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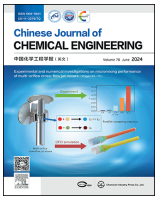

Full Length Article

Optimizing hemicelluloses pre-extraction in eucalyptus kraft pulping: A pathway towards enhancing pulp mill biorefineries

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ABSTRACT

A critical pathway towards enhancing pulp mill biorefineries is to integrate the extraction and utilization of hemicelluloses into the pulping processes. Hence, an industrial pre-extraction strategy for hemicelluloses targeting eucalyptus kraft pulping process was developed. Alkaline solution or pulping white liquor was used to pre-extract hemicelluloses before the actual pulping process. The response surface methodology (RSM) technique was applied to investigate the most suitable conditions to maximize the yield of these hemicelluloses while simultaneously minimizing the damage to pulp yields and properties. Temperature (105 to 155 °C), alkali concentration (3% to 8%), sulfidity (20% to 30%) and retention time (19 to 221 min) were combined to evaluate their effects on hemicellulose yields and chemical structures. The optimal pre-extraction conditions identified in this work (5.75% NaOH concentration, 25% sulfidity at 135°C for 60 min) successfully allowed recovering 4.8% of hemicelluloses (based on the wood dry mass) and limited damages to pulp yields and properties. The cellulose content in pulp can even be increased by about 10%. Hemicellulose emulsification properties were also evaluated, which were comparable to synthetic emulsifiers. This study provides an industrial pathway to effectively separate and utilize wood hemicelluloses from the pulping process, which has the potential to improve the economy and material utilization of pulp and paper mills.

1. Introduction

Cellulose, hemicelluloses and lignin are the main components in wood. In the pulping and paper-making process, most of the lignin is supposed to be removed leaving cellulose and some hemicelluloses to construct paper-based materials. During kraft pulping, approximately half of the hemicelluloses in wood dissolve in the cooking liquor, part of which are converted to degradation products such as furfural and hexenuronic acid, along with the degraded lignin. In order to recover chemicals, such as NaOH and Na_2S as well as energy used in the pulping process, black liquor is concentrated and burned. However, the combustion of dissolved hemicelluloses is not economical or optimally feasible, since hemicelluloses have a low heating value of 13.6 $MJ \cdot kg^{-1}$, compared to 26.9 $MJ \cdot kg^{-1}$ for lignin [1]. Effective separation and utilization of the hemicelluloses from pulping process is an important pathway to enhance the biorefineries for the integrated utilization of natural resources and improve the economic output of pulp mills.

Consequently, many researchers consider membrane filtration for separating hemicelluloses from black liquor. Sharma [2] used ZnO/PES ultrafiltration membranes achieving the highest rejection of hemicelluloses up to 90.7% at 0.4 MPa. Wallberg [3] used membranes with molecular weight cut-offs of 5000 and 15000 to recover hemicelluloses from black liquor. The retention of glucan, xylan, and arabinan was 80%–95%, whereas the retention of galactan and mannan was lower, 10%–70%. However, the above methods of separating hemicelluloses from black liquor require relatively expensive membrane materials, prolonged filtration time, regulation of transmembrane pressure and crossflow velocity, making the process complex and expensive, hindering large-scale separation of hemicelluloses from pulping process. Due to severe degradation [4], the hemicelluloses separated from black liquor have a very complex structure and inferior properties, compared to the commercial xylans extracted directly from wood. In accordance with the concept of value prior to pulping (VPP) [5], the hemicelluloses are extracted prior to pulping either partially or entirely for high value-added products, including ethanol [6], organic acids [1], polymers [7] and other chemicals, leading us to develop optimal industrial extraction strategies for hemicelluloses prior to kraft pulping.

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The extraction of hemicelluloses from wood using autohydrolysis or an alkaline solution before subsequent commercial pulping has been considered in recent years [8,9]. While autohydrolysis obtains hemicelluloses with low molecular weights aiming at platform chemical compound production, alkaline solution obtains hemicelluloses with high molecular weight aiming at materials utilization. Although this concept may seem appealing, it is necessary to balance the yield with the potential pulp property losses, as hemicelluloses greatly influence paper fibers' strength and inter-bonding [10].

Autohydrolysis at 180–200 °C causes acetylated polysaccharides in wood to release acetyl groups, forming acetic acid, and maintaining a pH of 3–4. This process results in random cleavage of hemicellulose and cellulose chains, making holocellulose more soluble, easier to peel and leading to a significant loss in pulp yield [11]. Mao [12] observed that kraft pulping of wood after autohydrolysis had pulping yields reduced by 3%–6%. Aspen chips were also shown to lose up to 13% of their total pulping yield after autohydrolysis as compared to the control cook in the study by Al-Dajani [9]. As cellulose also degrades during autohydrolysis pre-extraction, it is preferred to process the residual fibers to fermentable sugars instead of paper fibers.

In alkaline pre-extraction, hemicellulose yields are lower than autohydrolysis, but pulp yields and fiber properties remain comparable to the untreated group due to less fiber degradation in alkaline solutions. Different pre-extraction conditions affect hemicellulose recovery rates and overall pulp and paper qualities.

After pre-extraction under mild alkaline conditions of 50–90 °C, aspen chips had 4%–5% hemicellulose recoveries, but the same pulp yield and a slight decrease in tensile index, *e.g.* 10%, compared to pulping without hemicellulose pre-extraction [13]. By increasing the alkaline concentration and pre-extraction temperature, the extraction yield of hemicelluloses increases, but the pulp yield inevitably decreases. In a study by Testova [14], alkaline pre-extraction at 95 °C with 2.5 mol·L^{-1} NaOH resulted in the isolation of 6.6% xylan (based on the original wood) with a molar mass of 20 kDa; however, it yielded 4.9% less than the reference material after *E*-SAQ pulping. In recent years, some attention has been paid to using kraft pulping liquor (white liquor) for hemicelluloses pre-extraction due to its easy accessibility in pulp mills. Under white liquor extraction conditions (3% effective alkali charges, 60 min retention time, and 160 °C), hemicellulose yield was 5.44%, with subsequent wood chip pulping achieving a yield of 50.5%, preserving pulp physical properties [15]. It appears that Na_2S may also protect pulp properties, despite the much higher pre-extraction temperature with white liquor than with alkali. However, suitable applications for the white liquor-pre-extracted hemicelluloses have yet to be identified. Therefore, in order to upgrade pulp mills while preserving paper and pulp quality, the hemicelluloses alkali pre-extraction strategy is preferable to the autohydrolysis method.

Previous alkali pre-extraction studies often used small raw material sizes (0.25–0.42 mm wood powder) for extraction, but this method isn't practical for pulping wood chips due to its limited economic viability. Currently, the conditions for alkali pre-extraction using this raw material size remain unclear. Furthermore, the relationship between white liquor/alkaline pre-extraction conditions and the chemical structure of hemicelluloses remains unclear. Exploring how to balance the high-value utilization of high molecular weight hemicelluloses and subsequent pulp and paper production by adjusting pre-extraction conditions in pulp and paper mills is still needed [7,16–18].

Within this context, we evaluated alkali and white liquor extraction strategies for hemicelluloses prior to kraft pulping based on the large size of the eucalyptus wood chips for the first time. We also applied response surface methodology (RSM) technique [19] for the first time to evaluated the relationship between the chemical structure of hemicelluloses and extraction conditions such as pre-extraction temperature, time and alkali concentration. This way allowed pulp and paper mills to flexibly select the most suitable pre-extraction conditions to balance the high-value utilization of hemicelluloses and pulp and paper production. The high-value applications of the pre-extracted hemicelluloses on emulsions were also evaluated and proposed.

