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Optimized Furfural Production Using the Acid Catalytic Conversion of Xylan Liquor from Organosolv-Fractionated Rice Husk

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Abstract: This study determined the optimal production of furfural (FuR) from liquid hydrolysate xylan liquor obtained through a two-stage pretreatment process using NaOH for de-ashing and EtOH for the delignification of raw rice husk (RH). The de-ashing pretreatment was conducted at 150 °C, with 6.0% (*w*/*v*) NaOH and a reaction time of 40 min. The optimal conditions for delignification pretreatment, performed using an organosolv fractionation method with EtOH, were a reaction temperature of 150 °C, 60% (*v*/*v*) EtOH, 0.25% (*w*/*v*) H_2SO_4, and a reaction time of 90 min. Through a two-stage pretreatment process, a liquid hydrolysate in the form of xylan liquor was obtained, which was subjected to an acid catalytic conversion process to produce FuR. The process conditions were varied, with reaction temperatures of 130–170 °C, H_2SO_4 catalyst concentrations of 1.0–3.0 wt.%, and reaction times of 0–90 min. The Response Surface Methodology tool was used to identify the optimal FuR yield from xylan liquor. Ultimately, the optimal process conditions for the acid catalytic conversion were found to be a substrate-to-catalyst ratio of 2:8, a reaction temperature of 168.9 °C, a catalyst concentration of 1.9 wt.%, and a reaction time of 41.24 min, achieving an FuR yield of 67.31%.

Keywords: rice husk (RH); pretreatment; xylan liquor; acid catalytic conversion; RSM

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1. Introduction

With the growing global interest in sustainable chemical industries and renewable energy, the research on renewable resources such as biomass, hydropower, wind, and solar energy is expanding [1–3]. This trend reflects the ongoing concerns regarding environmental issues such as water pollution, air pollution, and global warming arising from the use of fossil fuels [4]. Additionally, fossil fuels are finite resources with limited reserves, making the development of alternative energy sources essential [5,6]. As an alternative to fossil fuels, biomass offers the advantages of being a nearly infinite resource that is widely distributed globally and is environmentally friendly [7–11].

Biomass is classified into the first, second, and third generations. First-generation biomass consists of edible crops such as sugarcane and corn. Second-generation biomass includes lignocellulosic nonedible crops, whereas third-generation biomass refers to marine plants such as microalgae and seaweed. Extensive research has focused on second-generation biomass, because first-generation biomass raises ethical issues related to food security, whereas third-generation biomass faces technological and geographical challenges [12,13]. Second-generation biomasses, known as lignocellulosic biomasses (LCBs), are composed of 30–50%

cellulose, 10–30% hemicellulose, 10–25% lignin, and other substances such as ash and protein [14,15]. Glucose and xylose are the monomers of cellulose and hemicellulose, respectively, which constitute LCBs. Both these substances can be converted into valuable products via chemical and biological processes [16]. For instance, levulinic acid derived from glucose and furfural (FuR) derived from xylose can serve as intermediates in the production of final products such as bio-oil, solvents, gasoline additives, pharmaceuticals, biopolymers, and jet fuel [17–23].

FuR, an organic compound belonging to the furan series, features an aldehyde group attached to the second carbon atom of the furan ring. Consequently, it is also called 2-furaldehyde or 2-furfural [24,25]. The pentagonal heterocyclic structure not only facilitates interactions with other substances but also stabilizes the structure of FuR. Additionally, the aldehyde group attached to the second carbon atom allows for various organic reactions, making it advantageous for chemical transformations. Because of its simple yet unique structure, FuR can serve as an intermediate in the synthesis of various compounds, making it a valuable substance across multiple industrial fields [26]. FuR can be obtained through the dehydration reaction of xylose, which is derived from the hydrolysis of xylan present in agricultural byproducts such as wheat meal, corncobs, and rice husk (RH) [19].

Rice production was as high as 523.9 million tons in 2023/24 [27], ensuring a substantial supply of the byproduct RH. However, the direct conversion of raw RH results in a low product yield. This is because RH, being an LCB, has a complex structure in which cellulose, hemicellulose, and lignin are intricately intertwined, making it recalcitrant to external attacks. Therefore, pretreatment to remove lignin is necessary [28,29]. Additionally, RH contains a high ash content of 10–20% compared to other LCBs. This ash is composed of 87–97% silica, which acts as an additional protective barrier against chemical attacks. Therefore, for more efficient FuR production, pretreatment to remove ash is essential [30]. Consequently, similar to other LCBs, RH undergoes various pretreatment methods using alkaline [31,32] and acidic solvents [33], as reported in numerous studies.

Among the various pretreatment methods, the use of alkaline NaOH to pretreat RH selectively removes the ash content (de-ashing), resulting in a significantly reduced ash content in the solid form of de-ashed RH [34]. When this de-ashed RH undergoes organosolv fractionation pretreatment using EtOH, delignification occurs, maintaining the purity of the carbohydrates. This process yields a solid fraction enriched in C6 (mainly glucan, a polymer of glucose monomers) and a liquor fraction enriched in C5 (mainly xylan and lignin) [35]. Since the liquid hydrolysate obtained from the two-stage pretreatment of de-ashing and delignification contains a large amount of xylan, it can be used to produce FuR through chemical conversion.

The aim of this study was to optimize FuR production from xylan liquor. We employed various pretreatment methods, including the degradation of xylan liquor and acid catalytic conversion. We identified efficient pretreatment methods by examining the correlations between process variables such as the reaction temperature, reaction time, and catalyst concentration used in the pretreatment stage. Additionally, the degradation reaction of xylan to xylose in liquid hydrolysate is discussed. The acid catalytic conversion process was optimized for FuR yield using the Box–Behnken design (B–B design) for the Response Surface Methodology (RSM) tool.

