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Potential Products of Coconut Shell Wood Vinegar

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ABSTRACT

Coconut shell is one part of the agricultural product with high economic value. Benefit of coconut shell not only for fuel, but also can produce wood vinegar through pyrolysis process. This wood vinegar has a good value raw material for agroindustries. The objective of this study was to find out the potential products from coconut shell wood vinegar. An identification of the potential product were carried out from literature review based on the chemical compound exist in the wood vinegar. It was selected the potential one that could be commercially developed. The chemical compound selected should contain at least 10% to be developed into new product. The compound determined were phenol, 2,6 dimethoxy phenol, 2 methoxy phenol, 2 methyl propyl ester butanoic acid, nitro 2 methyl 2 butane, 9-octadecenoic acid (Z)- tetradecyl ester (oleic acidtetradecyl ester)- $C_{32}H_{62}O_2$, 2-lauro 1-3 dodecoin- $C_{35}H_{66}O_6$, dodecanoid acid 1,2,3-propanetriyl ester (glyceryl tridodecanoate)- $C_{39}H_{74}O_6$, octanoid acid 1,2,3, propanetriyl ester- $C_{27}H_{50}O_6$, alkyl aryl ether, and acetic acid. These chemicals potentially used in food, chemical, pharmacy, cosmetics, and agricultural industrial products.

Keywords: coconut shell, potential product, pyrolysis, wood vinegar.

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INTRODUCTION

Coconut agroindusty has potency to develop in Indonesia. In fact, the production areas of coconut plant are large about 3.8 millions hectare, the third planting area after rice and palm oil. Thus, distribution of coconut area about 97% belongs to farmers. If each farmer has 1.0 hectare coconut planting area in average, so 3.8 millions farmers involve in maintaining, harvesting and post harvesting processes. Therefore, if in one farmer family has four persons, the dependency of farmers to coconut plants as income for family support are high about 15.2 millions persons [1].

Coconut fruit could use for food and non food products. But, in farmer level, development products of coconut based are still limited on fresh fruit, copra, sugar and coconut oil. Low diversification products impact on low add value of coconut[2]. Thus, in industry level, development products of coconut are produced as crude coconut oil dominantly about 78% with the low add value of US $ 94.6/ton, even with total income of US $ 529.830.000. Meanwhile, Production of active carcoal obtains the higher add value about US $ 635/ton, almost four fold benefit compared to crude coconut oil [3].

According to Asian Pacific Coconut Community,coconut export of Philippines is higher than Indonesia based on income value due to the high diversity of products i.e. coconut methyl ester, coconut fluor and fresh drink [4]. Currently, the diversity of development products of coconut in Philippines have more than 100 products, meanwhile, Indonesia has less than 20 products [5]. In this case, Philippines becomes the major exporter country in the world with market covering about 31.83% and Indonesia has covered about 11.78% only or one third compared to Philippines[6]. Moreover, Indonesia has not been known as exporter of oleochemical, VCO, and coir and active carcoal [5].

Export market demand of coconut development products tend increase in the world i.e. dessicated coconut and active carcoal but decline for crude coconut oil. Therefore, development products of coconut is important to do to meet consumer demand especially for coconut shell development products [5].

Based on national export data in year 2003, Indonesia exported coconut shell about 56%, meanwhile, other countries exported in active carcoal[5]. This the fact that Indonesia has been not yet developed the diversity of coconut products with the high add value. Coconut shell could develop to produce wood vinegar and active carcoal with other derivates and environmental friendly as well [7].

Wood vinegar has a high value as a part of agricultural product. Indonesia produces coconut shell about 3.1 million ton/year. Indonesia has a high advantage comparativeness to develop products based on coconut shell. However, there has still many problems arise by which it is difficult to increase its benefit. Currently, coconut shell is the important material needs for industry instead material as fuel [8].

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Through pyrolisis technology, coconut shell could produce wood vinegarfor industrial purposes[9, 10]. It is the big opportunity to maintain development products with the high add value by establishing the industries of coconut shell and directly enhance income of farmers. Objective of this study was to find out the new products of coconut shell wood vinegar based on chemical dominant compounds.

METHOD

Identification of new products was carried out as follows:

1 Identification the usage of some materials for wood vinegarthrough literatures study.
2 Inventory and identification the chemical compounds of coconut shell wood vinegar through literatures study.
3 Selection the potential chemical compounds to be developed as new products through expertise correspondency. Information was explored to identify potential chemical compounds of coconut shell wood vinegar to develop based on concentration level.
4 Figure out ideas of new products through exploration the usage of potential chemical compounds and production of wood vinegar on other materials.

