

Microwave-Assisted Urea-Based-Hydrotropic Pretreatment of Rice Straw: Experimental Data and Mechanistic Kinetic Models

Indah Hartati, Hary Sulistyono,* Wahyudi Budi Sediawan, Muhammad Mufti Azis, and Mohammad Fahrurrozi



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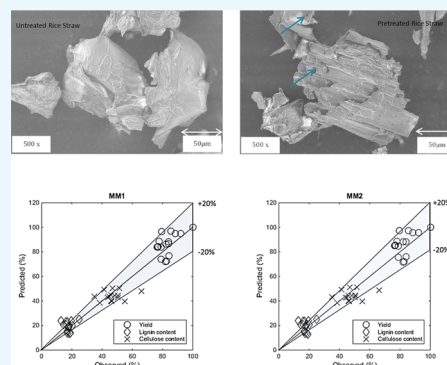
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ABSTRACT: The three major lignocellulose components can be transformed into various biomass-derived platform fuels, chemicals, and materials upon pretreatment and chemical upgrading. Lignocellulose pretreatment is an important step to obtain an eco-friendly, economical, and effective biomass utilization process. The combination of microwave heating and hydrotropic pretreatment is considered as a green method of lignocellulose pretreatment. Experimental data and two mechanistic kinetic models of microwave-assisted pretreatment of rice straw are presented. Here, the use of urea solution as the hydrotropic agent was examined to facilitate the degradation of three major lignocellulose components. The first kinetic model assumes that the soluble lignin does not undergo condensation, while the second one assumes that part of the soluble lignin condenses to a solid product. The mechanistic models were validated with a series of experimental data obtained from microwave-assisted hydrotropic pretreatment of rice straw. The results show that both models could generally describe the experimental data well. However, based on the evaluation of the results of the kinetic models, it turned out that the rate of lignin condensation was relatively slow compared to the rate of lignin degradation to soluble lignin (the value of k_c is relatively small compared to the value of k_{11}). Hence, the kinetic model with exclusion of lignin condensation is suggested more since it is mathematically simpler. The proposed mechanistic model can also predict the cellulose and hemicellulose dissolution and thereby can be used as a process optimization tool. The microwave-assisted urea-based hydrotropic pretreatment conducted at a solid–liquid ratio of 1:35, a urea concentration of 36.8%, a reaction temperature of 90 °C, and a pretreatment duration of 73.6 min is predicted to give a solid residue with low lignin content and high cellulose content which resulted in a cellulose to lignin ratio of 5.53. Cellulosic biomass characterization revealed that microwave-assisted hydrotropic pretreatment was able to produce higher crystallinity and thermally stable cellulosic biomass.



1. INTRODUCTION

Rice is an important staple food in Indonesia with a production rate of more than 70 million tons in 2018.¹ As one of the major rice-producing countries, Indonesia has huge biomass resources such as rice straw. Rice straw is the residue of rice production which can be burnt to improve the soil or used as livestock food. There has been a lot of interest in utilizing rice straw as a raw material for cellulose production. The broad potential application of cellulose has driven the development of lignocellulose pretreatment methods. In general, the lignocellulose pretreatment method can be classified into physical, chemical, physicochemical, and biological processes. Lignocellulose hierarchical structure complexity as well as its intractable characteristic has been considered as the critical challenge in lignocellulose pretreatment.

There has been huge interest in developing an environmentally friendly chemical pretreatment process such as the use of a hydrotrope solution.^{2,3} Hydrotropic chemistry denotes the application of a class of chemical compounds that cause

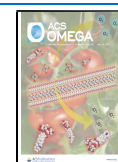
several-fold increase in the solubility of sparingly soluble organic compounds as well as water-insoluble compounds, including lignin, under normal conditions in aqueous solutions.⁴ Sodium xylene sulfonate,^{4,5} sodium cumene sulfonate,^{4,5} *p*-toluenesulfonic acid (*p*-TsOH),⁶ sodium benzoate,⁷ and urea^{8–10} are some hydrotropes that have been utilized in the lignocellulose fractionation of biomasses.

Urea solution is considered as a good hydrotrope for lignin removal due to its ability in breaking the inter- and intramolecular hydrogen bonds of lignin¹¹ as well as its less impact on other lignocellulose components.¹⁰ Urea is of great help in the lignin dissolution process due to its role in forming

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new hydrogen bonds with lignin. Urea also weakens π - π stacking in lignin by forming O- π structures.¹¹ Based on molecular simulations, it was described that hydrogen bonding of urea molecules and lignin occurs in the H-bond adsorption sites on hydroxyl groups of lignin which is supposed to be hydrophilic.¹²

Urea has been utilized in the pretreatment of rice straw,⁸ eucalyptus kraft pulp,⁹ wheat straw,¹⁰ corn waste,¹³ and oil palm waste.¹⁴ Dong et al.⁸ found that urea was able to remove as much as 29.97% of rice straw lignin in the delignification process at low temperatures. However, the addition of 8 M of urea solution to eucalyptus kraft pulp with 15% consistency and 2 h of treatment duration was able to remove as high as 19.4% of lignin content which is represented by its κ number.⁹

Furthermore, the recalcitrant nature of lignin and the heat transfer mechanism made the application of conventional heating on lignocellulose pretreatment result in the long duration of the process and the high energy consumed.¹⁵ Microwave-assisted pretreatment is stated as an efficient method as it offers several advantages compared to the conventional heating. Microwave heating is characterized as a high-energy-efficient process due to its rapid, uniform, direct, and selective heating. The low-energy requirement, the low-reaction temperature, the simplicity of the process, and the higher ability in removing the acetyl groups in hemicellulose are some interesting features of the microwave-assisted pretreatment process.¹⁶⁻¹⁸ A myriad of literature on lignocellulose pretreatment have also reported the combination of the microwave process with several chemicals such as alkali, deep eutectic solvents, subcritical water, ethanol, and acetic acid.^{16,19,20} The combination of microwave heating and hydrotrope in biomass pretreatment was also reported.²¹ It was reported that the cellulose concentration increased, while 44% of lignin was removed from the distillery stillage which was pretreated with sodium cumene sulfonate under microwave heating.²¹

Moreover, although the main objective of the pretreatment is lignin removal, it is important to note that pretreatment with chemical agents as well as microwave heating also resulted in the solubilization of cellulose and hemicellulose.^{4,22-24} Cellulose conversion into a water-soluble component in the NaOH/urea system was also reported.²⁵ Hence, investigating the behavior of lignocellulose component dissolution in the pretreatment process is important in order to get a better understanding toward the behavior of lignin, cellulose, and hemicellulose during pretreatment.

Kinetic modeling is a useful tool to quantify the conversion of lignocellulose components. Unfortunately, the available literature on the kinetic modeling of biomass, which present the lignocellulose component behavior during pretreatment, is limited. Dang and Nguyen²⁶ proposed a heterogeneous kinetic model of lignocellulose pretreatment based on the power law of growth and Avrami's nuclei growth concepts. Their proposed model was validated with data of several pretreatment processes of various biomasses and presented the lignin concentration profile as a function of time.²⁶ The heterogeneous kinetic model of hydrotropic pretreatment of sugarcane bagasse based on a general diffusion model for flat-shaped particles was proposed and validated by Ansari,⁵ while Hartati et al.²⁷ developed a mathematical model for hydrotropic lignin separation of slab-shaped particles, assuming that the delignification process occurs through simultaneous processes of hydrotrope intraparticle diffusion, second-order reaction of

lignin hydrotrope, and intraparticle soluble delignification product diffusion.

The heterogeneous structure of lignocellulose particles and mass-transfer effects of the reactants and products were often neglected which resulted in a pseudo-homogeneous system.^{28,29} Chemical reactions in the pretreatment process are numerous, but the overall process can be described as a conversion of lignin, cellulose, carbohydrates, xylan, and pretreatment chemical agents into dissolved components.³⁰ Further condensation of the dissolved lignin was reported that occur in kraft, organosolv, hydrothermal, and hydrotropic processes.³¹⁻³⁵ Lignin condensation in organosolv treatment is inevitable, even with the addition of a small amount of acid.³⁵ The condensed lignin, which re-deposits on the solid residue surface of the pretreatment process, has a detrimental impact on the enzymatic hydrolysis.³⁴ This undesirable reaction also results in a solid residue with lower cellulose purity and lower lignin removal. In terms of lignin recovery, condensation of lignin also results in a lower lignin yield. The condensed lignin is also reported to be more recalcitrant than the native one, hence hindering its further upgrading and incorporation into materials;³⁵ thus, several efforts have been made to minimize and to prevent lignin condensation as well as to investigate the kinetic models considering the condensation reaction.³⁶ However, due to the absence of acid and or the application of mild conditions, low-lignin condensation or even no occurrence of condensation reaction was also reported.^{29,37,38} A kinetic model of atmospheric formic acid pretreatment of wheat straw with negligible condensation of lignin and with the application of mild conditions was proposed and investigated.³⁷

Considering the possible solubilization of lignocellulose components, the condensation of soluble lignin, as well as the lack of a pseudo-homogeneous kinetic model of microwave-assisted hydrotropic pretreatment process, the objective of the present study is to develop a mechanistic model of microwave-assisted pretreatment of rice straw with urea solution as the hydrotropic agent. The proposed model was constructed based on a pseudo-homogeneous system to predict the conversion of lignocellulose components under a pretreatment step. The proposed kinetic model was also aimed to evaluate the role of a lignin condensation step by validating the model with the experimental data.

