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INFLUENCE OF PULPING PROCESS CONDITIONS TOWARDS BETTER WATER RESISTANT EFFECT OF DURIAN SHELL PAPER BY LIGNIN: TWO LEVEL FACTORIAL DESIGN APPROACH

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ABSTRACT

Chemical pulping of durian shell fiber is a comparatively new approach in the field of pulping, and the paper industry as a whole. Pressures of rising wood resource consumption have resulted in increased attention on the useof non-wood raw materials in the papermaking industry. This situation is due to trees being exploited in high numbers for the purpose of paper manufacturing. Thus, some alternative solutions have been developed to remedy this. Natural resources wastes like kenaf, bamboo and sugarcane bagasse are used as the raw material to produce these varied grades of paper. Additionally, cellulose fiber possesses a natural tendency to absorb moist and water vapor from the surrounding, producing weak mechanical properties and limiting paper's use. Therefore, in this study, lignin acts as a natural plasticizer in plant cell wall has been optimized to overcome the hygroscopic issue. An optimal amount of lignin will generate maximum hydrophobic effect to prepare for the production of water resistant paper. The process is optimized under the influence of three operational variables; 1) % of NaOH, 2) cooking temperature, and 3) period of cooking. To analyze the response, two level factorial design method by Design Expert v.6.0.8 software has been used. The results show that the highest water contact angle reading of 70.33° has been achieved at the condition of 17 % alkalinity, 140 °C of cooking temperature and 120 min of cooking period. At the same process condition, the highest amount of lignin (57.67 %) has also been obtained which showing the significant interaction between lignin and the hydrophobic effect. From the analysis of variance (ANOVA), all parameters have significantly affected the reading of water contact angle. The P-value of the experiment model is less than 0.0001 and the coefficient of determination value (R^2) is 1.000. This conclusively suggested that the model is significant and influences on the precision and process-ability of the production.

Keywords: durian shell, two level factorial design, lignin, soda pulping, hydrophobic.

INTRODUCTION

Recently, robust advantages of producing composite products from natural fibersare attracting researchers. Kenaf [1], [2], bamboo [3], sugarcane bagasse [4] and paddy straw [5] are some examples of the natural fibers that have currently gained much attraction. Durian shell is also now considered as a great potential source of natural fiber, capable of producing a variety of products. Some of its applications include activated carbon for toxic vapours adsorption [6], carbon electrode for electrochemical capacitor [7], activated carbon for dye removal [8] and insulated particleboard [9]. Like other natural fibers, the use of durian shell is justifiable in terms of renew ability, biodegradability and low-cost aspects. Hence, environmental pollution can be reduced and improved by the decreased number of organic wastes.

Globally, the top four durian producers are dominated by Southeast Asia itself. Thailand occupies the first place by contributing almost 42.62% durian production, followed by Indonesia (34.82 %), Malaysia (19.7%) and finally Philippines (2.87%). In Malaysia, durian (*Durio zibethinus*) is renowned for its culinary purposes, offering an assortment of use in cooking and feeding. The entire fruit is edible, which includes its leaves and flesh. The Department of Agricultural, Ministry of Agricultural and Agro-Based Industry Malaysia has stated that in 2012, durian plantation in Malaysia is the largest yet, occupying 73,933.2 hectares and producing 347,704.4 metric tonne per year [10]. Several Malaysian states that possess huge plantation areas are Johor, Pahang and Kelantan, where by the durian season typically occurs from July to September [10]. In season, durian shell waste dumping will inevitably happen. Therefore, this is a good opportunity to convert the wastes into other profitable and new product.

Durian shell fiber is a widely produced residue that contains cellulose (60.45 %), hemicellulose (13.09 %), lignin (15.45 %), ash (4.35 %) [11]. As an agricultural waste fiber, it is mainly composed of cellulose, a glucose-polymer with relatively high modulus. It is often known as the fibrillar component of many naturally occurring composites.

