Research Article

Subcritical Water Process for Reducing Sugar Production from Biomass: Optimization and Kinetics

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Abstract

The competitive reactions of lignocellulose hydrolysis and monosaccharide degradation in the subcritical water (SCW) hydrolysis of coconut husk were investigated to optimize the reducing sugar yield. Optimization analysis was performed by response surface methodology (RSM) and kinetics studies. Parameters of process optimization were varied at 130-170 °C for 15-45 min. The reducing sugars were measured using the Dinitro salicylic acid method. The sugar yield increased when the temperature increased from 130 °C to 170 °C. The highest reduction sugar yield of 4.946 g/L was obtained at 183.6 °C for 4.8 min and 23.4 liquid/solid ratio (LSR). Kinetics studies were carried out at temperature variations of 150, 170, and 190 °C and pressures of 60, 80, and 100 bar for 5 to 60 min. The yield of reducing sugar decreased with increasing temperature. The kinetic model 2B is the best method to explain the competitive reaction kinetics of coconut husk hydrolysis. This research is an innovation to increase the reducing sugar to make the process more commercially viable.

Keywords: Coconut Husk; Kinetic Model; Response Surface Methodology; Subcritical water

1. Introduction

An inevitable growth of human population has increased the fuel demand, used up the resources, and polluted the environment [1,2]. Fossil energy depletion has urged the innovation of alternative energy which is renewable such as lignocellulose from agricultural waste [3–5]. Lignocellulose is a potential feedstock for the production of biofuel and the other bioproducts, including chemicals, biofiber, biopulp, enzyme, adsorbent, *etc*. [6–9]. The energy from biofuel, such as biodiesel, bioethanol and biobutanol, biohydrogen, and bio-jet, has been widely applied for transportation sector and power plant because it is renewable, low cost, and environmental friendly [10–12].

The process determining biomass conversion is pretreatment to destruct the complex structure of biomass and hydrolysis to produce

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the sugars [13,14]. The conventional methods using acid, alkali, or oxidative delignification efficiently break the bonding of biomass structure, but require high energy and operational cost and cause hazardous risk to the environment [6,15,16]. Therefore, nowadays the researchers focused on the green technology for sustainable biomass utilization. Subcritical water (SCW) process functioning as pretreatment and hydrolysis simultaneously, has been an attractive technology in the last years [17]. The rapid reaction and environmentally friendly process made this technology as the most interesting biomass conversion process. Besides, the adjustable solvent properties by setting the temperature made the condition for hydrolysis optimizable [18,19].

Cellulose hydrolysis using subcritical water needs high temperature and pressure for reducing sugar production. Subcritical water is defined as the water condition between the boiling point (100 °C) and the critical point (374 °C) in the pressurized condition (0.1–22 MPa) [20]. Therefore, the optimization of reducing sugar yield by variable selection using experimental design to investigate the effects of the factors and minimum number of experiments should be conducted. In the previous study, we reported integrated process of subcritical water and enzymatic hydrolysis of coconut husk succeeded to enhance the fermentable sugar production [21]. The addition of surfactant to subcritical water process also increased the sugar production [22].

Reducing sugar result depends on the competitive reaction of the lignocellulose hydrolysis and monosaccharide degradation [23]. Thus, the kinetics study of cellulose hydrolysis should be investigated. The previous researches [24,25] reported that hydrolysis kinetics of garlic stalk and chitin using Coats−Redfern model resulted activation energy for hydrolysis zone with high correlation coefficient. The first order kinetics model is the most effective to express the hydrolysis kinetics.

Although it has been studied previously, the optimization and kinetics data of the subcritical water hydrolysis process have not been fully clarified. To best our knowledge, the optimization and kinetic study of the conversion of coconut husks using subcritical water for sugar production has not been reported. To fill these research gaps, in this work, SCW process condition have been examined and optimized by using response surface methodology (RSM) to produce maximum sugar yield. Furthermore, kinetics study will be carried out to develop a mathematical model that can represent the

subcritical water hydrolysis process for biomass to biofuel conversion. The optimization and kinetics of sugar production using SCW is projected making the processes more commercially viable.

2. Materials and Methods

2.1 Subcritical Water (SCW) Optimization

2.1.1 Material

Coconut husk was collected from Manado City, Sulawesi Utara, Indonesia. The preparation procedure of the sample was adapted from Muharja *et al.* [22]. Pro analysis grades of Dinitrosalycilic acid, commercial *cellulase,* and *xylanase* were purchased from Sigma Aldrich, Japan.

2.1.2 SCW process

The SCW equipment used in this study was modified from preceding work [26]. The process was run by supplying the Ultra-High Purity Nitrogen gas (PT. Aneka Gas, Sidoarjo, Indonesia) to the reactor with a constant pressure of 80 bar. Process parameters were varied at temperatures of 130 to 170 °C for 15 to 45 min since the condition reached. The sample was washed and dried in the oven at a constant temperature of 60 °C and stored at 4 °C prior to being analyzed.

2.1.3 Analytical method

The reducing sugar was obtained following SCW process. It was measured by using the Dinitrosalicylic acid method [27]. Hydrolysis data were analyzed by applying the two-way analysis of variance (ANOVA). Data are presented as mean standard deviation based on triplicate analyses.

2.1.4 Optimization

Central Composite Design (CCD) was applied to optimize the critical factor of the SCW process. The effect of three independent variables (liquid/solid ratio, time and temperature of reaction) at three levels toward sugar yield as the response was investigated by using Design Expert Software.

2.2 Kinetics

2.2.1 SCW process

Process parameters were varied at temperatures of 150, 170, 190 °C for 5 to 60 min since the condition reached. The process was run by supplying UHP Nitrogen gas to the

reactor with pressure variations of 60, 80, and 100 bar.

