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Influences of the Operating Variables of Formic Acid Pulping on Pulp Properties of Perimping Grass

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ABSTRACT

Perimping grass is one of lignocellulosic material which has not been fully utilized yet, so it is potential to be used as a raw material for pulp. The objective of this research is to study influences of the operating variables of formic acid pulping on pulp properties (bursting index, tearing index, and tensile index). Influences of the operating variables were studied by Response Surface Methodology (RSM) with Central Composite Design (CCD). The pulping experiments is carried out at the boiling temperature of cooking liquor on the atmospheric pressure, with 40 grams of perimping grass using formic acid concentrations of 60% - 80%, reaction time from 60 to 180 minutes, and liquid to solid ratio of 10/1 - 20/1, with HCl catalyst of 0.1% wt. The results showed that the physical properties of pulp from perimping grass are bursting index is 22-184,36 kPa m2/g, tearing index is 187-660 mN m2/g, and tensile index is 659.3-2.1149 N m/g.

KEY WORDS: *Formic acid, Organosolv pulping, Perimping grass, Response surface methodology*

1.0 INTRODUCTION

Production pulp in Indonesia in 2015 reaches 7.9 tons, and by 2017 it is estimated at around 10 million tons. Increased production of such pulp at raw material demand in 2017 will reach 45 million m3, up 27.5% from last year which reached 35.3 million m3 [Kemenperin, 2016]. While the availability of wood as a raw material for pulp tends to decrease due to deforestation. Non-wood plants such as grasses have shorter growth cycles, when compared to wood [Madakadze et al., 2010]. Therefore, the use of non-wood raw materials as alternative feedstock pulp can overcome the lack of wood supply.

One type of grass that can be used as an alternative wood is the perimping grass. The perimping grass is found in the tropics as a wild plant, as growth and rapid spread often make it a pest for agricultural land. Thus, the use of perimping grass as an alternative feedstock for pulp can be a solution for agricultural land and also can increase economic added value.

Organosolv pulping is one of the method for pulping which is the process of pulping using organic solvent as a cooking liquor. This method will be used to convert the raw material into a pulp. Organosolv pulping is selected because it uses less energy, chemicals, and this process is relatively environmentally friendly compared to the Kraft process. The resulting pulp is brighter and more easily bleaching, thus saving bleaching chemicals. Another advantage, the organosolv process is the process of hemicellulose hydrolysis and delignification process occurring simultaneously in one stage of the process [Jimenez et al., 2008].

Utilization of perimping grass as a raw material for pulp production has never been done. Therefore, the production of pulp from perimping grass using formic acid as cookingt liquor will be one of the efforts to utilize the grass perimping with products that have economic value and environmentally friendly process. So it can increase the use value of the grass primping and be a solution for the lack of raw materials supply of the pulp industry.

The aim of this study is to determine the effect of process conditions on the properties of pulp such as bursting index, tearing index, and tensile index from perimping grass. The effect between variables studied with RSM. Data from this study may provide information for the development of pulping from perimping grasses.

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2.0 METHODS

The raw materials used in this study were perimping grass, formic acid as a cooking liquor, and HCl as a catalyst. The initial treatment on the perimping grass is uniformed in size by cutting ± 2 cm, and dried in the sun until the water content reaches ± 10%. The pulping experiment was performed in a 1 liter reactor, which is equipped with an electric heater and a condenser. The flowchart of the experiment of pulping of perimping grass is given in Figure 1.