Lignin is one of the abundant organic polymers in plants, second to cellulose. According to Qingwen *et al.* [12], lignin of cell walls can act as a natural plasticizer. This reinforcement property is provided by polymer, characterized by the brownness amorphous "cement". They fill up the gaps between long and skinny saccharide fibers within the cell walls and bind them together. Lignin has complex structure, consisting of phenolic compounds and amorphous region [13]. The complex network of phenylpropanoid units contained in lignin is thought to be the result of oxidative polymerization on one or more of hydroxycinnamyl alcohol's three types of precursors[14]. Found in the secondary cell walls between cellulose, hemicelluloses and pectin components, it is a chemical compound derived from wood. Lignin is covalently linked to hemicelluloses and cross-linked to different polysaccharides, which is attributable to the mechanical strength of the cell wall and the whole plant. The polymers are hydrophobic and hence impermeable to water, whereas the polysaccharides are permeable to water. Its content varies considerably even in plants of the same species. Boon *et al.* [15] have also investigated the effect of lignin on moisture resistant and mechanical properties of binderless oil palm particleboard.

The optimum amount of lignin in the fibers will assist in the production of water resistant paper, due to its hydrophobic and natural plasticizer properties. Therefore, a lesser amount of chemicals or additives should be added to the paper surface as coating layer, in order to make it more hydrophobic or superhydophobic. In the sphere of open literature, there are no sources yet reporting on optimization of the process condition of pulping, towards determining the optimum amount of lignin for water resistant paper production. Therefore, the objective of this paper is to study the influence of process conditions in pulping parameters that determine the water resistant property of durian shell paper. The independent parameters involved are % of NaOH, cooking temperature and period of cooking on water contact angle reading using two level factorial design.

The traditional optimization process studies one factor at the time. This has led to independent variables' changes, while simultaneously keeping the other variables constant [16]. This approach is more time consuming, expensive and ineffective in finding the optimum parameter particularly when it comes to the interactions of each variable. The consequences include acquirement of false conditions and overlooked true significant factors during the process. To overcome these, two level factorial method of statistical software is used. It is useful when estimating the main and the interactive effects during pulping with only a few experimental runs as compared to the conventional method.

EXPERIMENTAL METHOD

Sample preparation

Durian shells were cleaned up and washed with tap water repeatedly to remove grime and unnecessary materials on its surfaces. Then, they were cut into blocks of approximately 2 to 3 cm long and about 0.3 cm thick. Next, the durian chips were dried at 50 ^oC for 24 hours in the drying oven to remove the moisture content.

Pulping

After the drying process, a dried durian shellnext underwent the process of pulping so as to remove lignin from cellulose. The selected pulping process was the soda pulping process, conducted using rotary digester machine. This process involves the use of sodium hydroxide (NaOH) to make the wood pulp. Approximately 300 g (oven-dried) durian chips were placed into the digester. The process was then carried out based on the half factorial design using two levels of each variable (high and low levels) as shown in Table-1. It consists of independent factors, namely % NaOH (17-21 %), cooking temperature (140-180 ^oC) and cooking period (60-120 min). The ratio of durian chips to cooking liquor was kept at a constant of1:10. The experimental design and statistical analysis were processed using Design Expert v.6.0.8 (Stat-Ease Inc. Minneapolis). The significance and adequacy of the model were tested through the analysis of varience (ANOVA). Once cooked, the unbleached durian shell pulp was washed, screened and centrifuged [17].

Table-1. Factors level used in two levels half factorial design.

Factor	Notation	Factor levels	
		Low (-)	High (+)
% NaOH (%)	A	17	21
Cooking temperature (^oC)	B	60	120
Cooking period (min)	C	1	10

Paper formation

Durianshell paper was made using a paper machine. The papers were pressed using Paper Press machinewith16 cmof diameter in a circular shape. Then, they were dried uniformly inside a control room with condition at 23.0±1°C and 50.0±2 % relative humidity for at least 24 hours before being characterized[17].

Determination of water contact angle (WCA) and lignin content

The water contact angles (WCA) of the samples were examined using FECA Contact-Angle Meter, while the lignin content was identified by TAPPI standard method (TAPPI T 222 om 11) at 23.0 ±1 °C and 50.0 ±2 % relative humidity.

RESULTS AND DISCUSSIONS

Water contact angle of durian shell paper

The water contact angle measurement is the important analytical aspect, in measuring the angle of the droplet on the durian shell paper surface. The WCA readingis contributory of the lignin content recorded. WCA result was set as the response for the experiments. Table-2 is the experimental design of the parameters involved with the response values.

