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Alkaline Fractionation and Subsequent Production of Nano-Structured Silica and Cellulose Nano-Fibrils for the Comprehensive Utilization of Rice Husk

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Abstract: The parameters of the alkaline fractionation process were investigated and optimized using a statistical analysis method to simultaneously remove hemicellulose and ash from rice husk (RH) concomitantly. After the alkaline fractionation process, the residual solid contained high cellulose, and the recovery yield of hemicellulose was enhanced in the fractionated liquid hydrolyzate. The hemicellulosic sugar recovery yield (71.6%), de-ashing yield (>99%), and lignin removal (>80%) were obtained at the reaction conditions of 150 °C of temperature, 40 min of reaction time, and 6% (*w/v*) of NaOH concentration. Subsequently, nano-structured silica was synthesized using black liquor obtained as a by-product of this fractionation process. For the production of nano-structured silica, it was observed that the pH of a black liquor and the heat treatment temperature significantly influenced the textural properties of silica product. In addition, the two-stage bleaching of solid residue followed by colloid milling for the production of high value-added CNF with was attempted. As a result, in addition to 119 g of fermentable sugar, 143 g of high-purity (>98%) silica with a surface area of 328 m²g^{−1} and 273.1 g of high-functional CNF with cellulose content of 80.1% were simultaneously obtained from 1000 g of RH.

Keywords: biorefinery; multi-objectives RSM; nano-silica; de-ashing; cellulose crystals

Citation: Jung, H.J.; Kwak, H.; Chun, J.; Oh, K.K. Alkaline Fractionation and Subsequent Production of Nano-Structured Silica and Cellulose Nano-Fibrils for the Comprehensive Utilization of Rice Husk. *Sustainability* **2021**, *13*, 1951. <https://doi.org/10.3390/su13041951>

Academic Editor: Dirk Enke

Received: 3 December 2020

Accepted: 8 February 2021

Published: 11 February 2021

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1. Introduction

In response to growing concerns about environmental pollution caused by excessive consumption of fossil fuels, many researchers are pursuing alternative bio-based resources that can be applied to related industries. Among various candidates, lignocellulosic biomass, including agro-industrial and agricultural wastes, has attracted an intensive interest in the production of biofuels and chemicals, which are desirable alternatives to conventional petroleum-based fuels and chemicals. The biodegradability, reproducibility, and abundance of lignocellulosic biomass make it a promising resource for the production of these bio-based products [1]. Thus, lignocellulosic biomass has emerged as a potential renewable resource due to its annual reproducibility and abundance.

To secure the economic feasibility of biorefinery, a biorefinery system for producing value-added chemicals, i.e., an integrated biomass conversion process, must be conceived. To operate the biorefining process efficiently, each component of biomass must be separated sequentially by an effective and technically feasible fractionation process [2,3]. Rice is one of the most cultivated crops in the world; in 2018, approximately 661 million tons of rice were cultivated worldwide. Therefore, rice husk (RH) is a major side product of the agricultural industry, because its weight accounts for approximately 20 wt.% of rice plant [4]. Since RH is obtained through the milling process, it has already been processed first, suitable

for further chemical and physical treatment without any additional drying or grinding process. In Korea, domestic RPCs (rice process complexes) perform rice milling according to demand, so they can produce relatively uniform amounts of RH throughout the year [5]. Nevertheless, most of the current RH is either burned in the field or used as compost in the soil as a quick and easy disposal method [6]. However, these methods of disposal are a major source of air pollution from smoke and greenhouse gases. In particular, RH combustion is evaluated as socially unacceptable due to the widespread air pollution increasing organic carbon emission [7]. The inclusion of some RH in the soil is a common management practice to improve soil fertility [8] and to prevent the harmful effects of long-term agricultural activities [9]. However, composting of RH increases emission of methane gas, one of the major greenhouse gases [10].

There has been a considerable amount of research on the use of RH over the past few years. Since RH is composed of a large amount of lignocellulose and ash, numerous studies have been focused on the preparation of high value-added products such as lignin, silica, and fermentable sugar to utilize RH as a raw material in various bio-based industries [11–13]. For examples, hemicellulose is hydrolyzed into sugars (mainly xylose) and substituted sugar oligomers [14,15], cellulose is hydrolyzed into glucose and then fermented into ethanol [16,17], and ash is used for preparation of pure fine silica [18,19]. In particular, the silicified surface of RH acts as a protective barrier, specifically conferring an outstanding recalcitrance toward biological threats, which leads to inefficient hydrolysis of cellulose and hemicellulose. Accordingly, the release of fermentable sugar from the tightly woven structure of cell wall is considered a prerequisite to obtaining bio-based products through the biological conversion process [20].

Interestingly, silica (SiO_2) accounts for 80–95% of the inorganic components in RH [21,22]. Therefore, after extraction of the cellulosic components through fractionation, silica-based products can be obtained from the byproduct liquor (black liquor). The morphology and purity of the silica products can be changed through post-treatment of black liquor. Therefore, the development of an appropriate post-treatment process with optimized conditions can lead to the production of high purity/grade nano-structured silica from black liquor. Currently, a large amount of silica is widely used in various industries. In particular, nano-structured silica with unique characteristics is required for various modern applications such as biosensors [23], drug delivery systems [24], wastewater treatment [25], and superhydrophobic coatings [26], which are expected to grow rapidly [27]. Accordingly, the facile preparation of high-purity nano-structured silica from RH is an important research theme, because the production of high value-added silica from a low-cost raw material and the effective treatment of waste biomass can be achieved simultaneously. Fernandes et al. [28] suggested that the effective production of silica from RH is generally based on a combination of appropriate chemical and heat treatment conditions.