2. MATERIALS AND METHODS

2.1. Materials. Solar dried rice straw collected from local rice fields in Semarang, Central Java, was chopped, grinded, and separated with a 60-mesh filter sieve. The cellulose, hemicellulose, lignin, ash, and hot water-soluble content of rice straw powder in the present study were 35.230.53, 20.11, 22.75 \pm 1.53, 9.85 \pm 1.02, and 8.77 \pm 1.03%, respectively. Urea with a purity of 98.57% was produced and supplied by PUSRI, an Indonesian fertilizer plant. In addition, sulfuric acid and sodium hydroxide were purchased from Merck.

2.2. Microwave-Assisted Hydrotropic Pretreatment. Fifteen grams of dry basis of rice straw powder was inserted into a three-neck glass jar followed by the addition of a urea solution. The three-neck glass jar was then inserted into the microwave (EMM2308X model from Electrolux) with a condenser and temperature and agitation speed controls. The microwave power level was set to medium level (450 W), the temperature was set to the target temperature of 363 K, and the agitation speed was set at 600 rpm. The parameter

Table 1. Experimental Process Variables

code	L/S ratio	hydrotrope concentration (%)	time (min)	code	L/S ratio	hydrotrope concentration (%)	time (min)
P1	30	10	20	P9	35	20	6.36
P2	30	10	60	P10	35	20	40
P3	30	30	20	P11	35	20	40
P4	30	30	60	P12	35	20	73.63
P5	40	10	20	P13	35	3.18	40
P6	40	10	60	P14	35	36.82	40
P7	40	30	20	P15	26.59	20	40
P8	40	30	60	P16	43.40	20	40

variations of the microwave-assisted hydrotropic pretreatment are listed in Table 1. The solid residue obtained from the hydrotropic pretreatment was separated by the filtration process. Subsequently, 800 mL of hot water was poured to wash the residue. The solid residue was then oven-dried at 378 K for approximately 4 h, and the pulp weight was recorded for pulp yield calculation.

2.3. Composition Analysis and Characterization of Cellulosic Biomass. The lignin content was determined based on the acid-insoluble lignin content. It was assessed gravimetrically as Klason lignin in accordance with the TAPPI T 222. The cellulose content was determined according to the TAPPI Method T249.

Cellulosic biomass characterization was conducted by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The solid residue obtained from microwave-assisted hydrotropic pretreatment was then subjected to FTIR analysis on a Nicolet iS-10 spectrometer from Thermo Fisher Scientific, USA. The pellet of KBr and sample was produced from a 100:1 mixture of KBr/sample. FTIR spectra were collected in the range of 400–4000 cm^{-1} with the spectral resolution set at 4 cm^{-1} . The solid residue was analyzed by SEM (Thermo Scientific Quattro S). Thermal analysis was performed using a thermogravimetric analyzer (PerkinElmer, TGA 4000). The sample placed in an alumina crucible was heated from 25 to 750 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ in the presence of nitrogen (30 mL/min).

2.4. Development of Mechanistic Models. The mechanistic model of hydrotropic pretreatment was constructed by assuming that reactions take place in a pseudo-homogeneous system since, before being processed, the straw was cut into small particles. In several cases of lignocellulose pretreatments, soluble lignin produced from depolymerization of solid phase lignin was reported to undergo repolymerization or the condensation reaction resulting in the formation of even more recalcitrant polymeric species,^{38,39} a solid state, as shown in the following equation



in which A , A_1 , and A_c represent solid phase of lignin, solubilized lignin, and condensed lignin, respectively; and k_{11} and k_c represent intrinsic solubilization reaction rate constant and condensation reaction rate constant, respectively.

The kinetic model proposed by Dong et al.⁴⁰ was then constructed which interpreted that solid phase lignin undergoes a simple solubilization to liquid phase lignin (eq 1bb).



Hence, in this study, the two possibilities were explored.

The reaction rate expressions for eq 1aa are as follow

$$-r_A = k_{11}C_A \quad (2a)$$

$$r_{A_c} = k_cC_{A_1} \quad (2b)$$

The reaction rate expressions for eq 1bb are similar to those, in which the value of k_c is set to be zero. Considering those two possible routes for lignin solubilization, the first mechanistic model proposed here was constructed by assuming that there is no lignin condensation and the second one was based on the fact that the solubilized lignin undergoes condensation.

Furthermore, polysaccharide solubilization into oligosaccharides and monomeric sugars was reported in several literatures;^{2,22,41} hence, for both possible mechanisms on lignin condensation, cellulose and hemicellulose were also assumed to be solubilized into soluble components (eqs 3 and 4). Hemicellulose and cellulose removal were occurring in hydrotropic treatment as it was revealed from X-ray diffraction and FTIR data analysis of hydrotropic pretreated corn stover.⁴² The application of *p*-toluenesulfonic acid in wood delignification showed that both lignin and hemicellulose were dissolved in the spent stream liquor.⁴³ The dissolution of cellulose and hemicellulose expression is represented in eqs 3 and 4. During the process, however, degradation of hydrotrope is encountered. The hydrotrope degradation rate was then modeled by (eq 5).



in which B , C , and H represent cellulose, hemicellulose, and hydrotrope, respectively, whereas B_1 and C_1 denote soluble cellulose and hemicellulose, respectively, and H_1 represents the hydrotrope degradation product. The intrinsic reaction rate constants for eqs 2a–3 are denoted by k_{12} , k_{13} , and k_4 , respectively.

Furthermore, reaction rates for eqs 2a–3 are modeled as first order, or mathematically

$$-r_B = k_{12}C_B \quad (6)$$

$$-r_C = k_{13}C_C \quad (7)$$

$$-r_H = k_4C_H \quad (8)$$

where C_B , C_C , and C_H are cellulose, hemicellulose, and hydrotrope concentrations in g/L, respectively. Hydrotropes were proven as an effective agent for lignin removal from lignocellulose biomass. It was then proposed that the reaction

Table 2. Assumption and Differential Equations of Mechanistic Model 1 (MM1) and Mechanistic Model 2 (MM2)

	MM1	MM2
assumption	pseudo-homogeneous system absence of lignin condensation	pseudo-homogeneous system occurrence of lignin condensation
lignin	$\frac{dC_A}{dt} = -k_1 C_A C_H$	$\frac{dC_A}{dt} = -k_1 C_A C_H$
solubilized lignin		$\frac{dC_{A_1}}{dt} = k_1 C_A C_H - k_c C_{A_1}$
condensed lignin		$\frac{dC_{A_c}}{dt} = k_c C_{A_1}$
cellulose	$\frac{dC_B}{dt} = -k_2 C_B C_H$	$\frac{dC_B}{dt} = -k_2 C_B C_H$
hemicellulose	$\frac{dC_C}{dt} = -k_3 C_C C_H$	$\frac{dC_C}{dt} = -k_3 C_C C_H$
hydrotrope	$\frac{dC_H}{dt} = -k_4 C_H$	$\frac{dC_H}{dt} = -k_4 C_H$
ash	$C_{ash} = C_{ash0} \times \frac{(C_A + C_B + C_C)}{C_{A0} + C_{B0} + C_{C0}}$	$C_{ash} = C_{ash0} \times \frac{(C_A + C_B + C_C)}{C_{A0} + C_{B0} + C_{C0}}$
lignin content	$LC = \frac{C_A}{C_A + C_B + C_C + C_{ash}} \times 100\%$	$LC = \frac{C_A + C_{A_c}}{C_A + C_B + C_C + C_{ash} + C_{A_c}} \times 100\%$
cellulose content	$CC = \frac{C_B}{C_A + C_B + C_C + C_{ash}} \times 100\%$	$CC = \frac{C_B}{C_A + C_B + C_C + C_{ash} + C_{A_c}} \times 100\%$
yield	$yield = \frac{C_A + C_B + C_C + C_{ash}}{C_{A0} + C_{B0} + C_{C0} + C_{ash0}} \times 100\%$	$yield = \frac{C_A + C_B + C_C + C_{ash} + C_{A_c}}{C_{A0} + C_{B0} + C_{C0} + C_{ash0}} \times 100\%$
initial conditions	$t = 0; C_A = C_{A0}; C_B = C_{B0}; C_C = C_{C0}; C_H = C_{H0}; C_{ash} = C_{ash0}$	$t = 0; C_A = C_{A0}; C_B = C_{B0}; C_C = C_{C0}; C_H = C_{H0}; C_{ash} = C_{ash0}; C_{A_1} = 0; C_{A_c} = 0$

rate constant of k_{11} , k_{12} , and k_{13} was function of hydrotrope concentration as in eqs 7–9.

$$k_{11} = k_1 C_H \quad (9)$$

$$k_{12} = k_2 C_H \quad (10)$$

$$k_{13} = k_3 C_H \quad (11)$$

where k_1 , k_2 , and k_3 symbolize the rate constants of lignin, cellulose, and hemicellulose, respectively.