2.2.2 Kinetics Model 1

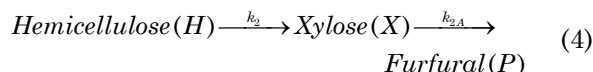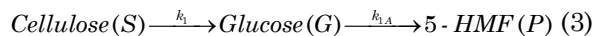Kinetic model 1 was derived based on the following reaction in Equation (1).

$$Biomass\,(SH) \xrightarrow{\;k_1\;} Reducing\,Sugar\,(R) \xrightarrow{\;k_2\;} Degradation\,Product\,(P) \tag{1}$$
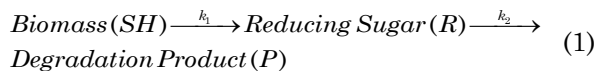
where, k_1 and k_2 are rate constants for the formation of reducing sugars and degradation products. The *SH* symbol represents the combination of cellulose (*S*) and hemicellulose (*H*) components that make up coconut husk, where these two components were degraded into reducing sugar (*R*). Then the kinetics equation can be given in Equation (2).

$$C_R = \frac{k_1 \cdot CSHO}{k_2 - k_1} \left(\exp(-k_1 t) - \exp(-k_2 t) \right) \tag{2}$$

The reaction rate constants k_1 and k_2 can be determined from the fitting of experimental data to Equation (2). The reaction rate constants k_1 and k_2 under different conditions can be determined from the fitting experimental data of the RR reducing sugar yield to Equation (2) using a solver from Microsoft Excel 365.

2.2.3 Kinetics Model 2A and 2B

The 2A kinetics method can be shown in the following Equations (3) and (4).

$$Cellulose\,(S) \xrightarrow{\;k_1\;} Glucose\,(G) \xrightarrow{\;k_{1A}\;} 5\text{-}HMF\,(P) \tag{3}$$

$$Hemicellulose\,(H) \xrightarrow{\;k_2\;} Xylose\,(X) \xrightarrow{\;k_{2A}\;} Furfural\,(P) \tag{4}$$

k_1 is the rate constant for the degradation reaction of cellulose, k_2 is the rate constant for the degradation of the hemicellulose, and k_3 is the rate constant for the degradation reaction of glucose and xylose reducing sugars.

$$C_S = C_{S0} e^{-k_1 t} \tag{5}$$

$$C_H = C_{H0} e^{-k_2 t} \tag{6}$$

$$C_R = \frac{k_1 CSO}{k_3 - k_1} \exp(-k_1 t) + \frac{k_2 CHO}{k_3 - k_2} \exp(-k_2 t) - \frac{k_1 CSO}{k_3 - k_1} - \frac{k_2 CHO}{k_3 - k_2} \exp(-k_3 t) \tag{7}$$

The reaction rate constants k_1, k_2 and k_3 can be obtained from the fitting data of cellulose and hemicellulose concentrations with Equations (5)–(7). The value of activation energy is obtained from the correlation between the reaction rate constant and the temperature of the Arrhenius equation as following Equation (8).

Table 1. Central composite design matrix along with predicted and experimental values for reducing sugar yield in SCW process.

Runs	Reaction time (min)	Liquid/solid ratio (LSR)	Reaction temperature (°C)	Reducing sugar yield (%)		MAPE (%)
				Observed	Predicted	
1	30	15	150	4.3	4.3	0.00
2	30	23.4	150	4.0	4.4	10.00
3	30	15	150	4.3	4.3	0.00
4	15	20	130	3.5	3.2	8.57
5	30	15	150	4.2	4.2	0.00
6	15	10	130	3.4	3.3	2.94
7	15	20	170	4.9	4.8	2.04
8	30	15	150	4.3	4.3	0.00
9	45	10	170	7.6	7.5	1.32
10	30	6.6	150	7.4	7.7	4.05
11	45	10	130	7.0	6.6	5.71
12	45	20	170	3.9	3.6	7.69
13	45	20	130	3.0	2.8	6.67
14	55.2	15	150	4.1	4.4	7.32
15	30	15	150	4.3	4.3	0.00
16	4.8	15	150	2.4	2.6	8.33
17	30	15	116.4	2.8	3.1	10.71
18	30	15	183.6	4.8	5.1	6.25
19	15	10	170	5.2	4.9	5.77
20	30	15	150	4.2	4.2	0.00
			Average			4.37

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (8)$$

where, Ea is the activation energy (kJ.mol^{-1}), k is the reaction rate constant (min^{-1}) for each temperature, R = 8.314 J.mol^{-1}.K^{-1} and A is the exponential factor (min^{-1}). Plot $-\ln (k)$ vs $1/T$ so that the slope is obtained as activation energy and intercept as an exponential factor.

3. Results and Discussion

3.1 Response Surface of SCW Process

At this work, three critical parameters of the SCW process were evaluated to determine variable which has a significant effect in reducing the concentration of sugar using response surface methodology (RSM). Table 1 shows the design and result of the three parameters in the SCW process using a central composite design (CCD). As shown in Table 1, the yields obtained from the SCW pretreatment process varied from 3.37% to 9.89%. The highest reducing sugar yield of 9.89% was attained under a reaction condition of 170°C for 15 min and the LSR

of 20. Mean Absolute Percentage Error (MAPE) and Root mean square error (RMSE) are 4.37 and 0.23, respectively.

The experiment data of sugar yield was used to determine the coefficient of the regression equation (see Equation 9) where X_1, X_2, and X_3 are reaction time, LSR, and temperature. The second-order polynomial equation can be used to predict the yield of reducing sugar.

$$\begin{aligned} Yield = {} & -20.4 + 0.513X_1 - 0.07X_2 + 0.192X_3 \\ & -0.00189X_1^2 + 0.0168X_2^2 - 0.0005X_3^2 \\ & -0.01531X_1X_2 - 0.00095X_1X_3 \\ & +0.00175X_2X_3 \end{aligned} \qquad (9)$$

