, the rubber wood has become an important source of timber, particularly for furniture. It is also extensively used to manufacture wood composites and panel products such as particleboard, block board and medium density fiberboard [38]. Recently, in tropical countries like Thailand and Malaysia, rubber wood has gained much importance as substitute for conventional timber. The rubber wood potential in exterior use has been hampered by its high susceptibility to biological degradation, while the growth of sapstain and surface mold on rubber wood poses serious problems for its utilization. The fungi that damaged rubber wood consist of three major groups: the white-rot, brown-rot and sap-staining fungi [39, 40].

7.4.2. Biochemistry of wood biodegradation mechanisms

In nature, cellulose, lignocellulose and lignin are major sources of plant biomass. Therefore their recycling is indispensable for the carbon cycle. Many organisms are capable of degrading and utilizing biopolymer as carbon source and energy sources. However the organisms predominantly responsible for lignocellulose degradation are fungi and the most rapid degraders in this group are basidiomycetes. The ability to degrade lignocellulose efficiently is thought to be associated with a mycelial growth habit that allows the fungus to transport scarce nutrients such as nitrogen. Each polymer is degraded by fungi which produce a battery of enzymes that work synergistically. There are two types of extracellular enzymatic systems; the hydrolytic system, which produces hydrolases that are responsible for polysaccharide degradation; and a unique oxidative and extracellular lignolytic system, which degrades lignin and opens phenyl rings. Consequently, many free radicals are produced for disrupting wood cell wall [41].

Cellulose biodegradation is synergistic interaction between cellulolytic and non-cellulolytic microorganisms leading to complete degradation of cellulose. Cellulose degrading enzymes are produced with different specificities working together namely cellulases. They are composed of a mixture of enzyme protein with different specificities to hydrolyze the β -1,4-glycosidic bonds. Cellulose degrading enzymes can be classified into three major enzyme activity classes; endoglucanase or endo-1,4-glucanase, cellobiohydrolase and β -glucosidase. Endoglucanase initiate attack randomly at multiple internal sites in the amorphous regions of the cellulose fiber, which opens-up site for subsequent attack by the cellobiohydrolase. It removes monomer and dimer from the end of the glucan chain. β -glucosidase hydrolyzes glucose dimer and in some cases cellulose oligosaccharides to glucose. To function correctly, those three enzymes must be stable in the extracellular environment and may form a tertiary complex with the substrate [42]. Generally, endoglucanase and cellobiohydrolase synergistically hydrolyse cellulose. However, the detail of mechanisms involved in the process are still unknown [41].

Hemicellulose biodegradation: the complete degradation of hemicellulose requires the cooperative action of variety of hydrolytic enzymes. Their action on substrates can be classified as endo-1,4- β -xylanase and generates oligosaccharides from the cleavage of xylan and xylan 1,4- β -xylosidase produces xylose from oligosaccharides. In addition, degradation of hemicellulose needs other enzymes such as xylan esterases, ferulic and p-coumaric esterases, α -1-arabinofuranosidases, and α -4-O-methyl glucuronosidases, acting synergistically to efficiently hydrolyze wood xylans and mannans. O-acetyl-4-O-methylglucuronoxylan is one of the most common hemicellulose, which was initially degraded by endomannases to rupture the polymer and then acetyl glucomannan esterase removes acetyl groups and α -galactosidases eliminates the galactose residue. Finally, β -mannosidase and β -glycosidase break down the endomannase-generated oligomeric β -1,4 bonds [41, 42].

Lignin biodegradation, is an oxidative process, which phenol oxidases from white-rot are used as major enzymes to degrade lignin. Among those enzyme, lignin peroxidase (LiP), manganese peroxidase (MnP) and laccases have been studied. LiP and MnP oxidize the substrate by two consecutive one-electron oxidation steps with intermediate cation radical formation [43]. LiP degrades non-phenolic lignin units, whereas MnP generates Mn^{3+} which acts as a diffusible oxidizer on phenolic or non-phenolic lignin via lipid peroxidation reactions. Laccase (blue