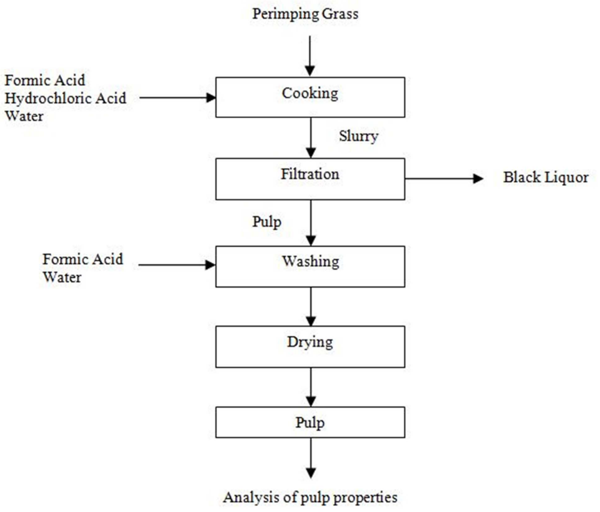

Figure 1. Flow Chart of Pulping Experiment of Perimping Grass

The experimental stage of this research is includes cooking, filtration, washing of pulp, drying, and analysis of pulp properties. The experimental design was performed on the basis of CCD, with 20 experimental and one replication. The effect of the variable on the response is modeled by the 2nd order polynomial equation. The result of the analysis of variation will be processed using STATISTICA 12.5 trial version.

The conditions of the cooking process used were 60%, 70%, and 80% formic acid concentrations, and 0.1% HCl catalysts with 40 grams over dry of raw materials. The reaction time used was 60 minutes, 120 minutes, and 180 minutes with a liquid to solids ratio of 10/1, 15/1, and 20/1 b/b. The solid (pulp) of the experimental results was tested strongly by the TAPPI T 403 om-97 method, strong tearing with TAPPI T 414 om-98 method, and tensile strength with TAPPI T 494 om-01 method. Data retrieval for testing is repeated twice (duplo), to minimize error due to changing circumstances.

3.0 RESULT AND DISCUSSION

The chemical composition of the perimping grass used in this study was 43% of cellulose, 26% of hemicellulose, and of 18% lignin content. The cellulose content from perimping grass is higher celluloce content elephant grass and cellulose content oil palm empty fruit bunches. Then, the hemicellulose content perimping grass lower than hemicellulose content elephant grass, but higher hemicellulose content oil palm empty fruit bunch. Meanwhile, the lignin content of the perimping grass was higher when compared to the elephant grass lignin level 17.70%, but lower when compared to lignin content in empty fruit bunch [Madakadze et al., 2010; Hong et al., 2013]. The perimping grass also has a chemical composition close to or nearly the same as hardwood and softwood as shown in Table 1.

Table 1: Chemical Composition of Various Biomass

Source	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Hardwood	43-47	25-35	16-24
Softwood	40-44	25-29	25-31
Agricultural Waste (Corn Cobs)	45,00	35,00	15,00
Crops Waste (Empty Fruit Bunches)	40,50	24,60	22,00
Plant Fiber (Cotton)	95,00	2,00	1,00
Grasses (Elephant Grass)	40,00	30,00	17,70
Perimping Grass (this research)	43,00	26,00	18,00

Source: Sixta, 2006; Madakadze *et al.*, 2010; Hong *et al.*, 2013; this research

The results of pulping experiment given pulp yield is 43.05% - 61.84%, with cellulose content is 83.56% - 93.10%, while lignin content is 3% - 15%. The average yield of perimping grass is 49.64%, lower than the pulp of dhaincha for yield pulp is 52.90%. While yield pulp of perimping grass is higher than 48.20% yield pulp of kash and 48.30% for banana stem. The average cellulose content of perimping grass is 88.40%, higher than the cellulose content of dhainca is 48.70%. While the average lignin content of pulp perimping grass is 8.43%, lower than that the lignin content of pulp dhainca is 8.50%.

However, lignin content of perimping grass is higher when compared with lignin content of pulp kash is 7.10% and pulp banana stem is 7.40%. Pulp chemical of perimping grass for

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yield pulp and lignin content are quite comparable to that of Jahat et al. [2007] which also uses non-wood raw materials namely dhaincha, kash, and banana stems. However, for cellulose content of pulp is quite different. This was due to the fact that the results obtained were naturally closely linked to experimental conditions, particularly acid and raw material structure used in cooking.