In the general SCW process, the temperature is one of the significant parameters toward cracking and hydrolysis performance of lignocellulose. It due to the properties of SCW which help in the hydrolysis process (*i.e.*, dielectric constant, density, viscosity, *etc*.) is a function of the temperature [28]. Figure 1 depicts a contour plot graph of the response surface for the reducing sugar yield. The dark blue area indicates the yield of reducing sugar with the lowest concentration, while the dark red area indicates the yield of reducing sugar with the highest concentration. As shown in Figure 1, by increasing temperature, reducing sugar production was increased. The degradation of hemicellulose and cellulose occurred at high temperatures because of water more reactive to break down the complex carbohydrate molecules. Hydrolysis biomass run slowly, on the temperature below 100 °C. Abaide *et al.* [15] revealed that free sugars and most hemicelluloses reacted above 170 °C. Muharja
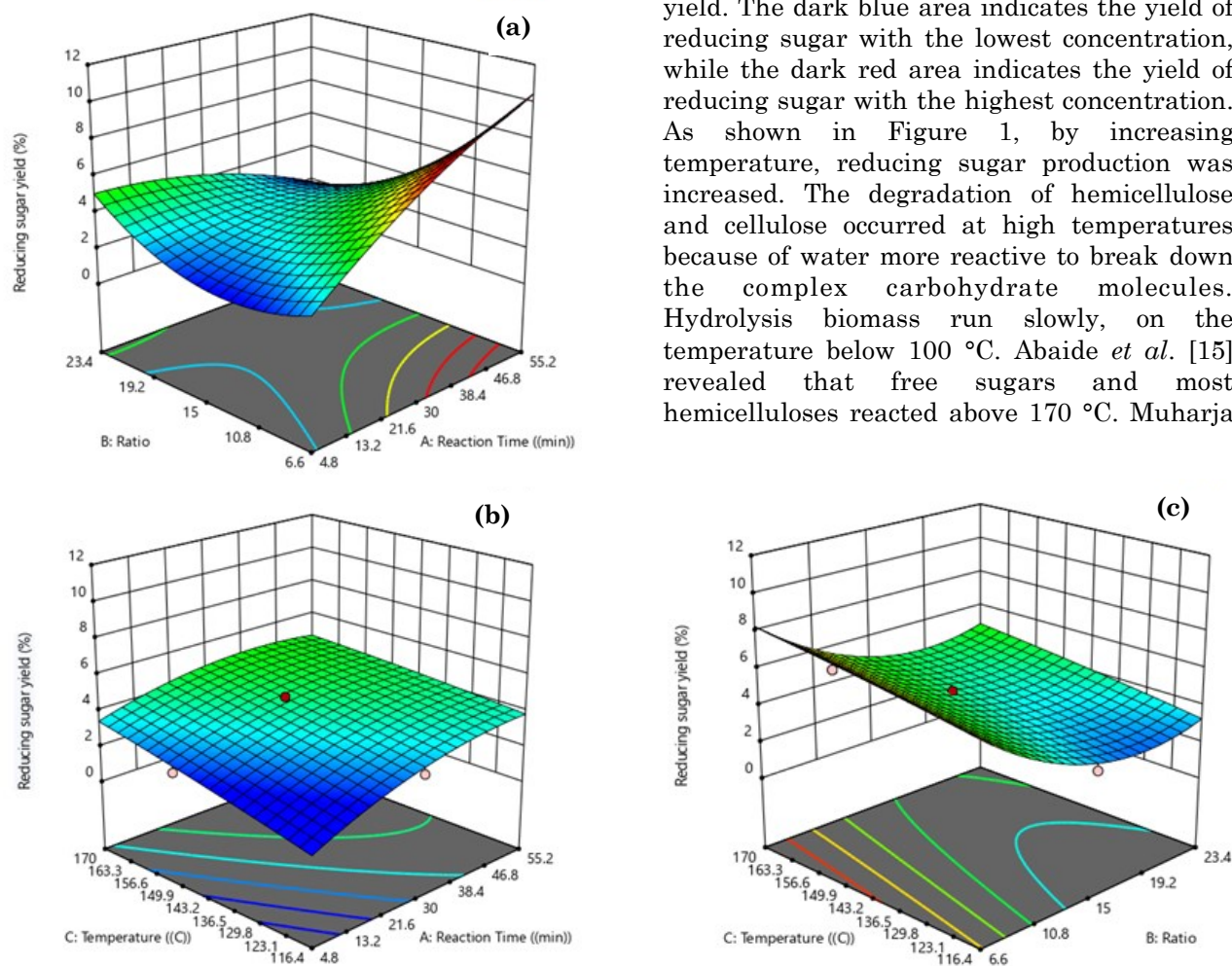

Figure 1. Surface response from RSM design.

et al. [29] showed the same result that hemicellulose extract from coconut husk increase from 67.8% to 73.94% with increasing temperature from 150 to 160 °C.

Another critical parameter on hydrolysis using SCW is reaction time. Reaction time has a significant effect on the recovery of reducing sugar. As shown in Figure 1, the yield of reducing sugar increased with increasing time of reaction and then decreased. This can be explained by the fact that the contact between

the liquid and the substrate causes the carbohydrate complex molecules to be increasingly hydrolyzed. This result is similar to the study of extraction of reducing sugars from date palm fruit by Rambabu *et al.* [30]. They revealed that reducing sugar increased at 5 to 11 min and then decreased.

The amount of water affected sugar yield. In this study, LSR is the most significant parameter in the hydrolysis process (see Table 2). As shown in Figure 1, hydrolysis of reducing sugar increased with increasing LSR. Based on the result of this study, more liquid used in the process cause complex carbohydrate molecules to be more easily hydrolyzed. Higher LSR caused the solution in the reactor is not easily saturated. In the batch process, the saturation of the solution becomes very important because it affects the solubility of the hydrolyzed sugar. The same result was reviewed by Abaide *et al.* [15] where sugar yield increased with increasing LSR for batch SCW system.