Substitution of eqs 7–9 into 2a, 2b and eqs 6 and 7 gives

$$-r_A = k_1 C_A C_H \quad (12)$$

$$-r_B = k_2 C_B C_H \quad (13)$$

$$-r_C = k_3 C_C C_H \quad (14)$$

$$r_{A_c} = k_c C_{A_1} \quad (15)$$

The mass balance of lignin (A) in the reacting system can be written as

$$0 - 0 - V \cdot k_1 C_A C_H = V \frac{dC_A}{dt} \quad (16)$$

After rearrangement, the following differential equation is formed

$$\frac{dC_A}{dt} = -k_1 C_A C_H \quad (17)$$

Similar to the construction of mass balance of lignin (A), the mass balance for cellulose (B), hemicellulose (C), hydrotrope

(H), solubilized lignin (A_1), and condensed lignin (A_c) is as follows

$$\frac{dC_B}{dt} = -k_2 C_B C_H \quad (18)$$

$$\frac{dC_C}{dt} = -k_3 C_C C_H \quad (19)$$

$$\frac{dC_H}{dt} = -k_4 C_H \quad (20)$$

$$\frac{dC_{A_1}}{dt} = k_1 C_A C_H - k_c C_{A_1} \quad (21)$$

$$\frac{dC_{A_c}}{dt} = k_c C_{A_1} \quad (22)$$

The initial conditions of the equation systems are

$$t = 0; C_A = C_{A0}; C_B = C_{B0}; C_C = C_{C0}; C_H = C_{H0}; C_{ash} = C_{ash0}; C_{A_1} = 0; C_{A_c} = 0 \quad (23)$$

The main component of lignocellulose solid particle comprises lignin, cellulose, and hemicellulose, while ash is concentrated within the bulk of solid particle. The concentration of ash is expressed according to eq 24.

$$\begin{aligned} \text{ash concentration} &= \text{initial ash content} \\ &\times \frac{\text{solid particle at } t = t}{\text{initial weight of solid particle}} \end{aligned} \quad (24)$$

Table 3. Chemical Composition of Rice Straw

references	components			
	cellulose (%)	hemicellulose (%)	lignin (%)	ash (%)
this work	35.23 ± 0.53	20.11 ± 0.07	22.75 ± 1.53	9.85 ± 1.02
Sarwar Jahan et al. ⁴⁵	38.2	23.5 ^a	26.2	14.6
Tutus et al. ⁴⁶	48.18 ± 0.19	24.50 ^a	17.20 ± 0.28	16.6 ± 0.26
Zhang et al. ⁴⁷	41.93 ± 0.31	24.99 ± 0.92	23.85 ± 0.64	
Pan et al. ⁴⁸	35.49 ± 0.55	18.54 ± 0.5 ^b	14.84	6.99 ± 0.23

^aCalculated as pentosan. ^bCalculated as the sum of xylan and arabinose.

Table 4. Yield, Lignin and Cellulose Contents of Microwave-Assisted Hydrotropic Pretreatment

code	exp		MM1		MM2		exp	MM1		MM2	
	yield_data (%)	yield_calc (%)	yield_data (%)	yield_calc (%)	LC_data (%)	LC_calc (%)		LC_data (%)	LC_calc (%)	CC_data (%)	CC_calc (%)
P1	88.53	95.11	95.79	15.99	23.16	23.45	45.88	40.26	40.09		
P2	77.86	88.63	88.53	14.59	20.67	20.72	43.81	42.67	42.92		
P3	83.95	86.60	88.32	18.21	19.86	20.64	44.79	43.49	43.01		
P4	82.54	72.26	72.12	18.54	13.68	13.75	51.53	50.20	51.02		
P5	92.15	95.01	95.71	16.93	23.13	23.42	46.36	40.30	40.12		
P6	83.89	88.42	88.32	16.14	20.59	20.64	50.37	42.75	43.01		
P7	82.20	86.36	88.11	20.15	19.76	20.55	35.04	43.58	43.10		
P8	82.07	71.86	71.72	17.34	13.50	13.57	46.91	50.41	51.25		
P9	79.39	96.59	97.24	19.53	23.71	23.97	55.05	39.75	39.57		
P10	76.48	84.04	84.99	17.71	18.81	19.31	50.59	44.55	44.45		
P11	76.79	84.04	84.99	17.63	18.81	19.31	50.39	44.55	44.45		
P12	84.11	76.93	75.82	17.09	15.77	15.41	66.16	47.81	48.95		
P13	85.44	97.08	97.28	12.86	23.89	23.98	46.12	39.58	39.56		
P14	78.92	74.14	75.52	16.81	14.53	15.28	41.53	49.21	49.11		
P15	77.00	84.33	85.27	17.93	18.93	19.42	48.18	44.43	44.33		
P16	78.91	83.86	84.82	19.14	14.06	12.74	45.98	44.63	44.53		

$$\text{ash concentration} = C_{\text{ash}0} \times \frac{(C_A + C_B + C_C)}{C_{A0} + C_{B0} + C_{C0}} \quad (25)$$

Furthermore, Xiao et al.⁴⁴ stated that condensed lignin was more preferential to re-deposit on the solid surface. The deposition of condensed lignin into pulp fiber was also mentioned by Chen et al.,⁴¹ and the produced condensed lignin is a more recalcitrant polymeric species than the native one. It was then logic if term of C_{A_i} was added into the numerator side of the yield representing equation for the mechanistic model with occurrence of lignin condensation (eq 26).

$$\text{yield} = \frac{C_A + C_B + C_C + C_{\text{ash}} + C_{A_c}}{C_{A0} + C_{B0} + C_{C0} + C_{\text{ash}0}} \times 100\% \quad (26)$$

while for the absence of lignin condensation assumption, yield is expressed as follows

$$\text{yield} = \frac{C_A + C_B + C_C + C_{\text{ash}}}{C_{A0} + C_{B0} + C_{C0} + C_{\text{ash}0}} \times 100\% \quad (27)$$

The residual lignin content for the mechanistic model with lignin condensation occurrence and lignin condensation absence was manifested in eqs 28aa and 28b, while the others for the cellulose content (C_B) are expressed by eqs 29aa and 29b.

$$\text{LC} = \frac{C_A + C_{A_c}}{C_A + C_B + C_C + C_{\text{ash}} + C_{A_c}} \times 100\% \quad (28a)$$

$$\text{LC} = \frac{C_A}{C_A + C_B + C_C + C_{\text{ash}}} \times 100\% \quad (28b)$$

$$\text{CC} = \frac{C_B}{C_A + C_B + C_C + C_{\text{ash}} + C_{A_c}} \times 100\% \quad (29a)$$

$$\text{CC} = \frac{C_B}{C_A + C_B + C_C + C_{\text{ash}}} \times 100\% \quad (29b)$$

The obtained differential equations representing the two mechanistic models proposed are summarized in Table 2.

The simultaneous differential equations of both of the mechanistic models were numerically solved by Euler's method where the step size (h) is 0.05 s. Four mechanistic model parameters, that is, k_1 , k_2 , k_3 , and k_4 of the first mechanistic model as well as five parameters, that is, k_1 , k_2 , k_3 , k_4 , and k_c of the second mechanistic model were determined by fitting to the experimental data obtained from microwave-assisted hydrotropic pretreatment of rice straw. The initial lignin content and cellulose content as well as the obtained experimental data of the lignin content, cellulose content, and yield presented in this work were all based on free extractive data. The initial lignin content and cellulose content were 24.93 and 38.61%, respectively. The fitting was based on minimization of sum of square error (SSE). The SSE was calculated according to eq 30 as follows

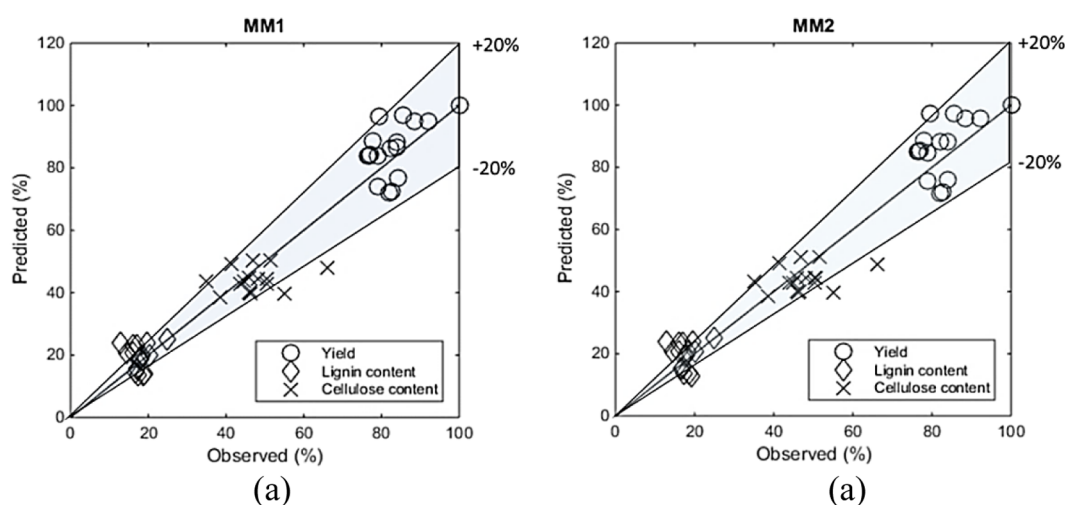


Figure 1. Profile of the calculated and experimental data of yield, residual lignin content, and cellulose content and of microwave-assisted hydrotropic pretreatment for (a) MM1 and (b) MM2.