RESULT AND DISCUSSION

Wood Vinegar for Industrial Application

Wood Vinegar in Food Industry

Wood vinegar has a big benefit for food industry as flavour, give the spesific aroma and food preservation due to the characters of anti-microbial and anti-oxidant. Therefore, application of wood vinegar is already wider than before that most meal industry in USA used wood vinegar as smoke flavour[11]. Moreover, the application of wood vinegar is also used for fish and vegetables canned, cheese, chilli sauce, food snack and mostly food flavour [12].

Anti-microbial

The role of wood vinegar as food preservation on meat, fish and other foods has been already applied in America, Europe, Africa, Australia, and South America[8]. Wood vinegar can be used as food preservation due to anti-microbial contents i.e. acid and its derivates (format, acetate, butyrate, propionate, methyl ester), alcohol (methyl, ethyl, propyl, alkyl and isobutyl alcohol), aldehyde (formaldehyde, acetaldehyde, furfural and methyl furfural), hydrocarbon (chumene and cimene), ketone (acetone, methyl ethyl ketone, methyl propyl ketone and ethyl propyl ketone), phenol, pyridine and methyl pyridine[11].

Anti-bacterial effect in food smoking obtained due to the presence of anti-microbial and anti-oxidant compounds, such as acids, aldehydes, carboxylic acids and phenols. Phenolic compounds in wood vinegar play a major contribution to anti-bacterial activity[13].The high concentration of phenolic compound will enhance the inhibition of bacteria growth[10].

Acidic compounds are much lower than phenolic compounds in wood vinegar but also shown anti-bacterial activity [14]. Acidic compound effectsthe degree of acidity [15]. The best quality of wood vinegar presented the low degree of pH[9]. pH 2.0 of wood vinegar causes stunted growth of harmful bacteria [14].

Anti-bacterial activities of wood vinegar have been applied in commercial applications[16, 17] such as for increasing shelf life on fishball [18], noodle[19], smoked *Katsuwonus pelamis L* fillet [20], *Monopterus albus*[21], smoked *Rastrelliger neglectus*[22], and fillets of trout (*Salmo gairdnerii*) [23]. Wood vinegar proved to suppress the growth of spoilage bacteria and pathogens such as *Escherichia coli*[24, 25], *Bacillus subtilis*, *Pseudomonas* and *Salmonella* groups[25, 26], *Bacillus cereus, Micrococcus luteus, Staphylococcus aureus*[25].

Anti-oxidant:

Wood vinegar is a viable source of anti-oxidants compounds which can play a role in food preservation and medical industries[27]. Phenols in wood vinegar are very important plant constituents because of their radical scavenging ability due to their hydroxyl groups. The phenolic content may contribute directly [28]. Phenol has capacity as anti-oxidant so it could be benefit to enhance the lenght of storage in any products[29].

Antioxidant properties of wood vinegar are similar to butylated hydroxyanisole (BHA)[30], but higher than black tea [27] and *Camellia sinensis*[31]. Wood vinegar can also be used as anti-oxidant that could inhibit lipid oxidation on smoked skipjack *(Katsuwonus pelamis)* that rich of unsaturated fatty acids such as eicosapentaenoic acid and docosahexaenoic acid [29].

Flavour

Carbonyl in wood vinegar smoked has a role in colouring and flavour of products. Reaction of carbonyl and protein results brown colour and phenol arises aromatic[32]. The kind of carbonyl in wood vinegar i.e. vanilyn and siringaldehyde have unique aroma of caramel on meat, fish and cheese [11]. Acid has potency to gain the spesific aromatic as well i.e. acetate, butirate and valerate [32].Wood vinegar is also used to improve aromatic taste on sauce, soup, vegetables canned, and others[8].

Recently, wood vinegar is widely use in food industry to improve aromatic, texture and specific taste on meat, fish and cheese [33]. The wood vinegar are easily applied because the concentration can be controlled, less effect on the environment and free of harmful compounds such as polycyclic aromatic hydrocarbons [11, 34]. Basedon microbial aspect and its distinctive smoked aroma, wood vinegar are possible to be applied as an alternative of traditional smoking method, such as in meat [25] and smoke fish industry in Sidoarjo, Indonesia[35].

