Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.7 No.12, 2015

Utilization of Rubber Seed Shells and Epicarp Wastes as Activated Biochar

Sumihar Hutapea [1] Ellen Lumisar Panggabean [1] Andi Wijaya [2]
1.Department of Agrotechnology, Agricultural Faculty of Medan Area University
2.Sungei Putih Research Center Galang-Deli Serdang, Po Box 1415 Medan 20001

Abstract
This research was investigated to find out activated biochar formulation and characteristic of rubber seed shell and *epicarp* that can be used as an amelioration of organic material in soil contaminated horticultural pesticide residues. Tests were carried out to study the effects of two processing parameters, namely, activation in HCl solution (0%, 5%, 10%, 15%, 20%) and activation temperature (600, 700, and 800 ^{o}C). The research had been performed using factorial completely randomized design. Parameters analyzed were ash content, moisture content, volatile matter content, fixed carbon, benzene and iodine number. Optimum conditions for producing activated biochar from rubber seed shell and *epicarp* wastes were at activation in HCl solution 15% and activation temperature 800 ^{o}C that resulted in rubber seed shell and *epicarp* activated carbon with the best characteristic, i.e moisture content of 3.97%; ash content of 3.78%; volatile matter of 30.91%; fixed carbon of 65,27%; absorption of iodine 875.97 mg g-1 and absorption of benzene 25.94%.
Keywords: activated biochar, formulation, activation time, and activation in HCl solution.

INTRODUCTION

Rubber plantations in Indonesia has an area of 3.2 million ha which consists of smallholder and state-owned plantations. Every year the number of smallholder rubber plantation rejuvenation program ranges from 50.000-70.000 ha (Supriadi, 2009). Potential rubber seed in the main grain season under normal circumstances is approximately 5,000-10,000 seeds per hectare of mature plants with an average weight of fresh seeds depending on the type of clones ranged 5.0-3.5 grams (Siagian, 2012).

Currently, rubber seed is widely used as a seed for the rubber plant breeding. Surely not all the seeds can be used as seed because it has specific criteria for the selection process of a good seed. So the rubber seed does not comply with the criteria of a good seed will be as waste. Not only that, *epicarp* which is skin of rubber seed, currently not utilized. So it need for studying to utilize rubber seeds shells and *epicarp* as a source of raw materials in the process.

Researchers have studied the production of activated carbon from various types of biomass such as palm-tree cob, plum kernel, cassava peel, bagasse, jute fibre, rice husk, olive stone, date pit, fruit stones and nutshell.

Activated carbon is an important component of filter material for the removal of hazardous components in exhaust gases for the purification of drinking water and for waste water treatment. The demand for activated carbon will continue to rise due to its wide range of use as a result of environmental compliances in many countries (Elisabeth et al., 2007).

Biomass has become one of the main sources of carbon for the production of activated carbon. The biomass used is usually waste materials or by-products in commercial activities. By reusing or recycling these low cost materials to produce activated carbon, we are providing another environmentally friendly alternative to dispose of the waste and by-product (Cheong, 2006).

The carbonisation process is to enrich the carbon content and create an initial porosity, and the activation process helps in enhancing the pore structure. Carbonisation takes place in the temperature range of 300–400 °C. During carbonisation, primary carbonisation gases are produced which can be categorised as permanent gases and oils (tars) if they are cooled to ambient temperature. The residue of the carbonization process is the primary charcoal which serves as base material for the activation step (Elisabeth et al., 2007).

The charcoal is then activated by steam in the same reactor at 650–800 °C. Some of the carbon is oxidised which leads to the generation of pores. It is very important at this step to keep the activation conditions constant. Steam activation at higher temperatures gave better activation and enhanced widening of the narrow pore network (Prakash Kumar et al., 2006).

The objective of this study was to obtain data on characteristic of activated biochar prepared from shell and *epicarp* of rubber seed residues. The present work also studied the influence of various process parameters such as activation time and activation in solution on activated biochar.

MATERIALS AND METHODS

The precursor material was shell and *epicarp*/skin of rubber seed from experimental estate of Sungei Putih Rubber Research Center. Experiments were conducted in a high temperature reactor with dimensions of 0.7 × 1.2 m (diameter of vessel × height). The reactor could produce 8 kg of activated carbon/day from 32 kg of raw materials.

