Extraction of Black Pepper Non-Volatile Components as an Industrial Material

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Abstract. Pepper (Piper nigrum L.) is a commodity that is quite important in Indonesia, both in terms of agribusiness and agro-industry aspects. From the aspect of agribusiness or cultivation, pepper can be seen as a potential plantation farming business as a plant industry because of its high productivity and selling value. [1] stated that pepper (can be cultivated, because it is one of the plantation commodities that has a high selling value and wide use. Plantation business is a combination of human components and physical and non-physical components [2]. This business is ecologically a system whose success is determined by the components mentioned above as subsystems, where these components influence each other and complement each other in the process of fulfilling the needs of human life. One of the innovations made by pepper farmers is in the form of environmentally friendly pepper cultivation. From the agro-industry aspect, pepper is a commodity that can be used as a variety of industrial materials from upstream to downstream, from the industrial extraction process to its use as raw material for finished products. The extraction result is in the form of oleoresin which is used as a flavor in the food industry as well as a raw material for the pharmaceutical and cosmetic industries. The by-products of the pepper processing process are made in the form of fertilizer and activated carbon.

1. Introduction
Humans are elements that cannot be separated from nature, because in nature humans are subjects who occupy and utilize this nature reciprocally to develop better and not only relationships with humans but also with physical and biological elements such as plants.

Organic and conventional cultivation systems have similar total environmental impacts per unit of product, with organic cultivation achieving lower environmental impacts in ‘freshwater eutrophication’, ‘climate change’, ‘terrestrial acidification’ and ‘marine eutrophication’ categories [10]. Conventional cultivation has a significantly greater effect on the freshwater eutrophication impact category, due to phosphate emissions arising from application of chemical fertilizers.

Pepper is a plant that grows in vines and lives in a tropical climate where the seeds are very often used as a cooking spice. The aroma and taste of pepper is very distinctive, so it is sometimes a part of mainstay recipes.

Indonesia has been known as the most important producer of pepper (Piper nigrum L.) since ancient times, as an important export commodity in producing spices and foreign exchange in the plantation sub-sector. As a pepper producing country, Indonesia ranks third after Malaysia and India.
However, it turns out that the productivity level of Indonesian pepper farmers is still very low, only an average of 500 kg per ha per year with an ideal productivity ranging from 1-1.2 tons per ha per year (www.perkebunan.go.id). Currently pepper plants are growing in Bangka, Lampung, West Kalimantan, East Kalimantan and Aceh [4].

The history of this plant dates back to the early days of the Netherlands 300 - 400 years ago, the development of pepper to this region was encouraged by the Dutch government, which controlled the world spice trade and was supported by farmers of Chinese descent who previously worked as tin miners. The spice known as The King of Spice had its ups and downs. However, because this commodity has its own market in the world spice trade, pepper plantations have continued to survive to this day.

Based on the difference in the time of picking and the processing process, it is known in two kinds, namely white pepper and black pepper. White pepper is a pepper fruit that is picked when it is fully ripe, then the skin is removed by soaking it. Soaking is carried out in running water for approximately two weeks, then dried in the sun for three days. Black pepper is a pepper fruit that is picked when it is ripe (the skin is still green) and immediately dried in the sun for three days without soaking it first (www.perkebunan.go.id).

Chemically black pepper has a composition as can be seen in table 1.

| Components            | Content (%) |
|-----------------------|-------------|
| Moisture              | 9,56-15,60  |
| Protein               | 10,80-12,66 |
| Essential oil         | 1-2         |
| Amidon & carbohydrate | 32,1-50     |
| Cellulose             | 11,9-15,5   |
| Ash                   | 3,4-5,9     |
| Dry alcohol           | 6,5-13,3    |

Source: Aksi Agraris K. (1980)

Pepper contains many components that have many benefits and properties, one of which is oleoresin. In addition, pepper contains saponins, flavonoids, essential oils, cavinic, starch, piperine, piperillin, piperonin, piperonal, dihydricarveol and others.

Oleoresin is one of the largest non-volatile components in pepper. Oleoresin is the result of extraction, followed by re-distillation of the solvent used. Black pepper oleoresin is extracted from black pepper (*Piper nigrum* L.) with organic solvents, in the form of a brown, light brown to greenish-brown paste with a characteristic peppery smell. Research on the extraction of black pepper oleoresin by combining the type of solvent, the fineness of the pepper powder and the extraction time has never been done. This study aims to increase the added value of pepper commodities by processing it into oleoresin with various combinations of treatments, so that the best treatment can be recommended in the black pepper extraction process.