The model coefficients and parameters of pysical properties pulp are shown in Table 2. The value of F_0 compared to the F_{table} value for each response is:

- The result of F_0 for bursting index pulp is less than F_{table} then hypothesis H_0 is accepted.
- The result of F_0 for tearing index pulp is less than F_{table} then hypothesis H_0 is accepted.
- The result of F_0 for tensile index pulp is greater than F_{table} then hypothesis H_0 is rejected.

The value of R^2 for bursting index is 0.1013, tearing index is 0,1000, and tensile index is 0.4065. The value of R^2 obtained is not too high indicates that the independent variable is less able to explain the variant of the dependent variable, which means that the independent variable does not significantly influence the bursting index, tearing index, and tensile index. Probably due to a large error variance (which indicates there is a relatively large data variation is found in the pulp handsheet). The empirical equations obtained for each response are shown in equations (1), (2), and (3).

$$\text{Bursting Index} = 77{,}9955 - 6{,}4152X_1 + 4{,}7478X_2 - 1{,}3996X_3 - 3{,}9313X_1^2 - 2{,}2838X_2^2 - 1{,}7513X_3^2 - 1{,}9994X_1X_2 + 1{,}0912X_2X_3 \quad (1)$$

$$\text{Tearing Index} = 342{,}9497 + 0{,}2002X_1 - 6{,}7113X_2 + 21{,}5361X_3 + 9{,}0435X_1^2 + 14{,}9680X_2^2 + 8{,}4249X_3^2 - 2{,}5625X_1X_2 + 20{,}3125X_1X_3 - 0{,}0625X_2X_3 \quad (2)$$

$$\text{Tensile Index} = 1533{,}3603 - 22{,}9040X_1 + 120{,}5690X_2 + 135{,}2370X_3 - 48{,}8250X_1^2 + 11{,}7330X_2^2 - 64{,}5540X_3^2 - 241{,}3060X_1X_2 + 129{,}1810X_1X_3 + 157{,}6810X_2X_3 \quad (3)$$

With,

X_1 = Concentration of formic acid (%)
X_2 = time (menit)
X_3 = Liquid to solid ratio (b/b)

Table 2: Model Coefficients and Statistical Parameters of pulp properties

Factor	Bursting Index	Tearing Index	Tensile Index
b_{oj}	77,9955	342,9497	1.533,3603
b_{1j}	-6,4152*	0,2002	-22,9040*
b_{2j}	4,7478	-6,7113*	120,5690
b_{3j}	-1,3996*	21,5361	135,2370
b_{11j}	-3,9313*	9,0435	-48,8250*
b_{22j}	-2,2838*	14,9680	11,7330
b_{33j}	-1,7513*	8,4249	-64,5540*
b_{12j}	-1,9994*	-2,5625*	-241,3060*
b_{13j}	1,2869	20,3125	129,1810
b_{23j}	1,0912	-0,0625*	157,6810
R^2	0,1013	0,1000	0,4065
F_o	0,3758	0,2822	2,2831

Note: (*) not significant on $\alpha = 0{,}05$

These pysichal properties of pulp from perimping grass differ from pysichal properties of pulp from dhaincha, kash, and banana stem [Jahan et al., 2007]. The low area shows a low response value with a high variable value, as shown in Figure 2. Bursting index decreases as the concentration of formic acid and reaction time increases. The results are in accordance with the research Lam et al. [2001] which mentions that bursting index value decreases as the concentration of formic acid increases.

Highly concentrated formic acid can cause fibers to become more hydrophobic, since hydrogen bonds are formed between hydroxyl groups in cellulose molecules. This causes the fibers to become more rigid and fragile. The bursting index values obtained in this study ranged from 22 to 84.36 kPa m^2/g. The highest bursting index was obtained at the 15/1 liqud/solid ratio with a reaction time of 120 minutes and a 70% formic acid concentration.