Table-2. Two level factorial design.

Run order	Factor 1 [A]	Factor 2 [B]	Factor 3 [C]	Response [Y]
	NaOH (%)	**Cooking temperature** (° C)	**Cooking period** (min)	**Water contact angle** (°)
1	19.00	160.00	90.00	0°
2	17.00	180.00	60.00	57.38°
3	21.00	180.00	120.00	61.50°
4	17.00	140.00	120.00	70.33°
5	21.00	140.00	60.00	56.33°
6	19.00	160.00	90.00	0°
7	19.00	160.00	90.00	0°

The highest water contact angle obtained is 70.33° on the sample in run 4. Next, the medium water contact angle is 61.50°on the sample in run 3. Meanwhile, the lowest water contact angle is 56.33° on the sample in run 5. Contrariwise, run 1, 6 and 7 show that no angle of water droplet is achieved as the water droplet on those samples' surface are absorbed immediately.

Figure-1 displays the image of water droplet angle for surface of the sample in run 4. As the highest reading obtained, it has occurred at process parameters of 17 % NaOH, 140 °C cooking temperature and 120 min cooking period. Therefore, these are the ideal process conditions in achieving the highest reading of water contact angle. Meanwhile, Figure-2 shows the image of medium water droplet angle reading, which is from sample in run number 3. Water contact angle of 61.50° is achieved under process parameters of involved were 21 % NaOH, 180 °C cooking temperature and 120 min cooking period. Finally, Figure-3 reveals the image of the lowest reading of water droplet angle. From condition sample run number 5, 56.33° reading is achieved. The process parameters involved are 21 % NaOH, 140°C cooking temperature and 60 min cooking period.

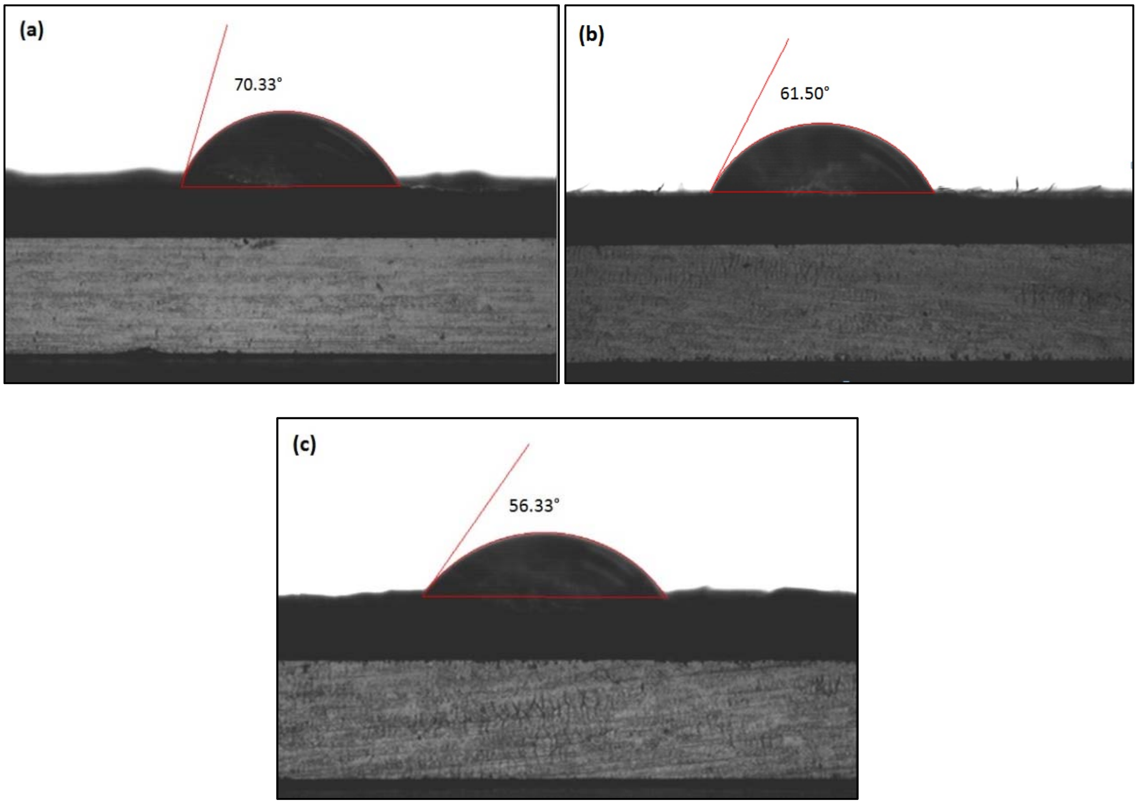

Figure-1. Image of water droplet on surface of (a) sample's run no. 4 (b) sample's run no. 3 and (c) sample's run no. 5.