After getting the results of the yield of reducing sugar, then the optimum response variable value needs to be calculated using the Derringer method. The Derringer method is used to determine the optimal conditions for obtaining the highest reducing sugar by using the optimum composition of reaction time,
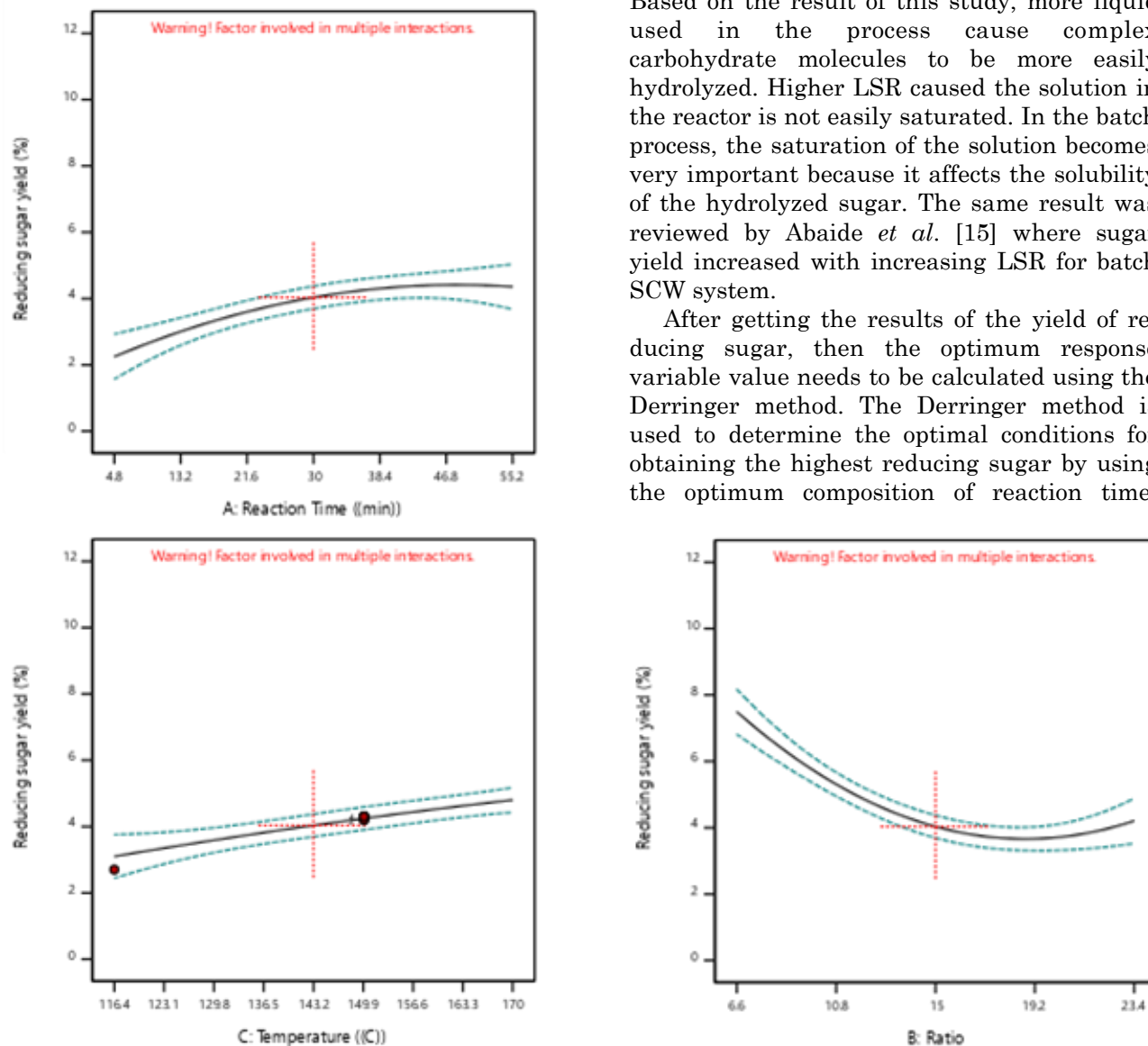

Figure 2. Derringer's desirability graph.

Table 2. Fit Summary of model parameters Reducing sugar yield.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0026	< 0.0001	0.5006	0.2292	
2FI	0.0459	< 0.0001	0.6609	0.4022	
Quadratic	**0.0003**	**< 0.0001**	**0.9295**	**0.7181**	**Suggested**
Cubic	0.9662	< 0.0001	0.8919	-6.4637	Aliased

ratio, and temperature as shown in Figure 2. In Figure 2, it is presented that the highest reducing sugar was obtained under conditions of 30 min of reaction time, 15 of LSR, and 143.2 of temperature.

3.2 Statistical Analysis and Model Fitting

P-value is a parameter to determine the significant factor of the experiment. A p-value of less than 0.05 indicates factors that are significant at the probability level of 95%. Ta-
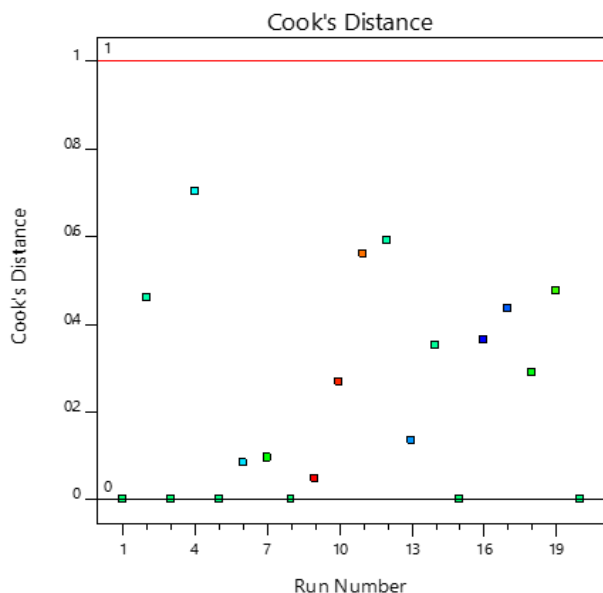
ble 2 is an analysis of variance (ANOVA) to fitness the models, the P-value of the quadratic model of <0.0001 indicates the model used has a significant effect. Based on Table 3, the P-values of reaction time, ratio, and temperature are 0.0002, <0.0001, and 0.0004, respectively, which means that they had a significant effect. The Model F-value of 28.85 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 106.92 implies the Lack of Fit is significant. There is only a 0.01% chance that a Lack of Fit F-value this large could occur due to noise. The value of R^2 (coefficient of determination) of 0.9629 shows the data that supports the model of 96.29% (see Table 4). Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study, ratio of 19.194 indicates an adequate signal. This model can be used to navigate the design space.

Figure 3 shows the plot of cook's distance vs experimental run for the two response cases. The plot shows that the cook's distance values for the responses are mostly within 0 and 1. The cook's distance test in regression analysis usually denoted by Di, is used to identify influential data points that may affect the model. Influential points are used for validity and to indicate which experimental design model is capable of achieving better performance.

Figure 3. The Cook's Distance plot.

Table 3. Analysis of variance (ANOVA) of model parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	37.36	9	4.15	28.85	**< 0.0001**
X_1-Reaction Time	4.49	1	4.49	31.19	**0.0002**
X_2-Ratio	10.92	1	10.92	75.87	**< 0.0001**
X_3-Temperature	3.82	1	3.82	26.58	**0.0004**
$X_1 X_2$	7.03	1	7.03	48.87	**< 0.0001**
$X_1 X_3$	0.2813	1	0.2813	1.95	0.1923
$X_2 X_3$	0.0013	1	0.0013	0.0087	0.9276
X_1^2	0.9693	1	0.9693	6.74	**0.0267**
X_2^2	5.95	1	5.95	41.37	**< 0.0001**
X_3^2	0.0320	1	0.0320	0.2222	0.6475
Residual	1.44	10	0.1439		
Lack of Fit	1.43	5	0.2851	106.92	**< 0.0001**
Pure Error	0.0133	5	0.0027		
Cor Total	38.80	19			

Note: The bold letter denoted the significant value (at a confidence level of 95%).
DF, Adj. SS, and Adj. MS means Degree of Freedom, Adjusted Sum of Squares, and Adjusted Mean of Squares, respectively.