On the other hand, due to the specific chemical and physical properties of biomass-derived cellulose, the interest in their research and development is rapidly increasing. However, cellulose is still limited in its use in industrial applications due to its unique properties such as water insolubility, hygroscopicity, and non-melting properties. Nevertheless, until recently, many researchers have found that when biomass cellulose is subjected to mechanical shear or controlled hydrolysis, elongated fibrils or defect-free rod-shaped crystal particles are obtained in the nanoscale range, and that they were named nano-cellulose [29]. Nano-cellulose has many advantages such as high mechanical strength, large aspect ratio, low density, high specific surface area, and excellent biocompatibility. In particular, by modifying the surface chemical properties of nano-cellulose through various development strategies, it is possible to change the properties to meet various industrial needs [30]. Thus, nano-cellulose can be a versatile source of various products in the form of commercial cellulose derivatives through chemical modification [31]. Typically, nano-cellulose is divided into two main types. That is, it can be broadly classified into cellulose nanocrystals (CNC) obtained from acid treatment and cellulose nano-fibrils (CNF) mainly produced by mechanical disintegration. CNF has become a more attractive material

for industrial use, and as CNF can be produced on a commercial scale, this material has become readily available through the market. Thus, CNF has received more attention in industrial applications. In relation to CNF from lignocellulosic biomass, many R&Ds have been proposed to develop and optimize production technologies or to impart new properties to materials of special and high industrial value [32–36].

In our previous work to effectively utilize the lignocellulosic biomass, glucose and xylose were produced as the raw materials for production of biofuel by hydrolyzing cellulose and hemicellulose through optimized fractionation process. In addition, ball milling combined in the presence of chemical catalyst has been shown to be an effective fractionation method because of increasing mixing effectiveness, reducing particle size and increasing larger accessible surface area, resulting in significantly improved fractionation of herbaceous biomass [37–39]. However, unavoidable substantial byproduct formation after recovery of the fermentable sugars incurs additional costs for the associated waste treatment, which can increase the production cost. Therefore, it is speculated that a conversion strategy for the utilizing by-products produced in the fractionation process is required [40].

In the current study, alkaline fractionation of RH has been attempted to selectively separate the components from RH. The objective of this study was to recover hemicellulosic sugar and ash (mainly silica), while retaining most of the cellulosic component in the solid residue. Numerous studies, however, have been conducted to produce bioethanol using xylose in liquid phase and cellulose in solid phase. Therefore, the focus of the research is on the multi-purpose optimization of the alkali fractionation process, which can simultaneously meet the recovery of hemicellulosic sugar (mainly xylose) and the de-ashing yield from RH. In addition, the studies were conducted to secure bio-based materials from rice husk other than biofuels. After fractionation of the RH, with the aim of producing high value-added bio-based materials from fractionation residues, new synthetic methods for producing high-purity nano-silica from liquid residues were investigated, and a series of experiments were conducted to produce CNF from solid residues.

2. Materials and Methods

2.1. Feedstock Preparation

RH was obtained as a by-product from local rice process complex (RPC); the rice was harvested from Gimpo, Gyeonggi-do, Korea, in the fall of 2017. Prior to the experiment, RH was dried for 48 h at 45 ± 5 °C using a convection drying oven (FC-PO-1500, Lab House, Seoul, Korea) and stored in an automatic dehumidification desiccator. The moisture content of the RH was 4.6% based on its oven-dried weight.

2.2. Compositional Analysis of Raw and Fractionated RH

The carbohydrate components of the fractionated or untreated RH were subjected to a two-stage acid hydrolysis extraction process, which was standardized according to the procedure specified in the corresponding Laboratory Analytical Procedure of the National Renewable Energy Laboratory (NREL-LAP) [41]. In addition, in the analysis of liquid samples obtained during the fractionation, glucose and hemicellulosic sugar (xmg: xylose, mannose, and galactose) were analyzed by high-performance liquid chromatography (HPLC; 1260 Infinity, Agilent Technologies Inc., Santa Clara, CA, USA). The analytical column and detector were an Aminex HPX-87H organic acid column (Bio-Rad) and a refractive index detector (1260 RID, Agilent Technologies Inc.), respectively. The operating conditions for the HPLC column were 65 °C and a mobile-phase (sulfuric acid) flow rate of 0.6 mL/min.

2.3. Experimental Setup and Operation of Bench-Scale Fractionation

A tubular reactor was used to optimize the lab-scale alkaline fractionation process. The reactor was made of stainless steel (SS-316L) and had an internal diameter of 10.7 mm and a length of 150 mm, with an internal volume of 13.5 mL. Five hundred milligrams

of oven-dried RH was placed in the reactor, and sufficient alkaline solution was added to give a solid-to-liquid ratio of 1:10. To increase the temperature of the reactor to the target temperature within approximately 1.0 min, it was first immersed in the first heating bath (molten salt) set at 240 °C. When the temperature of the reactor reached the target temperature, it was quickly transferred to the second bath (silicone oil) set to the target reaction temperature (116–184 °C). After the reaction was conducted for a fixed period of time, the reactor was quenched in an ice-water bath to quickly stop the reaction.