Table 5. Parameters of the Mechanistic Model

	mechanistic model parameters					SSE	MAE (%)
	k_1 (g min ⁻¹ L ⁻¹)	k_2 (g min ⁻¹ L ⁻¹)	k_3 (g min ⁻¹ L ⁻¹)	k_4 (min ⁻¹)	k_c (min ⁻¹)		
MM1	7.43×10^{-5}	5.03×10^{-6}	2.71×10^{-5}	9.99×10^{-3}	3.54×10^{-8}	2.13	5.86
MM2	5.73×10^{-5}	3.01×10^{-6}	2.33×10^{-5}	9.99×10^{-4}	3.54×10^{-8}	2.25	6.13

$$\begin{aligned}
 \text{SSE} = & \sum_{i=1}^n \left(\frac{\text{yield}_{\text{data}} - \text{yield}_{\text{calc}}}{\text{yield}_{\text{data}}} \right)^2 \\
 & + \sum_{i=1}^n \left(\frac{\text{XA}_{\text{data}} - \text{XA}_{\text{calc}}}{\text{XA}_{\text{data}}} \right)^2 + \sum_{i=1}^n \left(\frac{\text{XB}_{\text{data}} - \text{XB}_{\text{calc}}}{\text{XB}_{\text{data}}} \right)^2
 \end{aligned} \quad (30)$$

Furthermore, the mean absolute errors (MAE) as in eq 31 were also reported.

$$\begin{aligned}
 \text{MAE} = & \frac{100}{3n} \left(\sum_{i=1}^n \text{abs}|\text{yield}_{\text{data}} - \text{yield}_{\text{calc}}| \right. \\
 & + \sum_{i=1}^n \text{abs}|\text{XA}_{\text{data}} - \text{XA}_{\text{calc}}| \\
 & \left. + \sum_{i=1}^n \text{abs}|\text{XB}_{\text{data}} - \text{XB}_{\text{calc}}| \right)
 \end{aligned} \quad (31)$$

3. RESULTS AND DISCUSSION

3.1. Chemical Composition of Untreated Rice Straw.

The chemical composition of untreated rice straw found in this study as well as its comparison with literature values are tabulated in Table 3. The chemical composition variations might be due to rice varieties, producer area, and tissue parts. All the values found in this work were within the normal range as compared to the literature and thus provide an insight into their abundance and further potential utilization. It is interesting to note that cellulose accounts as the largest component in rice straw which accounts for ca. 35%. The composition of hemicellulose and lignin is relatively the same at ca. 20%. The ash content of untreated rice straw is 9.85% which is in close agreement with the literature.

3.2. Model Validation with Experimental Data.

The calculated and experimental data of the residual lignin content, cellulose content, and yield for both models are tabulated in Table 4 and illustrated in Figure 1.

Mechanistic model validation showed that SSE of both models is relatively similar (Table 5). The calculated and experimental data comparison of residual lignin, cellulose, and yield are shown in Figure 1. It is observed that the SSE and MAE of MM1 are only slightly smaller than those of MM2. Hence, it can be concluded that the assumption of neglecting the lignin condensation in microwave-assisted hydrotropic pretreatment assumption is conceivable. The relatively small effects of lignin condensation are also supported by a small value of the lignin condensation reaction rate, k_c , which is -8 order of magnitude (Table 5), compared to the ones of the solubilization rate of lignin (k_{11}), which is -3 order of magnitude for a hydrotrope concentration of 91.94 g/L.

The small value of lignin condensation reaction rate, k_c , results in the low concentration of condensed lignin produced. As an example, Figure 2a,b illustrate the concentration profile of calculated lignin, cellulose, hemicellulose, ash, soluble lignin, and condensed lignin of microwave-assisted hydrotropic pretreatment conducted at a solid liquid ratio of 1:35 and application of hydrotrope concentrations 20 and 36.8%. The figures show that the concentration of condensed lignin is very small compared to others. Moreover, the profile of ratio of condensed lignin to the initial lignin content (C_{Ac}/C_{A0}), as illustrated in Figure 2c, shows that the ratios of the condensed lignin concentration formed to the initial lignin concentration are all less than 1×10^{-3} for all process combination. The highest ratio of C_{Ac}/C_{A0} is obtained at a solid to liquid ratio of 1:35 and hydrotrope concentration of 36.8% (P14). It seems that the application of higher hydrotrope concentration results in a higher ratio of C_{Ac}/C_{A0} . Those phenomena are logic since the rate of condensed lignin production is proportional to the

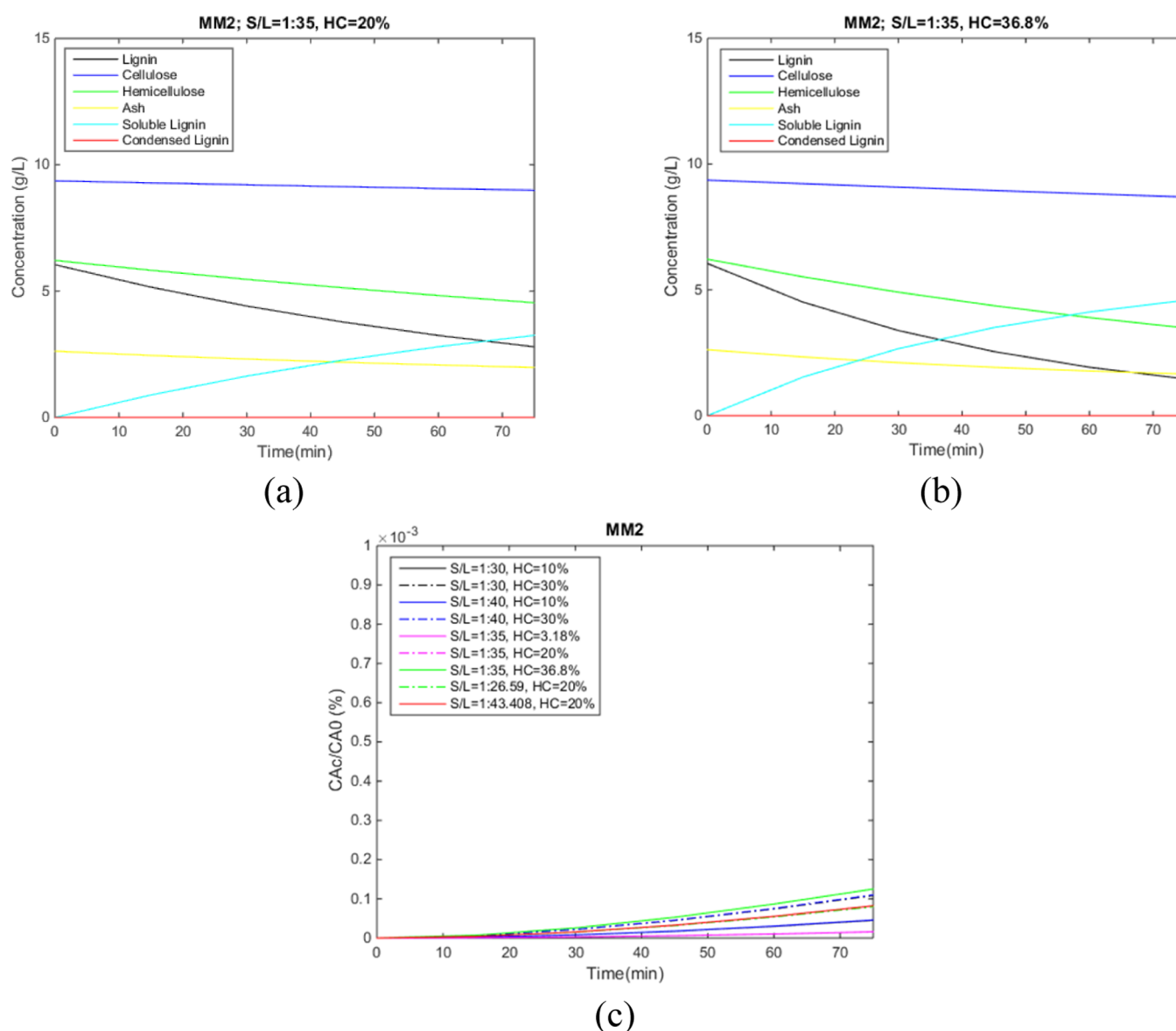


Figure 2. Concentration profile of calculated lignin, cellulose, hemicellulose, ash, soluble lignin, and condensed lignin based on mechanistic model 2 of microwave-assisted hydrotropic pretreatment conducted at a SL ratio of 1:35 and hydrotrope concentrations of (a) 20 and (b) 36.8% as well as at (c) the ratio of condensed lignin concentration formed to the initial lignin concentration.

soluble lignin concentration, as expressed in eq 23, while the higher the hydrotropic agent used in the pretreatment process, the higher the delignification degree and soluble lignin produced.