Wood Vinegar in Pharmacy and Cosmetics Industry

Wood vinegar products can be developed as deodorizer, soap, sun screen cream [36], sterilizing agent[37],anti-microbial agent for treatment in skin diasease such dandruff, anti-allergi [36]and eczema [17], scabies, atopic dermatitis, and other skin diseases [38].

Wood Vinegar in Chemical Industry

Latex coagulan and rubber sheet additive

There have been various attempts to apply wood vinegar to rubber production processes; for example, as coagulating agent for natural rubber sheet production, in preservative-treated rubber wood, and as additives of rubber sheets, improving the quality of sheets and, pests and diseases resistance[12, 39-41].

Wood vinegar can improve various properties in rubbers. It can reduce dirt, ash and nitrogen contents. It can also improve the initial plasticity, plasticity index, and Mooney viscosity. Additionally, it can retard fungal growth for the rubber since it contains acetic acid and phenolic compound and thus it can be used as also an anti-fungi chemical[42].

Wood vinegar has used as coagulating and anti-fungal agents to replace formic and acetic acids. Bamboo wood vinegar is more efficient as anti-fungal than *Eucalyptus* wood vinegar, acetic acid and formic acid onfungal growth area on natural rubber sheet surfaces[41]. The anti-fungal efficiency of the wood vinegars was strongly depended upon their phenolic compound contents and confirmed through the inhibitory growth of the main fungi, *Penicillium griseofulvum*, on potato dextrose agar[40].

Wood preservative:

Wood vinegars has termiticidal activity against termite worker, *Odontotermes*sp., and pesticidal activity against striped mealy bugs, *Ferrisiavirgate* [43]. This study shows that wood vinegar may be a worthy subtancefor termiticideon excluding termites from wood constructions and other wood products.

Beside having termicidal activity, wood vinegar can inhibite fungal growth against sapstaining fungi (*Ophiostoma flexuosum*, *Ophiostoma tetropii*, *Ophiostoma polonicum* and *Ophiostomaips.).*This study reported that compounds of wood vinegar inhibited fungal growth [44].

Wood Vinegar In Agricultural Purposes

According to Thailand's Department of Agriculture, wood vinegar have some benefits on improving of soil quality, eliminating of pests, increasing the population of beneficial microbes and promote plant growth (accelerate the development of roots, stems, tubers, leaves, flowers,

and fruits), increasing amounts of fruit produced in orchards, helping boost crop defenses against disease, using as repellent of nematodes on tomatoes, strawberries, and black pepper vines, and of insect pests on cabbage and Chinese cabbage [45].A substantial number of claims have been presented in the form of commercial advertisements, which indicates that more research is urgently needed to improve the scientific evidence ofthe use of wood vinegar in agriculture[46].

Pesticide

Wood vinegar has been used as a pesticide in countries where synthetic chemicals are not popular, or where the chemicals has been too expensive for small scale farmers. Globally, the need to minimize the environmental risks resulting from pesticides leaching to ground water and waterways has uncouraged the use of wood vinegar as a biocide and pesticide [47].

Wood vinegar showed potential biological activities as larvicidal, pupicidal, and adult deformities against *M. domestica*. The treated insect species showed deformities at larval, pupal and adult stages. After the treatment, development efficiency, metamorphosis, and growth were highly reduced depending on the concentrations. Due to the effects of wood vinegar, larval and pupal durations were elongated, the development was inhibited, and emerged adults' life span was decreased[48].

Fertilizer and Plant growth enhancer

Since the components of wood vinegar were naturally occurring organic compounds, therefore, it was highly suitable for use in organic and hydroponic farming, as well as for conventional farming. The improvement of activities of bacteria and small living creatures in soil was observed when apply wood vinegar to the soil[49].

A mixture of charcoal and wood vinegar has also shown to enhance soil fertility and the growth of bedding plants[50], rice [51], melon *(Cucumis melon)* [52], sweet potatoes *(Ipomoea batatas)* [53], sugarcane *(Sacharum officinarum)* [54], tomato [55]. Treatments with wood vinegar have also demonstrated an increase in vegetable growth of lettuce, cole, and cucumber [56].

Antifungal

Pyrolysis liquids may be effective fungicides in agricultural applications [57]. The anti-fungal inhibition of wood vinegar is strongly depends on its phenolic compounds [40].Wood vinegar exhibited anti-fungal activity against pathogenic fungus, *Alternariamali*[58], *Rhizoctonia solani*, *Sclerotium oryzae*, *Helminthosporium mayis*, *Pythium* sp., *Colletotrichum gloeosporioides* and *Choanephora cucurbitarum*[57].

