Journal of Applied Agricultural Science and Technology *E-ISSN: 2621-2528*
6(1): 11-19 (2022) *ISSN: 2621-4709*

DECREASED LEVELS OF CYANIDE AND FREE FATTY ACID ON RUBBER SEED OIL USING ZEOLITE ADSORBENT AND NONI EXTRACT ADDITION

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Abstract*. Rubber seed oil is not currently used optimally, due to the high content of cyanide and free fatty acid. Cyanide and free fatty acid can be decrease using zeolite adsorption process and addition of noni extract. This research aims to study the effect of noni extract for cyanide and free fatty acid of rubber seed oil. Rubber seed oil was purified using the zeolite adsorption method with the addition of 10% by weight of rubber seed oil. Research method used completely randomized design which consists of 4 treatments and each treatment was repeated 4 times. The treatments of noni extract addition were 40%, 45%, 50%, and 55% of total weight of rubber seed oil. Data were statistically analyzed by using analysis of variance and continued with Duncan New Multiple Range Test (DNMRT) at 5% level. The addition of noni extract significantly affected the decrease in cyanide acid content, acid number, specific gravity, and peroxide number. Based on this research, the best treatment was 55% noni extract addition which had average content of cyanide 0.500 ppm, specific gravity 0.862 g/ml, and acid number 4.325 mg KOH/g.*
Keywords: *rubber seed oil; cyanide; free fatty acid; noni extract*

1. Introduction

The name of rubber plant is taken from the latin *Hevea brasiliensis* which originated in Brazil. This plant is a major source of the world's natural rubber plant material. Based on statistical data, Riau Province has rubber plantation area about 329.005 ha in 2019 (Direktorat Jenderal Perkebunan, 2021). Rubber seeds are one of by-product from rubber plantations which hardly have any economic value and only used as generative purposes. Commonly rubber seed that is large and has hard shell, and its color is brown with blackish splotches patterned.

Rubber seeds are oval in shape with a length of 2.5-3 cm, which weighs 2-4 grams/seed. Rubber seeds consist of 40-50% brown hard skin, and 50-60% yellowish white kernel. Rubber seed kernel consists of linoleat acid 35-38%, 2.71% ash, 3.71% water, 22.17% protein and 24.21% carbohydrates, so that rubber seeds have the potential to be used as a source of oil (Hakim & Mukhtadi, 2018). Rubber seed oil can be used in industrial paint, lye, biodiesel, and as resin raw materials in the manufacture of roof tiles, steel industry, concrete, ceramic, cast and others. Compared to other than as a source of oil, rubber seed have nutrient content 10-22% protein, potential as raw material food (Eka *et al*., 2010). However, utilization of rubber seed as a food ingredient is not optimal, one of the barriers are is the high acid content of cyanide (HCN) and free fatty acids in the seed oil of rubber. In addition, rubber seed oil has been used in the cosmetic and personal care industries. This is because rubber seed oil which contains antioxidant activity shows

Received July 12, 2021; Accepted February 4, 2022; Published February 28, 2022
https://doi.org/10.55043/jaast.v6i1.25

a cellular protective effect of 0.001 mg/mL with cell viability of 99.72 ± 6.92% (Chaikul *et al*., 2017). In today's COVID-19 pandemic scenario, there is a multiple-fold increase in demand for soaps and handwash for personal hygiene. This demand shall continue to grow in the coming days, and the inclusion of rubber tree seed oil (RSO) in producing soaps may ease the burden on vegetable oil, which can be used for human consumption (Bhattacharjee *et al*., 2021).

The acid levels of cyanide (HCN) rubber seed oil according to Rahmawan and Mansyur (2008) showed a decrease during for processing rubber seed for cake by way of soaking and steaming. Chemically, steaming results for 30 minutes and immersion in flow water for 36 hours containing the lowest HCN about 39.11%, but the initial stages and submergence can increase the moisture content of the and it can lead to the hydrolysis reaction and produce of free fatty acids in the oil

High free fatty acids can lower the quality of the oil. Research results of (Rahmadanis *et al*., 2019) showed that rubber seed oil had a high free fatty acid content of 15.64%. The high level of free fatty acids in the control rubber seed oil was because the rubber seed oil was not treated with degumming and neutralization. The results showed that 3% bentonite was able to reduce free fatty acids to 6.5%. Besides bentonite, another natural ingredient that can reduce free fatty acids is zeolite. Zeolite is one of adsorbent that can be used to decrease free fatty acids in the oil. Research (Setiawan *et al*., 2016) showed that the zeolite was able to decrease free fatty acids in the seed oil of rubber up to 2.61 mg/KOH from 6.23 mg/KOH/ by using 25% zeolite and 14 hour time adsorption.