Design of experiment and statistical analysis

Figure-2 shows the half normal plot for factors affecting water contact angle response. The longer the distance of factors, the bigger effectis seen at the model. Factor C, which is cooking period, shows more effect compared to factors A and B, and becomes the biggest effect for the water contact angle. The red line exhibits the curve fitting of the half normal plot.

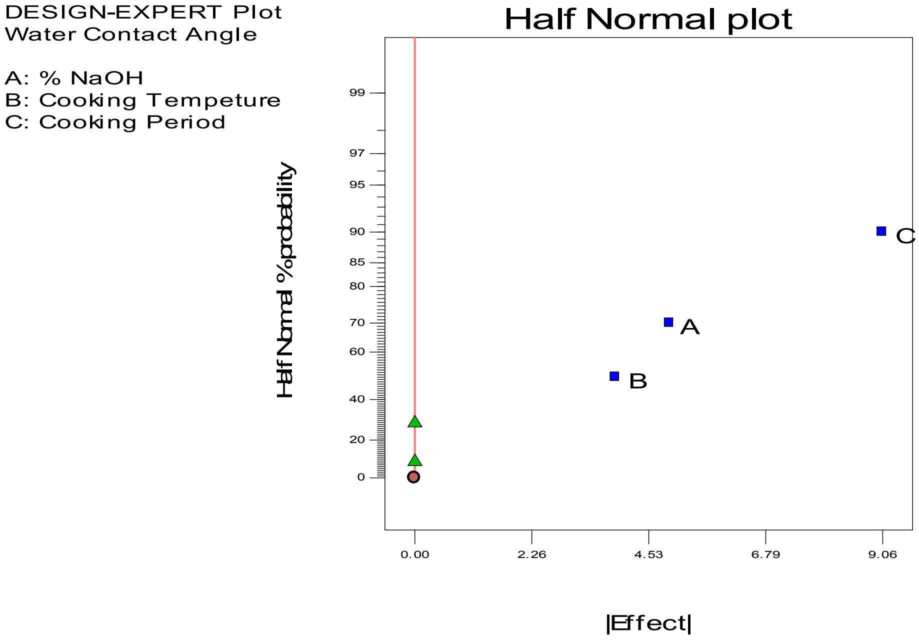

Figure-2. Half normal plot.

Table-3 displays the list of effects for each reference model for the process. Cooking period as factor C shows the most significant effect, with a percentage of contribution of1.24723 and sum of square of 82.0836. Factor A (% NaOH) follows, with a contribution percentage of 0.370805 and sum of square of 24.4036. The lowest affected factor is factor B (cooking temperature), with a percentage of contribution of 0.229927 and sum of square of 15.1321. Hence, factor C is more effective compared to factors A and B on the process model.

Table-3. List of effects for each reference model for the process.

Term	Effect	Sum of square	% Contribution
A	-4.94	24.4036	0.370805
B	-3.89	15.1321	0.229927
C	9.06	82.0836	1.24723

Table-4 depicts the result of second order response surface model fitting in the form of analysis of variance (ANOVA). "Prob > F" values less than 0.0500 indicate that model terms are significant. In this case, all three factors are significant model terms as their P-values are less than 0.001. The "Curvature F-value" of 6.33e+0.07 implies that there is significant curvature in the design space. This is measured by the difference between the average of the centre points and the average of the factorial points. There is only a 0.01% chance that a "Curvature F-value" of a value this large may have occurred due to noise. This model is therefore accurate and can be used for analysis.