3.3. Evaluation of the Effect of Lignin Condensation Term. Condensed lignin production prevention during the pretreatment processes is one of main objectives and success measurement of the pretreatment process.³³ The low lignin condensations in hydrotropic pretreatments were reported in several literatures. The application of *p*-toluenesulfonic acid (*p*-TsOH) in moderate temperature (≤ 80 °C) and short reaction time (≤ 30) of wood valorization resulted in low lignin condensation.⁴⁹ The low lignin condensation was also obtained in poplar wood fractionation using acid hydrotropes in a flow-through reaction under atmospheric pressure below the boiling point of water.³¹ Lignin condensation relies on the competition between the lignin de-polymerization rate through ether linkage cleavage and the rate of lignin condensation

through direct contact of the inter-ether moieties. The low condensation reaction rate of lignin compared to the lignin solubilization reaction rate found in this work is an indication that the combination of microwave heating and the use of urea as a hydrotropic agent is a potential hydrotrope for lignin depolymerization with low lignin condensation.

3.4. Evaluation of Lignin Solubilization. The values of the mechanistic model constants, as tabulated in Table S, show that cellulose and hemicellulose are solubilized during microwave-assisted hydrotropic pretreatment result in their concentration decreasing along with the time increasing. Decreasing concentration profile of lignin, cellulose, hemicellulose, and ash as a time function of microwave-assisted urea-based hydrotropic pretreatment conducted at varied conditions is presented in Figure 3.

Figure 3a shows that the lignin concentration decreases with the increase of urea concentration and that application of urea concentration of 36.8% and a solid – liquid ratio of 1:35 at the

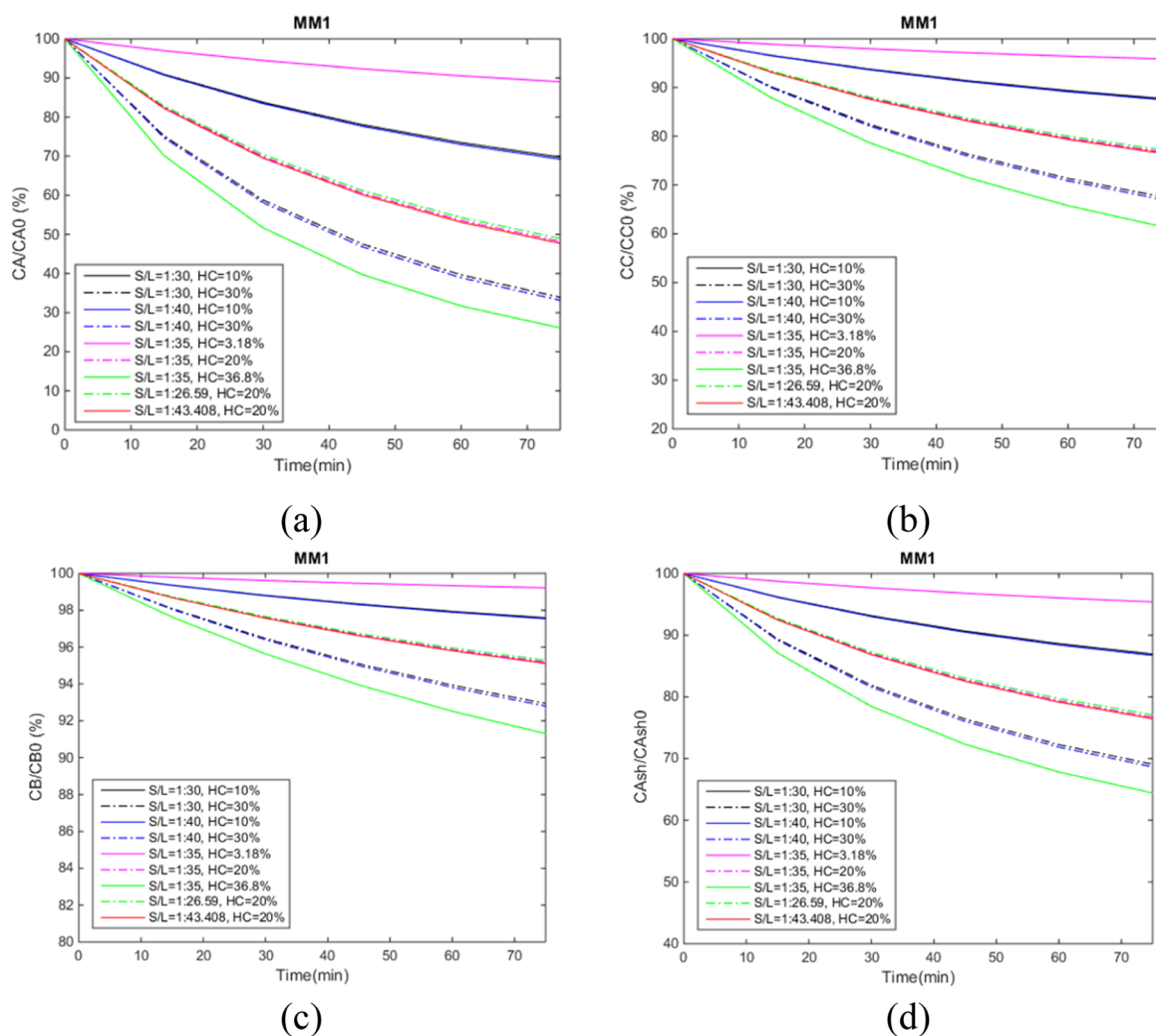


Figure 3. Concentration profile of (a) lignin, (b) hemicellulose, (c) cellulose, and (d) ash as a time function of microwave-assisted hydrotropic pretreatment.

microwave-assisted pretreatment of rice straw results in the solid residue having the lowest lignin concentration. The decrease of lignin concentration with the increase of hydrotrope concentration in various biomasses and hydrotropes were reported in several literatures.^{7,50} Denisova et al.,⁷ mentioned that hydrotropic solution solubilizing ability is known to increase with the increase of its concentration. Commonly, concentration of hydrotrope higher than 20% will give an appreciable solubilization effect. It was also stated that the effectiveness effects of most hydrotropic salt are valued when their content in the solution exceeds a part per three parts of water.⁷ 50% of *p*-TsOH aqueous solution was applied in the pulping process of rice straw,²⁴ while 35% solution of sodium benzoate was utilized for subsequent pulping of Miscanthus.⁷ However, no significant increase of lignin removal in rice straw lignin removal for bioethanol production was found when the sodium cumene sulfonate and sodium xylene sulfonate concentration applied were beyond 20%.⁵⁰ Lignin removal efficiency was increased marginally with the rise in hydrotrope concentrations from 10 to 20% for both sodium cumene sulfonate and sodium xylene sulfonate applied.⁵⁰

The effect of the solid–liquid ratio toward lignin dissolution is also depicted in Figure 3a. Figure 3a shows that at the same

hydrotrope concentration applied as an example in 10% of hydrotrope concentration, the value of C_A/C_{A0} on the addition of higher hydrotrope solution volume ($S/L = 1:40$) is just slightly lower than the one on the addition of lower hydrotrope solution volume ($S/L = 1:30$). It can be concluded that the solid–liquid ratio does not significantly affect the lignin solubilization of microwave-assisted urea-based hydrotropic pretreatment. The effect of the solid–liquid ratio in hydrotropic pretreatment of rice straw was also investigated.⁵⁰ It was found that biomass extractive percentage at the application of biomass loading of 5% in rice straw hydrotropic pretreatment is higher than the one of 2.5%, while the biomass extractive percentage was decreasing as the biomass loading applied is higher than 5%.

The capability of urea in dissolving lignin was studied by applied atomic force microscopy in quantitative analysis of molecular interaction among urea, water, and alkali lignin.¹¹ It was found that the presence of urea was able to reduce the intermolecular interaction of lignin molecules as the water–lignin mean adhesion force is as high as 32.3 mN/m, while urea–lignin mean adhesion force is 11.3 mN/m. The decreasing interaction indicates that in the presence of urea, the hydrogen bonds and π – π stackings in lignin are mostly broken, facilitating lignin disaggregation and dissolution.¹¹