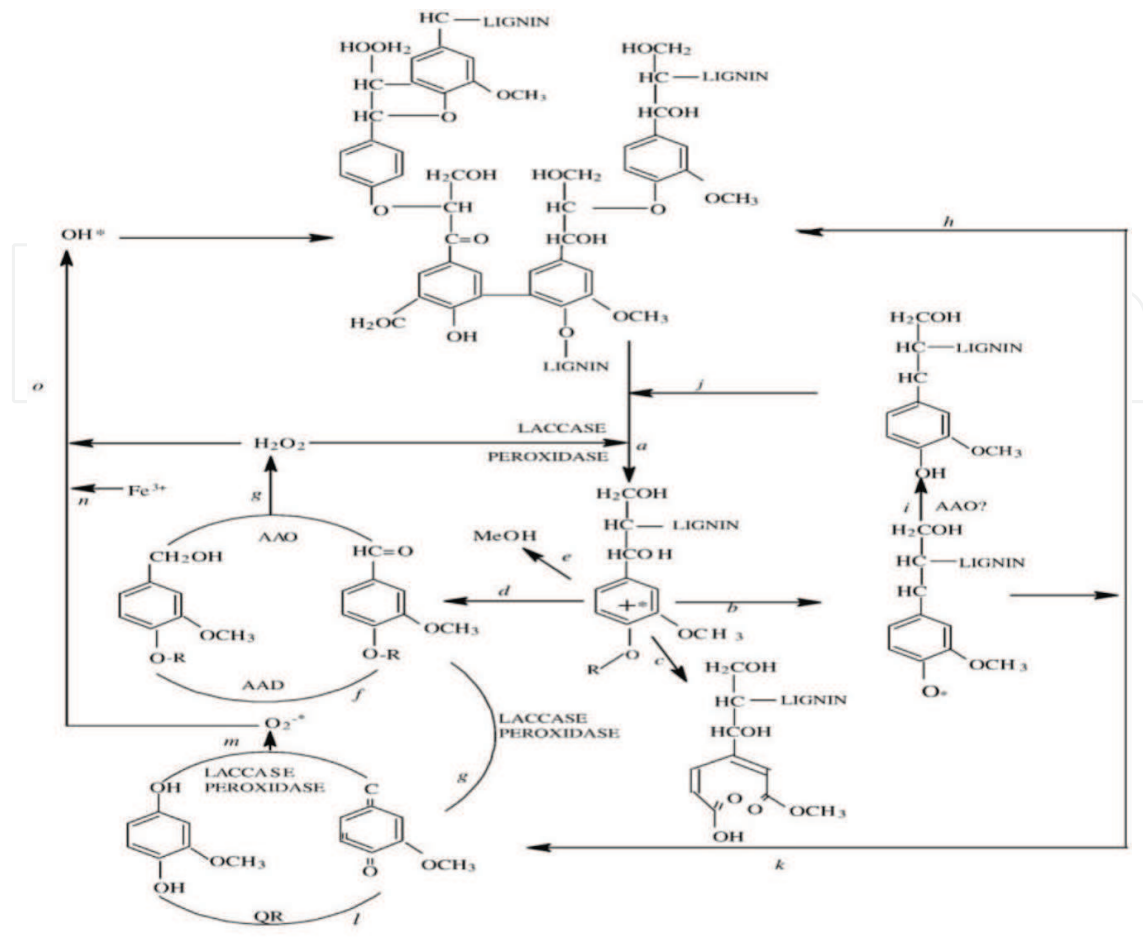


Figure 4. Biodegradation pathways of lignin by white rot fungi [41].

copper oxidases) catalyze the one-electron oxidation of phenolic and other substrate having rich electrons [43].

As shown in **Figure 4**, laccases or ligninolytic peroxidase such as LiP and MnP produced by white rot fungi, which generated aromatic radical by oxidizing the lignin polymer (a). These progress in different non-enzymatic reaction including C4-ether breakdown (b), aromatic ring cleavage (c), C α -C β breakdown (d), and demethoxylation (e). The aromatic aldehydes release from C α -C β breakdown of lignin or synthesize *de novo* by the fungus (g,f) are the substrates for H₂O₂ generation by aryl-alcohol dehydrogenases (AAD) in cyclic redox reaction. Phenoxyl radical from C-4 ether breakdown can repolymerize on the lignin polymer (h) if they are not first reduced by oxidases to phenolic compound (i). The phenolic compounds formed can be repeatedly reoxidized by laccases or peroxidase (j). Phenolic in radical form can also be subjected to C α -C β failure (k) yielding *p*-quinones. Quinones from g and k split oxygen activation in redox cycling reactions with quinone reductases (QR), laccases and peroxidase (l,m). This reaction reduced ferric iron present in wood (n), either by superoxide cation radical or directly by the semiquinone radicals. In addition, it reoxidized with concomitant reduction of H₂O₂ to a hydroxyl free radical OH^x (o) and then it is a very mobile and very strong oxidizer that can initially attack the lignin (p) in the first stages of wood decay when the small size of pores in the still-intact cell wall prevents the penetration of lignolytic enzymes. Then the enzymes described

above oxidize lignin. In the final steps, simple products from lignin degradation enter through the hyphae of fungal into intracellular and are incorporated catabolic routes.