2. Materials and Methods

2.1. Materials

Commercial eucalyptus wood chips supplied by Yunjing Forestry Paper Co., Ltd (Yunnan, China) were used for hemicellulose pre-extraction. The chemical composition of the wood chips is presented in Table 1. The chips were screened and collected with sizes of between 12 mm and 25 mm. The chips were further air-dried, sorted to remove knots and barks, and stored for subsequent pre-extraction and kraft cooking experiments.

Sodium hydroxide (NaOH), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), sodium chloride (NaCl), sodium phosphate dibasic (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4) and nitric acid (HNO_3) were all purchased from Guangzhou Chemical Reagent Co., Ltd (Guangzhou, China). Potassium permanganate ($KMnO_4$), sodium thiosulfate ($Na_2S_2O_3$), sodium bromate ($NaBrO_3$), sodium bromide (NaBr), acetic acid, absolute ethanol, aniline, potassium iodide (KI), starch indicator, phenolphthalein pH indicator solution, sodium sulfide nonahydrate ($Na_2S·9H_2O$), sodium dodecyl sulfate (SDS), Tween 80 (T80), Triton X-100 (TX100) were all purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Medium chain triglycerides (MCT, the carbon number of each fatty acid chain is 8–10) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). The chemicals used were all of analytical grade.

2.2. Experimental design by response surface methodology

The alkali pre-extraction parameters were optimized using RSM. Central composite design (CCD) with the distance of each star point from the center in CCD of 1.682. The 17 experimental points (8 factorial points, 6-star points and 3 center points) are shown in Table 2. Reaction temperature (H_1), retention time (H_2) and alkali concentration (H_3) were chosen as independent variables. The yield and molecular weight of hemicelluloses, the content of xylose and lignin were determined as the response variables (Y).

The relationship between the independent variables and response was calculated by the quadratic polynomial equation (1):

Table 1
Chemical composition of the raw eucalyptus wood chips

Component	Composition/% (mass)
Glucose	47.8 ± 1.3
Xylose	11.8 ± 0.7
Arabinose	0.2 ± 0.0
Galactose	1.1 ± 0.0
Mannose	1.7 ± 0.1
Acid soluble lignin	4.1 ± 0.0
Acid insoluble lignin	23.5 ± 1.2
Ash	0.2 ± 0.0
Extractives (Toluene/ethanol)	2.0 ± 0.3
Total	92.5 ± 3.6

Table 2
Code and actual level of the factor for three-factor CCD

Independent variables	Symbols	Actual level				
Reaction temperature/°C	H_1	105	115	130	145	155
Retention time/min	H_2	19	60	120	180	221
Alkali concentration/%	H_3	3	4	6	7	8

$$Y = \beta_0 + \beta_1 H_1 + \beta_2 H_2 + \beta_3 H_3 + \beta_{11} H_1^2 + \beta_{22} H_2^2 + \beta_{33} H_3^2 + \beta_{12} H_1 H_2 + \beta_{13} H_1 H_3 + \beta_{23} H_2 H_3 \quad (1)$$

where H_1, H_2 and H_3 are independent variables, which influence the response variable Y, β_0 is the intercept, β_1, β_2 and β_3 are the linear coefficient on the response Y; β_{11}, β_{22} and β_{33} are the quadratic coefficient and β_{12}, β_{13}, β_{23} respectively estimate the interaction effect between variables H_1 and H_2, variables H_1 and H_3, variables H_2 and H_3 on the response Y. The statistical software JMP (Version 13.2.0) was used for the regression analysis of the experimental data and the response surface plots. Analysis of variance (ANOVA) was used to estimate statistical parameters. Equation model to estimate alkali pre-extraction strategies was applied to obtain the optimum point based on alkali pre-extraction.

2.3. Alkali pre-extraction of hemicelluloses

Using the above conditions, alkali extraction was performed as follows. Approximately 100 g of air-dried chips were mixed with NaOH solution at a liquor-to-wood ratio of 4:1 in a 1 L batch-type digester, and the extraction conditions were kept at the desired reaction temperature, retention time and alkali concentration (Table 2). After the reactions were completed, the digesters were cooled with running water. The pre-extracted wood chips were collected and washed with de-ionized water and used for kraft pulping.

The liquor from the pre-extraction process was neutralized to pH = 5.5 with acetic acid, the liquor was concentrated to 1/3 of its original volume by rotary evaporation and then was precipitated in absolute ethanol of the volumes of three times the concentrated liquor. Finally, the hemicelluloses were separated by centrifugation, washed with 70% ethanol and freeze-dried for further use. Sample names of the alkali liquor extracted hemicelluloses are shown in Table 3.

2.4. White liquor pre-extraction of hemicelluloses

Approximately 100 g of dry chips were extracted by 400 ml 20%, 25% and 30% (percentage of Na_2S, expressed as NaOH) kraft white liquor in a 1 L batch-type digester. The extraction conditions were 135 °C, 60 min retention time and 5.75% alkali liquor concentration. After the reaction was completed, the digesters were cooled with running water. The extracted wood chips were collected and washed with de-ionized water and used for kraft pulping. The separation procedures of hemicelluloses from extraction liquor are the same as described in Section 2.2. Sample names of the white liquor extracted hemicelluloses are shown in Table 4.

2.5. Characterization of wood chips and hemicelluloses

Extractive-free milled wood samples (0.25–0.42 mm) and hemicellulose samples were first hydrolyzed and lignin content was determined according to Min [20]. The sugar compositions of the hemicelluloses were calculated based on the sugars in the hydrolysate. The neutral sugar contents in the hydrolysate were measured by an Ion Chromatography (940, Metrohm, Switzerland) equipped with a CarboPac PA10 column (2 × 250 mm, Dionex, US) and a PAD detector.

Molecular weight, including weight-average molecular weight (M_w) and number-average molecular weight (M_n), of hemicelluloses was measured by high-pressure liquid chromatography (HPLC) (1260 Infinity, Agilent Technologies, USA) equipped with a differential refractive index detector and GPC (gel permeation chromatography) columns (Polymer Laboratories (PL) aquagel-OH 60 and Polymer Laboratories (PL) aquagel-OH MIXED-H, Agilent Technologies, USA). Using $NaNO_3$–Na_2HPO_4 solution (0.1 $mol \cdot L^{-1}$:0.001 $mol \cdot L^{-1}$) as the mobile phase, approximately 6 mg of hemicelluloses sample was dissolved in 1.5 ml of mobile phase and 20 μl of the solution was injected for determination each time. The parameter settings used in the experiment were: the column and detector temperature were 35 °C and the flow rate was 0.6 $ml \cdot min^{-1}$. The standard curve was made by dextran with accurate peak M_W.