1.1. Potential of Pepper Plants
The pepper plant is native to the Western Ghat region of India. Pepper plants that are now scattered in Indonesia are believed to have originated from India brought by Hindu colonists who came to Java in 100 BC - 600 BC. In the 16th century, pepper plants in Indonesia were only cultivated on a small scale on the island of Java and in the 18th century the plant was on a large scale [5].

The center of pepper development in Indonesia was originally the Banten area. Before World War II, Indonesia was known as the largest pepper producing and exporting country in the world. However,
after World War II Indonesia's pepper exports declined due to the emergence of new pepper-exporting countries, such as Brazil, India, and Malaysia, as well as damage to pepper plants in production centers due to pests and diseases.

In Indonesia, pepper cultivation centers are located in Bangka Belitung, Lampung, South Sumatra, East Kalimantan, Bengkulu, West Kalimantan, South Kalimantan and South Sulawesi. Most pepper plantations are cultivated by farmers or smallholder plantations. In subsequent developments pepper plants are cultivated in more than 20 provinces, and currently pepper is grown in almost all provinces in Indonesia.

Pepper consists of many species, there are about 600-2,000 species of which are scattered in the tropics. Of these, only a few species have been cultivated, including *Piper nigrum* L. (pepper). Pepper flowering is seasonal. In the period of flowering or fruiting in the form of flower or fruit markings, numbering between 11-14 bunches, with a length of about 81-110 mm. Pepper plants begin to flower at the age of 10-12 months after transplanting. The period of flowering and fruiting (from flowering to ripe fruit) lasts for 7-9 months.

Pepper fruit is round to oval. Young fruit is green or light green, and after ripening turns orange red. The number of fruits per bunch ranges from 57-80 grains, with a potential yield per tree between 2.2-3.0 kg of dry pepper, depending on the variety.

As a plant that is propagated vegetatively, the genetic source of pepper germplasm is not much, from about 50 varieties in Indonesia so far it has not been widely described and tested. The priority for developing pepper plants is to produce superior varieties, including the Bulok Belantung, Jambi, Lampung Daun Lebar and Kerinci varieties.

Pepper fruit contains higher oleoresin than many other spices such as cinnamon, ginger, turmeric and cloves, except nutmeg and chili. The amount of oleoresin that can be extracted from various spices with organic solvents can be seen in table 2.

| Type of spice | Oleoresin content (%) |
|---------------|-----------------------|
| Pepper        | 11-13                 |
| Nutmeg        | 24-30                 |
| Chili         | 19-21                 |
| Ginger        | 11-12                 |
| Cinnamon      | 10-12                 |
| Clove         | 5-10                  |

*Source: Ketaren, 2004*

1.2. Harvesting of Pepper

Harvest time is determined by the type of pepper to be produced, black pepper or white pepper. Both types of pepper come from the same plant, the only difference being the time of harvest. Based on differences in harvest time and processing process, pepper is known in two types, namely black pepper and white pepper. Black pepper is the fruit of the pepper that is picked when it is ripe (the skin is still green), while the white pepper is the fruit of the pepper that is picked when it is fully ripe. Determination of a good harvest time by recording the time of planting pepper begins to flower. Ideally the fruit is ready to be picked after the plant is 7-9 months after flowering. Picking is done 3-4 times according to the picking requirements. At the last picking, all the unripe and ripe fruits are harvested (“rompes”).

The purpose of this fruit “perompesan” is to provide better and perfect vegetative growth opportunities so that plants are able to produce optimally. The production of this plant lasts until the age of 5-6 years, production begins to decline after the age of the plant 6-7 years.
After picking the peppers are sorted by ripeness or color. Green fruit is processed into black pepper, while yellow to red fruit is processed into white pepper.

1.3. Yield/Processing
The process of making black pepper is done from fruit that is really old but not yet ripe. The fruit that has been harvested and collected is then separated from the stalk. After that, it is dried in the sun. Before drying, the peppers should be soaked in hot water for a few minutes and then rinsed so that the fruits are separated from the panicles and the resulting black pepper is obtained more evenly and shiny. At the time of drying, it is best to use a mat and protect it from disturbance of the surrounding animals, so that cleanliness is guaranteed. If the sun is shining all day long, within 3-4 days the pepper will be dark black with a moisture content of about 14%. Water content of about 14% is indicated by the pepper will break apart when squeezed and then winnowed to clean, after that the pepper can be packaged and marketed. The yield of black pepper obtained from the drying process is between 33-36 kg.

The process of making white pepper is done after the fruit is harvested and sorted. Different from making black pepper, the fruit is put in a sack and then soaked for 7-10 days so that the seed coat rots. After the skin rots, it is then trampled so that the algae skin is clean. The seeds of pepper that are skinned and other parts are used up, then washed and filtered. Furthermore, the seeds are dried in the sun for 3-4 days depending on the weather. The yield of white pepper processing obtained ranges from 24-27 kg.