2. Materials and Methods

2.1. Materials

RH was used as the biomass for pretreatment and acid catalytic conversion processes. The RH was harvested in 2017 and purchased from a local rice-processing complex (RPC), and the RH was harvested from Gipmo, Gyeonggi-do, Republic of Korea, in the fall of 2017. It was dried in a convection oven (FC-RP-1500, Lab House, Seoul, Republic of Korea) at 45 ± 5 °C for more than 48 h. Before use in the experiments, the RH was stored in an automatic de-humidification desiccator. At this stage, the moisture content of the RH was 4.6% based on the oven-dry weight [36].

The pretreatment of RH used in the experiments was performed by SugarEn Co., Ltd. (#B207, Seogwan, 152, Jukjeon-ro, Suji-gu, Yongin-si, Gyeonggi-do, 16890, Republic of Korea). Owing to the high content of ash and lignin in the RH, a two-step pretreatment process consisting of de-ashing pretreatment and delignification pretreatment was performed [36].

De-ashed RH was obtained by mixing the RH with NaOH, which resulted in solid-form carbohydrates. Delignified RH was achieved through an organosolv reaction with ethanol, removing lignin and separating the carbohydrates into C6 (glucan-rich) solids and C5 (xylan-rich) liquids. In this study, xylan liquor, a C5 (xylan-rich) liquid carbohydrate was used.

2.2. Methods

2.2.1. Pretreatment Using Alkaline Solution for De-Ashing of Raw RH

An alkaline fractionation process was employed to simultaneously remove hemicellulose and ash from the RH. The process utilized a tubular reactor made of SS-316 with an inner diameter of 10.7 mm, a length of 150 mm, and an internal volume of 13.5 mL. Oven-dried RH (0.5 g) and an alkaline solution (10 mL) were used to achieve a solid-to-liquid ratio of 1:10. To quickly preheat the reactor to the desired temperature, the reactor was immersed in molten salt set at 240 °C, with a target time of 1.0 min to reach the desired temperature. Upon reaching this temperature, the reactor was transferred to silicon oil, maintaining a reaction temperature between 116 and 184 °C, reaction times of 6–74 min, and a NaOH concentration of 1.0–6.0%. After the designated time, the reaction was rapidly quenched to stop it.

For the pretreatment at bench-scale, a ball-milling reactor with a 30 L capacity was used. It operated at 60 rpm under a pressure of 20 $\mathrm{kg_f\ cm^{-2}}$, with alumina balls of 10 mm diameter and 3.6 $\mathrm{g\ cm^{-3}}$ density. The de-ashing process used a ball-to-RH-to-alkaline solution ratio of 30:1:10. The residual solids were thoroughly washed with clean distilled water to prepare for the delignification pretreatment using the organosolv fractionation method [36,37].

2.2.2. Delignification Pretreatment of De-Ashed RH

For the delignification pretreatment of the de-ashed RH, an organosolv fractionation process was employed using ethanol as the organic solvent. Ethanol allows for the dissolution of hemicellulose (xylan-rich) and lignin in the liquid hydrolysate while retaining a high content of cellulose (glucan-rich) in the residual solid. The process was performed at a reaction temperature of 130–170 °C, with 60% ethanol concentration, and reaction times ranging from 30 to 120 min. The sulfuric acid concentration and sol-to-liquid ratio were maintained at 0.25% (w/v) and 1:10, respectively.

Adding sulfuric acid to ethanol-based organosolv fractionation reduces the severity of the reaction and increases lignin solubility [38]. The delignification process followed the same procedure as the de-ashing process. However, a different reactor, with an inner diameter (ID) of 21.0 mm, length of 140 mm, and internal volume of 48.5 $\mathrm{cm^3}$, was used.

2.2.3. Degradation Reactions of Xylan Liquor

The degradation of xylan to xylose was used to accurately measure the initial concentration of xylose. We applied the secondary hydrolysis method from the National Renewable Energy Laboratory (NREL) report NREL/TP-510-42623 [39]. The procedure for the degradation reaction proceeded as follows:

First, the liquid xylan was placed in a 250 mL media bottle and then autoclaved at 121 °C for 1 h using a high-pressure steam sterilizer (HS-2321SD, Hanshin Medical Co., Ltd., 166, Pyeongcheon-ro, Bupyeong-gu, Incheon, Republic of Korea) to ensure the sufficient degradation of xylan to xylose. The samples used for the subsequent acid conversion experiments always contained xylan that had been degraded under these conditions.

2.2.4. Acid Catalytic Conversion in Batch Reaction

The acid catalytic conversion reaction of the degraded xylan liquor was performed using an SS-316 batch reactor (outer diameter of 1/2 inch, length of 19.5 cm, internal volume of 19 cm^3). The acid catalytic conversion reactions were conducted at a reaction temperature range of 130–170 °C and reaction times ranging from 0 to 90 min. The substrate/catalyst ratio was 2:8. The reaction system, as shown in the diagram (Figure 1) below, consisted of a preheating oil bath to preheat the reactor, a main oil bath to maintain the reaction at specific times, and a cooling bath. Both the oil baths were equipped with temperature controllers to allow precise temperature settings. It required approximately 5 min to preheat the reactor to the set reaction temperature. After reaching the set reaction temperature, the batch reactor was removed at specific intervals and placed in a cooling bath for a set cooling period. All experiments were conducted at least three times to ensure reproducibility, and the results were calculated as average values.