Table-4. Analysis of variance (ANOVA) of experimental data using quantity ratio calculation.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value > F
Model	121.62	3	40.54	6.366E+007	< 0.0001
A	24.40	1	24.40	6.366E+007	< 0.0001
B	15.13	1	15.13	6.366E+007	< 0.0001
C	82.08	1	82.08	6.366E+007	< 0.0001
Curvature	6459.63	1	6459.63	6.366E+007	< 0.0001
Pure Error	0.000	2	0.000		
Cor Total	6581.25	6			

A regression model is used to predict the response at any point encompassing experiments by factors in the design [18]. Figure-3 represents a three-dimensional (3D) plot of response water contact angle effectiveness, based on the first stage model selected using factor A (% NaOH) and factor C (cooking period) coefficient. Response surface obtained are caused by interactions on the first stage plane. Based on an examination of the corresponding surfaces, the highest effectiveness of water contact angle shown is at the longest cooking period (120 minutes) and the lowest percentage of NaOH (17 %). Contrariwise, the lowest effectiveness of water contact angle point is seen at the highest percentage of NaOH (21 %) and the shortest cooking period (60 minutes).

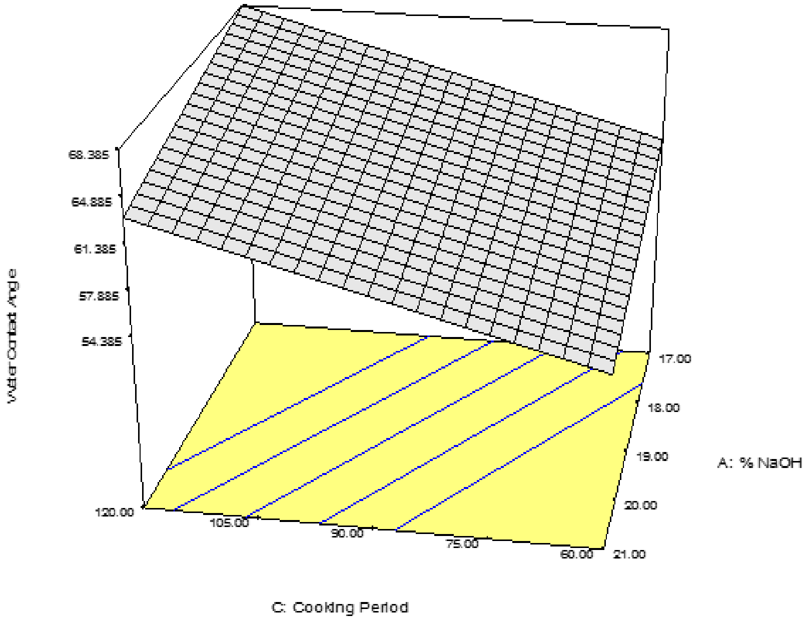

Figure-3. 3D plot shows the effect of cooking period (min) and % NaOH (%), and their mutual interaction on water contact angle.

Figure-4 represents a 3D plot of effectiveness of the response water contact angle, based on the model selected in the first stage. It utilizes factor A (% NaOH) and factor B (cooking temperature) coefficients to show response surface caused by the interaction on the first stage plane. Based on an examination of the corresponding surface, the most effective water contact angle point is seen at the lowest NaOH percentage (17 %) and cooking temperature (140 °C). Contrariwise, the least effective water contact angle point is seen at the highest cooking temperature (180 °C) and percentage of NaOH (21 %).