1.4. Industrial Uses of Pepper
Pepper can be widely used in both food and non-food industries, so pepper is an important ingredient in the spice trade. In the food industry, pepper is used as a spice and preservative in various dishes. Pepper as a cooking spice can give a delicious smell and add to the delicacy of food. Some food products made from pepper are chili sauce, green pepper sauce, bottled pepper, pepper mayonnaise and pepper yogurt.

In the non-food industry, pepper is used in the pharmaceutical and cosmetic industries. In the pharmaceutical industry or medicine (pepper in medical use) it is used both in traditional and modern medicine. In the cosmetic industry, it is used as perfume (pepper perfume) such as perfume products. In industry, as is the use of pepper, oleoresin is used in the food, pharmaceutical and cosmetic industries. In the food industry, oleoresin is used in various products such as processed meat (sausage and ham), fish and other marine products, bread, cakes, puddings, syrups, sauces and others. In the pharmaceutical industry it is used for rheumatism / gout, balsam, ayurvedic treatment (stimulating the digestive system), treatment of nausea and lack of appetite.

1.5. Pepper Oleoresin
Further processing of pepper seeds needs to be developed because in a whole state pepper seeds have weaknesses, namely the aroma will be lost and also easily damaged due to fungus during storage. Processed pepper products include oleoresin and ground pepper. Oleoresin is an extract or plant extract that has undergone solvent evaporation. Pepper oleoresin has advantages compared to other processed products from pepper, namely it has a uniform aroma and does not contain microbes so that it is more durable.

Oleoresin is one of the largest non-volatile components in pepper. Oleoresin is the result of the extraction process followed by re-distillation of the solvent used, so that the resulting oleoresin is free from solvent. According to [7], black pepper oleoresin is defined as oleoresin extracted from black pepper (Piper nigrum L.) with organic solvents, in the form of a brown, light brown to greenish brown paste with a characteristic peppery smell.

- Oleoresin which is the largest non-volatile component of black pepper, consists of various components which include:

- Piperine, an alkaloid that gives pepper its sharp taste, its content is about 35-45%
Chavicine, is an isomer of piperine and is the component that also gives pepper its pungent odor.
- Piperitin, as well as isoperic, chavinic and isochavinic acids, are the parts that give pepper its important flavor, which is spicy, which is about 5-10%. Piperitin is an alkaloid like piperine.
- Other undetermined resins, which also enrich the taste and aroma of black pepper oleoresin.

According to the Indonesian National Standard for Black Pepper Oleoresin, the specifications for the quality requirements of black pepper oleoresin oleoresin can be seen in table 3.

| Test type                        | Requirements                                           |
|----------------------------------|--------------------------------------------------------|
| **Appearance:**                  |                                                        |
| - Colour                         | Light brown, greenish brown                            |
| - Form                           | Liquid paste, thick paste Pepper special               |
| - Smell                           |                                                        |
| Piperine (%w/w)                  | Min. 35.0                                              |
| Essential oil (%v/w)             | Min. 10.0                                              |
| Oil refractive index (nD 25)      | 1.4820-1.4960                                          |
| Residual solvent (ppm)           | Max. In accordance with the regulations in the importing country |

Source: SNI 01-0025-1987

2. Methods

2.1. Tools and Material
The materials used consist of main ingredients and auxiliary materials. The main ingredients used are black pepper seeds, while the auxiliary materials include ethanol, acetone, hexane and aquadest as well as other chemicals for analysis.

The equipment used in the research includes grinders, extractors, distillers, vacuum filters, scales, volume measuring instruments, glassware, extraction containers, as well as sample testing equipment such as spectrophotometers, refractometers, distillation sets, hotplates, water baths and aluminum foil.

2.2. The Stages of The Research
The research was conducted in five stages of the process, namely:
- Preparation Process
- Black Pepper Refining Process
- Stirring/Extraction Process (homogenization of black pepper powder with solvent)
- Black Pepper Oleoresin Separation Process
- Sample Test

2.2.1. Preparation Process. In the preparation process, the dirt, moldy seeds and others contained in black pepper are sorted which will be used as experimental raw materials. After sorting, the black pepper is then dried in the sun for about 3 hours.

2.2.2. Black Pepper Refining Process. In the refining process, black pepper is used which has been dried for about 3 hours in the sun. First ground black pepper with a spice grinder, then sifted. Black
pepper refining is carried out up to several levels of fineness (mesh), namely 70 mesh, 80 mesh, and 90 mesh.