Table 4. Fit Statistics of Model.

Std. Dev.	Mean	C.V. %	R^2	Adjusted R^2	Predicted R^2	Adeq Precision
0.3793	4.48	8.48	0.9629	0.9295	0.7181	19.1944

Figure 4 shows the average leverage which is the sum in the model divided by the number of trials, presented as a design plot. The leverage test is used to determine how much influence a point has on the fit of the model. The model can be said to be appropriate and in accordance with the observations at a point if the point has a leverage value of 1.00. It can be seen in Figure 4, that the plot results show that the mean scores for the responses are mostly within 0 and 1. This means that the model fits the observations very well.

3.3 Determination of Subcritical Water Hydrolysis Kinetics

The kinetics of the degradation reaction of cellulose and hemicellulose to reducing sugars and the reaction kinetics of the degradation of reducing sugars to further degradation products are assumed to follow irreversible first-order reaction kinetics. In this study, the reaction rate constants were obtained by fitting experimental data using Solver non-linear regression in Excel 365. Response rate constants were calculated by several models, including kinetics model 1, kinetics model 2A, and kinetics model 2B whose results can be shown in Table 5.

The 2A kinetics model gave the worst R^2 value. This is probably due to the inaccuracy of cellulose and hemicellulose concentration data

as measured by the gravimetric method. This method is quite long and requires a very high level of skill and accuracy so that it gives the possibility of a high error rate. Table 5 shows that the kinetics models 1 and 2B give fairly good results. Both kinetics models use experimental data on sugar concentrations measured by the DNS method which is known to be quite simple and accurate. Kinetic model 2B is the best method for determining reaction rate constants. This can be seen from the value of R^2 in the kinetics model 2B which is better than the kinetics model 1 and kinetics model 2A.

Hydrolysis of coconut husk SCW was started from reaction time of 5, 20, 40 and 60 min. Figure 5 shows that the reduced sugar yield increased from 0 to 20 min, then decreased from 20 min to 60 min. The increase in reducing sugars is due to the degradation of cellulose and hemicellulose into monomer sugars such as glucose, xylose arabinose, etc. The reduction in yield of reducing sugars that occurs from 20 to 60 min is due to the decomposition of reducing sugars into further degradation products such as furfural. In the GC analysis, the furfural content after SCW hydrolysis was 21.7 mmol/ml at 170°C and 60 bar. The pathway of degraded products such as 5-HMF (5-hydroxymethyl-furfural), furfural, dihydroxyacetone, aldehyde, glycol etc. This is the same as the research from Benito-Román *et al.* [31] that the yield of reducing sugar has decreased at 180 °C and 190 °C from 45 to 180 min.

The reducing sugar yield of coconut husk by SCW hydrolysis was studied from a temperature range of 150 °C to 190 °C which can be shown in Figure 5. In Figure 5 it can be seen that most of the data show that the yield of reducing sugars decreases with increasing temperature. The results of this study indicate that the SCW hydrolysis has a high severity condition where reducing sugars are originally produced from degradation of cellulose and hemicellulose which are then degraded into degradation products such as furfural and 5-HMF [21]. At low severity conditions, the reducing sugar concentration increases when the SCW hydrolysis temperature increases. This was obtained at a reaction time of 5 min. This phenomenon is associated with an
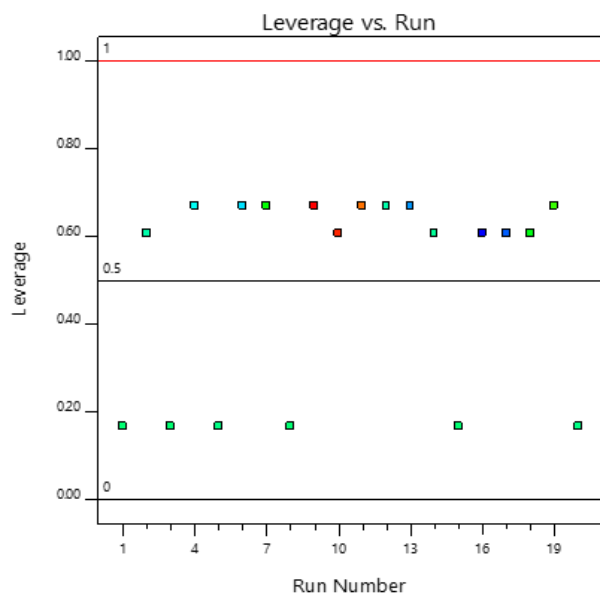

Figure 4. Leverage vs. Run plot.

Table 5. The reaction rate constants k_1, k_2, and k_3 using the various kinetics model.

Model	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	R^2
Model 1	0.0383	0.0336	-	0.9433
Model 2 (2A)	0.0131	0.0229	0.6525	0.5753
Model 3 (2B)	0.0015	0.0056	0.1352	0.9941

increase in the ionization constant (*Kw*) at high temperatures where the concentration of hydroxide ions and hydronium ions has increased. Furthermore, hydronium ions and hydroxide ions break the glycosidic bonds in

cellulose into glucose by attack from electrophilic hydrogen atoms [32]. However, at high severity conditions there is further degradation of reducing sugars where the rate of degradation is higher than the rate of formation.

Several other researchers also experienced an increase in reducing sugar yield at a temperature of 150 to 170 °C and a decrease at a temperature of 170 to 190 °C. Yee *et al.* [33] reported that the yield of sugar increased 81.9% from 5.4 to 29.7 g/L when the temperature was raised from 150 to 170 °C. Then yield of sugar decreased rapidly with increasing temperature where the furfural content at 170 to 190 °C increased from 1.0 to 6.9 g/L. Pattnaik *et al.* [34] reported that the total reducing sugar concentration in the SCW hydrolysis of reed grass increased from 130 to 170 °C and then decreased sharply above 190 °C. Likewise with the results of research from Vedovatto *et al.* [35] that with increasing temperatures above 220 °C in a reactor with a solid to liquid ratio of 9 g/g, reducing sugars were degraded to furfural, while galactose to 5-HMF. The yield of furan increases with increasing temperature and hydrolysis time.