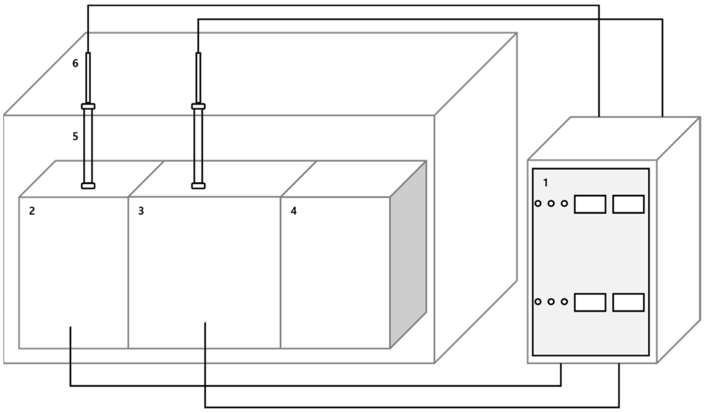


Figure 1. Schematic diagram of the batch reaction system: (1) temperature set controller; (2) preheating oil bath; (3) main oil bath for acid catalytic conversion reaction; (4) cooling bath; (5) SS-316 reactor for thermocouple installation in each bath; (6) thermocouple.

2.2.5. Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a tool used to analyze the effects of input variables on outcomes in complex processes or systems and to determine optimal conditions. It is used in various fields, such as chemical processes, manufacturing processes, and food engineering. RSM plays a crucial role in effectively collecting data through experimental design, data analysis, and the creation of mathematical models. By analyzing the response surfaces, optimal conditions can be predicted, reducing the number of experiments and the costs. This maximizes experimental efficiency and enhances the reliability of the results. In this study, we used a B–B design with three independent variables: reaction temperature, catalyst concentration, and reaction time [40].

2.3. Analysis and Determination of Samples

For the analysis samples, we used D-(+)-Glucose (Sigma-Aldrich Co., St.Louis, MO, USA, Cas No. 50-99-7), D-(+)-Xylose (Sigma, Cas No. 58-86-6), formic acid (Sigma, Cas No. 64-18-6), levulinic acid (Sigma, Cas No. 123-76-2), 5-HMF (Sigma, Cas No. 67-47-0), and FuR (Sigma, Cas No. 98-01-1). Sulfuric acid (SAMCHUN, Seoul, Republic of Korea, CAS No. 7664-93-9) was used as the catalyst and was diluted to 1.0–3.0 wt.% with distilled water. Calcium carbonate (DUKSAN, Gyeonggi, Republic of Korea, Cas No. 471-34-1) was used to neutralize the conversion liquid for the component analysis of the acid catalytic conversion liquid.

Solid analysis of the pretreated RH was conducted using the NREL/TP-510-42618 analytical method [41]. Liquid analyses of the initial xylan liquor, degraded xylan liquor, and products from the acid catalytic conversion were performed using high-performance liquid chromatography (HPLC). The main analytes were monosaccharides (glucose and xylose), organic acids (formic acid and levulinic acid), and furanic compounds (5-HMF and FuR). The HPLC system consisted of a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm; Bio-Rad. Inc., Hercules, CA, USA) and a refractive index detector (RID–410, Shimadzu, Kyoto, Japan). The mobile phase was 5 mM sulfuric acid pumped at a flow rate of 0.6 mL/min. The column oven was set at 60 °C, and the RI detector was set at 50 °C. Before injecting the samples into the HPLC, they were centrifuged at 14,000 rpm and filtered through a 0.45 µm syringe filter [42,43].

Because the sulfuric acid used in the acid catalytic conversion process can affect the peaks of the reducing sugars, each sample was neutralized with calcium carbonate before analysis. After neutralization, the samples were centrifuged, and only the supernatant was collected for analysis [44]. The xylose conversion, FuR yield, and selectivity were calculated using the following equations [45]:

$$\text{xylose conversion (\%)} = \text{(moles of reacted xylose)}/\text{(moles of initial xylose)} \times 100 \quad (1)$$

$$\text{FuR yield (\%)} = \text{(moles of produced FuR)}/\text{(moles of initial xylose)} \times 100 \quad (2)$$

$$\text{FuR selectivity (\%)} = \text{(moles of produced FuR)}/\text{(moles of reacted xylose)} \times 100 \quad (3)$$

3. Results and Discussions

3.1. Pretreatment of Raw RH

3.1.1. De-Ashing Pretreatment of Raw RH

De-ashed RH with selectively removed ash was used to produce an efficient carbohydrate feedstock, as listed in Table 1. During the de-ashing process, it was presumed that the chemical bonds and dense structure of RH were disrupted, allowing relatively mild reaction conditions to determine the optimal pretreatment conditions. The process variables included a reaction temperature range of 116–184 °C, reaction times of 6–74 min, and NaOH concentrations of 1.0–6.0%. The optimal de-ashing yield was achieved at 150 °C, a reaction time of 40 min, and a NaOH concentration of 6.0% (*w*/*v*) [37]. The de-ashed RH was obtained in solid form, showing a decrease in ash content from 16.2 to 0.9 wt.%, which led to an increase in the relative contents of glucan and xylan. Therefore, the de-ashing pretreatment of raw RH using NaOH not only effectively removed the ash surrounding the RH but also preserved the high yield of carbohydrates.