2.2.3. Stirring/Extraction Process. Black pepper that has been ground at various levels of fineness (70 mesh, 80 mesh and 90 mesh) is weighed as much as 2 kg each, then put into the extractor. Then added 5000 ml of organic alcohol solvent and stirred with an extractor for one hour. After finishing the stirring process, the mixture of black pepper and alcohol was filtered using a vacuum filter. The rest of the filter is accommodated into a holding container, while the resulting liquid (filtrate) is separated from the solvent from the oleoresin.

2.2.4. The same process was carried out for 80 mesh and 90 mesh fineness black pepper, with different solvents (ethanol, hexane and acetone) at various stages with a time of one hour for each step.

2.2.5. Black Pepper Oleoresin Separation Process. The oleoresin separation process carried out lasted for three hours, with three stages of distillation. At each stage the distillation was carried out for one hour.

2.2.6. The oleoresin separation process procedure can be described as follows. First, the distillation/separator equipment is prepared by connecting the water faucet pipe and running water to the cooler. In addition, a container for the remaining solvent and a water cooler is prepared. Furthermore, the filter results obtained from the final process of distillation, set the temperature at 60°C and time for one hour (stage I). After the refining process for one hour, the oleoresin yield was measured/calculated. In the same way as in step I, the treatment was repeated again to obtain oleoresin from the extraction in the second hour (stage II) and the third hour (stage III).

2.2.7. Sample Test. The test was carried out based on the Indonesian National Standard on Black Pepper Oleoresin (SNI 01-0025-1987). Testing or analysis of samples is carried out on physical and chemical properties. Physical analysis was carried out on the appearance of oleoresin which included color, shape and smell. While the chemical analysis includes piperine content, essential oil content, residual solvent and oil refractive index (nD 25).

3. Results and Discussion

3.1. The Oleoresin Yield
In the extraction process, black pepper oleoresin and various residual organic solvents were used. The yield or oleoresin content of each treatment was different from each other. The average yield of black pepper oleoresin with the best ethanol solvent was obtained from the 70 mesh pepper fineness treatment with an average hourly yield of 12.48% and the highest was obtained at the second 1 hour extraction time (14.00%). With hexane solvent, the highest average hourly yield was obtained at 70 mesh pepper fineness (11.37% yield) and the highest was obtained in the first 1 hour extraction time (13.50%). With hexane solvent, the highest yield was obtained at the fineness of 70 mesh (6.33% yield) and the highest at the first 1 hour extraction time. The yield of oleoresin produced from black pepper extraction in various treatments can be seen in figure 1.
The study showed that the average yield of black pepper oleoresin produced in the optimal treatment was quite high and was the maximum amount of yield for pepper. [6] stated that the oleoresin content of dry pepper ranged from 11-13%.

Black pepper has a higher oleoresin yield than white pepper, and therefore black pepper is usually used as a raw material to produce oleoresin. In addition, the price of black pepper is cheaper with a plant essence content that is almost the same as white pepper. Oleoresin is in the form of concentrated liquid, semi-concentrated and paste [8].

The increase in oleoresin yield was influenced by the type of solvent. The alcohol solvent produced a higher yield than the other two solvents, for each solvent it was influenced by the length of the extraction time. The extraction process of oleoresin in black pepper occurs because of the coagulation of the extract in the solvent. The solvent that has been mixed with the material in the form of black pepper powder will penetrate the capillaries of the black pepper powder and dissolve the extract solution with a higher concentration formed on the inside of the extraction material. Based on the type of solvent, a high yield was obtained in the type of alcohol solvent to extract oleoresin compared to acetone and hexane solvents. Research shows that hexane solvent produces the lowest oleoresin yield compared to other solvents. Black pepper oleoresin extraction with hexane solvent, the ratio of ingredients to solvents 1:15 (w/v), obtained a yield of 5.13%, while [9] stated that the major component of both ethanol and ethyl acetate oleoresins was found to contain piperine (63.9 and 39.0%), with many other components in lesser amounts.

3.2. Quality Test
Black pepper oleoresin obtained from the extraction process is in the form of a brown, light brown to greenish brown paste with a distinctive peppery smell, extracted with organic solvents and then tested for quality parameters of appearance, refractive index, and piperine content.