In different with pulp result of citrus sinensis by Moral et al. [2015], pulp of perimping grass has a higher value for tearing index. The different tearing index values due to differences in bond strength between pulp fibers results. Dehydrated fibers are relatively stiff, fragile, inflexible, and easily cut, different to hydrated fibers [Lam et al., 2001]. Pulp perimping grass with

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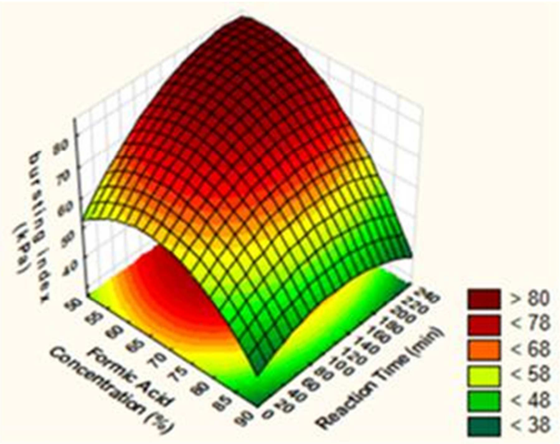
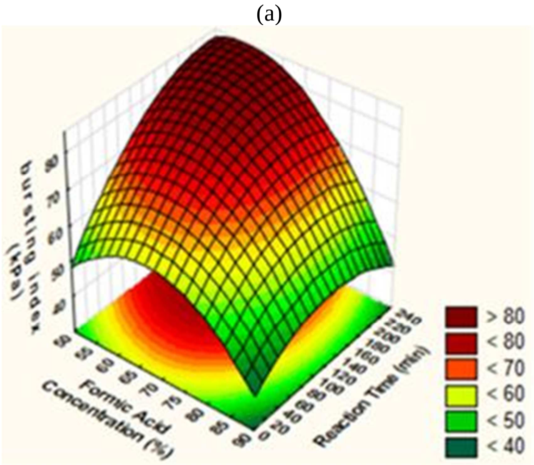
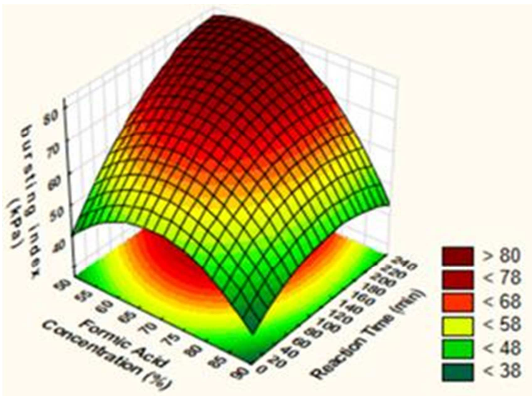
hydrated fibrous formiat acid, because it is relatively rigid, not easily broken, relatively flexible, and not easily cut.



(a)



(b)

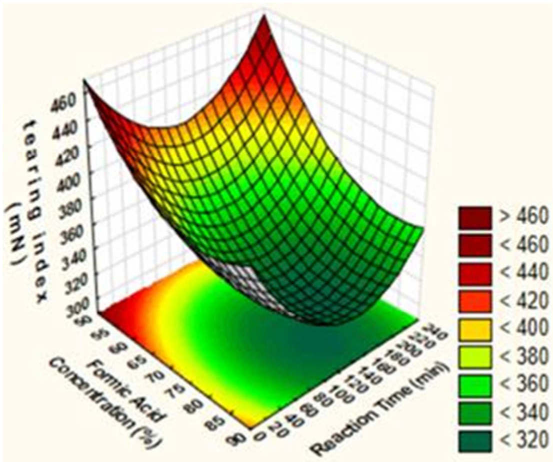


(c)