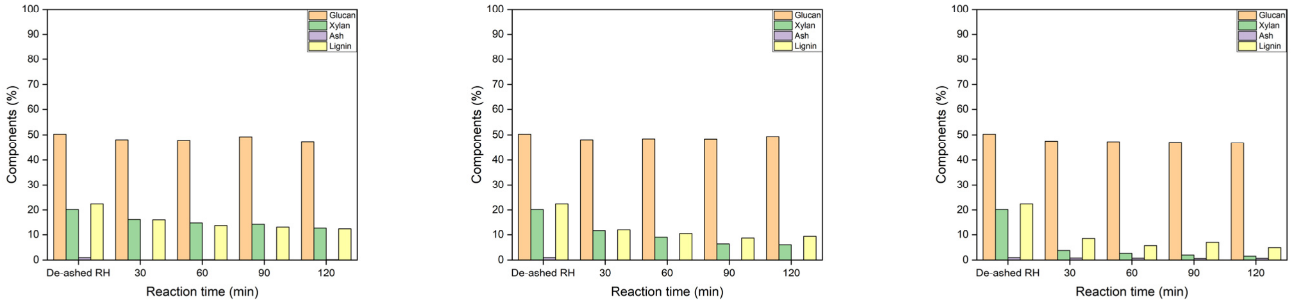
Table 1. Composition of de-ashed RH.

Components		Concentration [wt.%]	
		Raw RH	**De-Ashed RH**
Carbohydrates	Glucan	34.4 ± 0.1	50.3 ± 0.2
	Xylan	15.6 ± 0.0	20.2 ± 0.6
	Galactan	1.8 ± 0.2	1.5 ± 0.0
	Arabinan	1.9 ± 0.0	2.5 ± 0.0
	Mannan	0.3 ± 0.0	0.3 ± 0.0
Lignins	Acid-insoluble lignin	23.2 ± 0.0	22.4 ± 0.1
	Acid-soluble lignin	1.0 ± 0.0	0.8 ± 0.0
Ash		16.2 ± 0.2	0.9 ± 0.1

3.1.2. Organosolv Fractionation for Delignification Pretreatment of De-Ashed RH

Because the de-ashed RH still contained significant amounts of lignin, which acted as an inhibitor of downstream processes, a two-stage pretreatment process was employed. The initial de-ashing pretreatment was followed by a delignification pretreatment using organosolv fractionation. For the delignification, a 0.25% (*w*/*w*) sulfuric acid catalyst was used in 60% (*v*/*v*) ethanol as the organic solvent, with reaction temperatures ranging from 130° to 170 °C and reaction times ranging from 0 to 120 min.

Figure 2 illustrates the changes in the contents of glucan, xylan, ash, and lignin in the solid fraction when reacting de-ashed RH with an organic solvent at a solid-to-liquid ratio of 1:10, within the temperature range of 130° to 170 °C and reaction times from 30 min to 120 min. Glucan showed a decreasing trend in the amount preserved in the solid fraction as the reaction conditions became harsher; however, its preservation rate remained high, ranging from 93.1% to 98.1%. Conversely, xylan was largely extracted at temperatures above 170 °C, with an extraction rate ranging from 19.6% to 92.5% across the temperature range.



(**a**) (**b**) (**c**)

Figure 2. Results for composition changes by reaction time in delignification pretreatment of de-ashed RH using organosolv fractionation. Note: Untreated means de-ashed RH. Pretreatment conditions: EtOH 60% (*v*/*v*), 0.25% (*w*/*v*) H_2SO_4, solid-to-catalyst ratio of 1:10; (**a**) 130 °C, (**b**) 150 °C, (**c**) 170 °C.

Figure 3 shows the results for the liquid fraction. The graph shows changes in component contents under similar conditions, with a ratio of 1:10 and reaction temperatures from 130° to 170 °C over 30 to 120 min. As the reaction time increased, the xylose content initially increased but then decreased, while the FuR content showed an increasing trend. Xylose was converted to FuR as the reaction conditions became more severe, so the highest xylose preservation with minimal conversion to FuR was observed at 150 °C and 90 min. Thus, these conditions were selected as the optimal conditions for delignification pretreatment using organosolv fractionation. The glucan, xylan, lignin, and ash contents in the residual solids after the fractionation process, depending on the reaction time and temperature, are shown in Table 2.

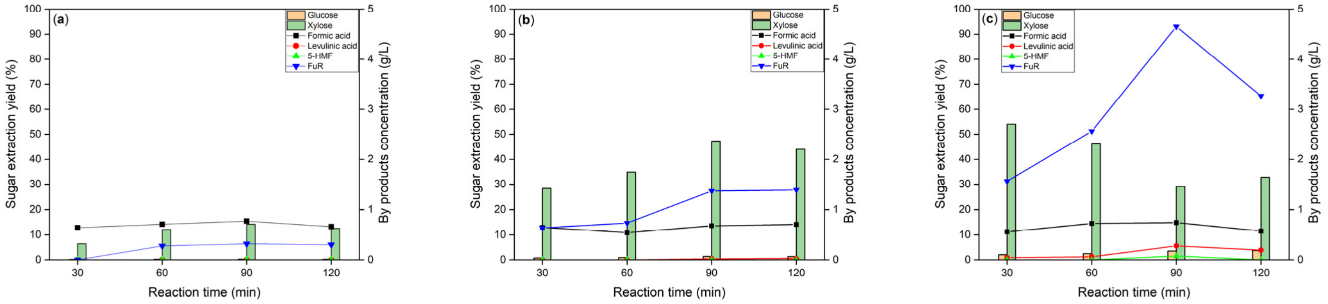


Figure 3. Results of sugar extraction yield and byproduct mass concentration by reaction time from delignification pretreatment using organosolv fractionation. Pretreatment conditions: EtOH 60% (*v*/*v*), 0.25% (*w*/*v*) H_2SO_4, solid-to-catalyst ratio of 1:10; (**a**) 130 °C, (**b**) 150 °C, (**c**) 170 °C.

Table 3 lists the changes in glucan, xylan, and other components before and after delignification pretreatment. This comparison highlights the effectiveness of the organosolv fractionation delignification pretreatment.