Carbonisation and activation processes

For the carbonisation and activation processes, sehell and *epicarp* of rubber seed wastes were cut and air dried to moisture contents of 13–15%. Thirty two kg of dried samples were taken for each run and fed into the reactor after which the vessel was heated to temperature between 300 and 400 °C in the absence of air. The carbonisation reaction was completed when the emitted gas turned bluish in colour. The charcoal prepared from the carbonization process was activated in HCl solution (0%, 5%, 10%, 15%, and 20%) and activated in muffle at different activation temperature (600, 700, and 800 ^{o}C).

Proximate analysis

Proximate analysis in this research was moisture content, ash content, volatile matter and fixed carbon, absorption of iodine and benzene of shell and epicarp of rubber seed activated carbon were carried out using.

a. Mouisture Content

Procedure of determination of mouisture content refers to Indonesian National Standard (SNI) 06-3730-1995 about quality requirements and testing of activated charcoal. Sample is weighed as much as 5 g, dried in an oven at (103 ± 2) °C until its weight is constant. Then put in a desiccator until weight is fixed and determined mouisture content in percent (%). Moisture content of activated charcoal is calculated with the following formula:

$$\text{Mouisture content}(\%) = \frac{\text{wet sample weight (gr)} - \text{Dry sample weight (gr)}}{\text{wet sample weight (gr)}} \text{ x } 100\%$$

b. Ash content

Procedure of determination of ash content refers to the Indonesian National Standard (SNI) 06-3730-1995 about quality requirements and testing of activated charcoal. 2 g sample is weighed and then put in a cup that is already known dry weight, then the cup was placed in a furnace, slowly heated from room temperature up to 600 ^{o}C for 6 hours. Further cooled in a desiccator until its weight is constant, then it is weighed. Calculation ash content using the formula:

$$\text{Ash content (\%)} = \frac{\text{ash sampel weight (gr)}}{\text{sampel weight (gr)}} \text{ x } 100\%$$

c. Volatile matter

Determination of volatile matter content aims to find compounds that have not been vaporized at carbonisation and activation process, but evaporate at temperature of 950 ^{o}C. According to Smisek and Cerny (1970) that the components contained in the activated charcoal is water, ash, fixed carbon, nitrogen, and sulfur. On heating above 900 ° C nitrogen and sulfur will evaporate. This component is referred to as a volatile matter content. As much as 2 g dry sample is inserted into porcelain cup dry which is known its weight. Furthermore, the sample is heated in a furnace to temperature of 950 ^{o}C for 10 minutes, and then cooled in a desiccator for 1 hour and sample is weighed.

$$\text{volatile matter content (\%)} = \frac{a - b}{a} \text{ x } 100\%$$

a = sample weight before heated (gr)
b = sample weight after heated (gr)

d. Fixed carbon

Procedure of fixed carbon content refers to the Indonesian National Standard (SNI) 06-3730-1995 about quality requirements and testing of activated charcoal. Fixed carbon is carbon-bound fraction in the room besides the fraction of water, volatile matter, and ash. Measurement of fixed carbon content is calculated using the formula:
Fixed carbon (%) = 100% - (volatile matter content + ash content)%

e. Absorption of Iodine

Determination of iodine absorption refers to Indonesian National Standard (SNI) 06-3730-1995 about quality requirements and testing of activated charcoal. Sample of activated charcoal is weighed as much as ± 0.25 g and put into the erlenmeyer flask. Then sample is treated with a solution of iodine 25 ml, stirred for ± 15 minutes. The solution was stirred and then filtered using filter paper, and the results pipette 10 ml for titration using a solution of thio (Na2S2O3). Titration is done until the sample solution changes color to clear. The amount of iodine absorption is calculated by the formula:

Absorption of Iodine (%) =

$$\frac{10 - (\text{N } Na_2S_2O_3 \text{ x ml titration } Na_2S_2O_3 / \text{N } I_2) \text{ x } 12.693 \text{ x } 2.5}{\text{sample weight}}$$

f. Absorption of Benzene

Determination of Benzene absorption refers to the Indonesian National Standard (SNI) 06-3730-1995 about quality requirements and testing of activated charcoal. Petridish which has dried is weighed, then sample placed on a petridish which is still above the balance of the scales. The sample is flattened to cover all the surface of the petridish and the weight recorded. then insert to absorbent tools of benzene, allowed for ± 24 hours, and after that sample is weighed. Absorption of benzene calculated by the following formula:

Absorption of benzene (%) =

$$\frac{\text{Sample after absorption (gr)} - \text{Sample before absorption (gr)}}{\text{Sample before absorption (gr)}} \times 100\%$$

RESULTS AND DISCUSSION

Results of testing the characteristics of activated biochar from shell and epicarp of rubber seed can be seen in Table 1.