Rubber seed oil has a high content of unsaturated fatty acids (Linoleat 35-38% and Linolenat acid 21-24%). The high content of unsaturated fatty acids caused the oil easily damaged; allow the occurrence of contact with oxygen from the outside air to ease of oxidation reaction in the oil to form the cluster and produces peroxide radicals free. According to (Fakriah *et al*., 2019) , Free radicals are molecules that have lost one electron from their lone pair, or in other words, are the result of hemolytic separation of a covalent bond. Various chronic diseases caused by accumulated free radicals due to continuous exposure. Therefore we need free radical scavenging substances known as antioxidants. Various antioxidants found in nature, one of which is noni extract.

(Singh, 2012) reported that noni has bioactive activities such as antibacterial, antiviral, antihelmintic antifungal, antioxidant, hepatoprotective, antiobesity, hypoglycaemic, analgesic, anxiolytic, anti-inflammatory, hypotensive, cardiovascular activity, estrogenic, immunological and anticancer activity. This is supported by earlier research of (Anwar & Triyasmono, 2016) which proved that noni had a phenolic compounds and flavonoids. The total phenolic content of the noni fruit ethanol extract was 14.44 ± 0.82 mg equivalent to pyrogalol (PE)/gr, while the total flavonoid content was 5.69±0.21 mg equivalence to routine (RE)/gr. The addition of noni extract in waste cooking oil, can prevent the oxidation of food components that are sensitive to oxygen

and can lower the levels of acid fat free and peroxide (Mulyati *et al*., 2006). In addition, the noni fruit has been used as an antioxidant as well as an antimicrobial, the noni fruit has been used in noni flour as a feed additive (Kurniawan, 2018).

The research on purification of rubber seed oil was carried out using the adsorption method using zeolite and noni extract addition. Noni fruit extract was used in this study with treatment variations of 40%, 45%, 50%, and 55% of the weight of oil which is a modification of the research of Irwan *et al*. (2010). This research has produced rubber oil which has good quality with cyanide acid content and free fatty acids which are minimized by the use of noni extract as an antioxidant.

2. Methods

2.1. Materials

Materials used in this study were rubber seeds obtained in Sejati Village, Rambah Hilir District, Rokan Hulu. Other materials used in this research were noni extract, aquades and zeolite.

2.2. Research Method

The method used in this study was a non-factorial Completely Randomized Design (CRD) consisting of four treatments and each treatment was repeated four times to obtain 16 experimental units. The treatment is a variation of the addition of noni extract which is a modification of the research of Irwan *et al*. (2010). The zeolite used for adsorption was 10% of the weight of the oil, with an adsorption time of 14 hours, which was selected based on the results of Setiawan (2016). The treatment is as follows:

P0 : Without the addition of noni extract as a control
P1 : 40% addition of noni extract to crude rubber seed oil
P2 : 45% addition of noni extract to crude rubber seed oil
P3 : 50% addition of noni extract to crude rubber seed oil
P4 : 55% addition of noni extract to crude rubber seed oil

2.3. Research Procedure

Rubber seeds are peeled from the shell first using a hammer. The peeled rubber seeds are then cleaned and soaked for 3 days. The rubber seeds that have been soaked are then mashed with a blender with a ratio of rubber seeds and water (1: 2) become rubber seed pulp. Rubber seed porridge is squeezed to produce coconut milk. Coconut milk is filtered so that there is no rubber seed pulp. Coconut milk is heated using low heat while stirring slowly until all the water evaporates. Rubber seed oil is separated from blondo by squeezing it using filter cloth (Lestari, 2014).