After pretreatment, the glucan content decreased by 1.2 g compared to the initial amount, whereas the xylan content decreased by 4.3 g. The loss of glucan was less significant than the loss of xylan. Lignin content was significantly reduced to approximately 62.5% in the delignificated RH in solid form, and the proportion of ash also decreased. Consequently, the solid fraction obtained after the delignification pretreatment primarily consisted of C6-rich glucan, whereas the liquid fraction mainly contained C5-rich xylan and dissolved lignin in ethanol. The substrate used in the experiment was a C5-rich xylan liquor obtained via this pretreatment process.

Table 2. Remaining yield for the solid part by the reaction conditions of delignification pretreatment.

Reaction Conditions			Remaining Yield			
Biomass	Temperature [°C]	Time [min]	Glucan [%]	Xylan [%]	Lignin [%]	Ash [%]
RH	130	30	57.1	19.3	19.1	0.0
		60	59.7	18.6	17.3	0.2
		90	61.5	18.0	16.5	0.0
		120	61.9	16.8	16.4	0.2
	150	30	63.7	15.5	16.1	0.0
		60	67.8	12.7	16.1	0.0
		90	73.1	9.7	14.7	0.4
		120	72.8	9.0	13.1	0.0
	170	30	76.1	6.1	13.7	1.2
		60	81.8	4.5	9.8	1.2
		90	80.7	3.4	12.0	1.0
		120	84.6	2.7	8.9	1.2

Table 3. Compositions of delignificated RH.

Component	De-Ashed RH (100 g)	After Organosolv Fractionation	
		Solid (66.2 g)	Liquid
Glucan	50.3 g	48.4 g	0.7 g
Xylan	20.2 g	6.4 g	9.5 g
Lignin	23.2 g	8.7 g	14.5 g
Ash	0.9 g	0.2 g	0.7 g
Other	5.4 g	-	-

3.2. Degradation Reactions of Xylan Liquor

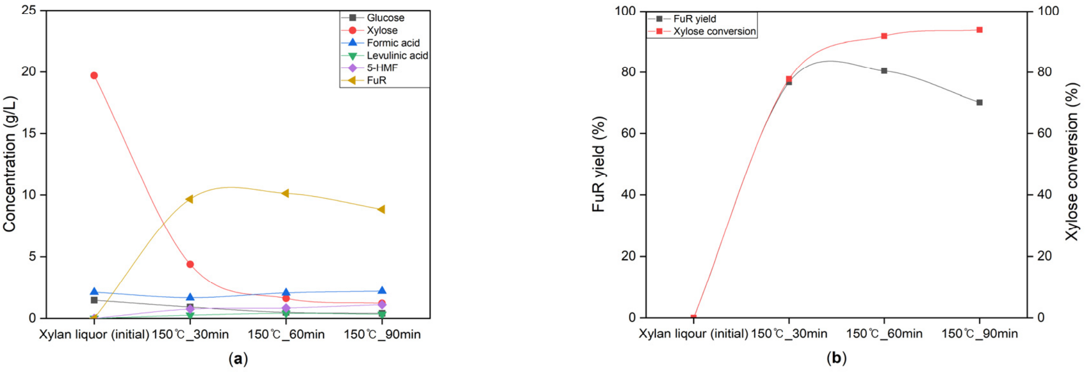
The composition of the xylan liquor after the two-stage pretreatment comprising de-ashing and delignification is shown in Table 4. The xylan liquor delignificated via organosolv fractionation contained a small amount of glucose, with xylan as the main component. It was confirmed that the xylan liquor was C5-enriched, containing approximately 25.86 g/L of xylan in both monomer and oligomer forms. Because a significant amount of xylan dissolved in the liquid phase, the goal was to obtain FuR using an acid catalytic conversion process.

Table 4. Compositions of initial xylan liquor.

Components		Concentration [g/L]	
		Monomer	Oligomer [1]
Carbohydrates	Glucan	1.25	1.16
	Xylan	17.87	7.99
	Arabinose	4.08	N/D [2]
	Subtotal	23.2	9.15

[1] Concentrations of oligomer have been calculated by the inversed calculation method during the secondary hydrolysis process. [2] N/D means not analyzed due to not being of significant value.

As a result of the acid conversion process experiment for FuR production, it was confirmed that the yield of FuR was calculated to be excessively high at 80.41% under the conditions of 150 °C reaction temperature, 3.0 wt.% sulfuric acid catalyst concentration, and a 60 min reaction time, as shown in Figure 4b. This indicated the need to re-evaluate the initial concentration of xylose. The pretreated xylan liquor contained xylose, which could be directly converted to FuR, xylan, and xylo-oligomers. As the reaction progressed, the breakdown of xylan and xylo-oligomers into xylose occurred simultaneously, making the initial concentration of xylose ambiguous. Therefore, to determine the initial concentration of xylose, a xylan degradation reaction was conducted by referring to NREL/TP-510-42623, which was used for biomass component analysis. The degradation reaction was performed in xylan liquor in an autoclave at 121 °C for 1 h. The composition of the liquid xylan after the reaction is shown in Table 5. After the degradation reaction, it was found that the concentration of xylose in monomer form increased from 17.87 g/L to approximately 27.148 g/L, an increase of about 9.3 g/L. This confirmed the presence of xylan and xylo-oligomers that had not been broken down into xylose. When a substrate from the degradation reaction of xylan liquor was used, the FuR yield in the acid catalytic conversion process was consistently calculated.



(**a**) (**b**)

Figure 4. Acid catalytic conversion reaction of initial xylan liquor: 150 °C reaction temperature, 3.0 wt.% sulfuric acid concentration, 30 to 90 min reaction time; (**a**) mass concentration of detected sample and (**b**) xylose conversion and FuR yield of reacted samples.