The bench-scale (30 L) combined ball milling reactor used for the production of hemicellulosic sugar and black liquor via an alkaline fractionation of RH [42]; this reactor was designed to be capable of operating at 60 rpm at a pressure of 20 kg_f cm^{−2} and a temperature of 200 °C (Sugaren Co. Ltd., Yongin, Korea). Alumina balls (HD, sphere type, 10 mm diameter, and 3.6 g cm^{−3} density) were additionally placed in the reactor to improve the mixing efficiency. The ball/biomass/alkaline solution ratio was 30:1:10 (*w/w/v*). Upon completion of the reaction, the solid and liquid inside the reactor were separated. The remaining solid samples were washed and then used for glucose production by enzymatic hydrolysis.

2.4. Optimization of the Process Variables Using Response Surface Methodology (RSM)

A second-order model was used to fit the data individually for the response of hemicellulosic sugar extraction yield and de-ashing yield by the general model with three variables in the alkaline fractionation of rice husk: reaction temperature, reaction time, and NaOH concentration [43]. The range of process variables in the central composite design (CCD) are shown in Table 1.

Table 1. Process variables and their levels for 3³ central composite design (CCD).

Process Variables	Coded Levels and Actual Conditions				
	−1.68	−1	0	+1	+1.68
Temperature (°C)	116	130	150	170	184
Time (min)	6	20	40	60	74
NaOH Conc. (%)	1	2	3.5	5	6

To achieve high hemicellulosic sugar extraction yield and de-ashing yield from RH, the alkaline fractionation conditions were optimized by response surface methodology (RSM) based on the 3³ factorial CCD. To determine the optimal conditions for extracting hemicellulosic sugar and de-ashing, analysis of variance (ANOVA) and multiple regression analysis were performed using Design Expert (Ver 8, Stat-Ease, Minneapolis, MN, USA).

2.5. Preparation of Nano-Structured Silica Powders from Black Liquor

Nano-structured silica powders (NSP series) were obtained from a black liquor. A block diagram according to the preparing sequence and conditions is shown in Figure 1. In a typical preparation of NSP-1, 450 mL of the black liquor diluted with 50 mL of distilled water was used. First, the pH of the black liquor was adjusted to ~7.0 by addition of acetic acid. After the resulting solution was stirred for 12 h at room temperature (~25 °C), it was centrifuged at 5000 rpm for 5 min; the supernatant was then decanted away. The remaining products were washed several times with distilled water and dried overnight at 80 °C. Finally, the dried powders were heat-treated at 600 °C for 2 h under air atmosphere. Through this process, we obtained ~15.5 g of silica powders per liter of black liquor. The overall synthesis procedure of NSP-2 and NSP-3 was similar to that of NSP-1, except that the pH of the black liquor was adjusted to ~6.0 and ~8.0, respectively.

Figure 1. Block diagram depicting the preparation of nanostructured silica powder (NSP) from black liquor under different conditions.

In the case of NSP-4 and NSP-5, the overall synthetic procedure was the same as that of NSP-1, except that the heat-treatment temperatures at the last step were 450 °C and 300 °C, respectively. NSP-6 was prepared by a procedure similar to that used for NSP-1, except that the dried powders at 80 °C were further treated with HCl solution before the heat treatment at 600 °C; specifically, the dried powders were placed in 100 mL of 10 wt% HCl solution and then stirred at 90 °C for 2 h. After reaction, the powders were filtered and washed with distilled water. After drying overnight at 80 °C, the final products were obtained by the heat treatment at 600 °C for 2 h under air atmosphere.

2.6. Preparation of Cellulose Nano-Fibrils from Fractionated Residual Solid

The two-stage bleaching process was performed using hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2) to remove residual lignin from fractionated solid phase. In the first step, the solid/liquid ratio was set to 10% using 5% (*v/v*) H_2O_2 , and reacted at 100 °C for 60 min. In a second step using 5% (*v/v*) ClO_2 , the pH was controlled to 3 to 4 using CH_3COOH , reacted at 70 °C for 90 min, then washed with distilled water and dried at 45 °C. A 2 wt.% (*w/v*) dry solid suspension was prepared using distilled water, and CNF was prepared by grinding with a colloid milling device, Super Mass Colloider (MKCA6-5J, Masuko Sangyo Co., Kawaguchi, Japan). A non-porous grinder (MKGA10-80, Masuko Sangyo Co., Kawaguchi, Japan) that prevents contamination of bacteria and can add catalysts was used, for which the grinder interval was 150 μm and the rotation speed was 1600 rpm.

2.7. Material Characterization of Nano-Structured Silica Powders and Cellulose Nano-Fibril

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max 2500/PC diffractometer (Japan). The material morphologies were investigated by scanning electron microscopy (SEM; X-Max T50, Oxford Instruments, Abingdon, UK) and transmission electron microscopy (TEM; JEM-2000EX, JEOL Ltd., Tokyo, Japan). The nitrogen (N_2) physisorption isotherms were obtained at 77 K using a Tristar II 3020 system (Micromeritics Inc., Norcross, GA, USA). The surface areas of materials were calculated from the measured isotherms according to the Brunauer–Emmett–Teller (BET) method, and the pore volumes were taken at the $P/P_0 \approx 0.995$ single point. The pore size distributions of materials were

calculated by the Barrett–Joyner–Halenda (BJH) method from the adsorption branches of the isotherms. The inorganic chemical composition and carbon content of silica were determined using a sequential X-ray fluorescence (XRF) spectrometer (ZSX100, Rigaku, Akishima, Japan) and an elemental analyzer (Elementar Analysensysteme GmbH, vario MICRO cube, Langensfeld, Germany), respectively.