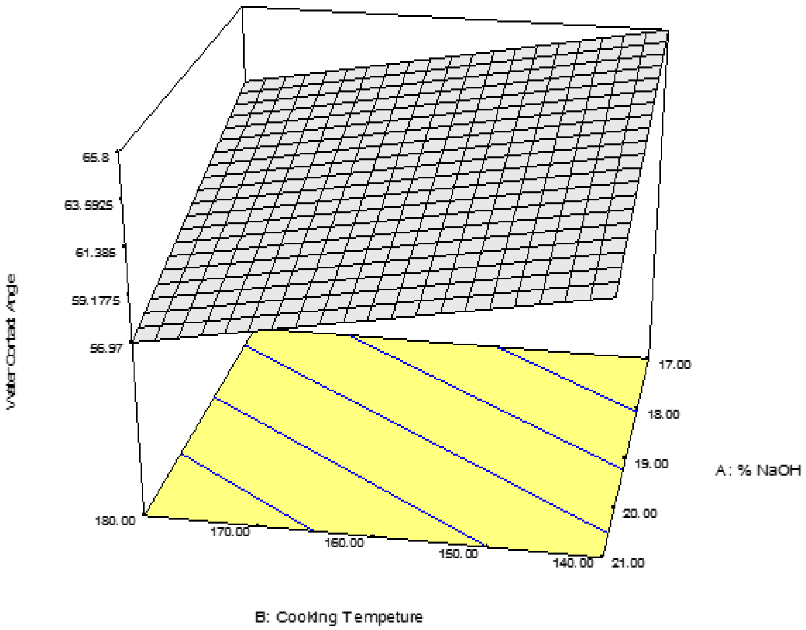

Figure-4. 3D plot shows the effect of cooking temperature (°C) and % NaOH (%), and their mutual interaction on water contact angle.

Lignin content

The amounts of lignin in all of the water contact angles are also calculated. The analysis has been conducted using standard TAPPI 222 os-74. This method describes a procedure that isapplicable to distinguish acid-insoluble lignin in wood and in all grades of unbleached pulps. Table-5 shows the results of lignin content with the parameter process conditions respectively.

Table-5. Two level factorial design with lignin content.

Run	Factor 1 % NaOH	Factor 2 Cooking temperature (° C)	Factor 3 Cooking period (min)	Lignin content (%)
1	19.00	160.00	90.00	-
2	17.00	180.00	60.00	37.13
3	21.00	180.00	120.00	38.00
4	17.00	140.00	120.00	57.67
5	21.00	140.00	60.00	33.15
6	19.00	160.00	90.00	-
7	19.00	160.00	90.00	-

Effect of cooking period on lignin content

Generally, the longer the cooking period is, the higher the degree of lignin removal is seen. A longer period of pulping process will decrease the pulp quality itself, causing it to overcook. It influenced by certain factors such as the nature of fiber materials, conditions and methods of pulping, and the topochemistry of lignin dissolution. As the durian shell pulp is cooked for longer time, condensation of lignin on fiber takes place which results in black liquor. This will resist the delignification from durian shell. This is why black liquor is obtained after a certain time.

Effect of percentage of NaOH on lignin content

As soda is used as the liquor on lignin, it is therefore called as soda lignin which originates from soda or soda-anthraquinone pulping processes. Lignin and hemicelluloses were dissolved instantaneously during the cooking process. Reaction between lignocellulosic components in durian shell and cooking chemicals which is NaOH started at certain reactive sites numbers that are exposed to the chemicals [19]. The reactive sites could be the surface or inside of the durian shell. The reaction causes the opening of the lignocellulosic components that let the chemicals to penetrate the durian shell structure. This results in further decomposition of durian shell components and alteration of its structure as the pulping process proceeds. The number of reactive sites that involved at the starting pulping process might also be influenced by the cooking temperature and chemical concentration that bordered the durian shell.

Increasing the cooking time at a specific temperature, will decrease pH of liquor. It is because, during cooking, the contact between hydroxide ions and durian shell components resulted in deacetylation reactions [20] while pulping causes carbohydrate degradation forming hydroxy acids which lower the pH of the liquor [21]. Table-5 exhibitsthat the lignin content is decreased when the amount of soda liquor increases, indicating that lignin content is reliant on the percentage of soda.

Effect of temperature on lignin content

The amount of lignin content is decreased as the time of reaction process decreases due to its degradation. However, rising the temperature will increase the rate of lignin dissolution. The pulp quality will be affected in a few additional minutes as the delignification reactions are very rapid at high temperatures. Table-5 shows the decreasing amount of lignin by increasing the temperature.

CONCLUSIONS

As a conclusion, the investigation for the relationship between temperature, cooking period and percentage of NaOH towards lignin content and hydrophobicity has been successfully achieved using two-level factorial design. Increased NaOH percentage and cooking temperature both affect lignin content as increased solvent and increased cooking temperature enhance lignin dissolution respectively. Cooking period which is the last effect, also affect lignin content as a longer duration of pulping enhances the degree of lignin removal. All factors contributing towards increased or decreased water contact angle have resulted in hydrophobicity. The highest amount of lignin content acting as natural plasticizer has contributed to the highest of water contact angle.

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