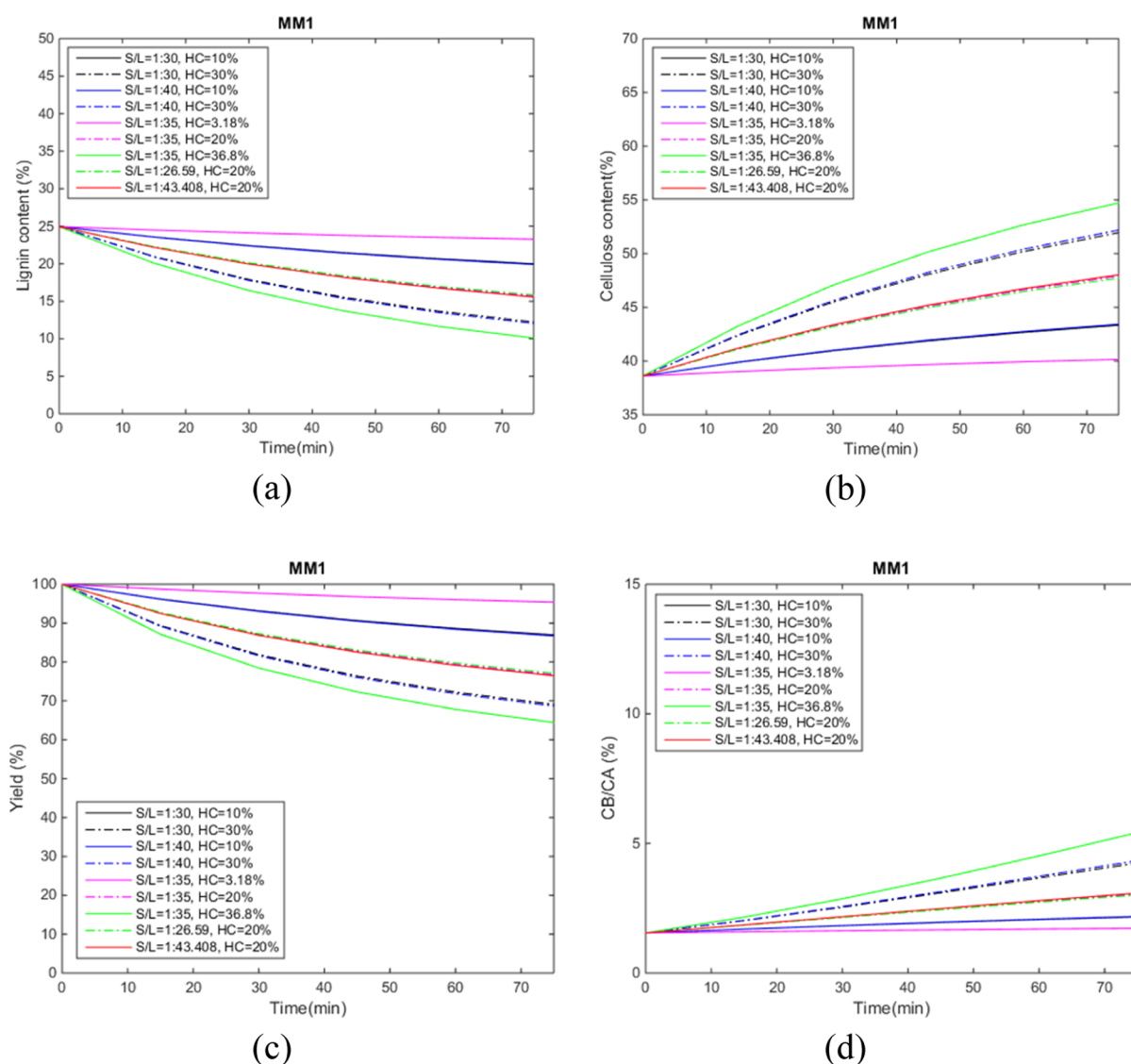


Figure 4. Profile of (a) lignin content, (b) cellulose content, (c) yield, and (d) C_A/C_B ratio for the microwave-assisted urea-based hydrotropic pretreatment of rice straw conducted under varied process conditions.

The dissolved lignin in hydrotropic pretreatment can be further recovered by the precipitate upon dilution with water, while the remaining spent solution can be further concentrated to be reused. The success of soluble lignin separation from hydrotropic pretreatment as well as the reusability of the spent solution of the hydrotropic process were reported by several researchers.^{5,22,32} Moreover, some inhibitors such as furans, aliphatic acid, benzoquinones, and pentose sugars are commonly produced from the lignocellulose pretreatment process as the result of lignin and/or hemicellulose solubilization and degradation.⁵¹ However, the absence of inhibitor formation in hydrotropic pretreatments was reported by several researchers. It was found that there was no inhibitor produced in microwave-assisted hydrotropic pretreatment of maize distillery stillage²¹ and in hydrotropic pretreatment of cotton stalk.⁵² Moreover, although some literatures reported the absence of inhibitor production in their microwave-assisted pretreatment, in this kinetic model, the formation of inhibitors was represented by the term of formation of soluble lignin from lignin (eq 1bb) as well as formation of soluble hemicellulose from hemicellulose (eq 4).

3.5. Evaluation of Hemicellulose Solubilization. The mechanistic model of urea-based hydrotropic pretreatment proposed in this work also informed us the profile of hemicellulose dissolution, as presented in Figure 3b. As seen in Figure 3b, hemicellulose dissolution increases with the increase of urea concentration, while the solid–liquid ratio does not give any significant effect. Hemicellulose removal during hydrotropic pretreatment was reported in several literatures.^{4,22,24,53,54} Hemicellulose dissolution during the rice straw pulping process with 50% *p*-TsOH aqueous solution at temperature 70–100 °C and the pulping process for 0–360 min was reported.²⁴ A significant part of hemicellulose was also removed from Birchwood in modified hydrotropic treatment. The presence of hemicellulose together with sugar monomers, furfural, and acetic and formic acids were reported in sugarcane bagasse treated with sodium xylene sulphonate which was acidified with formic acid.²² Both of hemicellulose and lignin were found in the wood pretreatment spent liquor which utilized a recyclable aromatic acid, *p*-toluenesulfonic acid (*p*-TsOH), as the chemical agent.⁵³ Delignification and hemicellulose solubilization were also reinforced by the application

of hydrotropic and acid treatment combination processes, whereas the cellulose retained well in the pretreated solid fraction.²³ The hydrolytic process occurring during hydro-tropic pretreatment was stated as the cause of hemicellulose removal.^{4,53}

3.6. Evaluation of Cellulose Solubilization. The effect of urea-based pretreatment and microwave heating on cellulose dissolution in rice straw based on the mechanistic model, assuming that there is no lignin condensation, is presented in Figure 3c. It appears that cellulose converted into soluble cellulose. Figure 3c shows the similar cellulose dissolution characteristic to the lignin. It was found that urea promotes cellulose dissolution as the dissolution increases with the increase of urea concentration. A molecular dynamic simulation in the investigation of the interaction between single chain of cellulose and urea–water system was carried out and reported.^{25,55} It was found that at the same temperature, the interaction energy between cellulose and urea in the solvent mixture is lower than those of cellulose and water. The low interaction energy is an indication that the cellulose chain prefers to form hydrogen bonds with urea rather than with water.⁵⁵ As compared to cellulose–water interactions, the interaction between urea and cellulose is stronger and more stable, which then promotes the formation of the inclusion layer.⁵⁵ The formed inclusion layer would then decrease the self-interaction of cellulose chains and promote dissolution of cellulose in the urea-containing solvent mixture.⁵⁵ Moreover, cellulose dissolution over the presence of urea was also studied.⁵⁶ Based on molecular dynamic simulation, urea was found to solubilize cellulose by solvating hydrophobic portions of cellulose. Solubilization of amphiphilic compound such as cellulose can also be promoted by adding co-solute, which has the tendency to weaken hydrophobic interaction such as in urea.⁵⁷

Cellulose dissolution due to hydrotropic pretreatment is also reported,⁵⁸ as well as dissolution of cellulose in the presence of urea in the alkaline system.^{59,60} Hydrotropic pretreatment was reported to be able to remove up to 50% of the substrate lignin of willow and corn stover at the application of *p*-TsOH at temperatures as low as 50 °C. *p*-TsOH treatment performed at temperature 50 °C also dissolved >10% of the cellulose.⁶¹ However, utilization of sodium xylene sulfonate in sugarcane bagasse valorization did not result in cellulose dissolution as the amount of cellulose in untreated bagasse and in pulp was nearly the same.²² The utilization of alkybenzene sulfonates in sugarcane bagasse delignification did not exhibit any significant effect to cellulose.⁵ It seems that cellulose dissolution in hydrotropic delignification is influenced by the type of hydrotrope compound used in the pretreatment process.

The cellulose dissolution occurrence in microwave-assisted urea-based hydrotropic pretreatment is expressed by its solubilization rate which is obtained from the mechanistic models proposed. The value of the cellulose dissolution rate is 1 order magnitude smaller than those of lignin and hemicellulose (Table 5). The low cellulose solubilization rate compared to others indicates that in the case of cellulose-focused pretreatment, the application of urea and its combination with microwave heating give positive effect as the dissolved component is less than those of lignin and hemicellulose.

3.7. Evaluation of Ash Solubilization. Furthermore, the mechanistic model proposed here is capable in capturing and presenting the ash concentration profile (Figure 3d). It seems

that ash concentration decreases with the increase of time. It was found that 44.29% of ash were solubilized in microwave-assisted urea-based hydrotropic pretreatment on rice straw conducted at a solid–liquid ratio of 1:35, temperature of 90 °C, and application of urea concentration of 36.8%. The decrease in the ash content as the result of the increase of pretreatment chemical was also reported,⁶² and 55.29% of ash rice straw was solubilized as the result of rice straw 4 h soaking in 2% (w/v) NaOH solution and at room temperature, followed by the heating process in an autoclave at 121 °C for 15 min.⁶⁴

3.8. Evaluation of Lignin Content. The decreasing concentration of lignin, cellulose, hemicellulose, and ash of rice straw during microwave-assisted urea-based hydrotropic pretreatment resulted in the decrease of the lignin content, the increase of cellulose content, and the decrease of yield of the solid residue obtained (Figure 4a–d). As seen in Figure 4a, the lignin content of the solid residue is decreased as the lignin solubilized during microwave-assisted urea-based hydrotropic pretreatment. The high lignin solubilization rate compared to that of cellulose results in the decreased lignin content. Figure 4a shows that the predicted lignin content of the solid residue, obtained from microwave-assisted urea-based hydrotropic pretreatment on rice straw conducted at a solid–liquid ratio of 1:35 and application of urea concentration of 36.8% (P14), is the lowest compared to the those obtained from the other process condition. The lignin content of the solid residue of P14 at pretreatment duration of 40 min is predicted to be 14.52%, while upon experiment, the lignin content is 16.81%, which, in terms of lignin removal, represents 41.74 and 32.57%, respectively.