3. Results

3.1. Compositional Analysis of Raw and Fractionated RH

Table 2 summarizes the chemical constituents of the raw and NaOH-fractionated RH. The composition of carbohydrates in the raw RH was measured to be $35.6 \pm 0.8\%$ of cellulose, $13.6 \pm 0.4\%$ of hemicellulose, $0.8 \pm 0.1\%$ of galactan, and $1.7 \pm 0.0\%$ of arabinan; thus, the total carbohydrates account for $51.7 \pm 1.3\%$. In addition, the noncarbohydrate component was analyzed to consist of $23.4 \pm 0.2\%$ lignin, $4.2 \pm 0.1\%$ extractives, 3.2% protein, 0.5% lipid, and $15.7 \pm 0.2\%$ ash. Therefore, the mass closure of each constituent of raw RH was reached at $99.6 \pm 1.6\%$ for oven-dried biomass. The results of the component analysis of the NaOH-fractionated RH in the second row in Table 2 were used to compare the changes in content of each component.

Table 2. Chemical composition of raw and NaOH-fractionated rice husk based on an oven-dry biomass.

Components	Carbohydrates			Lignin		Extractives		Protein (²)	Lipid (³)	Ash	Mass Closure
	Glucan	XMG (²)	Arabinan	Insoluble Lignin	Soluble Lignin	Water	Ethanol				
Raw rice husk	35.6 ± 0.8	13.6 ± 0.4	0.8 ± 0.1	22.7 ± 0.0	0.7 ± 0.2	3.5 ± 0.1	0.7 ± 0.0	3.2	0.5	15.7 ± 0.2	97.9
Fractionated rice husk (¹)	73.9 ± 1.1	13.4 ± 0.6	1.1 ± 0.2	11.5 ± 0.3							99.9

(¹) NaOH-fractionated at optimized reaction conditions; reaction temperature of $150\text{ }^{\circ}\text{C}$, reaction time of 45 min, and NaOH concentration of $6\%(w/v)$ with solid remaining of 35.5% . (²) XMG: Major component of hemicellulose (Xylan, Mannan, and Galactan). (³), (⁴) Protein and lipid contents were analyzed by KFRI, Korea Food Research Institute. *N-factor* = 5.95.

Only carbohydrate and lignin contents are shown for fractionated rice husk, because most of the noncarbohydrate components, including ash, were estimated to have been extracted into liquid by-product during the fractionation, resulting in no analysis. Similar studies have reported that alkaline fractionation facilitates the degradation of lignin and hemicellulose because of saponification of the intermolecular crosslinking between hemicellulose and lignin. In addition, significant changes in physical properties such as increased porosity, cellulose expansion and destruction of carbohydrate–lignin complexes can also be the cause [44,45].

The cellulose content of the NaOH-fractionated RH increased from 35.6% to 73.9% , and the hemicellulosic sugar content was found to be very slightly reduced. Meanwhile, the lignin content was greatly reduced from 22.7% to 11.5% . These values are relative, because the noncarbohydrate fraction and some of the hemicellulose and lignin fractions were solubilized during the fractionation; given the amount of residual solids, the hemicellulose and lignin fractions correspond to 26.2% cellulose, 4.8% hemicellulose, and 4.1% lignin based on the raw RH. These results are in good agreement with those of Shahabazuddin et al., who reported that the cellulose content increased from 32.7% to 51.7% and that the hemicellulose and lignin contents decreased from 18.1% to 16.1% and 26.7% to 12.3% , respectively [46]. Compositional analysis was established from three replicate measurements performed independently; error values are expressed as standard deviations.

3.2. Effects of Process Variables for Alkaline Fractionation

The effects of independent variables, reaction temperature, reaction time, and NaOH concentration, were evaluated to maximize the extraction of lignin, ash, and hemicellulosic sugar. In the 17 experimental conditions investigated in this study, the hemicellulosic sugar extraction yields ranged from 21.7% to 77.4% , and the de-ashing yields ranged from 69.2% to 95.6% (Table S1). In examining the influence of each independent variable, we

observed that hemicellulosic sugar extraction and de-ashing yields tended to increase proportionally as the level of all of the independent variables increased. The effects of each independent variable on hemicellulosic sugar extraction and de-ashing yields were evaluated based on ANOVA (Table S2). The effect of NaOH concentration on the hemicellulosic sugar extraction yield was found to be greatest, followed by the effect of reaction time and temperature. By contrast, in the case of the de-ashing yield, significance was confirmed in the order of NaOH concentration, reaction temperature, and reaction time. The coefficients of determination (R^2), which measure the fitness of the second-order regression equations for hemicellulosic sugar extraction and de-ashing yield, as derived using the CCD, were evaluated as 0.9803 and 0.8372, respectively. The p -values were 0.0001 and 0.0406, respectively, indicating that the confidence intervals were within 95%. The highest yields of hemicellulosic sugar extraction and de-ashing at 150 °C, 40 min of reaction time, and 6% (w/v) NaOH concentration were 77.4% and 95.6%, respectively. These results are consistent with previous reports that lignin and ash were extracted as black liquor with increasing NaOH concentration.