Table 5. Compositions of degraded xylan liquor.

Components		**Concentration [g/L]**
Carbohydrates	Glucose	2.149
	Xylose	27.148
	Arabinose	-

3.3. FuR Production

3.3.1. Acid Catalytic Conversion of Degraded Xylan Liquor

The acid catalytic conversion of the xylan liquor after the degradation reaction was performed with the same substrate-to-catalyst ratio and reaction time (0–90 min). The initial concentration of xylose was approximately 5.5 ± 0.2 g/L, and the experiments were conducted under consistent concentration conditions. To determine the yield of FuR, the reaction temperature was set between 130 and 170 °C, and the experiments were performed in a batch reactor system using sulfuric acid catalyst concentrations of 1.0 to 3.0 wt.%. Figure 5 shows FuR yields at different reaction temperatures. Figure 5a shows the results of the acid conversion experiment conducted at a reaction temperature of 130 °C. The yield of FuR was approximately 16.60% when 3.0 wt.% sulfuric acid was used, indicating that the reaction of xylose with FuR was not sufficient within the given reaction time. Therefore, a longer reaction time was required to achieve a higher FuR yield, which was considered inefficient for the experimental conditions. Figure 5b,c show the results of experiments conducted at reaction temperatures of 150 and 170 °C, respectively. At 150 °C, the yield of FuR was approximately 63.43% after 80 min reaction time when using 2.0 wt.% sulfuric acid. At 170 °C, the yield of FuR was approximately 65.56% after 40 min reaction time when using 2.0 wt.% sulfuric acid. Unlike the 130 °C condition, both the 150 °C and 170 °C conditions showed a tendency for the FuR yield to decrease over time when using 3.0 wt.% sulfuric acid compared to 2.0 wt.%. This suggests that an overreaction occurred, converting FuR into subsequent products due to the higher concentration of sulfuric acid [46,47].

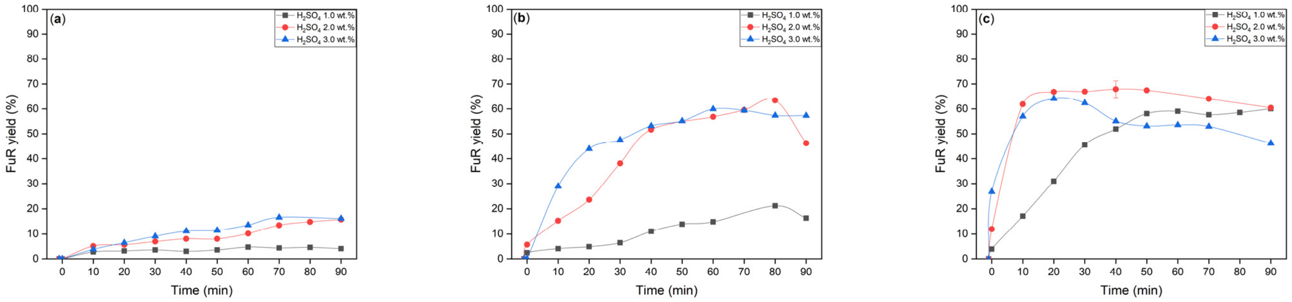


Figure 5. FuR yield from degraded xylan liquor by acid catalytic conversion at different temperatures: (**a**) 130 °C; (**b**) 150 °C; (**c**) 170 °C. All experiments were conducted at a substrate-to-catalyst ratio of 2 mL/8 mL and with a reaction time from 0 to 90 min.

3.3.2. Optimization Variables for Acid Catalytic Conversion of Degraded Xylan Liquor

To clearly determine the optimal conditions, we aimed to identify them using the B–B design of the RSM based on the experimental results. The independent variables in the experiment were set as reaction temperature (130–170 °C), sulfuric acid catalyst concentration (1.0–3.0 wt.%), and reaction time (0–90 min), as shown in Table 6.

Table 6. B–B design conditions for the acid catalytic conversion of degraded xylan liquor.

Variable	Factor	Levels		
Reaction temperature (°C)	X_1	130	150	170
Catalyst concentration (wt.%)	X_2	1.0	2.0	3.0
Reaction time (min)	X_3	10	50	90

The response values of the B–B design included the conversion rate of xylose and yield of FuR, as shown in Table 7. The RSM describes the optimal conditions for the acid conversion of xylan liquor after the degradation reaction. A predictive model for the optimal FuR yield was developed based on the results of the acid conversion process through batch reactions. The coefficient of determination (R^2) for the predictive model for the xylose conversion rate was 0.9450 for the quadratic model, indicating high reliability, whereas the predictive model for FuR yield showed a value of 0.8997, indicating a good fit.

The optimal conditions for each variable for FuR yield were predicted to be a reaction temperature of 168.97 °C, sulfuric acid catalyst concentration of 1.91 wt.%, and reaction time of 41.2 min. Under these conditions, the conversion rate of xylose and the yield of FuR were predicted to be 93.6192% and 67.5545%, respectively. These results are represented by Equations (4) and (5):

$$\begin{gathered}\text{Predicted xylose conversion } (\%) = 67.38 + 34.60X_1 + 8.79X_2 + 12.87X_3 + \\ 2.69X_1X_2 - 1.68X_1X_3 + 8.23X_2X_3 - 3.43X_1^2 - 9.47X_2^2 - 0.75\,X_3^2\end{gathered} \tag{4}$$

$$\begin{gathered}\text{Predicted FuR yield } (\%) = 49.11 + 23.61X_1 + 8.43X_2 + 6.64X_3 - 3.30X_1X_2 - \\ 5.29X_1X_3 + 3.41X_2X_3 - 4.33X_1^2 - 13.30X_2^2 - 8.75\,X_3^2\end{gathered} \tag{5}$$

The 3D response surface curves were obtained by plotting two variables on the X- and Y-axes while keeping the remaining variable at mid-level (0). Figure 6 shows the contour and surface plots for optimizing FuR yield conditions. Figure 6a illustrates the effects of the reaction temperature and sulfuric acid catalyst concentration on the FuR yield. As the reaction temperature increased, the FuR yield also increased. However, when both the reaction temperature and sulfuric acid catalyst concentration increased together, the FuR yield initially increased and then showed a decreasing trend. An improved FuR yield was observed at near 170 °C with moderate catalyst concentrations.