A higher lignin removal when hydrotrope of sodium cumene sulfonate is utilized in the pretreatment process of rice straw was reported.⁵⁰ More than 50% of lignin was removed from rice straw when 5% biomass loading was subjected to 20% of hydrotropic solution pretreatment at 121 °C for 1 h. The higher lignin removal compared to the one obtained from this work might be due to their application of higher temperature and longer time of pretreatment. A higher lignin removal was also obtained from the other process, that is, almost complete removal of rice straw lignin was obtained from flow-through hydrothermal pretreatment at 200 °C for 10 min at a flow rate of 160 mL/min.⁶³ The high temperature of the subcritical water seems to work well in solubilizing lignin. Moreover, the utilization of urea in rice straw lignin removal performed in this work is found to be better than the utilization of sodium hydroxide in rice straw lignin removal as the application of 5% of sodium hydroxide solution at 155 min and temperature of 89 °C resulted in lignin removal up to 44.09%.⁶⁴

3.9. Evaluation of Cellulose Content. Microwave-assisted urea-based hydrotropic pretreatment results in producing the rich cellulose–solid residue; the predicted cellulose content profile of the solid residue is represented in Figure 4b. Figure 4b shows that the predicted cellulose content of the solid residue obtained from microwave-assisted urea-based hydrotropic pretreatment on rice straw conducted at a solid–liquid ratio of 1:35 and application of urea concentration of 36.8% (P14) is the highest compared to the those obtained from the other process condition. The cellulose content of the solid residue of P14 at pretreatment duration of 40 min is predicted to have a cellulose content of 49.21%, while upon experiment, the cellulose content is 41.53%. Cellulose contents of the solid residue obtained from the treatment with 20%

aqueous solution of sodium cumene sulfonate (NaCS) and sodium xylene sulfonate (NaX) at 121 °C for 1 h with 5% biomass loading were 39.29 and 38.88%, respectively.⁵⁰ The higher cellulose content found in this work might be caused by the dissolution of lignin and the other component such as hemicellulose and ash, while in the application of sodium cumene sulfonate (NaCS) and sodium xylene sulfonate (NaX), it was reported that there was no loss of hemicellulose during rice straw pretreatment.⁵⁰

3.10. Evaluation of Yield. The lignin, cellulose, hemicellulose, and ash dissolution resulted in the decrease of yield of the solid residues (Figure 4c). The higher the lignocellulose component dissolution, the lower the yield of the solid residue obtained. The microwave-assisted urea-based hydrotropic pretreatment on rice straw conducted at a solid–liquid ratio of 1:35 and application of urea concentration of 36.8% (P14) at pretreatment duration of 40 min is predicted to give a solid residue yield of 74.14%, while upon experiment, the yield is 78.92%. The yield value obtained in this work is higher than the yield of rice straw treated by other processes. Dutta et al.⁶⁴ reported that $46.10 \pm 0.07\%$ of the solid fraction of rice straw was obtained from the application of 5% sodium hydroxide solution on the pretreatment process performed at a temperature of 89 °C and 155 min reaction time. Moreover, the utilization of a novel biphasic organic solvent comprising 70% of 2-phenoxyethanol (EPH) and 0.05 M H₂SO₄ in rice straw pretreatment conducted at a temperature of 130 °C for 120 min resulted in a lower yield (49.12%).⁶⁵

3.11. Process Selectivity. The low solid residue yield resulted in pretreatment processes or rice straw are acceptable since rice straw is considered as a low-cost biomass; thus, the pretreatment process would focus on the selection of the selective pretreatment route which resulted in producing the cellulose-rich and low lignin solid residue other than pursuing a high yield of the solid residue.

Lignocellulose pretreatment selectivity could be observed from the ratio of solubilization rate constant of lignin to the one of cellulose (k_1/k_2).⁶⁶ The higher the ratio, the more the lignin solubilized than the cellulose which results in higher process selectivity. A ratio of (k_1/k_2) as high as 15.3 was obtained from the application of tetrahydrofurfuryl alcohol (THFA) over the presence of 0.02 M of HCl for rice straw lignin removal conducted at 120 °C and 120 min of solubilization reaction,⁶⁶ while the ratio of (k_1/k_2) found in this work is 14.76 from the mechanistic model with assumption of the absence of lignin condensation. The lower (k_1/k_2) ratio found in this work might be due to the microwave-assisted hydrotropic pretreatment which was conducted in lower system temperature, that is, 90 °C and the application of different chemicals.

Process selectivity can be evaluated also by observing the profile of C_B/C_A ratio. The profile of the C_B/C_A ratio for the microwave-assisted urea-based hydrotropic pretreatment of rice straw conducted at varied process conditions is illustrated in Figure 4d. As seen in Figure 4d, the solid residue, obtained from microwave-assisted urea-based hydrotropic pretreatment conducted at a solid–liquid ratio of 1:35, application of urea concentration of 36.8%, reaction temperature of 90 °C, and pretreatment duration of 73.6 min, is predicted to have the highest ratio of the cellulose to lignin concentration ($\frac{C_B}{C_A} = 5.33$).

This ratio is higher than the C_B/C_A ratio obtained from the utilization of a novel biphasic organic solvent comprising 70% of 2-phenoxyethanol (EPH) and 0.05 M H₂SO₄ in rice straw pretreatment conducted at a temperature of 130 °C for 120 min in which the ratio of cellulose to lignin in their solid residue was 4.46.⁶⁵ Moreover, the ratio of cellulose to lignin concentration found in this work is lower than the one obtained from the application of the flow-through hydrothermal system in which lignin was almost completely removed from rice straw.⁶³ Even though better pretreatment results were obtained by other pretreatment methods such as the hydrothermal process, the application of microwave-assisted urea-based-hydrotropic pretreatment offers several advantages such as (i) urea is cheaper than the other chemicals commonly applied in the pretreatment system, (ii) urea is readily available and abundant, (iii) urea is considered as a green chemical due to its non-corrosiveness, its low volatility, and its lower risk to human health as well as to environment, (iv) urea gives less impact on other lignocellulose components, and (v) urea can be employed and transported at regular temperatures and pressure without extra equipment cost.¹³

3.12. Cellulosic Biomass Characterization. The characteristic bands of molecules of untreated rice straw and microwave-assisted hydrotropic pretreated rice straw exhibiting the highest ratio of cellulose–lignin were shown by the FTIR spectra (Figure 5). The absorption bands at 3298.34 and

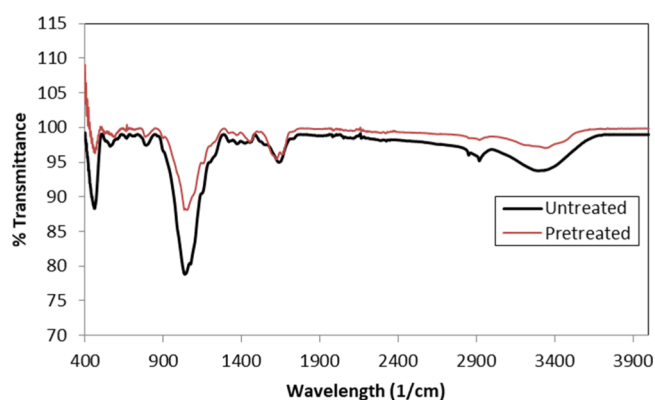


Figure 5. FTIR spectra of untreated rice straw and pretreated rice straw.

3340.31 cm^{-1} (between 3100 and 3600 cm^{-1}) mainly reflect the $-\text{OH}$ -stretching vibration for untreated and pretreated samples, respectively. The $-\text{OH}$ -stretching vibration are attributed to the hydrophilic tendency of the samples and attributed to polymeric lignin.⁶⁷ The absorption peaks at 2918.14 and 2917.97 cm^{-1} (between 2500 and 3200 cm^{-1}) for untreated and pretreated sample, respectively, are mainly formed by the stretching vibration of $\text{C}-\text{H}$ and assigned to the cellulose crystalline order.⁶⁸ At the interval of 1300 – 1500 cm^{-1} , peaks at 1371.52 and 1454.55 cm^{-1} mainly provide information on the $\text{C}-\text{H}$ -bending vibrations, which are associated with cellulose main chains. The crystalline band of the pretreated sample, which is represented by the band at 1430 cm^{-1} , is slightly higher compared to that of the untreated sample. It is an indication that the crystallinity degree of the pretreated sample was increased as the result of microwave-assisted hydrotropic pretreatment.