3.3. Multi-Objectives Optimization of the Alkaline Fractionation of RH

The second-order polynomial equations related to hemicellulosic sugar extraction yield and de-ashing yield were obtained from the regression analysis and given by Equations (1) and (2).

$$Y_{\text{xmg}} = 49.35 + 2.14 \times X_1 - 0.34 \times X_2 + 14.56X_3 - 2.18X_1 X_2 - 2.84X_1 X_3 - 1.17X_2 X_3 - 6.20X_1^2 - 1.60X_2^2 + 0.076X_3^2 \quad (1)$$

$$Y_{\text{de-ashing}} = 93.65 + 1.25 X_1 + 1.68 X_2 + 5.47 X_3 - 0.10 X_1 X_2 + 0.13 X_1 X_3 + 0.25 X_2 X_3 + 0.083 X_1^2 - 1.19 X_2^2 - 3.37 X_3^2 \quad (2)$$

where X_1 : reaction temperature; X_2 : reaction time; X_3 : NaOH concentration.

The coefficients of determination (R^2), which measure the fitness of the second-order regression equations for hemicellulosic sugar extraction and de-ashing yield, were evaluated as 0.9803 and 0.8372, respectively, which further indicated that the model was suitable for adequately representing the real relationships among the selected reaction variables. The statistical significance of the model was evaluated by the F-test that showed that the regression was statistically significant. For the case of hemicellulosic sugar extraction yield, the “ $Prob > F$ ” represented as p -value for the model was <0.0001, which indicated that the model was statistically significant with a confidence level of 99.99%.

The predicted maximum yield of hemicellulosic sugar extraction from the regression equation of dependent variable hemicellulosic sugar extraction yield was 74.7% at 148.1 °C reaction temperature, 27.0 min reaction time, and 5.9% NaOH concentration, respectively. Furthermore, the predicted maximum de-ashing yield was 96.1% at 142.8 °C reaction temperature, 60.6 min reaction time, and 4.9% NaOH concentration. The conditions for highest yields of hemicellulosic sugar extraction and de-ashing were determined by the analysis of the statistical model generated.

Figure 2 attempts to represent the change of dependent variables by overlaid contour lines for the interactions between the independent variables; therefore, the gray-toned contours represent the changes in the de-ashing yield, and the black-toned contours were expressed for the changes in the hemicellulosic sugar extraction yield. Since a relatively high de-ashing yield was obtained in most of the experimental range, the optimization criterion was given priority to the range in which the hemicellulosic sugar extraction yield could be obtained more than 70%. It was determined that the de-ashing yield was high, and the overlapping portion appeared to be suitable for the purpose of the processing, which was indicated in grayscale. Figure 2a shows that over 72% hemicellulosic sugar extraction yield and 94% de-ashing yield can be obtained in the range of reaction temperature of about 146 to 158 °C and reaction time of about 41 to 55 min. Likewise, in the case of reaction temperature, there was a possibility to obtain an hemicellulosic sugar extraction yield of 70% or more and a de-ashing yield of 93% or more in a wide range of about 140 to 160 °C,

but the NaOH concentration to meet these yields was determined to be possible only in a narrow experimental range of about 5.8–6.3% (Figure 2b).

Figure 2. Multi-objective optimization on hemicellulosic sugar recovery and ash removal as a function of reaction temperature, reaction time and NaOH concentration, where, (a) NaOH concentration; 3.5 (w/v)%, (b) Reaction time; 40 min., (c) Reaction temperature; 150 °C.

It can be seen in Figure 2c that NaOH concentration greatly influences the sugar recovery and ash removal in the alkaline fractionation process of RHs. The reaction range capable of simultaneously matching the hemicellulosic sugar yield of 75% and the de-ashing yield of 92% or higher was possible in the entire range of reaction time. However, the effect of NaOH concentration was significant, as it was found to be possible only in the range of about 6.0% to 6.3%.

By overlapping the response surfaces of the resultant dependent variables, the optimized reaction conditions were estimated with a reaction temperature of 149.8 °C, a reaction time of 45.1 min, and a NaOH concentration of 5.9 wt.%, under which the hemicellulosic sugar extraction and de-ashing yields were estimated to be 73.2% and 93.9%, respectively. When the RH was fractionated under the optimized conditions; 150 °C, a reaction time of 45 min, and a NaOH concentration of 6.0 wt.%, it was confirmed that the extraction yield of hemicellulosic sugar was 71.6% and the de-ashing yield was greater than 99%, which are in good agreement with the estimated values obtained from the optimized conditions.

3.4. Synthesis of Nano-Structured Silica from the Residual Black Liquor

Residual black liquor is a type of basic silicate solution that contains both hemicellulosic sugar and lignin components. To obtain silica powders from black liquor preventing excessive precipitation of other components (e.g., lignin), the pH of black liquor was adjusted to neutral using a certain amount of acid solution. In this study, we used acetic acid instead of sulfuric acid for pH adjustment, because the former is weaker and less harmful than the latter. After purification of precipitated silica by centrifugation and washing, trace organic components were removed by heat treatment under an air atmosphere.