Table 7. Results for coded factor levels for a B–B design.

Run	X_1	X_2	X_3	Xylose Conversion (%)	FuR Yield (%)
1	150	2.0	50	64.5689	48.1429
2	150	1.0	10	34.2083	3.6286
3	150	2.0	50	60.9909	39.5519
4	150	2.0	50	67.1875	56.7985
5	170	2.0	10	84.9209	61.9103
6	150	2.0	50	74.5416	49.3514
7	130	2.0	90	44.8293	20.7164
8	130	2.0	10	23.0202	5.1464
9	170	3.0	50	100	53.1180
10	130	3.0	50	14.7813	11.4535
11	150	2.0	50	69.5976	51.6818
12	170	1.0	50	88.7973	58.0865
13	150	3.0	90	96.5595	57.3082
14	150	1.0	90	50.7911	18.3826
15	170	2.0	90	100	56.3274
16	150	3.0	10	47.0739	28.9095
17	130	1.0	50	14.3225	3.2147

Figure 6b shows the response surface for the FuR yield concerning reaction temperature and reaction time. As the reaction time increased, the FuR yield initially increased and then decreased, suggesting that prolonged reaction times at a given temperature led to an overreaction and a subsequent decrease in FuR yield. The optimal FuR yield was observed between 40 and 50 min near 170 °C of reaction temperature.

Figure 6c shows the correlation between the sulfuric acid catalyst concentration and reaction time. As shown in Figure 6a,b, the FuR yield did not increase continuously with higher values of both variables but showed improved yields at moderate values.

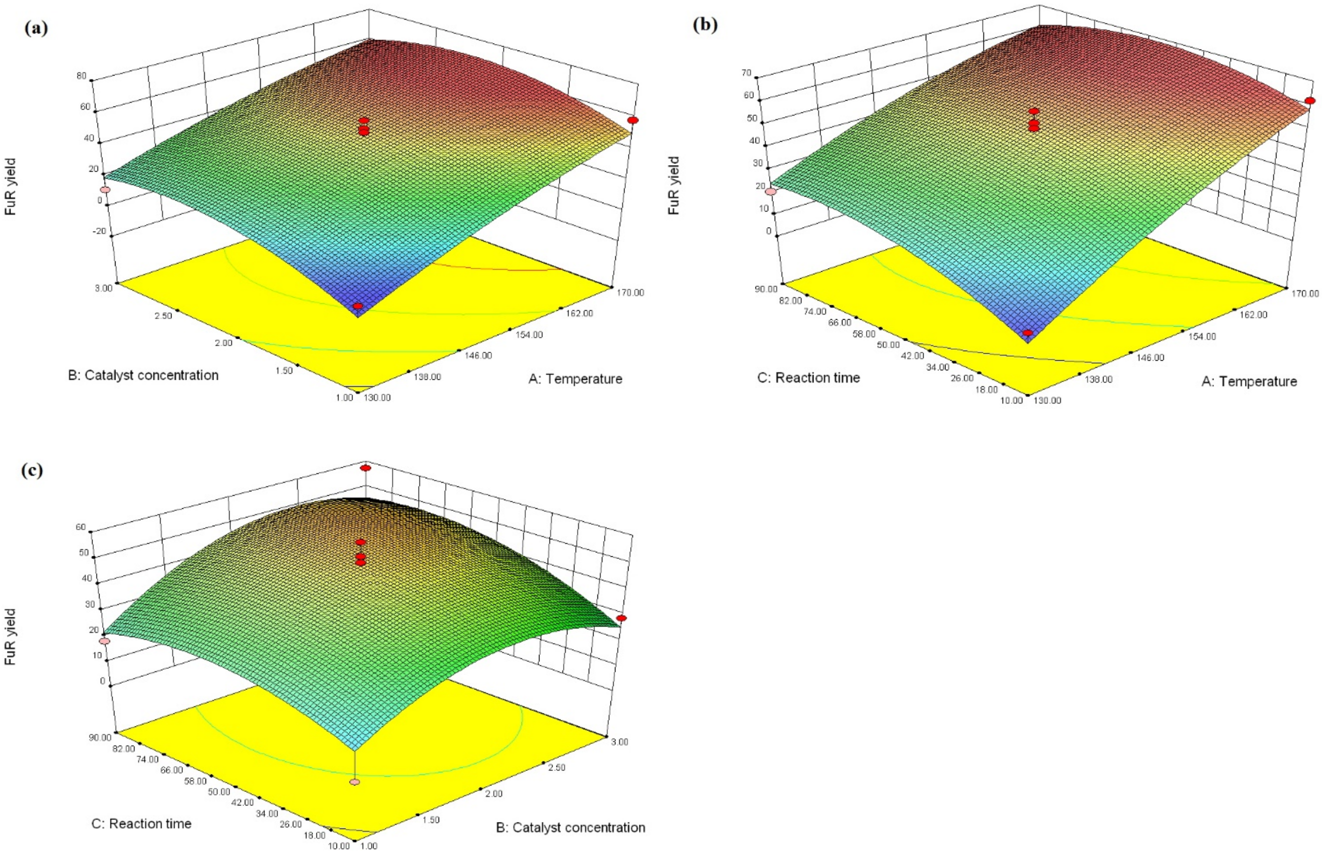


Figure 6. Response surface plots for acid catalytic conversion by degraded xylan liquor: (**a**) interaction between reaction temperature and catalyst concentration; (**b**) interaction between reaction temperature and reaction time; and (**c**) interaction between catalyst concentration and reaction time. Note: Blue region has a low expected value for FuR yield and red region is high.