The formation of reducing sugars and degradation products in SCW is represented by the activation energy (*Ea*) and pre-exponential factor (*A*). The kinetics constant used in the calculation of the activation energy is based on the kinetics constant in the kinetics model 2B which is the best kinetics model. Parameters are obtained from the plot between ln *k* vs 1/*T* based on Equation (8). From Figure 6, the slope shows the activation energy and the
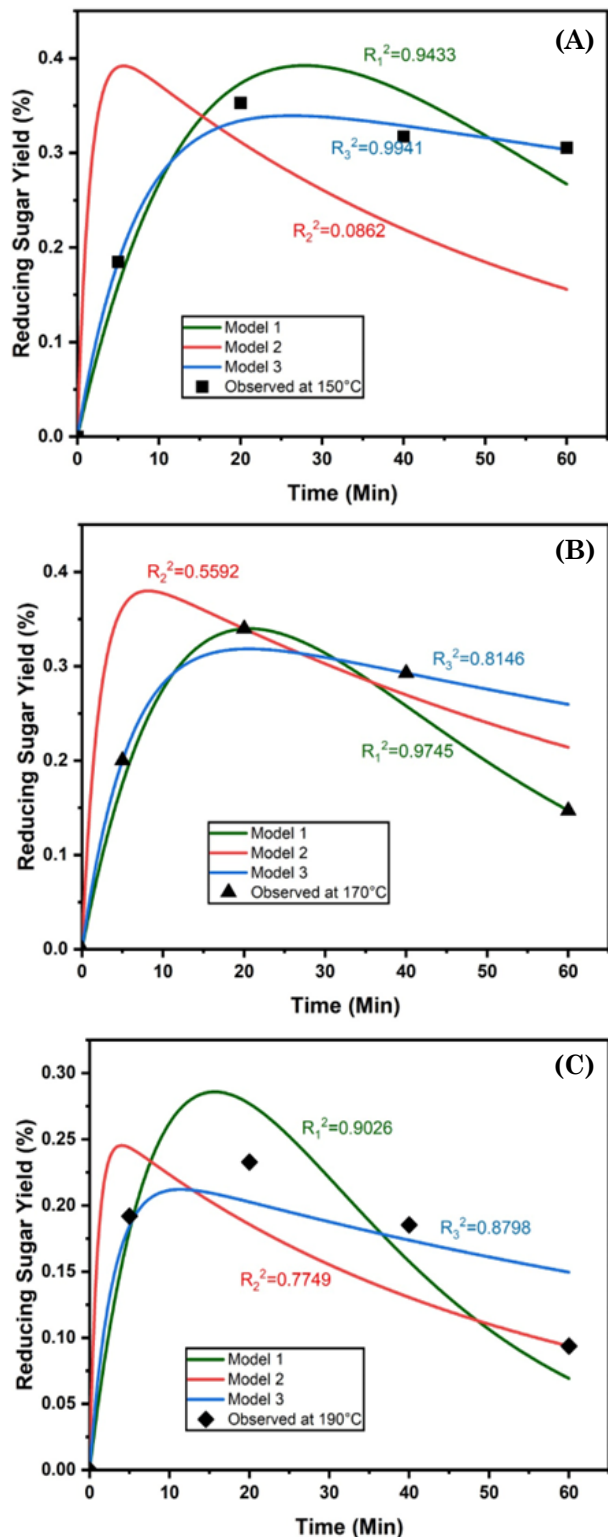

Figure 5. Model validation on the rate of reducing sugar production at temperature of (a) 150 °C, (b) 170 °C, and (c) 190 °C.
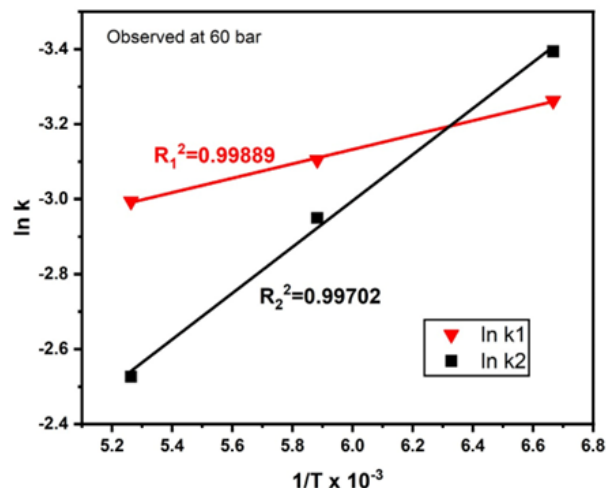

Figure 6. Linier fitting of models constant in various temperature for the formation of reducing sugars and degradation products in SCW.

intercept shows the pre-exponential factor. The activation energy decreases with increasing pressure. This shows that with SCW hydrolysis at high pressure it is easier to form reducing sugars than degradation products. In general, the small activation energy causes the catalytic process in hydrolysis to be better. Under conditions of 60 bar and 150 °C, the activation energy of reducing sugar formation of 15.95 kJ.mol^{-1} is smaller than that of reducing sugar decomposition of 51.24 kJ.mol^{-1}. Alimny *et al.* [36] explained that the activation energy for the formation of reducing sugars is greater than the decomposition of reducing sugars so that it is necessary to increase the performance of SCW at high temperatures. From the research results, the activation energy for the formation of reducing sugars is smaller than the decomposition of reducing sugars, so the process is not required at high temperatures. This is both in terms of energy requirements which are more economical and reduce the presence of inhibitors.

4. Conclusions

Reducing sugar has been successfully gained from coconut husk using subcritical water hydrolysis. The highest yield of sugar was 9.89% with a sugar concentration of 4.946 g/L. The variable water-solid ratio has a significant effect, where the high ratio will produce a high yield. From the optimization, the concentration of reducing sugar from the RSM model was obtained at 183.6 °C for 4.8 min and 23.4 LSR. Kinetic model 2B is the best method for elucidating the competitive reaction kinetics of coconut husk hydrolysis.