To prepare an initial test sample (NSP-1), the pH of black liquor was adjusted to approximately 7.0 using acetic acid, followed by heat treatment at a high temperature (600 °C) to completely remove the organic components. The XRD pattern of NSP-1 exhibited a broad diffraction near 20°, which is typical for amorphous silica (Figure 3a). It was seen that silica content among the inorganic components of NSP-1 was as high as 98.0%, and a small amount (1.76%) of sodium compound was also measured. SEM and TEM images of NSP-1 showed that the small nano-particles aggregated into large particles with sizes of a few hundred nanometers (Figure 3b,c). These types of hierarchical nano-structures impart NSP-1 with a large surface area of 175 m² g^{−1} and a pore volume of 0.81 cm³ g^{−1} (Table 3).

Figure 3. (a) XRD pattern, (b) SEM image, and (c) TEM image of NSP-1. (d) N₂ physisorption isotherms and pore size distributions (inset) of NSP-1, NSP-2, and NSP-3.

Table 3. Experimental conditions and characterization results of NSP series.

	NSP-1	NSP-2	NSP-3	NSP-4	NSP-5	NSP-6
pH control	~7.0	~6.0	~8.0	~7.0	~7.0	~7.0
Acid leaching	–	–	–	–	–	O
Heat treatment temperature (°C)	600	600	600	450	300	600
Surface area (m ² g ^{−1})	175	113	109	273	328	392
Pore volume (cm ³ g ^{−1})	0.81	0.23	0.45	0.57	0.61	0.65
Main pore size (nm)	~25	~7	~20	~10	~10	~10
SiO ₂ (%) among the inorganic components	98.0	95.5	97.2	98.2	98.1	99.8

In the synthesis procedure, it was confirmed that the pH of black liquor and the heat-treatment temperature affected the textural properties of silica products substantially. NSP-2 and NSP-3 were obtained using the same procedure used for NSP-1, except that the pH levels of the black liquor were adjusted to approximately 6.0 and 8.0, respectively. Although the pH levels of NSP-2 and NSP-3 only differed from that of NSP-1 by approximately ± 1.0 pH unit, their surface areas and pore volumes were noticeably small. NSP-2 exhibited a surface area of 113 m² g^{−1} and a pore volume of 0.23 cm³ g^{−1}. A similar tendency was observed for NSP-3 (Table 3), which exhibited a surface area of 109 m² g^{−1} and a pore volume of 0.45 cm³ g^{−1}. We speculated that these differences in textural properties resulted from the different rates of condensation reactions. After the formation of silicic acid by the addition of acetic acid, the condensation reaction of silicic acid was strongly dependent

on the pH of the reactant solution [47]. Since the formation of the silica framework was affected by the condensation reaction rate, the textural properties of NSP powder were also altered by the pH of the solution.

3.5. Optimization for the Synthesis of Nano-Structured Silica with Large Surface Area

NSP-4 and NSP-5 were prepared following the same synthesis procedure used for NSP-1, except that the heat-treatment temperature at the last step was decreased to 450 °C and 300 °C, respectively. Because of the lower heat-treatment temperatures, the surface area of the silica substantially increased (Table 3). Between NSP-4 and NSP-5, NSP-5 showed a surface area of 328 m² g^{−1}, which was nearly two times larger than that of NSP-1.

The main pore sizes of NSP-4 and NSP-5 were approximately 10 nm, whereas that of NSP-1 was approximately 25 nm (Figure 4a). This phenomenon might be induced by the residual sodium contents in the NSP powders, because the melting points of sodium silicates are substantially lower than that of pure silica [48]. Therefore, a small sodium content could reduce the melting point of the silica. In addition, because the particle size decreased to the nano-scale, the melting point of the material also decreased [49]. Accordingly, the nanosized silica framework of the NSP series could be easily melted and aggregated even at 600 °C. This process leads to the generation of large mesopores through the collapse of small mesopores, resulting in the decrease of surface area. Inevitably, because of the low heat-treatment temperature, the carbon content (0.61 wt.%) of NSP-5 was greater than that (0.06 wt.%) of NSP-1. However, we found that nano-structured silica with a high surface area could be readily prepared through a simple optimization of the established process.

Figure 4. (a) N₂ physisorption isotherms and pore size distributions (inset) of NSP-1, NSP-4, and NSP-5. (b) N₂ physisorption isotherms and pore size distributions (inset) of NSP-1 and NSP-6. (c) SEM and (d) TEM images of NSP-6.

It was also found that high purity silica can be obtained without compromising textural properties through additional acid leaching. After centrifugation and washing, dried powders were further treated with HCl solution before heat treatment at high temperature.

Through this acid leaching process, residual sodium compounds could be completely removed. XRF analysis results showed that the purity of the silica product (NSP-6) was as high as 99.8%, but that of the sodium compound was less than 0.2%. Interestingly, although NSP-6 was obtained through heat treatment at 600 °C, it retained a high surface area of 392 m² g^{−1} with a main pore size of ~10 nm (Table 3 and Figure 4b). In comparison with the TEM image in Figure 4c, the high-magnification TEM image of NSP-6 (Figure 4d) clearly showed the preservation of small-sized nanopores without agglomeration of the framework. This result supports the fact that the residual sodium content strongly affects the surface area of silica by deforming the silica framework during heat treatment at high temperatures. Because of its high treatment temperature, NSP-6 contained practically no carbon (0.06 wt.%). Therefore, high-purity silica with a large surface area could be successfully obtained from a black liquor. In particular, the surface area of NSP-6 is much greater than that of RH-derived silica prepared in previous studies [50,51], despite the absence of the use of additional surfactants or block copolymers.