3.2.1. Appearance. The results of the appearance test were carried out on color, shape and odor, as shown in table 4. The test results (table 4) showed that the appearance of black pepper oleoresin obtained met the requirements set out in the Indonesian National Standard (SNI 01-0025-1987), as shown in table 4.
Table 4. Appearance of extracted oleoresin at each level of fineness and type of solvent.

| Degree of fineness (mesh) | Type of solvent | Colour          | Shape        | Smell         |
|----------------------------|-----------------|-----------------|--------------|--------------|
| 70                         | Ethanol         | Greenish brown  | Liquid paste | Pepper special|
|                            | Acetone         | Greenish brown  | Thick paste  | Pepper special|
|                            | Hexane          | Brown           | Thick paste  | Pepper special|
| 80                         | Ethanol         | Greenish brown  | Liquid paste | Pepper special|
|                            | Acetone         | Brown           | Liquid paste | Pepper special|
|                            | Hexane          | Brown           | Thick paste  | Pepper special|
| 90                         | Etanol          | Greenish brown  | Liquid paste | Pepper special|
|                            | Aseton          | Brown           | Liquid paste | Pepper special|
|                            | Heksan          | Brown           | Thick paste  | Pepper special|

3.2.2. Refractive Index. The average results of the non-volatile refractive index/oleoresin of black pepper obtained ranged from 1.4012 - 1.4269, as shown in figure 2.

![Figure 2](image)

**Figure 2.** The chart of oleoresin refractive index averages for each solvent and degree of fineness (mesh).

Figure 2 shows that the value of the refractive index resulting from this study is relatively small, this can be caused because in black pepper oleoresin there are also molecules that are relatively high in unsaturated bonds or oxygen groups such as B-karyophyllin and dihydrocarveol.

3.2.3. Piperine Content. The average level of piperine oleoresin test results in black pepper produced in the study ranged from 10.50 to 37.50, as can be seen in figure 3.
Figure 3 shows that at the level of fineness of black pepper 70 mesh and 80 mesh and 90 mesh with hexane solvent produced relatively lower piperine levels compared to the use of other solvents. This can be caused by the solvent hexane is a non-polar solvent.

4. Conclusion
The best oleoresin yield from this study was obtained by extraction with a fineness level of 70 mesh black pepper and alcohol as a solvent. The results of the oleoresin quality test obtained from the study for the appearance parameters met the requirements of the SNI Black Pepper Oleoresin, while the piperine content partially met the SNI requirements, namely at a fineness level of 70 mesh for ethanol and acetone solvents, respectively 37.50% and 35.90%. The resulting refractive index ranged from 1.4012-1.4269, with the highest yield at the level of fineness of 80 mesh black pepper with hexane solvent, which was 1.4269.

From the results of the study, it is recommended that the black pepper oleoresin extraction process be carried out at a fineness level of 70 mesh with alcohol solvent. On a commercial production scale with the use of larger raw materials, it is expected that the refractive index of the oleoresin produced will be higher.

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References
[1] Rismunandar and Riski M H 2003 Budi Daya dan Tata Niaga Lada (Jakarta: Penebar Swadaya)
[2] Utami D 2007 Analisis Geografi Terhadap Produksi Tanaman Kopi Di Kecamatan Buay Pemaca Kabupaten Ogan Komering Ulu Selatan Sumatera Selatan Thesis (Universitas Muhammadiyah Surakarta)
[3] Mediatani 2015 Cara Sukses Menanam Lada dengan Mudah http://mediatani.com/
[4] Nuryawan A, Haryati Y and Bandjar H 2007 Lada (Piper nigrum Linn) sebagai salah satu pangan fungsional penghasil devisa (Bogor: BPTP)
[5] Aksi Agraris Kanisius 1980 Bercocok Tanam Lada (Yogyakarta: Kanisius)
[6] Ketaren S 2004 Kondisi minyak atsiri indonesia saat ini dan pengembangannya ditinjau dari aspek teknologi. Panduan Seminar Minyak Atsiri Indonesia (Jakarta: Balai Besar Industri agro)

[7] Standar Nasional Indonesia 1988 SNI 01-0025-1987 Oleoresin Lada Hitam (Jakarta: Badan Standardisasi Nasional)

[8] Sulhatun, Jalaluddin and Tisara 2013 Pemanfaatan lada hitam sebagai bahan baku pembuatan oleoresin dengan metod ekstraksi Jurnal Teknologi Kimia Unimal 2 16–30

[9] Kapoor I P S, Singh B, Singh G, De Heluani C S, De Lampasona M P and Cesar A N C 2009 Chemistry and in Vitro Antioxidant Activity of Volatile Oil and Oleoresins of Black Pepper (Piper nigrum) J. Agric. Food Chem. 57 5358–5364

[10] Chatzisymeon E, Foteinis S and Alistair G L B 2017 Life cycle assessment of the environmental performance of conventional and organic methods of open field pepper cultivation system Int. J. Life Cycle Assess. 22 896–908