7.4.3. *Synthetic wood preservation*

In comparison with the other structural materials such as concrete, steel and plastic, wood is of biological origin which is considered to be the lesser durability, whereas it poses the higher tensile strength. This problem is principally due to its susceptible to fungi and termites. To increase service life, therefore, preservative treatment using some chemical is introduced in wood industries. It has been concluded that there are 3 major groups of fungi involving to the problem, namely: white-rot, brown-rot and sap-staining fungi [39, 40].

On the basis of solubility, chemicals use in wood preservative may be classified into water soluble type (water-based) and organic soluble type (oil-based). Because copper is an excellent broad spectrum fungicidal property, low mammalian toxicity, relatively low price (Hingston et al. [45]), and is mostly water soluble compound, it is used as a primarily ingredient in wood preservative formulation. These include chromate copper arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), chromate copper boron (CCB), chromate copper phosphate (CCP), alkaline copper quaternary ammonium (ACQ) and copper azole, etc. Among them, CCA appeared to be the most potent wood preservative mixture because it posed a wide range of effects on fungi, termite, bacteria and marine borers, but its use is restricted in many countries [44]. In Thailand, CCB has been accepted for using as wood preservative.

7.4.4. *Environmental friendly wood preservative from wood vinegar*

As health and environmental concern, the conventional chemicals used in wood treatment are considered to be toxic agents. Therefore, an alternative eco-friendly preservative is underway of research. Some investigators reported that the settled tar of bio-oil from fast pyrolysis showed a high potential to use as organic wood preservative [4, 45], [48]. They also suggested that phenolic compounds seem to play an important role to inhibit growth of wood-degrading fungi.

Recently, some investigators reported that bio-oil and wood vinegar prepared from fast pyrolysis have high potential to be used as wood preservative, and they suggested that phenolic compounds seem to play an important role on growth inhibition and decay resistance test of fungi [4, 45, 46]. Moreover, wood block treated with the filtrates obtained from the slurry fuel of several woods such as sugi (*Cryptomeria japonica*) and acacia, (*Acacia mangium*) exhibit resistance against brown-rot fungus (*Fomitopsis palustris*) and white-rot fungus (*Trametes versicolor*). However, the filtrates did not increase the durability of wood blocks against subterranean termites (*Coptotermes formosanus*) [45]. Also, it has been showed that the liquid from pyrolysis of solid wood and wood-based composite such as particleboard, plywood and medium density fiber board with phenol or urea type adhesive have a high potential to inhibit growth of wood-degrading fungi. Bio-assay test shown that the liquid form wood-based composites bonded with phenol-type adhesive at the higher temperature and the liquid from the composites with urea-type adhesive at lower temperature showed a high antifungal activity [46].

In addition, decay and termite resistance of wood treated with tar oil obtained from commercial pyrolysis product of macadamia nutshells has been investigated. It was found growth of

white-rot fungi *Trametes versicolor*, sap-staining fungi *Pleurotus ostreatus*, brown-rot fungi *Fomitopsis palustris* on wood specimens which had been applied with the tar oil 460 at kg/m^{-3} , was effectively inhibited [47].

8. Conclusion

Wood vinegar is prepared from pyrolysis of lignocellulose waste and biomass by fast and slow pyrolysis. The characteristics and properties of obtained wood vinegar are influenced by the type of feedstocks and production techniques. The vinegar is a complex mixture of polar and non-polar chemicals compositions, in which water, acetic acid and phenols are main proportions. Some physical properties such as pH (2–4), specific gravity within (1.005–1.016 g/mL), color, odor, dissolved tar content (0.23–0.89% wt.), and transparency have been evaluated as quality index of wood vinegar product. Wood vinegar, as a natural product, has beneficial applications in wildy fields; including agriculture, pharmacy and biomedicine, veterinary and animal production, food processing and wood preservative.

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