The results showed that the process of activation with a solution of HCl concentration and activation temperature gives different effect on the value of moisture content, ash content, volatile matter, fixed carbon, the absorption of iodine number, and the absorption of benzene. In the analysis parameters , the lowest moisture content contained in the treatment K0S3 by 3.12% and the highest value contained in K3S1 treatment of 12.82%. The lowest value on ash content contained in 1.77% of K1S1 treatment and the highest value contained in K0S1 treatment by 20.39%. For volatile matter of the lowest value contained in K4S2 treatment of 20.69%, and the highest value contained in K3S1 treatment of 66.12%.

The lowest value of fixed carbon contained in K0S1 treatment amounted to 17.75% and the highest value contained in K2S2 treatment of 66.60%. For the lowest iodine absorption value contained in K0S2 treatment of 483.95 mg / g and the highest value contained in K3S3 treatment of 875.97 mg / g. Absorption of benzene number for the lowest K1S2 treatment of 8.09% and the highest value contained in K3S3 treatment of 25.94%.

Tabel 1. Characteristic of activated biochar from shell and epicarp of rubber seed

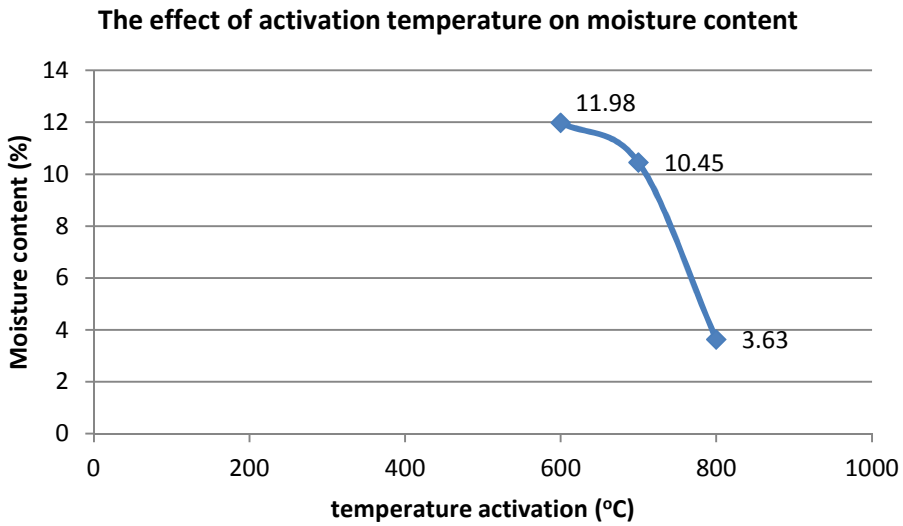
Treatmen	Parameters					
	Mouisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Absorption of Iodine (mg/g)	Absorption of Benzene (%)
K0S1	10.66	20.39	61.97	17.75	558.93	10.08
K0S2	6.91	15.92	22.35	61.32	483.95	10.72
K0S3	3.12	11.36	36.25	52.43	817.81	25.33
K1S1	11.88	1.77	61.98	35.11	507.08	10.36
K1S2	11.29	14.30	24.49	60.78	582.82	8.09
K1S3	3.37	6.94	29.81	63.59	829.28	24.15
K2S1	12.24	5.95	65.45	28.15	511.37	10.27
K2S2	11.91	4.52	28.45	66.60	645.04	9.73
K2S3	3.56	8.26	27.16	65.20	759.77	22.40
K3S1	12.82	4.24	66.12	29.52	539.17	10.88
K3S2	12.76	4.38	28.72	64.90	728.49	10.50
K3S3	3.97	3.78	30.91	65.27	875.97	25.94
K4S1	12.31	7.18	38.05	53.94	498.34	8.73
K4S2	9.39	19.20	20.69	59.57	506.14	8.22
K4S3	4.14	16.65	25.42	57.18	671.47	19.52