3.6. Characteristics of CNF Prepared from Fractionated Residual Solid

Figure 5 shows the changes in chemical composition of raw RH and sequentially treated RH fibers. The untreated RH showed component content of cellulose 35.6%, hemicellulose 13.6%, lignin 23.4%, and ash 15.7%. The relative composition of the residual solid fractionated by NaOH showed 70.8% of cellulose, 12.3% of hemicellulose, 12.2% of lignin, and 0% of ash, confirming that all ash and a significant amount of lignin were removed through the optimized NaOH fractionation, whose conditions were 150 °C, a reaction time of 45 min, and a NaOH concentration of 6.0 wt.%. As a result of the first bleaching stage (H₂O₂) on the NaOH fractionated residual solid, the relative content of the 1st bleached solid was shown as cellulose of 81.1%, hemicellulose of 12.0%, and lignin of 6.1%, representing that some of the lignin was removed. In the case of the second bleached (ClO₂) RH, the relative composition of cellulose 85.2%, hemicellulose 10.4%, and lignin 0.6% were shown, so that most of the lignin was removed, resulting in highly pure cellulose.

Figure 5. Changes in chemical composition and whiteness of rice husk fiber according to sequential treatment: untreated RH, NaOH fractionated RH fiber, first bleached RH fiber, second bleached RH fiber.

In addition, figures of residual solids for each sequential bleaching were intended to be shown at the top of Figure 5. After the second-stage bleaching process, the residual solid had a white color, which was believed to be due to the removal of lignin and other impurities as the bleaching proceeds sequentially. The change in the colors of the residual solids in each sequence well explained the change in the chemical composition as the bleaching progresses.

Figure 6a shows the results of XRD analysis to compare the change in crystallinity of RH and RH fibers according to each sequence. RH raw material, NaOH-treated RH fiber, and first-stage bleached RH fiber showed Cellulose I form, which is the crystal structure of lignocellulose that exists in nature. On the other hand, CNF obtained after second-stage bleaching showed a Cellulose II form. It is believed that this is because the number of hydrogen bonds between molecules increases as hydroxyl groups are exposed due to mechanical shear and friction forces, resulting in a more stable crystal structure. The crystallization index (CrI) at each stage of bleaching was the lowest at 37.3% in RH raw samples, 51.6% in NaOH-treated RH fiber, and 60.5% in first-stage bleached RH fiber. On the other hand, the crystallinity of the CNF obtained after proceeding to the second-stage bleaching was measured to be 57.1%, which was slightly lowered. This result is in good agreement with the results of Liu et al., which suggested that the crystallinity of CNF increased as the proportion of cellulose increases due to the removal of amorphous components such as lignin or hemicellulose during chemical bleaching step [52].

Figure 6. (a) XRD patterns, (b) FT-IR patterns, (c) SEM image of CNF, (d) N_2 physisorption isotherms and pore size distributions (inset) of NaOH + bleaching treated RH, CNF.

Figure 6b shows the FT-IR spectra of raw RH and RH fibers obtained by chemical bleaching for each stage. All samples exhibited major absorption areas in the range of $900\text{--}1600\text{ cm}^{-1}$, $2900\text{--}3400\text{ cm}^{-1}$. Compared to the raw RH raw material, the narrow and high peak of $3335\text{--}3344\text{ cm}^{-1}$ in the chemically treated RH fiber indicates that it contains more -OH groups. The $1159\text{--}1108\text{ cm}^{-1}$ peak, $1027\text{--}1051\text{ cm}^{-1}$ peak, and $896\text{--}897\text{ cm}^{-1}$ peak represent typical β -(1-4) glycosidic bonds in cellulose including C-O-C stretching and pyranose ring skeleton vibration. As the bleaching progressed, more significant effects were observed, which is believed to be due to the increase in the proportion of cellulose due to the removal of non-cellulosic substances by chemical bleaching. The peak at 1734 cm^{-1} in the spectrum of the RH raw material (a) is due to C=O bonding, and it was found that most of the hemicellulose and lignin components were removed as the peak disappeared in the

treated RH fiber. In the CNF spectrum (d), characteristic peaks were 1429 and 1370 cm^{-1} , which were related to CH_2 bending and O-H bending, respectively.

As a result of the FE-SEM analysis, it was confirmed that the nano-fibrillation of the milled RH fibril was properly performed compared to the unmilled RH fiber (image is not shown) as shown in Figure 6c. Before colloid milling, the diameter of RH fiber was observed to be 10–50 μm , and after colloid milling, the diameter of RH fibril was observed to be 19–21 nm, confirming that the nano-sized fibril was properly formed.

In order to observe the structural characteristics of CNF, BET analysis was performed (Figure 6d), and the results of analysis of the specific surface area, pore volume, and pore size of RH fibrils before and after colloid milling are summarized in Table 4. The surface area of RH fibril before milling was $0.79 \text{ m}^2 \text{ g}^{-1}$, the pore volume was $0.0026 \text{ cm}^3 \text{ g}^{-1}$, and the pore size was 14.81 nm. After milling, the surface area, pore volume, the pore size of CNF were all increased; i.e., $110.52 \text{ m}^2 \text{ g}^{-1}$, $0.52 \text{ cm}^3 \text{ g}^{-1}$, and 15.82 nm, respectively. It was confirmed that the aspect ratio and specific surface area were greatly improved during colloid milling, and colloid milling can be used as an effective CNF manufacturing method.