Wood vinegar and medium density fiberboard pyrolysis condensate liquids under different pyrolysis conditions were applied to identify fungicidal effectiveness against white rot

fungus *Coriolusversicolorm* and brown rot fungus *Gloeophyllum trabeum*. The result showed that wood vinegar had obvious inhibition to both of the fungi [46].

Feed-Stuff

Wood vinegar was a source of acids help to promote acidity in large intestine,resulting in inhibition the growth of bad bacteria, reducing absorption of alkaline carcinogen, enhancing calcium and magnesium absorption and increasing blood circulation[36].Wood vinegar was not only consumed as prebiotics for human but it also used in animal. It could promote digestion system, increase nutrient adsorption, and reduce diarrhea. Wood vinegar liquid could reduce the number of *Cryptosporidium parvumoocyst*[59].

Wood vinegar has a potential additive in animal production such as anti-biotic alternative [60], inducing a significant increase in egg production and improvements in the feed efficiency of chicken [61],improving the growth performance in duck [62] and piglet [60], apparenting nutrient digestibility, and inhibiting the harmful coliforms in pig [63].

Repellent and Insecticide

Wood vinegar has been widely used with husbandries flies, tick and fleas, control external parasites[27], and insects [36]. Wood tars pyrolysed were effective repellentsfor control of the vole (*Clethriono mysrufocanus bedfordiae*), slugs (*Arionlusitanicus*) and snails(*Arantaarbustorum*)[64].

The chemical compounds of coconut shell wood vinegar

Coconut shell contains 32% hemicellulose, 14% cellulose and 46% lignin [65] with water content of 8% [66]. Coconut consist of 19.5% shell [8]. Pyrolisis technology could apply to produce wood vinegar with the contains of thousands chemical compounds for industrial purposes[7, 10, 67]. Decomposition of hemicellulose, cellulose and lignin can be done by pyrolisis to produce wood vinegar under high temperature i.e. hemicellulose (200-250^{o}C), cellulose (280-350 ^{o}C) and lignin (300-450 ^{o}C) [11].

Previously studies using Gas Chromatography Mass Spectrometryfound that coconut shell wood vinegar contains many chemical compounds[7, 8, 14, 68-74], i.e. phenol (14 types), ketone (21 types), acid (15 types), alcohol (4 types), aldehyde (4 types), carbonyl (1 type), pyridine (4 types), benzene (1 types), catechol (1 type), ester (6 types), furans (3 types), alkane (5 types), amine (2 types), pyrazine(1 type), and sterol (1 type). Types and concentrations of all chemical components as mentioned above were vary among others due to different treatments such as temperature, solution and standar procedure of pyrolisis[7, 15].

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Development of new products based on potential chemical compounds

Through deep discussion with two expertises from National Research and Development on Forest Product in Indonesia about wood vinegar has been gotten the information that only spesific chemical compounds with the concentration above 10% can be selected to develop as potential products due to it will be commercial and efficient.

In Table 1 is shown that dominant chemical compounds on wood vinegar are phenol and its derivates, and acetate acid. Both of them has been used widely in industry. Currently, phenol is extracted in big scale from petroleum[75], and acetate acid is obtained as sintetic product and by fermentation process[76]. Coconut shell as a waste is usefull for raw material in industry due to by using technology of pyrolisis could produce chemical compound and environmental friendly. Therefore, pyrolisis technology is an alternative solution to meet demand of industries instead petroleum and others organic materials[10, 77].