Specification : K0 = without activation in HCl solution (control); K1 = with activation in HCl solution 5%; K2 = with activation in HCl solution 10%; K3 = with activation in HCl solution 15%; K4 = with activation in HCl solution 20%; S1 = activation temperture 600 ^{o}C; S2 = activation temperture 700 ^{o}C; S3 = activation temperture 800 ^{o}C.

a. Moisture content

Determination of moisture content of biochar aims to determine the hygroscopic properties of activated charcoal. Moisture content produced in this study ranged from 3.12% to 12.82%. The value of mouisture content of all samples is meet SNI standards stipulated a maximum of 15%.

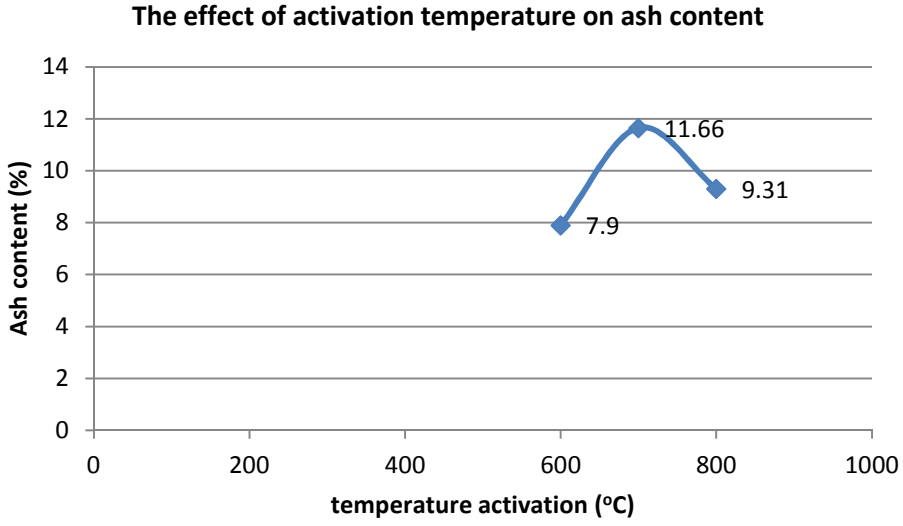
Theoretically, increasing of activation temperature can enhace evaporation of water level, hence the water level is too less. Time and conditions of storage and processing of activated charcoal, such as milling and sieving will also affect the value of the moisture content of activated charcoal, since the activated charcoal is hygroscopic which can absorb moisture or other molecules in contact with the air, so its ability to adsorb gases or other liquids will decline. This happens because the pores of the activated charcoal has been filled or covered by another atom or molecule (Pari, 1996).



b. Ash content

Ash is an inorganic components remaining after the material is heated at a temperature of 500-600 ° C and consisting of potassium, sodium, magnesium, calcium and other components in small quantities. Determination of ash content aims to determine the content of the metal oxide contained in biochar. Sudrajat (1985) said the high ash content can reduce the ability of activated charcoal to absorb the gas and solution. The value of all the ash content of the resulting samples ranged from 1.77 to 20.39% . It means that only some of the treatments only meets the SNI standard, ash content is a maximum of 10%.

Theoretically, an increase in the activation temperature tends to increase ash content of active charcoal because the high temperature activation will be oxidized easily and produce inorganic components. In addition, the high temperature activation can result metal oxide from the interaction of chemicals reagent between furnace (muffle) hence the content of inorganic components on activated charcoal is much. Sudrajat (1985) said the high ash content can reduce the ability of activated charcoal to absorb gases and solutions for the minerals contained in the ashes spread in the lattice of activated charcoal.