Acknowledgments

CRediT Author Statement

Author Contributions: Maktum Muharja: Conceptualization, Methodology, Investigation, Resources, Writing; Arief Widjaja: Supervision, Review and Editing Formal Analysis; Rizki Fitria Darmayanti: Writing, Validation, Review and Editing; Nur Fadhilah: Writing and Analysis; Bramantyo Airlangga: Writing, Validation, Data Curation, Software, Abdul Halim: Review and Editing; Siska Nuri Fadilah: Writting Draft Preparation, Project Administration; I Made Arimbawa:, Data Curation, Visualization; All authors have read and agreed to the published version of the manuscript.

References

[1] Nanda, S., Berruti, F. (2021). Municipal solid waste management and landfilling technologies: a review. *Environmental Chemistry Letters*, 19(2), 1433–1456. DOI: 10.1007/s10311-020-01100-y.

[2] Sharma, H.K., Xu, C., Qin, W. (2019). Biological Pretreatment of Lignocellulosic Biomass for Biofuels and Bioproducts: An Overview. *Waste and Biomass Valorization*, 10(2), 235–251. DOI: 10.1007/s12649-017-0059-y.

[3] Sarker, T.R., Pattnaik, F., Nanda, S., Dalai, A.K., Meda, V., Naik, S. (2021). Hydrothermal pretreatment technologies for lignocellulosic biomass: A review of steam explosion and subcritical water hydrolysis. *Chemosphere*, 284, 131372. DOI: 10.1016/j.chemosphere.2021.131372.

[4] Djali, M., Kayaputri, I.L., Kurniati, D., Sukarminah, E., Mudjenan, I.M.H., Utama, G.L. (2021). Degradation of Lignocelluloses Cocoa Shell (*Theobroma cacao* L.) by Various Types of Mould Treatments. *Journal of Food Quality*, 2021, 6127029. DOI: 10.1155/2021/6127029.

[5] Rahardjo, A.H., Azmi, R.M., Muharja, M., Aparamarta, H.W., Widjaja, A. (2021). Pretreatment of Tropical Lignocellulosic Biomass for Industrial Biofuel Production : A Review Pretreatment of Tropical Lignocellulosic Biomass for Industrial Biofuel Production : A Review. *IOP Conf Series: Materials Science and Engineering*, 1053, 012097. DOI: 10.1088/1757-899X/1053/1/012097.

[6] Bardhan, P., Deka, A., Bhattacharya, S.S., Mandal, M., Kataki, R. (2022). Economical aspect in biomass to biofuel production. In: *Value-Chain of Biofuels*. Elsevier, pp. 395–427. DOI: 10.1016/B978-0-12-824388-6.00003-8.

[7] Shehu, M.R. (2022). The Production of Bio-Aviation Fuel Precursor (Isoprenol) from Engineered E. coli Using Different Feedstocks. *Thesis*, Southern Illinois University Edwardsville.

[8] Muharja, M., Darmayanti, R.F., Palupi, B., Rahmawati, I., Fachri, B.A., Setiawan, F.A., Amini, H.W., Rizkiana, M.F., Rahmawati, A., Susanti, A., Putri, D.K.Y. (2021). Optimization of microwave-assisted alkali pretreatment for enhancement of delignification process of cocoa pod husk. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(1), 31–43. DOI: 10.9767/bcrec.16.1.8872.31-43.

[9] Muharja, M., Fadilah, S.N., Arimbawa, I.M., Hasanah, S., Darmayanti, R.F., Rois, M.F., Asrofi, M. (2022). Low-cost, sustainable, and high-capacity magnetite–cellulose adsorbent from Ramie stem (Boehmeria nivea L.) as oil spill solution. *Chemical Papers*, 76, 7429–7440. DOI: 10.1007/s11696-022-02423-6.

[10] Malolan, R., Panchamoorthy, K., Dai, G., Vo, V.N., Sai, R. (2021). Green ionic liquids and deep eutectic solvents for desulphurization, denitrification, biomass, biodiesel, bioethanol and hydrogen fuels : a review. *Environmental Chemistry Letters*, 19(2), 1001–1023. DOI: 10.1007/s10311-020-01113-7.

[11] Darmayanti, R.F., Susanti, A., Setiawan, F.A., Rizkiana, M.F., Muharja, M., Aji, B.B., Prasiefa, M.G., Dewi, L.T., Yanti, Z.A. (2021). Exploring Starch Sources for the Refreshment Process of Acetone-Butanol-Ethanol Fermentation with Clostridium Saccharoperbutylacetonicum N1-4. *International Journal of Technology*, 12(2), 309–319. DOI: 10.14716/ijtech.v12i2.4354.

[12] Muharja, M., Darmayanti, R.F., Fachri, B.A., Palupi, B., Rahmawati, I., Putri, D.K.Y., Amini, H.W., Setiawan, F.A., Asrofi, M., Widjaja, A., Halim, A. (2022). Biobutanol Production from Cocoa Pod Husk Through a Sequential Green Method: Depectination, Delignification, Enzymatic Hydrolysis, and Extractive Fermentation. *Bioresource Technology Reports*, 21, 101298. DOI: 10.1016/j.biteb.2022.101298.

[13] Zhou, Z., Liu, D., Zhao, X. (2021). Conversion of lignocellulose to biofuels and chemicals via sugar platform: An updated review on chemistry and mechanisms of acid hydrolysis of lignocellulose. *Renewable and Sustainable Energy Reviews*, 146, 111169. DOI: 10.1016/j.rser.2021.111169.

[14] Hashemi, S.S., Karimi, K., Mirmohamadsadeghi, Safoora (2019). Hydrothermal Pretreatment of Safflower Straw to Enhance Biogas Production. *Energy*, 172, 545–554. DOI: 10.1016/j.energy.2019.01.149.

[15] Abaide, E.R., Ugalde, G., Di Luccio, M., Moreira, R. de F.P.M., Tres, M. V, Zabot, G.L., Mazutti, M.A. (2019). Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode. *Bioresource Technology*, 272, 510–520. DOI: 10.1016/j.biortech.2018.10.075.

[16] Batista, G., Souza, R.B.A., Pratto, B., dos Santos-Rocha, M.S.R., Cruz, A.J.G. (2019). Effect of severity factor on the hydrothermal pretreatment of sugarcane straw. *Bioresource Technology*, 275, 321–327. DOI: 10.1016/j.biortech.2018.12.073.

[17] Cocero, M.J., Cabeza, Á., Abad, N., Adamovic, T., Vaquerizo, L., Martínez, C.M., Pazo-Cepeda, M.V. (2018). Understanding biomass fractionation in subcritical & supercritical water. *Journal of Supercritical Fluids*, 133, 550–565. DOI: 10.1016/j.supflu.2017.08.012.