The noni fruit is sorted, then washed, after that the blanching process is carried out with hot water at a temperature of 65-70^{0}C for 2-3 minutes, then drained. The skin and noni seeds are then separated, the noni is crushed using a blender (without water) to obtain noni liquid, then the

noni liquid is filtered to obtain noni fruit extract. The addition of noni extract to crude rubber seed oil was carried out with various treatments of 40%, 45%, 50%, and 55% of the weight of the rubber seed oil.

Rubber seed oil added to zeolite by as much as 10% of the weight of oil that later adsorption for 14 hours. Rubber seed oil is then separated from the zeolite using centrifugation for 15 minutes with a speed of 3000 rpm, then filtered with a filter paper (Setiawan *et al*., 2016) Rubber seed oil adsorption result heated water bath with 70°C temperature and addition noni extract with treatment (40% 45%, 50% and 55%) (Irwan *et al*., 2010). Rubber seed oil is then separated from the noni extract using centrifugation for 15 minutes with a speed of 3000 rpm, then filtered with a filter paper (Setiawan *et al*., 2016).

2.4. Analysis of rubber seed oil

Analysis of oil in this research is content of cyanide and acid number referring to Sudarmadji *et al*. (1997), and specific gravity referring to Ketaren (2008).

3. Results and Discussion

3.1. Levels of Cyanide

The results of variance showed that the noni fruit extract in the refining process of rubber seed oil had a real influence on the levels of cyanide acid (HCN) produced. The average value of cyanide acid (HCN) produced after further testing of DNMRT at the 5% level is presented in Figure 1.

Figure 1 shows that tthe acid content of cyanide (HCN) rubber seed oil with the addition of 10% of the zeolite and without adding noni extracts (control) of 3.11 ppm. The average cyanide acid content of rubber seed oil ranges between 0.5-2.02 ppm. The more addition of noni extract of seed oil in rubber, then the lower acid content of cyanide produced. This is because the water content in the extract of noni starred as polar solvents. Based on Pudjaatmaka and Hadyana (2002) cyanide acid polar in nature, so that the cyanide acid will join together to extract soluble pace added.

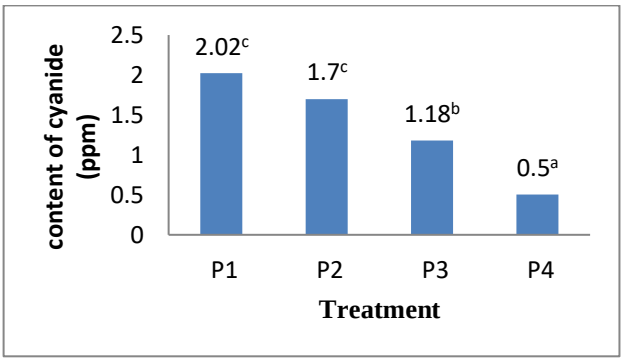

Figure 1. Reduction of Cianida Levels in Rubber Seed Oil

Note: numbers that are followed by small letters of the same unreal test according to different 5% level DNMRT

Figures 1 hows that the more noni extract was added to the rubber seed oil, the lower the cyanide acid content produced. The average cyanide content of rubber seed oil ranged from 2,02 ppm-0.50 ppm. Based on quality standard the P4 treatment has fulfil the standard, which is a maximum of 1 ppm. The cyanide acid of rubber seed oil in this study overall decreased. The decrease in cyanide acid levels was caused by the water content in the noni extract which acts as a polar solvent. Cyanide acid is polar, so the cyanide acid will dissolve along with the added noni extract. This is in line with the opinion of Pudjaatmaka and Hadyana (2002) which states that cyanide is polar.

Cyanide has a solubility which runs slow on organic solvents. Therefore inneed's energy to optimize the solubility conditions of cyanide that is, one is the stirring process. Stirring done for dissolve cyanide acid content in seed oil of rubber together with extract of noni. Cyanide Acid that has been dissolved in the noni extract is then separated from the rubber seed oil through the process of centrifugation.

Decrease in cyanide is also influenced by the preliminary treatment during the extraction of rubber seed oil which is soaking and heating. Rubber seeds soaked with water for 3 days can reduce cyanide acid (HCN). This is in accordance with the study of (Atklistiyanti. C, Herwitarahman. A, Rivai. R R, Santoso. Y S, 2013) that immersion can reduce cyanide acid of rubber seeds from 128 ppm to <3 ppm. Rubber seeds that have been soaked are then given water and mashed using a blender until they become coconut milk seeds. Coconut milk seeds which still contain cyanide are then heated at ± 100 ° C, while cyanide has a boiling point of 25.6 ° C so that when heated cyanide will evaporate. The longer the heating time, the more cyanide will evaporate.