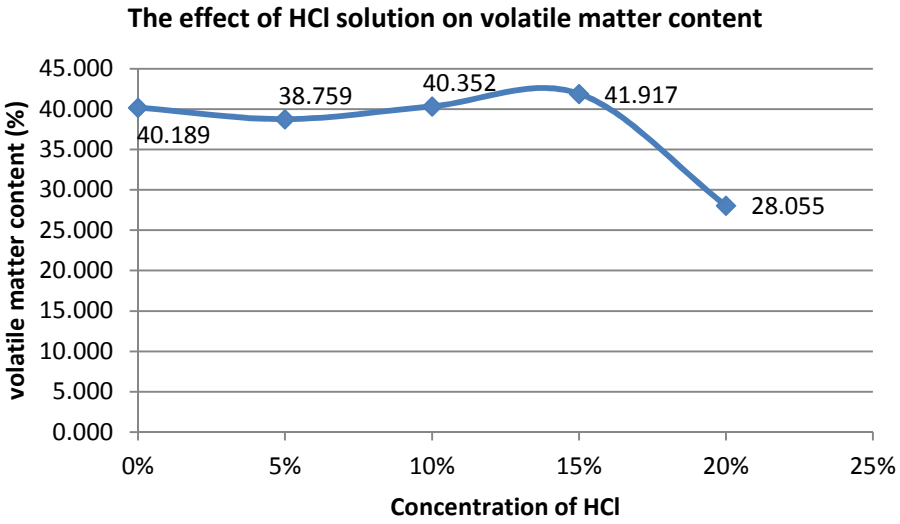


c. Volatile matter

Determine of volatile matter aims to find compounds that have not been vaporized in the process of carbonization and activation, but evaporate at a temperature of 950 °C. Value levels of volatile matter generated from this study ranged from 20.69 to 66.12%. In theory, an increase in HCl concentration tends to increase the levels of substances evaporate anyway. This is due to HCl is added to the charcoal pervasive, coat, protect materials from heat. High levels of volatile substances would reduce the ability of biochar to absorb gases and solutions. Levels of substances

evaporate all samples yielded not meet SNI standards, namely a maximum of 25%.

Theoretically, increasing concentration of HCl will increase the levels of volatile matter. This is because HCl is used will coat and protect the material from the heat, so the higher concentration of HCl then the less sulfur and nitrogen in the material that burned and vaporized at temperature of 950 ^{o}C. High content of volatile matter will reduce absorbency because there are pores of activated charcoal which is still covered with volatile matter such as carbon, sulfur and nitrogen. Increased activation temperature will reduce levels of volatile matter content. This happens because the high temperature will reduce non-carbon compounds such as CO_2, CO, CH_4 and H_2 which can react perfectly (Kuriyama, 1961).



d. Fixed carbon

Activated biochar from shell and epicarp of rubber seeds contain fairly high and it ranged from 17.75 to 66.60%. The higher concentration of substances evaporate and ash content, the carbon content, will make the lower bound. Fixed carbon content of all samples is not yet meet the standards of activated charcoal powder according to SNI is a minimum of 65%.

Fixed carbon content is strongly influenced by the concentration of volatile matter and ash content. As much as concentration of volatile matter and ash content, the fixed carbon content is to be lower. Fixed carbon content is directly proportional to the activated charcoal adsorption ability, so that the high level of fixed carbon effect on the ability of activated charcoal to absorb the gas (Sudrajat et al., 2005).

e. Absorption of iodine number

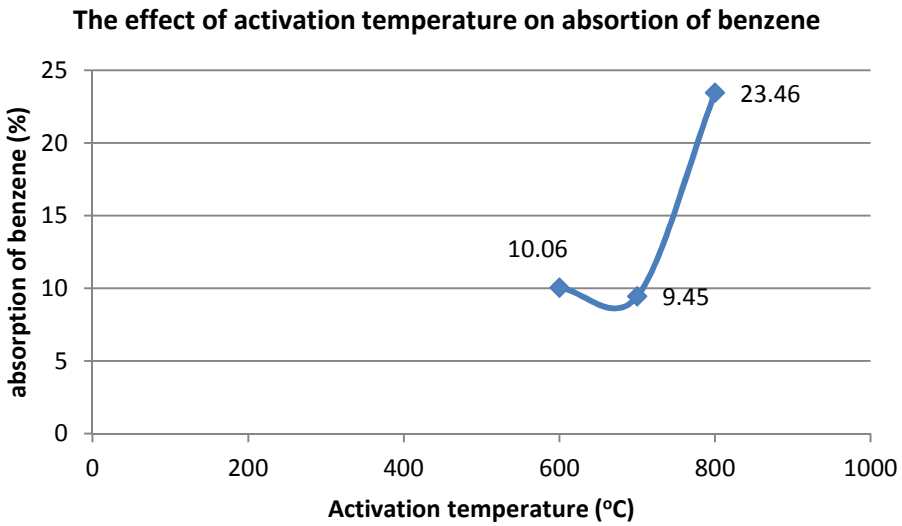
Determination of iodine absorption of active charcoal/biochar aims to find out the ability of biochar to absorb colored solution/dirty. The amount of biochar to the iodine absorption is an indication of the magnitude of the pore diameter of biochar that can be penetrated by molecules whose size is no greater than 10 A and the number of microporous structures formed (Pari, 1996). Iodine absorption of some samples not allowed to SNI standard activated charcoal powder where it has a minimum iodine number of 750 mg/g.