2.6. Preparation and characterization of pulp and paper hand sheets

For the pulping process, 100 g of pre-extracted wood chips or original wood chips were used. Cooking liquor was composed of 25% sulfide (percentage of Na_2S, expressed in NaOH) and 23% effective alkali (expressed in NaOH, based on oven-dried wood mass). Cooking was performed in a 1 L batch-type digester and with a maximum temperature of 165 °C, a liquor-to-wood ratio of 4:1, a total cooking time of 50 min and a retention time of 70 min. As soon

Table 3
Response surface experimental design and results

Sample	H_1/°C	H_2/min	H_3/%	Yield/%	Xylose/%	Glucose/%	Lignin/%	M_n	M_w
y1	130	120	2.98	2.06	45.26 ± 7.32	2.98 ± 0.05	31.68 ± 5.12	49287	57109
y2	115	60	4.00	2.54	39.98 ± 5.84	4.36 ± 0.55	27.98 ± 4.09	50584	71018
y3	145	60	4.00	2.76	36.23 ± 8.06	8.53 ± 2.20	25.36 ± 5.64	38676	63138
y4	115	180	4.00	2.40	27.35 ± 8.63	4.61 ± 0.36	29.14 ± 6.04	32707	55476
y5	145	180	4.00	2.64	46.46 ± 4.04	5.90 ± 0.51	32.52 ± 2.83	31792	55054
y6	130	120	5.50	3.42	32.98 ± 5.33	3.35 ± 0.46	30.08 ± 3.73	52235	73318
y7	130	120	5.50	3.02	32.75 ± 7.87	3.48 ± 0.62	29.93 ± 5.51	52771	74929
y8	130	120	5.50	3.27	29.39 ± 2.10	3.65 ± 0.31	20.57 ± 1.47	50016	77424
y9	155	120	5.50	1.96	43.22 ± 9.94	4.26 ± 1.01	30.25 ± 6.96	23080	35092
y10	130	19	5.50	3.08	40.41 ± 1.95	3.49 ± 0.27	28.29 ± 1.36	52971	63835
y11	105	120	5.50	1.96	43.86 ± 8.64	5.72 ± 1.21	30.70 ± 6.05	27168	31932
y12	130	221	5.50	3.95	53.11 ± 4.20	5.68 ± 0.43	37.18 ± 2.94	29475	40792
y13	115	60	7.00	3.59	45.38 ± 0.75	2.53 ± 0.06	21.77 ± 0.52	65345	79915
y14	145	60	7.00	3.87	58.40 ± 1.21	6.13 ± 0.09	20.88 ± 0.85	54722	64903
y15	145	180	7.00	5.03	58.14 ± 3.15	6.42 ± 0.37	30.70 ± 2.20	35436	39900
y16	115	180	7.00	3.57	34.66 ± 1.04	4.04 ± 0.90	24.27 ± 0.73	33205	56348
y17	130	120	8.02	4.48	55.98 ± 0.71	3.41 ± 0.03	23.49 ± 0.50	54950	76870

Note: Yield (%) = absolute dry hemicelluloses quality/absolute dry wood chip quality.

as the cook was completed, the kraft pulp was recovered and washed with deionized water until pH turned neutral. Afterward, the pulp was disintegrated, screened on a screen separator using a 0.15 mm slotted screen and yield (mass fraction of screened pulp based on original non-extracted chip mass) was calculated. The lignin and xylan contents of screened pulp were determined according to the methods described in Section 2.5. The cellulose content of the screened pulp was determined by the nitric acid-ethanol method [21].

For the papermaking properties evaluation, firstly, the pulps were screened by Somerville-type screening equipment with 0.15 mm slit widths' screen plates. Subsequently, the screened pulps were refined in a "PFI" type refiner to achieve a (45 ± 2) SR beating degree with a 3.33 $N \cdot mm^{-1}$ beating pressure. Hand sheets with the grammage approximately 60 $g \cdot m^{-2}$ were prepared using a KCL model machine. Tensile index, tear index and burst index of the hand sheets physical properties were measured using National Standard of the People's Republic of China methods: GB/T 12914—2008, GB/T 455—2002 and GB/T 454—2020, respectively.

2.7. Emulsifying properties of the hemicelluloses

Hemicellulose aqueous dispersions were obtained by dispersing hemicelluloses with an ultrasonic cell grinder (JY99-IIDN, Ningbo Xinzhi Biological Co., Ltd., Ningbo, China) at 15 $W \cdot ml^{-1}$ for 10 min. Emulsions were prepared by mixing hemicelluloses aqueous dispersions with medium chain triglycerides (MCT) at a water-oil ratio of 8:2 homogenized by an ultrasonic cell grinder at 10 $W \cdot ml^{-1}$ for 15 min.

The emulsifying activity (EA) and emulsion cream index (ECI) were evaluated according to previous studies [7,18]. For EA measurement, approximately 30 μl of emulsion was mixed with 15 ml 0.1% (mass) sodium dodecyl sulfate (SDS, AR) aqueous solution, and the absorbance was measured at 500 nm by a UV–vis spectrophotometer (Shanghai Mapada Instrument Co., Ltd., Shanghai, China). For ECI measurement, the fresh emulsion was continuously standing up for 7 d, the layering of the emulsion at different times was recorded, and the ECI was calculated as following equation (2):

$$ECI = \frac{H_A}{H_T} \times 100\% \quad (2)$$

where H_A is the height of the upper phase and H_T is the total height of emulsion.

3. Results and Discussion

3.1. Response surfaces and analysis of variance

In this study, xylans were pre-extrected before kraft pulping following the scheme shown in Fig. 1. Xylan is a major type of hemicelluloses in eucalyptus, with β-(1→4)-linked D-xylopyranosyl backbone. These hemicelluloses are linked to lignin *via* α-ether and phenolic glycosidic bonds. During alkali pre-extraction, some sugar units on the side chains, such as 4-*O*-methyl-D-glucuronic acid and L-arabinofuranosyl acid units are prone to detachment and degradation, thereby reducing the molecular weight of hemicelluloses. Consequently, the yield and molecular weights of hemicelluloses, as well as the xylose content are considered as the response variables (Y) for optimizing the extraction conditions favoring high molecular weights hemicelluloses aiming at materials utilization. In line with subsequent pulping processes, no bleaching was conducted during pre-extraction, and the lignin linked to hemicelluloses is also considered as a response variable (Y).

The experimental conditions and results of 17 runs are shown in Table 3. The results of an analysis of variance (ANOVA) are presented in Table S1 in Supplementary Material p-values and F-values are used to verify the significance of coefficients. Specifically, p-value Prob > F values less than 0.05 indicate that model coefficients are significant, and the values greater than 0.05 indicate that coefficients are not significant. According to these parameters, p-value Prob > F less than 0.05 indicates that all 5 models are significant, and there is only a 0.05% probability of such a large "model F-value" being the result of noise in the model. Moreover, the non-significant lack of fit values suggest that the model fits the experimental observations well. Additionally, for the yield of hemicelluloses, H_1, H_3 model parameters