[18] Torres-Mayanga, P.C., Azambuja, S.P.H., Tyufekchiev, M., Tompsett, G.A., Timko, M.T., Goldbeck, R., Rostagno, M.A., Forster-Carneiro, T. (2019). Subcritical water hydrolysis of brewer's spent grains: Selective production of hemicellulosic sugars (C-5 sugars). *The Journal of Supercritical Fluids*, 145, 19–30. DOI: 10.1016/j.supflu.2018.11.019.

[19] Abaide, E.R., Mortari, S.R., Ugalde, G., Valério, A., Amorim, S.M., Di Luccio, M., Moreira, R. de F.P.M., Kuhn, R.C., Priamo, W.L., Tres, M. V., Zabot, G.L., Mazutti, M.A. (2019). Subcritical water hydrolysis of rice straw in a semi-continuous mode. *Journal of Cleaner Production*, 209, 386–397. DOI: 10.1016/j.jclepro.2018.10.259.

[20] Okolie, J.A., Mukherjee, A., Nanda, S., Dalai, A.K., Kozinski, J.A. (2021). Next-generation biofuels and platform biochemicals from lignocellulosic biomass. *International Journal of Energy Research*, 45(10), 14145–14169. DOI: 10.1002/er.6697.

[21] Muharja, M., Junianti, F., Ranggina, D., Nurtono, T., Widjaja, A. (2018). An integrated green process: Subcritical water, enzymatic hydrolysis, and fermentation, for biohydrogen production from coconut husk. *Bioresource Technology*, 249, 268–275. DOI: 10.1016/j.biortech.2017.10.024.

[22] Muharja, M., Umam, D.K., Pertiwi, D., Zuhdan, J., Nurtono, T., Widjaja, A. (2019). Enhancement of sugar production from coconut husk based on the impact of the combination of surfactant-assisted subcritical water and enzymatic hydrolysis. *Bioresource Technology*, 274, 89–96. DOI: 10.1016/j.biortech.2018.11.074.

[23] Muharja, M., Fadhilah, N., Darmayanti, R.F., Sangian, H.F., Nurtono, T., Widjaja, A. (2020). Effect of severity factor on the subcritical water and enzymatic hydrolysis of coconut husk for reducing sugar production. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15(3), 786–797. DOI: 10.9767/bcrec.15.3.8870.786-797.

[24] Yang, W., Wang, H., Zhou, J., Wu, S. (2018). Hydrolysis kinetics and mechanism of chitin in subcritical water. *Journal of Supercritical Fluids*, 135, 254–262. DOI: 10.1016/j.supflu.2018.01.029.

[25] Singh, S., Sawarkar, A.N. (2020). Thermal decomposition aspects and kinetics of pyrolysis of garlic stalk. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 1–11. DOI: 10.1080/15567036.2020.1716891.

[26] Muharja, M., Fadhilah, N., Nurtono, T., Widjaja, A. (2020). Enhancing enzymatic digestibility of coconut husk using nitrogen-assisted subcritical water for sugar production. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15(1), 84–95. DOI: 10.9767/bcrec.15.1.5337.84-95.

[27] Yu, G., Zhao, J., Wei, Y., Huang, L., Li, F., Zhang, Y., Li, Q. (2021). Physicochemical Properties and Antioxidant Activity of Pumpkin Polysaccharide (Cucurbita moschata Duchesne ex Poiret) Modified by Subcritical Water. *Foods*, 10(1), 197. DOI: 10.3390/foods10010197

[28] Alper, K., Tekin, K., Karagöz, S., Ragauskas, A.J. (2020). Sustainable energy and fuels from biomass: a review focusing on hydrothermal biomass processing. *Sustainable Energy & Fuels*, 4(9), 4390–4414. DOI: 10.1039/D0SE00784F.

[29] Muharja, M., Junianti, F., Nurtono, T., Widjaja, A. (2017). Combined subcritical water and enzymatic hydrolysis for reducing sugar production from coconut husk. *AIP Conference Proceedings*, 1840, 030004. DOI: 10.1063/1.4982264.

[30] Rambabu, K., AlYammahi, J., Thanigaivelan, A., Bharath, G., Sivarajasekar, N., Velu, S., Banat, F. (2022). Sub-critical water extraction of reducing sugars and phenolic compounds from date palm fruit. Biomass *Convers Biorefinery*, in press. DOI: 10.1007/s13399-022-02386-4

[31] Benito-Román, Ó., Alonso-Riaño, P., Díaz de Cerio, E., Sanz, M.T., Beltrán, S. (2022). Semi-continuous hydrolysis of onion skin wastes with subcritical water: Pectin recovery and oligomers identification. *Journal of Environmental Chemical Engineering*, 10(3), 107439. DOI: 10.1016/j.jece.2022.107439.

[32] Zhao, Y., Lu, K., Xu, H., Zhu, L., Wang, S. (2021). A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion. *Renewable and Sustainable Energy Reviews*, 139, 110706. DOI: 10.1016/j.rser.2021.110706.

[33] Cheng Yee, L., Shamsudin, S., Farihan Kasim, K. (2020). Comparative Study of Various Pretreatment on Sugar Production from Mixed Rice Biomass. *IOP Conference Series: Materials Science and Engineering*, 864(1), 12209. DOI: 10.1088/1757-899X/864/1/012209.

[34] Pattnaik, F., Nanda, S., Kumar, V., Naik, S., Dalai, A.K. (2022). Isolation of cellulose fibers from wetland reed grass through an integrated subcritical water hydrolysis-pulping-bleaching process. *Fuel*, 311, 122618. DOI: 10.1016/j.fuel.2021.122618.

[35] Vedovatto, F., Ugalde, G., Bonatto, C., Bazoti, S.F., Treichel, H., Mazutti, M.A., Zabot, G.L., Tres, M.V. (2021). Subcritical water hydrolysis of soybean residues for obtaining fermentable sugars. *Journal of Supercritical Fluids*, 167, 105043. DOI: 10.1016/j.supflu.2020.105043.

[36] Alimny, A.N., Muharja, M., Widjaja, A. (2019). Kinetics of Reducing Sugar Formation from Coconut Husk by Subcritical Water Hydrolysis. *Journal of Physics: Conference Series*, 1373(1), 012006. DOI: 10.1088/1742-6596/1373/1/012006.