Activated charcoal absorption to iodine ranges from 483.95 mg/g - 875.97 mg/g. Activated charcoal absorption value of the lowest iodine obtained from the samples treated with HCl 0% and activation temperature of 700 °C, while the highest value obtained from the samples treated with HCl 15% and activation temperature of 800 ^{o}C.

f. Absorption of benzene number

Determination of benzene absorption biochar aims to find out the ability of biochar to absorb gas. Absorption of benzene number of biochar ranged from 8.09 to 25.94%. Benzene absorption of some activated biochar did not allowed to SNI standard activated charcoal powder where it has a minimum benzene number of 25%.

Theoretically, an increase on activation temperature can increase the absorption of active charcoal on benzene. This is because the higher temperature will cause carbon plates to shift and push hydrocarbons and other organic compounds to come out at activation. The low value of benzene absorption due to activated charcoal pore is covered by non-carbon compounds which are not pushed out of the surface of activated charcoal at activation (Pari, 1996).



CONCLUSION

Activation solution in HCl and activation temperature were important parameters affecting the activated carbon produced. The best conditions were at 15% HCl solution activation and 800 °C activation temperature. This gave the highest iodine number of 875.97 mg g-1. Increasing temperature and concentration of HCl increased iodine number which subsequently increased adsorption capacity of the activated carbon. When the temperature exceeded 800 °C, the particles were burned out completely. This indicates that rubber seed shell and epicarp has the potential to be a promising precursor for the production of activated carbon.

REFERENCES

National Standardization Agency. (1995). Technical Active Charcoal. *SNI 06-3730-1995*. http://sisni.bsn.go.id/index.php?/sni_main/sni/detail_sni/4156. Access on 08 November 2013.

Cheong, Ww. 2006. Preparation and characterization of activated carbons from bamboo for adsorption studies on the removal of surfactants. Thesis, Universiti Teknologi Malaysia, Skudai.

Elisabeth S, Klaus T, Christine W, Andreas H & Vander T. 2007. Experiments on the generation of activated carbon from biomass. *Journal of Analytical and Applied Pyrolysis* 79: 106–111.

Kuriyama, A. 1961. Destructive Distillation of Wood. Ministry of Agriculture and Forestry Overseas. Technical Cooperation Agency, Tokyo.

Pari, G. 1996. Active Charcoal quality of five wood type. *Forest Products Research Bulletin*. Vol. 14(2):60-68. Forest Products Research and Development Center, Bogor.

Prakash Kumar BG , Shivakamy K, Miranda LR & Velan M. 2006. Preparation of steam activated carbon from rubberwood sawdust (*Hevea brasiliensis*) and its adsorption kinetics. *Journal of Hazardous Materials* B136: 922–929.

Siagian, N. (2012). Seeding and Planting Material Rubber Procurement Excellence. Sungei Putih Research Institute, Rubber Research Center. Deliserdang, Medan.

Smisek, M. dan S. Cerny. (1970). Active Carbon: Manufacture, Properties and Application. Elsevier Publishing Co., New York.

Sudrajat, R. (1985). The Effect of Some Processing Factors on Activated Carbon. *Journal of Forest Research*. Vol.5(11):343-349. Forest Products Research and Development Center, Bogor.

Sudrajat, R.. D. (2005). Active Charcoal manufacture of seeds shell of Jatropha. *Journal of Forest Research*. Vol 23(2):143-159.

Supriadi, M. (2009). Implementation of a participatory model of rejuvenation in a rubber plantation revitalization program. *Warta Perkaretan*. 28(1): 76-86.