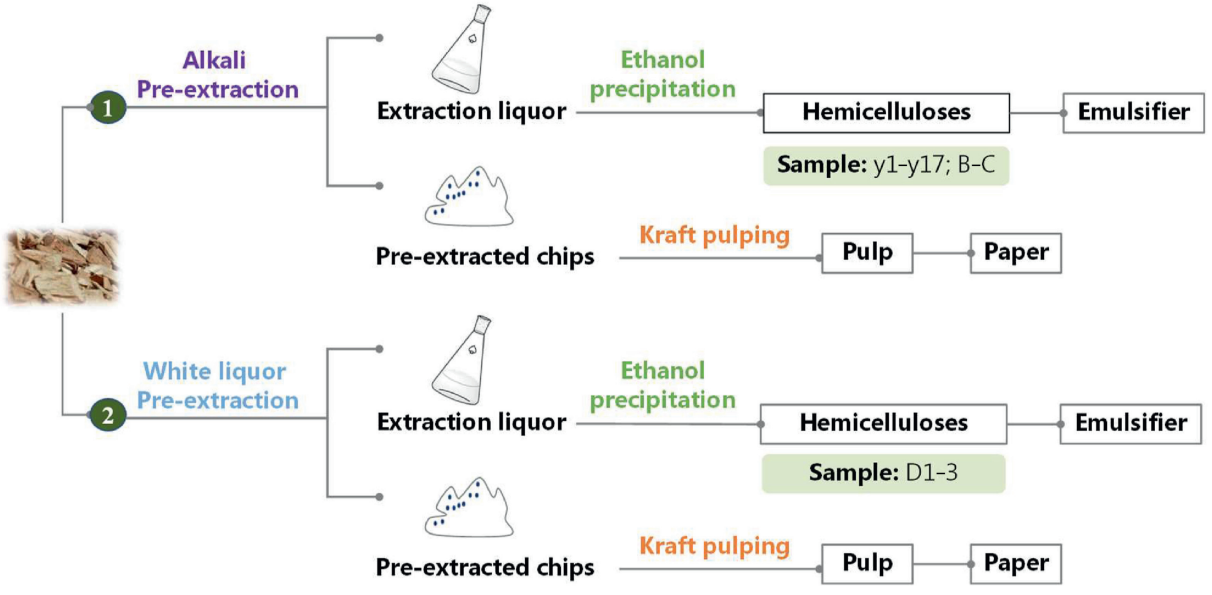

Fig. 1. Scheme of kraft pulping after hemicellulose pre-extractions using white liquor and alkali solution. (Sample codes are indicated in each case).

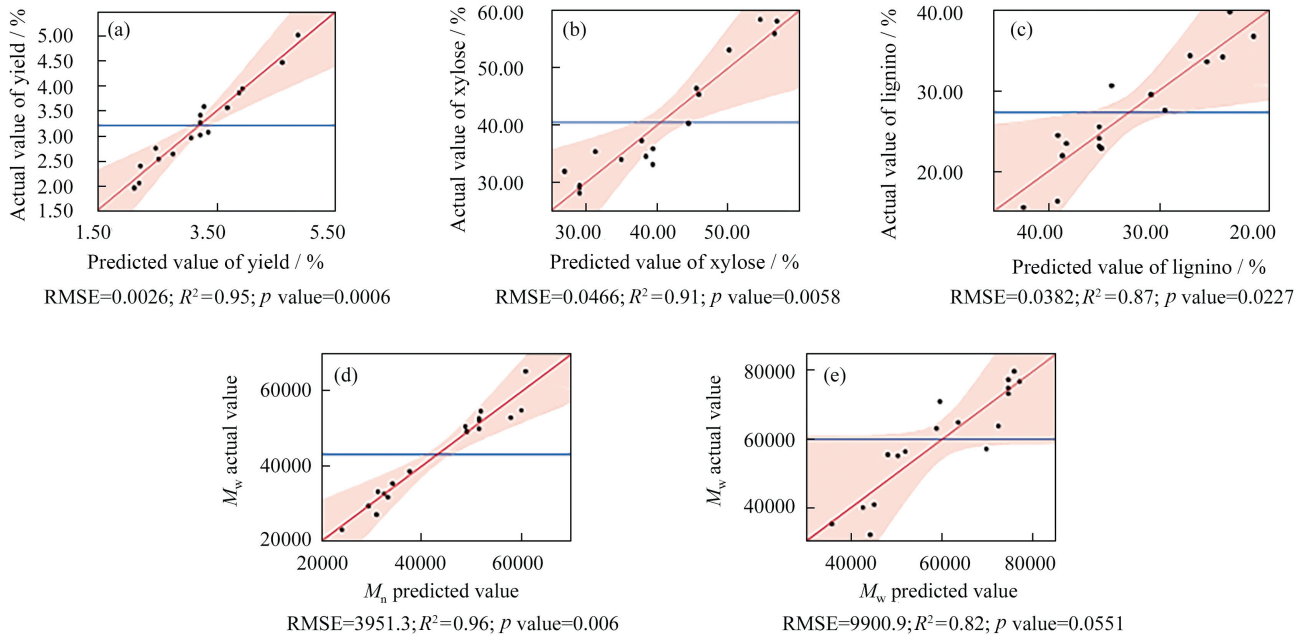

Fig. 2. Actual-by-predicted value of (a) yield, (b) xylose content, (c) lignin content, (d) M_n and (e) M_w.

were found to be significant at a level of $p < 0.01$ or $p < 0.001$ with a coefficient of determination (R^2) of 0.9549. $H_2, H_3, H_1^2, H_2^2, H_2H_3$ model parameters were significant for M_n, while H_2, H_1^2 model parameters were significant for M_w at the lever of $p < 0.05$ or $p < 0.001$. The R^2 values for M_n and M_w were 0.9552 and 0.8195, respectively. H_1, H_3, H_2^2, H_3^2 model parameters were significant for xylose content, while H_2, H_3, H_2H_3 model parameters were significant for lignin content at the level of $p < 0.05$ or $p < 0.01$. The R^2 value for xylose and lignin content were 0.9125 and 0.8654, respectively (Fig. 2). A good fit of the model can be determined by the R^2 which value is closer to 1.00, the better the model can predict the response. Normally, a regression model with an R^2 higher than 0.80 suggests high correlation [22].

Above all, it is confirmed that the experimental models succeed. The regression equation could be used to predict the effects of reaction temperature (H_1), retention time (H_2) and alkali concentration (H_3) on hemicelluloses yield, M_n, M_w, xylose and lignin content. The final equations (3)–(7) in terms of actual factors can be described as follows:

$$Y_{Yield} = -0.086 - 0.986H_3 - 0.003843H_2 + 0.002H_1 + 2.77H_3^2 + 0.0000004138H_3^2 - 0.000009957H_1^2 + 0.002H_3H_2 + 0.007H_3H_1 + 0.000001667H_1H_2 \quad (3)$$

$$Y_{M_n} = 515249.893 - 175885.9187\,H_3 - 181.825H_2 + 9135.747H_1 + 4703483.808\,H_3^2 - 0.776H_2^2 - 37.714H_1^2 - 3703.472H_3H_2 + 2461.667H_3H_1 + 3.312H_2H_1 \quad (4)$$

$$Y_{M_w} = -945134.834 + 2434637.2161H_3 + 319.850H_2 + 14593.362\,H_1 - 1834725.2665H_3^2 - 1.556H_2^2 - 54.440H_1^2 - 3464.444H_3H_2 - 12865.556H_3H_1 + 0.836H_1H_2 \quad (5)$$

$$Y_{Xylose} = 3.1203 - 41.382H_3 - 0.006H_2 - 0.025H_1 + 284.125H_3^2 + 0.00001784H_2^2 + 0.00006424H_1^2 - 0.03305H_2H_3 + 0.137H_3H_1 + 0.00002717H_2H_1 \quad (6)$$

$$Y_{Lignin} = 2.580 - 18.377H_3 - 0.005H_2 - 0.022H_1 + 69.797 + 0.000002202H_2^2 + 0.00004567H_1^2 - 0.0138H_2H_3 + 0.0724H_1H_3 + 0.00004554H_2H_1 \quad (7)$$

3.2. Effects of alkali pre-extraction conditions on the yield, composition and molecular weight of hemicelluloses

The two-dimensional contour plot and three-dimensional response surface are graphical representations of the regression equation, which are used to evaluate the interaction between variables and predict the optimum value for each variable at maximum value.

ANOVA results indicate that reaction temperature and alkali concentration have significant effects on the yield of hemicelluloses with p-values of 0.005394561 and $p = 2.12317 \times 10^{-5}$ ($p < 0.01$), respectively. To further analyze the interaction between these variables regarding hemicellulose yield, response contour plots and 3D response surface plots were generated (Fig. 3(a)).