Figure 2: Effect of Formic Acid Concentration and Time of Reaction on Bursting Index at Liqud to solid ratio (a) 10/1, (b) 15/1, and (c) 20/1

Tearing index value decreases when reaction time and formic acid concentration increase. The high area shows a high response value with a low variable value as shown in Figure 3. The results are in accordance with the results of the research lam et al. [2001], because hydrogen bonds are formed directly between hydroxyl groups in cellulose molecules. The tearing index value obtained in this study ranged from 187-660 mN m2/g. The highest tearing index was obtained at the 20/1 liquid/solid ratio with 60 minutes reaction time and 80% formic acid concentration.

The value of the tensile index decreases as the concentration of formic acid increases at the 10/1 and 20/1 liquid-solids ratios, as shown in Figures 4 (a) and (c). As for the tensile index value with the 15/1 liquid to solids ratio there is an increase as the reaction time increases, as shown in Figure 4 (b). These results are partially in accordance with the results of Moral et al. [2015], which mentions the increasing reaction time there is an increase in the tensile index. That a high degree of depolymerization is not directly implied on the low physical properties of the pulp. Because of the stronger fiber bonds are formed and not easily broken.



(a)

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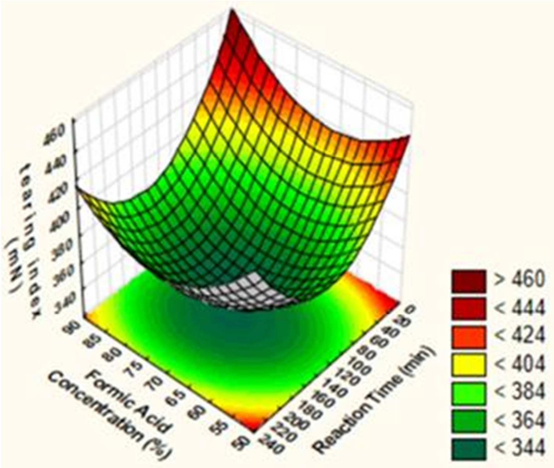

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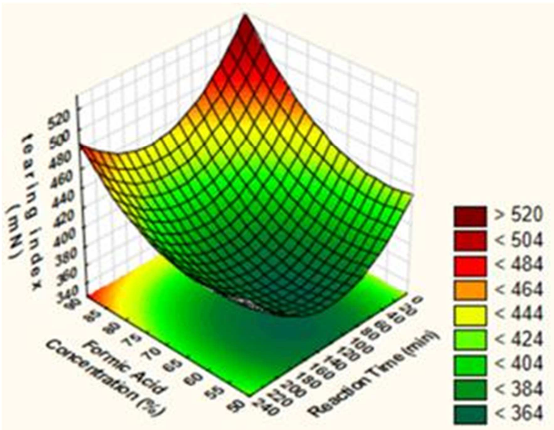

(c)

Figure 3. Effect of Formic Acid Concentration and Time of Reaction on Tearing Index at Liquid to solid ratio (a) 10/1, (b) 15/1, and (c) 20/1

High concentrated formic acid lowers the value of the tensile index as in the bursting and tearing index. Since high concentration formic acid produces direct hydrogen bonds between hydroxyl groups of cellulose molecules [Lam et al., 2001]. The value of tensile index of pulp obtained in this study ranged from 659.3-2149 N m/g. The highest pulp tensile index was obtained in both process conditions, reaction time 180 min, 60% formic acid concentration at solid to liquor ratio is 10/1 and solid to liquor ration is 20/1 liquid/solid.

4.0 CONCLUSIONS

Interaction between variables (concentration of formic acid and reaction time) is a factor that affects pulp tensile index. But none of the factors that affect the bursting index and tearing index. The values obtained for bursting index is 22 - 184.36 kPa m2/g, tearing index is 187 – 660 mNm2/g, and tensile index is 659.3 - 2,149 Nm/g.

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