The surface morphology evaluation of cellulosic biomass was performed by SEM. Images of the untreated rice straw and

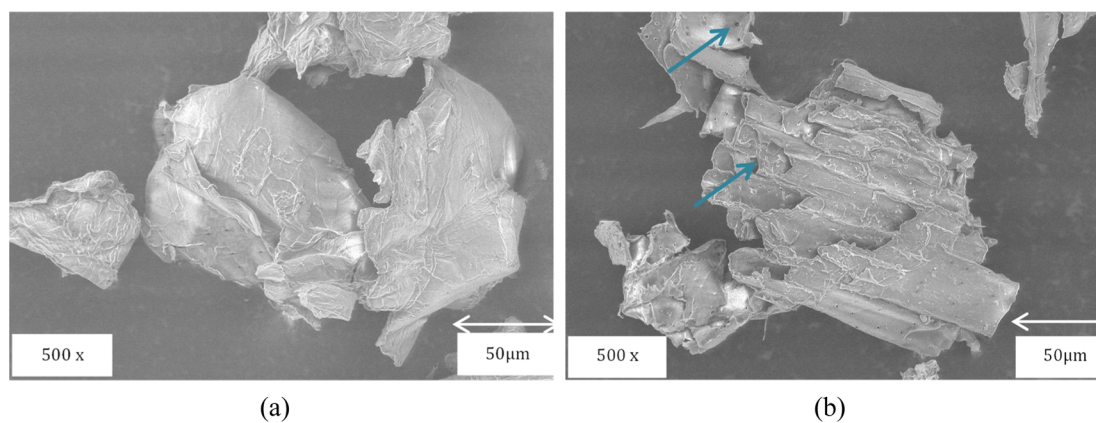


Figure 6. SEM images of (a) untreated rice straw and (b) pretreated rice straw.

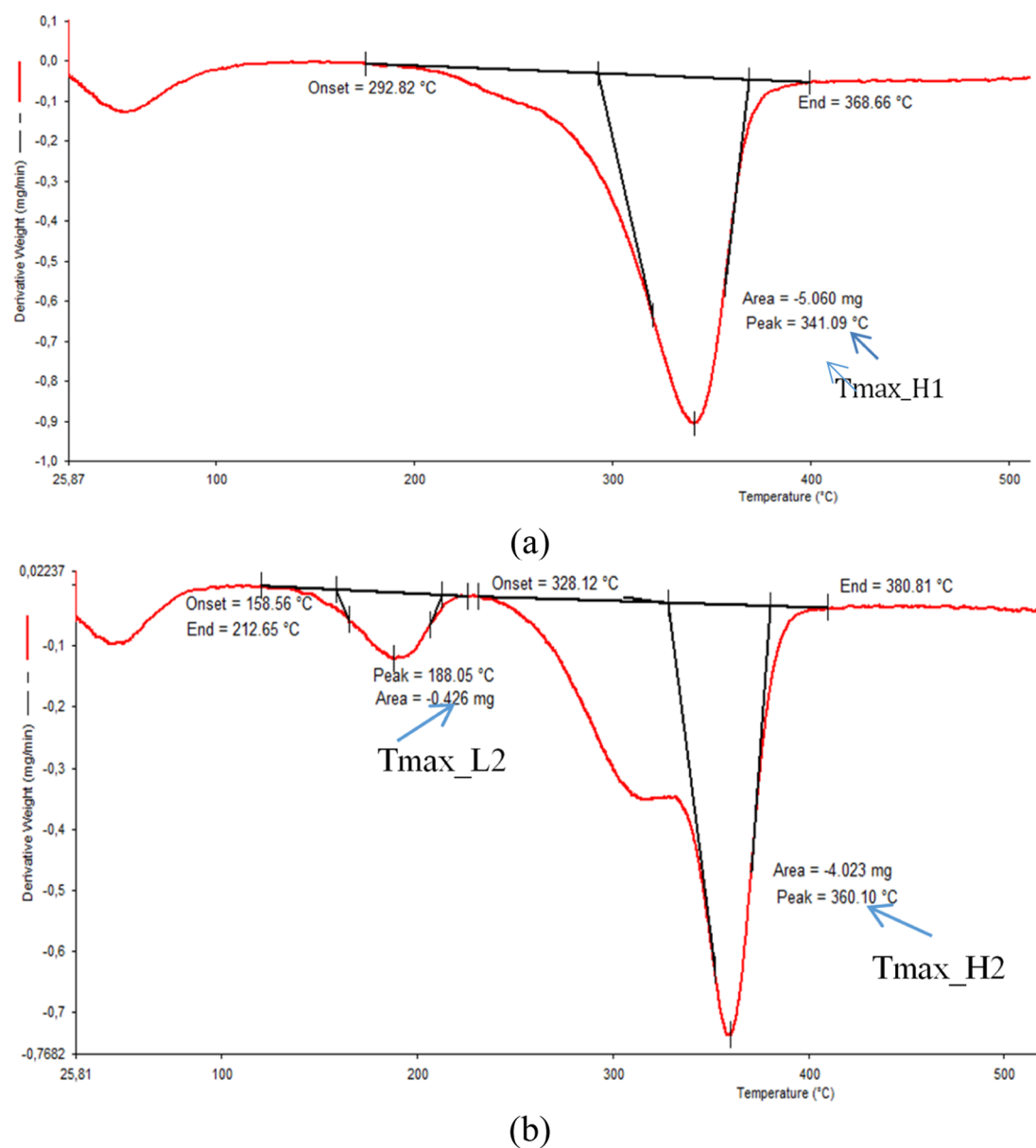


Figure 7. DTGA curves of (a) untreated rice straw and (b) pretreated rice straw.

microwave-assisted hydrotropic pretreated rice straw are shown in Figure 6. SEM images obtained at 500 time

magnifications showed that the untreated rice straw is a flat shape particle having smooth structured surface area. Figure 6b

shows that the surface structure of pretreated rice straw is disorganized and dots are exposed. It indicated the combination of microwave and hydrotropic solution disrupted the lignocellulose structure and thus facilitating the dissolution of lignocellulose components. The disruption of lignocellulose components as the result of microwave heating and/or by hydrotropic agents was also reported by several researchers.⁶⁹

The thermal decomposition curves of untreated rice straw and pretreated rice straw are shown in Figure 7. It is shown that single high temperature peak with a peak value (T_{\max_H1}) of 341.09 °C was obtained from the untreated rice straw. Moreover, a low temperature peak with a peak value of 188.05 °C (T_{\max_L2}) and a high temperature peak with a peak value of 360.10 °C (T_{\max_H2}) were obtained from the microwave-assisted hydrotropic pretreated rice straw. The value of T_{\max} derived from TGA data represents the temperature at which the maximum decomposition rate occurs as well as the thermal stability of biomass samples.⁷⁰ The high-temperature peak corresponds to the degradation of cellulose type II. It seems that the solid residue, obtained from the microwave-assisted hydrotropic pretreatment conducted at a solid–liquid ratio of 1:35, application of urea concentration of 36.8%, reaction temperature of 90 °C, and pretreatment duration of 40 min, is more thermally stable than that of the untreated since the T_{\max_H2} (360.10 °C) is higher than T_{\max_H1} (341.09 °C).

4. CONCLUSIONS

The combination of microwave heating and urea-based hydrotropic pretreatment turned out to be a potential route for the rice straw fractionation process. Based on the results of the kinetic models, it was observed that the rate of lignin condensation is relatively slow compared to the rate of lignin degradation to soluble lignin since the value of k_c is relatively small compared to the value of k_{f1} . Hence, due to its simplicity, the first kinetic model is suggested. The mechanistic model proposed can be used to predict the cellulose and hemicellulose dissolution quantitatively. As a result, the mechanistic model can also be applied to determine the process conditions giving the desirable results. The predicted profiles of lignin, cellulose, hemicellulose, and ash concentration, as well as the profiles of yield, lignin content, and cellulose content of the solid residue at various times, are expected to give a better understanding of the phenomena related to the microwave-assisted urea-based hydrotropic pretreatment of rice straw. Process selectivity can be determined by observing the ratio of the cellulose to lignin concentration, C_B/C_A . The microwave-assisted urea-based hydrotropic pretreatment conducted at a solid–liquid ratio of 1:35, application of urea concentration of 36.8%, a reaction temperature of 90 °C, and a pretreatment duration of 40 min is predicted to give a solid residue with a low lignin content, a high cellulose content, and a high ratio of cellulose to lignin concentration, C_B/C_A , of 9.78. The surface morphology evaluation of cellulosic biomass performed by SEM illustrated the disruption of the lignocellulose structure and facilitated the dissolution of lignocellulose components due to the application of microwave heating and hydrotropic solution. FTIR analysis indicates that as a result of microwave-assisted hydrotropic pretreatment, the crystallinity degree of pretreated rice straw was slightly higher compared to the one of untreated biomass, while thermogravimetric analysis shows that the pretreated rice straw is more thermally stable than the untreated rice straw.

AUTHOR INFORMATION

Corresponding Author

Hary Sulistyono – Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia; orcid.org/0000-0002-2941-3840; Email: hary@ugm.ac.id

Authors

Indah Hartati – Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia; Department of Chemical Engineering, Faculty of Engineering, Universitas Wahid Hasyim, Semarang 50236, Indonesia

Wahyudi Budi Sediawan – Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

Muhammad Mufti Azis – Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

Mohammad Fahrurrozi – Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.1c01084>

Notes

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