It is evident that temperature exerts a notable impact on hemicelluloses extraction yield at lower alkali concentration. When the NaOH concentration falls below 5.28%, the yield experiences an increase, reaching its peak before declining as temperature continues to rise. Additionally, the elliptical curvature of the contour lines illustrates that excessively high reaction temperatures (>140 °C) result in reduced extraction yields. Conversely, when the NaOH concentration surpasses 5.93%, the yield increases once more, signifying a higher NaOH concentration requirement for efficient hemicellulose dissolution.

Fig. 3(d) illustrates the substantial increase in xylose content when the NaOH concentration is raised from 2% to 8%. Conversely,

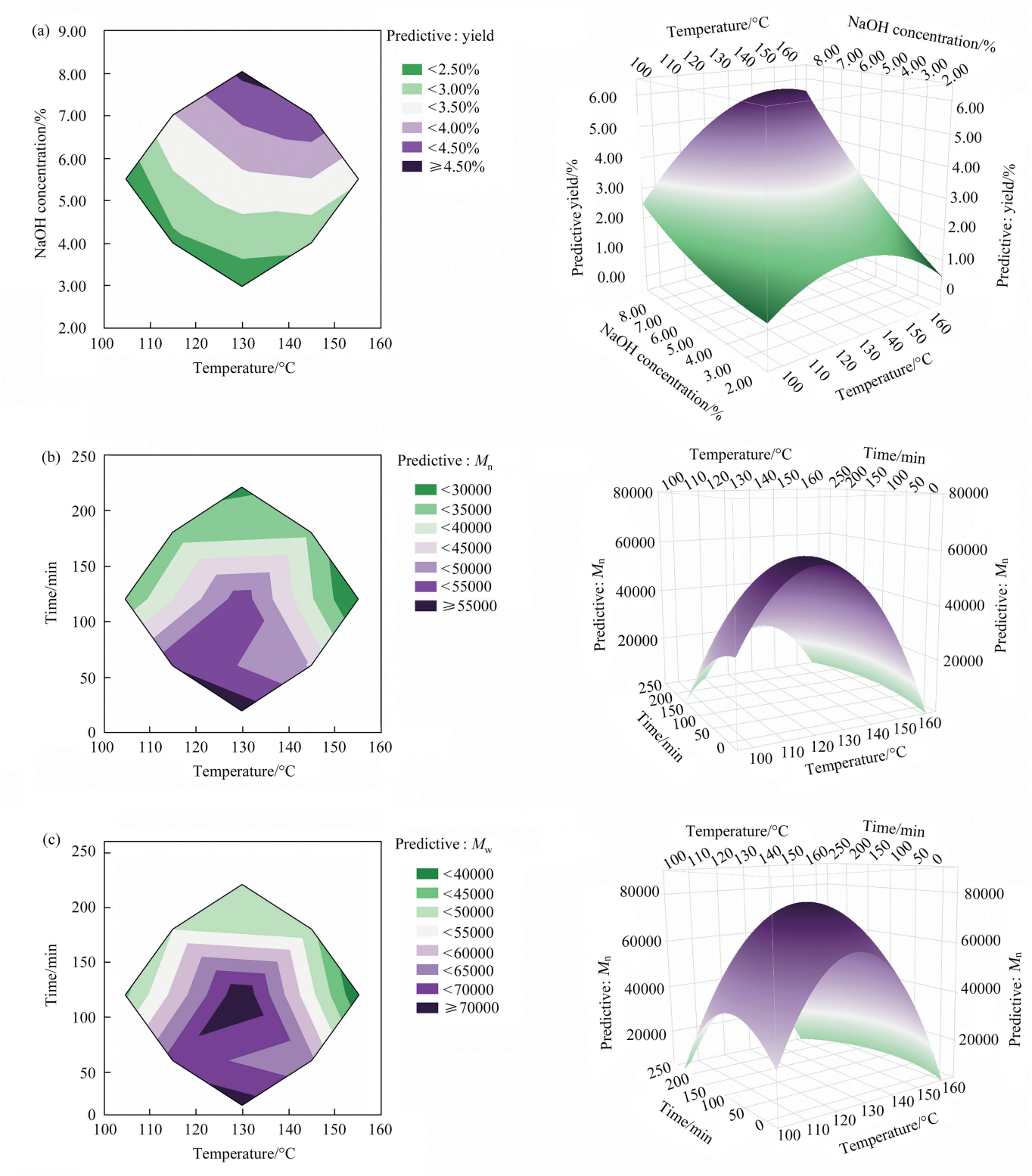

Fig. 3. (a) The effects of reaction temperature (105–155 °C) and alkali concentration (2.98%–8.02%) on hemicellulose yields; (b), (c) the effects of reaction temperature (105–155 °C) and retention time (19–221 min) on M_n and M_w of the extracted hemicelluloses; (d), (e) the effects of alkali concentration (2.98% to 8.02%) and retention time (19–221 min) on xylose and lignin contents of the extracted hemicelluloses.

retention time exhibits a pronounced quadratic effect. Specifically, an extension of retention time from 60 min to 135 min leads to a significant reduction in xylose content, whereas further prolongation of the extraction time demonstrates a noticeable increase. However, that trend is exclusively observed at alkali concentrations < 6.5%.

The reasons for this phenomenon may be as follows: (1) hemicelluloses dissolved in low alkali concentration may undergo