Zeolites also plays a role in lowering the levels of cyanide acid rubber seed oil through the process of adsorption. Based on the research results (Setiawan *et al*., 2016) in the refining of rubber seed cooking oil with adsorption zeolite time 14 hours, the cyanide acid degradation be 1.97 ppm of 14.06 ppm. This is because the cations in zeolites are capable of binding ions CN^- in HCN, so that when the process of centrifugation will separate the oil and the HCN has been tied to the zeolite.

3.2. Acid Number

The results of variance showed that the noni fruit extract in the refining process of rubber seed oil had a real influence on acid number. The average acid number generated after further testing DNMRT at the 5% level is presented in Figure 2.

Figure 2 indicates that shows the acid number of rubber seed oil by the addition of 10% of the zeolite and without adding noni extracts (control) of 5.67 mg KOH/g. The average number of rubber seed oil acid ranges between 5, 49 mg KOH/g-4.33 mg KOH/g. The more addition of noni extract of seed oil in rubber, then the lower the resulting acid number. This is because the free

fatty acids are polar will join together to extract soluble pace added. This is in line with the opinion of (Ayu & Hamzah, 2010) the stating that free fatty acids cannot bind dirt due to polar in nature. In addition, the presence of compounds alkaloids in noni extract can decrease the number of acid in the seed oil of rubber. A compound alkaloid compounds in alkaline nitrogen, so the more the addition of noni extract, then the acid number of rubber seed oil would getting lower. This is confirmed by the results of the research of Mulyati *et al. (*2006), stating that the fruit of noni have alkaloid compounds.

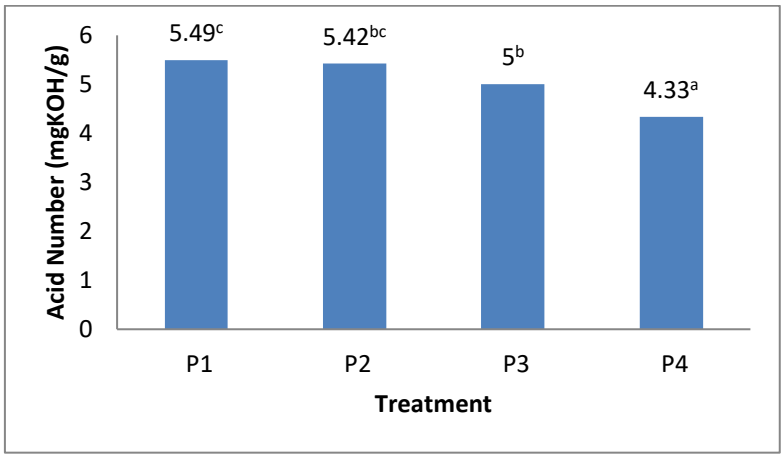

Figure 2. Reduction of Acid Number in Rubber Seed Oil

Note: numbers that are followed by small letters of the same unreal test according to different 5% level DNMRT

Refining of rubber seed oil by zeolite adsorbent also plays a role in the decrease in the number of the acid in the seed oil of rubber. Zeolite is used as adsorbent previously activated in advance with warming in the oven at a temperature of 200°C for 15 minutes. This is supported by the statement Kusumastuti (2004), zeolite has a greater ability in absorbing free fatty acids than natural zeolite. The activation process led to the evaporation of water, change the comparison of Si/Al, increased surface area and porosity occurrence of zeolite. This will enhance the ability of the zeolite adsorption and thus more efficient oil purification.

3.3. Specific Gravity

The results of variance showed that the noni fruit extract in the refining process of rubber seed oil had a real influence on specific gravity. The average specific gravity generated after further testing DNMRT at the 5% level is presented in Figure 3.