Table 4. Effects of colloid milling treatment on characteristics of CNF.

Sample	BET Surface Area ($\text{m}^2 \text{ g}^{-1}$)	Pore Volume (cm^3)	Pore Size (nm)
Before milling treatment	0.79	<0.01	14.81
After milling treatment	110.52	0.52	15.82

3.7. Overall Mass Balance on the Comprehensive Utilization of RH

Figure 7 summarizes the simplified flow diagram and overall mass balance for each sequential process aimed at producing high value-added bio-based materials from RH. Based on 1000 g of RH input, the cellulose and hemicellulose, lignin, and ash contents were 356, 136, 227, and 157 g, respectively. Under the optimized fractionation conditions, approximately 64.5% of the input biomass mass was solubilized into the black liquor, with 26.2% cellulose, 64.7% hemicellulose, and nearly 100% of ash from the raw RH.

Figure 7. Simplified flow diagram of the RH process including the overall mass balance of RH fractionation process for cellulose nano-fibril and nano-structured silica.

Black liquor from alkaline fractionation contained 24 g of glucose, 95 g of hemicellulosic sugar, and 152 g of ash, and 262 g of cellulose and 48 g of hemicellulose were retained unhydrolyzed in 355 g of the residual solid based on 1 kg of raw RH. During the alkaline fractionation process, the undetected 79 g of glucose, which corresponded to 20.3% of cellulose, was presumed to be in the sugar filtrate as a cello-oligomer, because small

amounts of degradation products from glucose, such as HMF and levulinic acid, were found in the analysis.

The black liquor resulting from the alkaline fractionation was subjected to consecutive precipitation and calcination, yielding 143 g of high-purity nano-structured silica.

In order to produce the CNF from the fractionated solid, a two-stage bleaching process using hydrogen peroxide and chlorine dioxide followed by colloid milling was performed, which resulted in 273.1 g of CNF (80.1% of cellulose content). After the bleaching process, 41.6 g (12.2%) of lignin was almost removed, and the whiteness of the cellulose could be enhanced. As a result, 96.3% of 283.5 g of cellulose was converted to CNF throughout the colloid milling process.

4. Discussion

For production of high value-added materials from lignocellulosic biomass, there have been many previous reports on the cellulose nano-crystals [53] and silica [54]. In addition, recent studies have focused on the opportunity to simultaneously fractionate and recover the useful components of biomass through unique fractionation methods using various catalytic solutions [55,56].

In this work, an alkaline fractionation was selected for the fractionation of the lignocellulosic materials, because the NaOH solutions are widely employed to remove lignin from wood and non-woody lignocellulosic materials [57,58]. It should be noted that the alkaline fractionation is also able to effectively solubilize hemicellulose, residual extractives, and ashes [59]. It is also important that the large amount of ash confers RH an outstanding recalcitrance toward biological and environmental threats. It was observed that the 30 L-bench scale alkaline fractionation completely removed ash from RH, in addition to the effective production of hemicellulosic sugars. We have already confirmed that the integration of mechanical and chemical pretreatment can be implemented in a large-scale reactor system [37].

RH is a naturally ash-rich agricultural by-product, which has more than 90% of this inorganic fraction as a pure silica [60], and the natural silica obtained from it represents an economically viable raw material that can be effectively used in life science and health care industries including cosmetics and pharmaceuticals. In this study, it was verified that silica can be recovered from the fractionated liquid phase generated and there was an advantage in recovering cellulose nanofibrils (CNF) in solid phase. CNF are attracting much attention due to their high nano-sized surface area, low density and high mechanical strength, as well as their solubility and biodegradability properties. In these days, CNF is promising to be used in a variety of applications in fields such as paper, composites, packaging, coatings, biomedicine, and automobiles due to its outstanding properties [61].

5. Conclusions

One of the most impeding negatives for the biorefinery industry is how to improve low economics. To overcome this problem, it is important to achieve effective utilization of lignocellulosic biomass and improve overall process economy by simultaneous production of high value-added materials. In our study, we have demonstrated the excellent properties, physical properties, and purity of the fractions produced through the fractionation method, which can maximize the added value of each component. In conclusion, it was confirmed that rice husk is a resource with very high economic potential. For this reason, this study attempted to increase the added value of by-products for the development of efficient biorefinery process technology, and is currently conducting research on technologies and applications such as separation/purification of high value-added silica and production of cellulose fiber.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2071-1050/13/4/1951/s1>: Figure S1. Central composite experimental design and responses obtained for the alkaline fractionation of rice husk on the yields of xmg extraction and de-ashing, Figure S2. Analysis of variance (ANOVA) for the adjusted quadratic model for alkaline fractionation of rice husk on the xmg extraction yield and de-ashing yield.

Author Contributions: Conceptualization: H.J.J., J.C. and H.K.; methodology: H.J.J. and H.K.; validation: H.K.; formal analysis: H.J.J. and J.C.; investigation: H.J.J., J.C. and K.K.O.; resources: H.J.J.; data curation: H.J.J., J.C. and H.K.; writing—original draft preparation: K.K.O. and J.C.; writing—review and editing: K.K.O. and J.C.; visualization: H.J.J.; supervision: K.K.O.; project administration: K.K.O.; funding acquisition: K.K.O. and J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the R&D program of Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Trade, Industry, and Energy (MOTIE), the Republic of Korea (No. 20183030091950).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts 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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