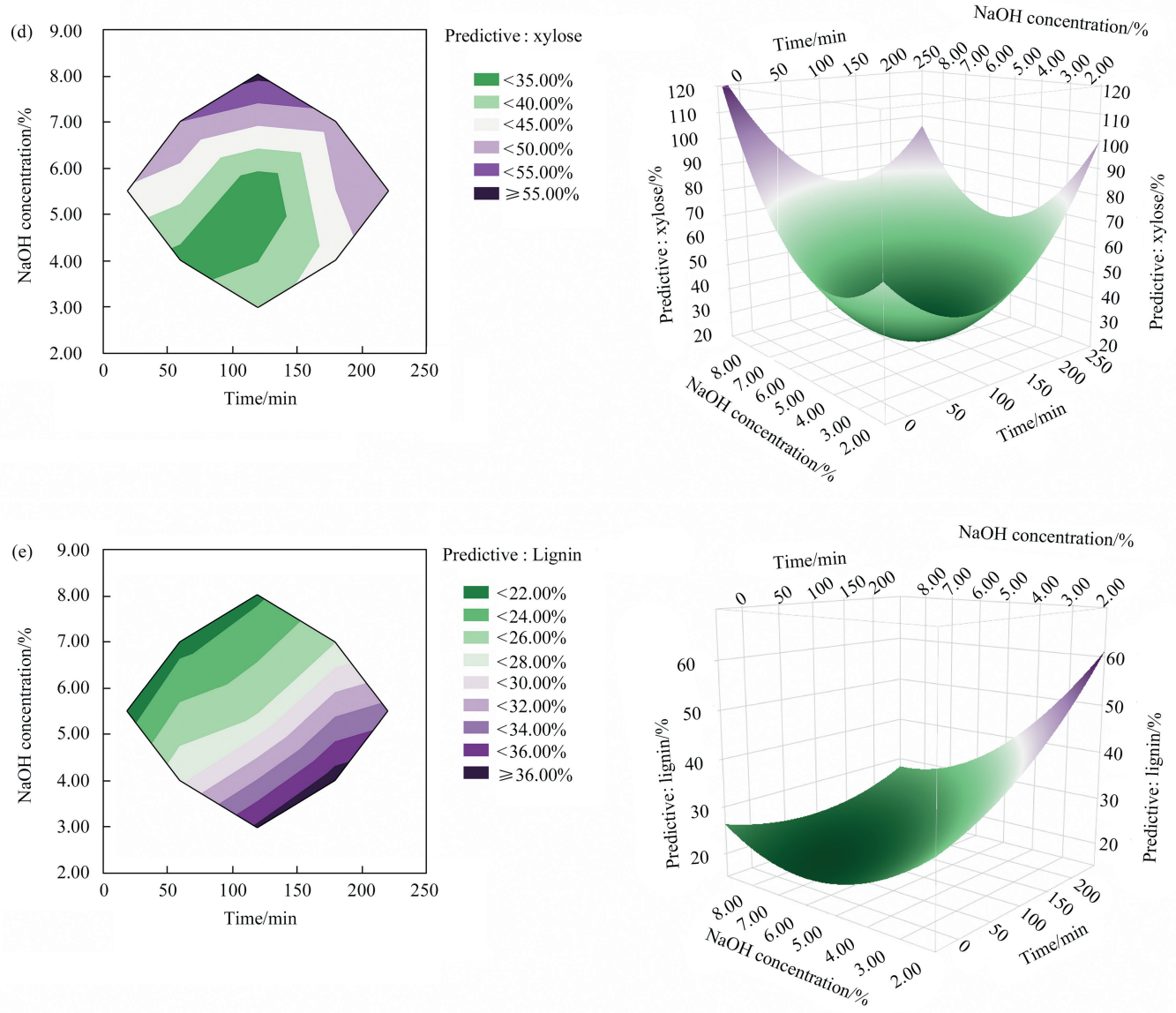

Fig. 3. (continued)

partial degradation into acids and furfural as the retention time extends from 60 to 135 min, resulting in a decrease in xylose content; however, as time continues to extend, it enhances the penetration of the alkaline solution deeper into the raw materials, causing the dissolution of the deeper hemicelluloses and subsequently increasing the xylose levels [23,24]. As a result, pulping factory large wood chips exhibit different reaction characteristics compared to the common laboratory raw material size (0.425–0.85 mm). Correspondingly, cellulose will also undergo partial degradation, resulting in an increase in glucose content. For example, the samples of y6, y12 in Table 3 were at the same condition of 130 °C, 5.5% alkali concentration, only the retention time was lengthened from 120 min to 221 min, the xylose content increased by 20% and the glucose content grew by 2%. (2) Hemicelluloses dissolution efficiency with high alkali concentration is higher which is comparable to the increase of xylose content with low alkali concentration and long retention time [24]. According to Table 3, for the sample of y5, y12 at 145 °C, the retention time decreased from 180 min to 60 min, the alkali concentration increased from 4% to 7%, the xylose content increased by 12%, whereas the glucose content barely changed.

ANOVA shows that retention time and alkali concentration are significant with $p = 0.010601005$ and $p = 0.00368524$, respectively, on the lignin content. Based on these results, the interaction of the above variables on the hemicelluloses yield is further analyzed by response contour plot and 3D response surface plot (Fig. 3(e)). With a constant retention time, lignin content showed a negative correlation with alkali concentration: the higher alkali concentration, the less lignin. Conversely, hemicelluloses yields were positively correlated with NaOH concentration. This implies that a strong negative correlation was observed between total lignin content and hemicelluloses yield. In many studies, it has been suggested that the differences in hemicelluloses extractability are explained by the recalcitrance from lignin [25,26]. Previous studies have [27] demonstrated that a greater presence of lignin resulted in lower hemicelluloses solubilization. Also, when the retention time was longer than 60 min, residual lignin increased, especially if the alkali concentration was lower than 4%.

The contour plot and 3D response surface plot show the interaction between temperature and retention time on molecular weight (Fig. 3(b) and (c)). During the temperature increase from 105 °C to 135 °C, the molecular weight increases from <40000 to >70000. Simultaneously, when the retention time exceeds 60 min,

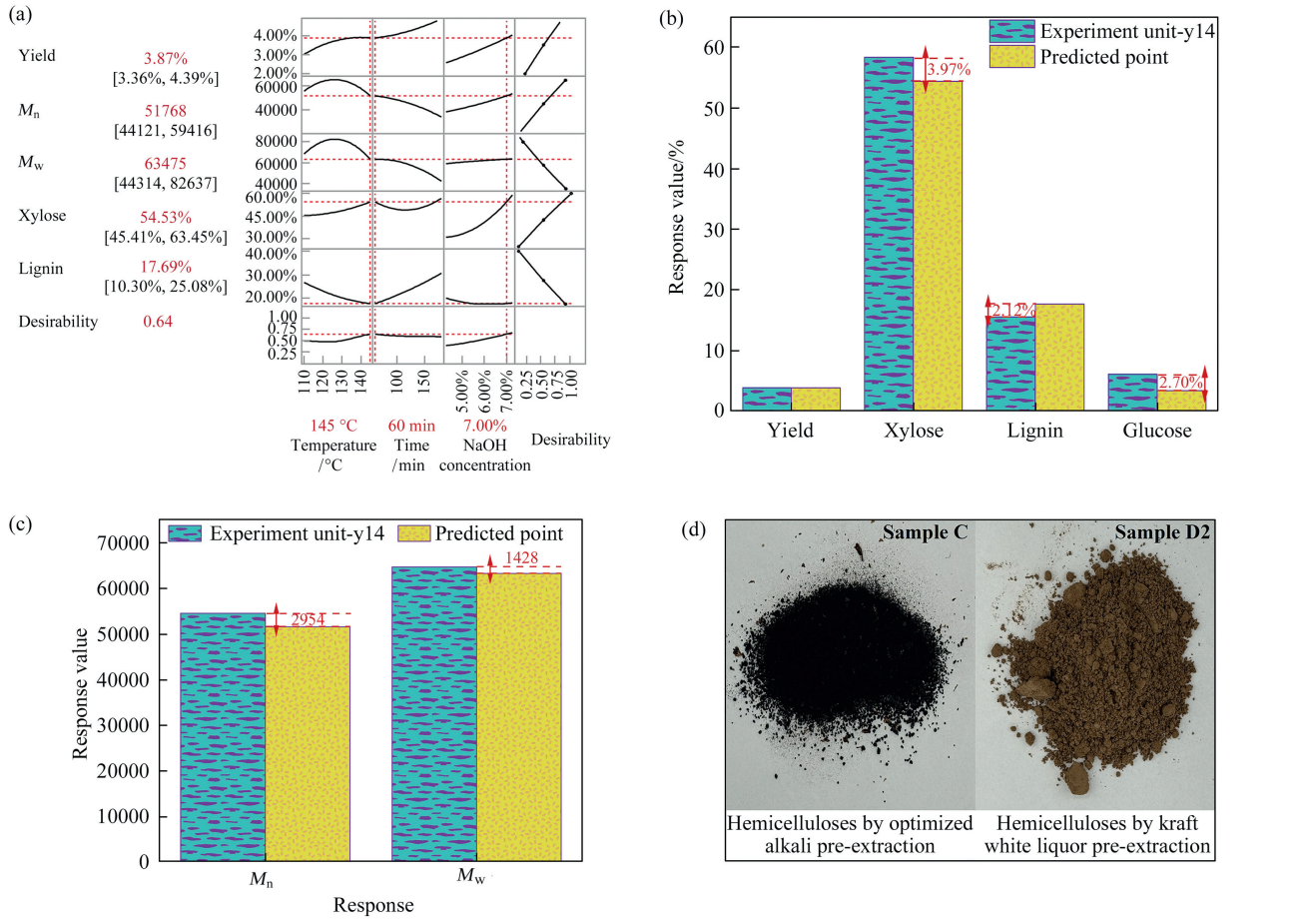

Fig. 4. (a) The optimal alkali pre-extraction conditions for hemicelluloses: 145 °C reaction temperature, 60 min retention time, 7.00% NaOH concentration, as predicted by profiler; (b), (c) validation of the models; (d) hemicellulose samples obtained after optimized alkali and white liquor pre-extraction.

even at the same temperature (*e.g.*, 115 °C), the molecular weights after 60 min were approximately 20000 higher than that after 180 min. This is due to proper temperature and retention time accelerating the hydrolysis process and the cleavage of bonds between lignin and hemicelluloses [28]; Higher temperature and longer time resulted in serious degradation of hemicelluloses into soluble mono- and oligosaccharides [29].