Table 1 shows that the heavy type of rubber seed oil with the addition of 10% of the zeolite and without adding noni extracts (control) of 0.86 g/ml. The average weight of a type of rubber seed oil ranges between 0.88 g/ml-0.86 g/ml. The more addition of noni extract of seed oil in rubber, then the lower the weight of the resulting type. This it can be caused due to the moisture content and weight-fraction fraction like dirt in rubber seed oil soluble noni extract that appended together. Noni extract will then separate from rubber seed oil at a time when the process of centrifugation due to the difference in specific gravity.

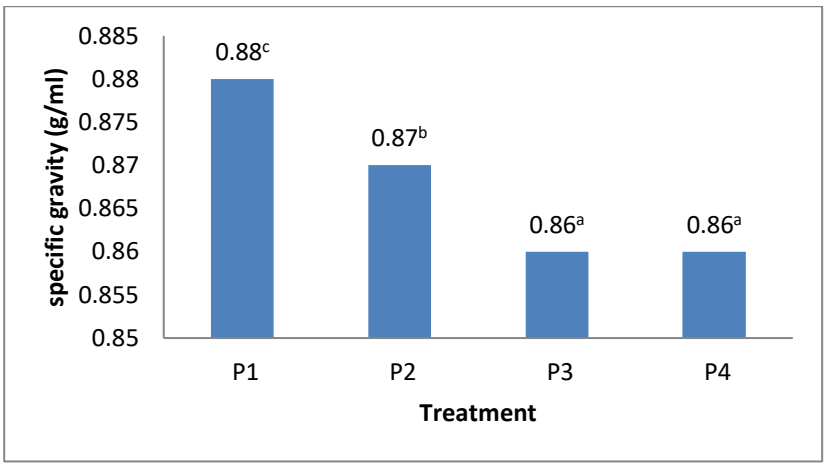

Figure 3. Reduction of Specific Gravity in Rubber Seed Oil

Note: numbers that are followed by small letters of the same unreal test according to different 5% level DNMRT

Zeolites also plays a role in lowering the weight of different types of rubber seed oil by adsorption. Based on the results of research (Setiawan *et al*., 2016), refining of rubber seed oil, gravity has decreased from 0.906 g/ml into 0.898 g/ml. This is caused by the ability of the zeolite in absorbing particles in rubber seed oil, so when the process of centrifugation will separate oil with water and the particles of rubber seed oil.

3.4. Assessment and Determination Rubber Seed Oil Selected Treatment

Rubber seed oil is expected to meet the cooking oil quality standards set by the Indonesian National Standard (SNI). The recapitulation data based on parameters of cyanide acid (HCN), acid number, and specific gravity are presented in Table 1.

Table 1 show that the levels of cyanide acid (HCN) have different values for each treatment. The treatments P4 treatments had fulfilled the SNI standard. The acid numbers of all treatments did not meet SNI standards. The peroxide number of all treatments met the SNI standard, which is a maximum of 2 Meq / kg. The specific gravity of all treatments met the SNI standard which is a maximum of 0.921 g / ml. Based on the recapitulation results of the analysis, the best treatment of rubber seed oil selected was P4 treatment (10% zeolite + 55% addition noni fruit extract). Rubber seed oil in P4 treatment has a cyanide acid content of 0.50 ppm, an acid number of 4.33 mg KOH / g, and a specific gravity of 0.86 g / ml.

Table 1. Recapitulation of data chemical analysis rubber seed oil

Parameters	SNI*	Treatment			
		P_1 (40% M)	P_2 (45% M)	P_3 (50% M)	P_4 (55% M)
Cyanide acid	Max. 1 ppm	2.02^{c}	1.70^{c}	1.18^{b}	**0.50^{a}**
Acid number	Max. 0.6 mg KOH/g	5.49^{c}	5.42^{bc}	5.00^{b}	4.33^{a}
Specific gravity	Max. 0.921 g/ml	**0.88^{c}**	**0.87^{b}**	**0.86^{a}**	**0.86^{a}**

* (BSN, 2013)

Note: numbers that are followed by small letters of the same unreal test according to different 5% level DNMRT

4. Conclusion

The addition of noni extract significantly affected the decrease in on the content of cyanide, acid number, and specific gravity. The best treatment of rubber seed oil namely treatment P_4 (noni extract addition 55% of total weight of rubber seed oil) with content of cyanide 0.500 ppm, acid number 4.325 mg KOH/g, and specific gravity 0.862 g/ml.

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