Table 1. Dominant chemical compounds of coconut shell wood vinegar

Compound	Procedure	Concentration (%)	Reference
Phenol	Condensation at 300^{o}C	34,45	[68]
	Condensation at 500^{o}C	31,93	[68]
	Condensation at 300^{o}C	19,28	[71]
	NA	14,87	[74]
	NA	44,13	[8]
	NA	19,90	[70]
2,6 dimethoxy phenol	Condensation at 300^{o}C	12,57	[68]
	Condensation at 500^{o}C	12,44	[68]
	Condensation at 300^{o}C	11,98	[71]
	Condensation at 300^{o}C	12,53	[71]
2 methoxy phenol	Condensation at 300^{o}C	18,29	[71]
	Condensation at 300^{o}C	21,71	[14]
	NA	11,5	[8]
2 methyl propyl ester butanoic acid	Condensation at 300^{o}C	30,76	[71]
Nitro 2 methyl 2 butane	Condensation at 300^{o}C	34,99	[71]
9-Octadecenoic acid (Z)-, tetradecyl ester (Oleic acid. tetradecyl ester)- $C_{32}H_{62}O_2$	Distillation at227-251,8^{o}C	71,68	[69]
2-Lauro, 1-3 dodecoin- $C_{35}H_{66}O_6$	Distillation at 336,6-427,8^{o}C	37,53	[69]
Dodecanoid acid, 1,2,3-propanetriyl ester (Glyceryl tridodecanoate)- $C_{39}H_{74}O_6$	Distillation at 336,6-427,8^{o}C	37,18	[69]
Octanoid acid, 1,2,3, propanetriyl ester- $C_{27}H_{50}O_6$	Distillation at 336,6-427,8^{o}C	15,25	[69]
Alkyl aryl ether	NA	69,01	[74]
Acetic acid	NA	51,99	[70]

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Table 2.The commercial usage of wood vinegar dominant chemical compound

Chemical compound	Usage	Reference
Phenol	anti-microbial	[13]
	anti-oxidant	[28]
	flavour	[15, 33]
	deodorizer	[37]
	sterilizing agent	[37]
	anti-dandruff	[36]
	anti-eczema	[17]
	anti-scabies	[78]
	anti-atopic dermatitis	[78]
	anti-allergic	[36]
	sun screen lotion	[36]
	soap	[36]
	oral analgesic	[36]
	coagulating agent for rubber	[41]
	additive for rubber sheet	[12]
	rubber preservative	[41]
	wood preservative	[43]
	pesticide	[47]
2 MethoxyPhenol	smoke taste	[32]
	anti-microbial	[14]
	anti-oxidant	[14]
	food colour	[14]
	flavour	[14]
	wood preservative	[79]
2,6 Dimethoxy Phenol	anti-fungal	[44]
	anti-oxidant	[44]
	anti-bacterial	[44]
	deodorizer	[44]
	anti-eczema	[78]
	anti-scabies	[78]
	anti-atopic dermatitis	[78]
	flavour	[32, 80]
2 Methoxy Phenol	anti-microbial	[15, 81]
	anti-fungal	[36]
	expectorant	[36]
	local anesthetic	[36]
	deodorizer	[15]
	fertilizer	[15]
Acetic acid	fertilizer	[50]
	pesticides	[82]
	anti-fungal	[57]
	feed stuff	[83]
	repellent	[27]
	termicides	[43]
	additive for rubber sheet production (coagulant, anti-fungal)	[39]
	wood preservative	[79]
	sterilizing agent	[15]

	deodorizer	[15]
	anti-bacterial	[57]
	anti-virus	[57]
	pesticide	[82]
	plant grow promoting agent	[82]
	weed control	[36]
	herbicide	[36]

Table 3: Potential products of coconut shell wood vinegar

Industry	Product
Food	anti-microbial, anti-oxidant, flavour, smoke taste, and food colour
Pharmacy and cosmetic	medicine for eczema, scabies, anti-allergy, anti-dandruff, and other skin diseases, sun screen lotion, soap, local anesthetic, and expectorant
Chemical	anti-protozoa, anti-bacterial. sterilizing agent, preservative for wood (anti-fungal and termicides for wood), additive for rubber (coagulant, anti-fungal), insecticide, and deodorizer
Agriculture	population increaser of beneficial microbes, plant growth promoter, weed grow inhibitor, repelent., pest control, anti-pathogenic fungal, and feed stuff

Idea of new products based on the usage of dominant chemical compound

The next step in this study was to find out the idea of new products based on dominant chemical compounds on wood vinegar especially phenol and acetate acid. In Table 2, phenol along with its derivates has been used in industries i.e. food, chemical, pharmacy,cosmetic,and agriculture. Acetate acid is also used in chemical and agricultural industries. All products is already commercially and few of them still in exploration by research i.e. as anti-bacterial and anti-oxidant.In Table 3 is shown that some products could possible to develope by using coconut shell wood vinegar.

CONCLUSION

Coconut shell wood vinegar has some potential chemical compounds to be developed for any products. Two dominant chemical compounds arise are phenol and acetate acid. Both chemical compounds are usefull for industry i.e. food, chemical, pharmacy, cosmetic and agriculture.

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