3.3. Optimization and verification of the alkali pre-extraction process

A prediction profiler was utilized to maximize model accuracy. The optimized conditions for alkali pre-extraction of hemicelluloses, as predicted by the profiler, include a reaction temperature of 145 °C, a retention time of 60 min, and a NaOH concentration of 7.00% (Fig. 4(a)). The model exhibits high accuracy, with less than a 5.50% difference between the optimal and experimental points, effectively predicting experimental values for hemicellulose alkali pre-extraction (Fig. 4(b)–(c)).

In addition, using the predicted conditions and considering practical industrial operations, the author modified the optimal experimental conditions (Table 4). Considering the structural characteristics of hemicelluloses and their subsequent integration with the pulp and paper production, we further refined and optimized the alkali extraction model, resulting in the optimal conditions and outcomes presented in Table 4, specifically as samples B and C. The average extraction yield and xylose content of two samples (B, C) was 5% and 63% respectively, higher than in the existing experiments, while the molecular weight and lignin content were similar to that.

Table 4
The yields, chemical compositions and molecular weight of hemicelluloses obtained by white liquor extraction and optimized alkali pre-extraction

Sample	B	C	D1	D2	D3
Temperature/°C	135	135	135	135	135
Retention time/min	60	60	60	60	60
Alkali Concentration/%	7	5.75	5.75	5.75	5.75
Sulfidity/%	–	–	20	25	30
Yield/%	5.30 ± 0.34	4.72 ± 0.02	4.31 ± 0.38	4.82 ± 0.50	4.92 ± 0.04
Xylose/%	62.18 ± 0.29	65.99 ± 1.51	70.05 ± 2.44	71.70 ± 1.99	55.88 ± 2.91
Glucose/%	6.77 ± 3.43	4.86 ± 0.62	5.72 ± 0.48	6.77 ± 0.06	6.62 ± 0.21
Lignin/%	30.81 ± 1.10	26.78 ± 1.59	23.05 ± 1.50	22.10 ± 2.55	27.26 ± 1.68
M_n	49131	62766	50722	54737	42536
M_w	74158	74424	70583	80080	72870

3.4. Comparison of white liquor and alkali solution for pre-extraction of hemicelluloses

When sulfidity increases from 20% to 25%, as observed in sample D1-2, hemicelluloses exhibit higher xylose contents and molecular weights, along with reduced residual lignin. This indicates that Na_2S effectively preserves carbohydrates from degradation and removes lignin efficiently. However, at 30% sulfidity, with a significant increase in HS^- and S^{2-} concentrations and a decrease in OH^- concentration [30], there is reduced xylan extraction efficiency, leading to lower xylose content in white liquor (D3) compared to optimized alkali pre-extraction (C). Although the hemicellulose yield of sample D3 exceeds that of D1-2, this is primarily due to a higher residual lignin content within the hemicelluloses.

Furthermore, lignin has been observed to be soluble and co-precipitates with hemicelluloses in ethanol [25,31], implying potential chemical bonding through lignin-carbohydrate complex (LCC) bonds [27]. A comparison between samples subjected to white liquor pre-extraction and optimized alkali pre-extraction (C, D1, D2) clearly illustrates that Na_2S effectively weakens LCC chemical bonds, leading to reduced lignin content and bleaching of hemicellulose samples (Fig. 4(d)).

3.5. Effects of hemicelluloses pre-extraction on pulp and paper properties

Solid residues by white liquor pre-extraction (D1-3) and optimized alkali pre-extraction (B, C) were selected for subsequent kraft pulping with non-extracted eucalyptus chips (A) used as a control. Table 5 shows the effects of the above pre-extraction conditions on kraft pulping yields and chemical compositions.

The screened pulp yield of extracted chips under identical kraft cooking conditions ranged from 40% to 44%, lower than the control sample at 47%. In contrast, the cellulose content of the screened pulp after pre-extraction process reached 81%–84%, marking a significant 6%–9% increase compared to the unextracted pulp. The decrease in pulp yield was due to the removal of part of xylan and lignin during pre-extraction.

Maintaining an optimal level of hemicelluloses or xylans in the pulp can enhance fiber bonding, improving overall pulp performance [32]. Therefore, one of our purposes is to optimize the pre-extraction process condition to balance the performance of the pulp and the yields and properties of the extracted xylans. Notably, pre-extraction with a lower alkali concentration (5.75%) improved xylan content and subsequent performance of the pulp and reduced the loss of screened pulp yield compared to pre-extraction with 7.0% alkali concentration. This phenomenon could be attributed to the lower alkali content resulting in reduced hemicellulose yields during pre-extraction, retaining more xylan in the wood chips, thus improving both the screened pulp yield and pentose content. Furthermore, the samples of B, C and D1–3 show that increased sulfide during the pre-extraction led to a greater increase in xylan content in the fine pulp, but had little effect on yield and cellulose content.

Another noticeable benefit of using pre-extracted wood chips for kraft pulping is the lower lignin content, which is about 2%–3%, compared to up to 27% in the control unextracted chips. The porous structure of the extracted chips allows for better penetration of cooking chemicals, resulting in a more uniform cook [33]. Jun [34] also obtained a good degree of delignification (screened pulp residue Klason lignin mass fraction about 2.27%–3.31%) after pre-extraction with white liquor. However, that process requires a longer pretreatment time (4 h) and more stringent cooking conditions (H factor 865) to achieve similar delignification and pulp quality as ours.

Table 5 presents the paper results obtained after white liquor pre-extraction and optimized alkali pre-extraction.

The tensile and burst index of samples (D1–3) extracted after white liquor pre-extraction, generally surpass those of samples B and C, extracted after optimized alkali pre-extraction. This improvement is attributed to the higher xylan content in samples D1-3, enhancing fiber bonding strength [35]. Additionally, Na_2S provides better cellulose protection during pre-extraction, preventing degradation and resulting in enhanced paper strength properties. Although there is still some disparity in paper performance between the pre-extracted samples and the control group, our paper still meets the tensile index requirement for producing first-grade quality bag paper that complies with GB/T 7968—2015. In addition, we can effectively improve the paper performance by incorporating fillers during the papermaking process.

The tear index serves as an effective indicator for assessing the tightness of fiber interactions within paper [36]. Adding Na_2S during pre-extraction can effectively enhance fiber interactions or inter-fiber forces. For example, the tear index of white liquor extracted samples (D1–3) is higher than sample C without Na_2S and close to the unextracted sample A.

3.6. Emulsifying properties of the pre-extracted hemicelluloses

Hemicelluloses colloidal dispersions (y1–y17, B, C, D1–3) served as emulsifiers for creating oil-water emulsions, and their performance was compared to well-known non-ionic surfactants Tween 80 (T80) and Triton X-100 (TX100), commonly used in industries such as coloring and detergent production [37–39]. These emulsions were evaluated using two critical parameters: emulsifying activity (EA) and emulsion cream index (ECI), where EA quantifies emulsion formation capability, and ECI assesses stability [40].

The hemicelluloses dispersions exhibited impressive emulsifying properties, rivaling synthetic emulsifiers (Fig. 5(a)). Notably, y15 displayed the highest EA (1.28), equivalent to TX100 and

Table 5
Effects of the pre-extraction conditions on the kraft pulp and paper properties

	A	B	C	D1	D2	D3
Pre-extraction temperature/°C	–	135	135	135	135	135
Pre-extraction retention time/min	–	60	60	60	60	60
Pre-extraction alkali concentration/%	–	7	5.75	5.75	5.75	5.75
Pre-extraction sulfidity/%	–	–	–	20	25	30
Screened pulp yield/%	47.05 ± 1.75	39.74 ± 0.80	43.75 ± 0.31	41.23 ± 0.97	40.86 ± 0.47	43.67 ± 0.23
Screened pulp xylan content/%	21.30 ± 0.42	13.89 ± 0.24	15.78 ± 0.19	16.59 ± 0.48	14.47 ± 0.01	16.04 ± 0.84
Screened pulp lignin content/%	3.14 ± 0.07	2.13 ± 0.04	2.32 ± 0.00	2.34 ± 0.06	2.32 ± 0.37	2.16 ± 0.01
Screened pulp cellulose content/%	75.57 ± 0.49	83.99 ± 0.20	81.90 ± 0.19	81.07 ± 0.42	83.22 ± 0.36	81.80 ± 0.83
Tensile index/$N\cdot m\cdot g^{-1}$	94.92 ± 12.83	57.50 ± 9.75	60.13 ± 7.88	63.21 ± 11.32	76.13 ± 4.11	77.51 ± 8.10
Burst index/$kPa\cdot m^2\cdot g^{-1}$	6.60 ± 0.32	4.01 ± 0.31	4.30 ± 0.55	4.42 ± 0.25	4.52 ± 0.21	4.77 ± 0.61
Tear index/$mN\cdot m^2\cdot g^{-1}$	10.20 ± 0.59	8.99 ± 0.88	7.60 ± 0.59	10.68 ± 1.21	7.71 ± 0.63	10.17 ± 0.53

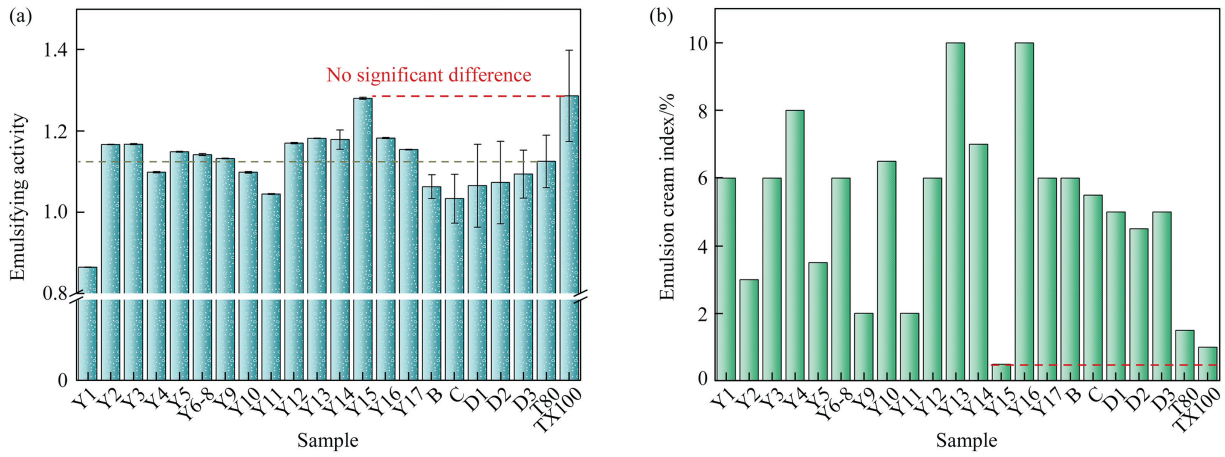

Fig. 5. (a) The emulsifying activities of hemicelluloses obtained by different pre-extraction conditions; (b) the emulsion cream indexes of hemicelluloses obtained by different pre-extraction conditions after standing for 7 days.

exceeding T80 emulsifiers (1.13 for T80). Additionally, y2, y3, y5–7, y12–17 also surpassed T80 in EA. Concerning ECI (Fig. 5(b)), y15 demonstrated superior emulsion stability, even after a 7-day standing period.

The potential for emulsion production using hemicelluloses offers a sustainable pathway for expanding their industrial utility. Importantly, unlike small-molecule chemicals such as xylitol and ethanol, which often necessitate extensive catalyst treatments, our emulsion production process is highly environmentally friendly, reducing the need for chemical treatments.

4. Conclusions

This study demonstrates the feasibility of pre-extracting hemicelluloses from eucalyptus chips using alkaline solution or pulping white liquor before commercial kraft pulping. This approach maximizes the potential of high-value hemicellulose applications while synchronizing pulp and paper production.

Hemicellulose yields are significantly affected by both alkali concentration and temperature, with alkali concentration exhibiting a more pronounced influence. Increased alkali concentration has a beneficial impact on yield, while elevating the temperature (not exceeding 140 °C) under lower alkali concentration conditions promotes yield. Molecular weight is significantly affected by the temperature and retention time. Hemicelluloses with higher molecular weights are favored for dissolution within the temperature range of 105–135 °C. However, excessively prolonged retention time (>60 min) leads to a reduction in hemicelluloses molecular weights. Raising alkali concentration or extending holding time under low alkali conditions both increase xylan content. Residual lignin in hemicelluloses is notably impacted by alkali concentration and retention time. Higher alkali concentration reduces lignin content, while prolonged retention time increases it. Hence, under low alkali conditions with holding time exceeding 60 min, hemicelluloses retain more lignin. During white liquor pre-extraction, hemicelluloses yields are still significantly affected by the alkali concentration. However, hemicelluloses obtained through this method have lower lignin residues, higher xylose content, and a similar molecular weight compared to alkali-extracted hemicelluloses.

The screened pulp yield from the wood chips after pre-extraction of hemicelluloses results in approximately 1%–4% reduction compared to the control group. The differences are attributed to the extraction of some hemicelluloses for high-value applications. Notably, there is a significant 10% increase in cellulose content, indicating substantial potential for dissolving pulp production. The physical properties of the final paper products are suitable for paper production. The slight differences in mechanical performance compared to the control group can be easily compensated in the papermaking process by adding inexpensive fillers like $CaCO_3$.

We further evaluated the emulsifying properties of the hemicelluloses pre-extracted by alkali and white liquor processes. Hemicellulose-based emulsifiers demonstrate emulsifying activity and stability akin to commercial emulsifiers, with the potential for high-value chemical applications. This provides a feasible pathway for traditional pulp mills to be upgraded to advanced pulp mill biorefineries while harnessing the valuable attributes of by-products without interfering with pulp and paper production.

CRediT Author Contribution Statement

Yuhan Wang: Formal analysis, Investigation, Writing – original draft. Danqi Xue: Investigation. Jingjing Zhuo: Investigation. Zhouyang Xiang: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2024.03.017.

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