3.3.3. Validation of the RSM Results

Using the conditions predicted by the RSM model for the optimal FuR yield, as specified in Equation (4), the acid catalytic conversion of xylan liquor after the degradation reaction was conducted, and the results are shown in Figure 7. The process conditions included a substrate-to-catalyst ratio of 2 mL/8 mL, a reaction temperature of 169 °C, a catalyst concentration of 1.9 wt.%, and a reaction time of 0–90 min, including the verification of the predicted value for reaction time (41.24 min). The resulting FuR yield was 67.31%, which was close to the RSM-predicted value of 67.5545%. The ANOVA results for the FuR yield, particularly the lack-of-fit tests for the quadratic model, suggested a *p*-value of 0.0749 and an F-value of 5.09, indicating potential noise. Nevertheless, results similar to the model predictions were obtained through experiments with more than three replicates, confirming the reliability of the model.

The reaction temperature, catalyst concentration, and reaction time play crucial roles in FuR production. To validate the optimal process based on the correlations between these variables, the relationship between FuR yield and selectivity was examined and is shown in Figure 8. In Figure 8a, the concentration of FuR was the highest at 2.34 g/L at a reaction time of 41.2 min, indicating that the reaction conditions are highly effective for FuR production. Additionally, the concentrations of FuR and formic acid decreased as xylose participated in the reaction. This supports the earlier observation of an overreaction of FuR after a certain reaction time.

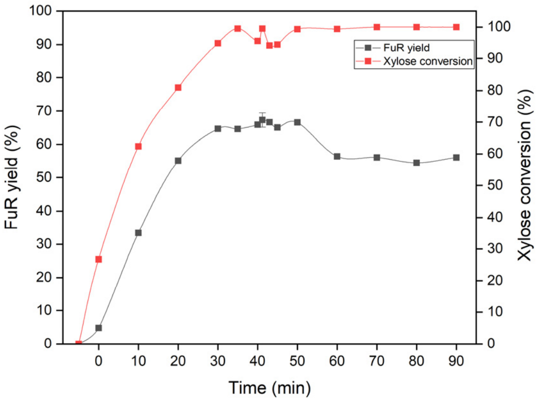


Figure 7. Experimental values according to RSM analysis results: 169 °C reaction temperature, 1.9 wt.% sulfuric acid concentration, 0–90 min reaction time.

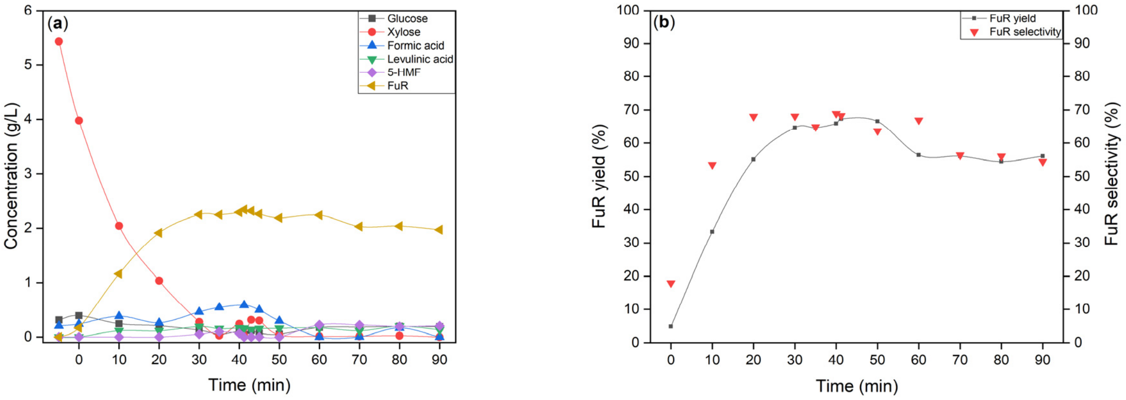


Figure 8. Reaction product molar concentration (**a**) and FuR yield and reaction selectivity (**b**) in the degraded xylan liquor to acid catalytic conversion process according to reaction time: reaction temperature (169 °C), catalyst concentration (1.9 wt.%), reaction time (0–90 min).

Figure 8b shows the selectivity of FuR for xylose. At a reaction time of 41.2 min, the selectivity for FuR was 67.64%, meaning that about two-thirds of the substance produced from xylose in the reaction comprised FuR, which is considered relatively high selectivity. In another study on the acid catalytic conversion of pure xylose using the same reactor [48], under the conditions of an initial xylose concentration of 10 g/L, a reaction temperature of 180 °C, a reaction time of 10 min, and a sulfuric acid catalyst concentration of 3.0 wt.%, the yield of FuR was 65.79%, and the selectivity was 66.24%. Although the reaction conditions used by Lee and Kim were harsher, the yield and selectivity of FuR from the acid catalytic conversion of xylose in liquor form show a similar trend to the results of this study. Therefore, it can be concluded that under similar experimental conditions, the yield of FuR from xylose is expected to be 65 to 70%.

As the concentration of FuR decreased, the selectivity of FuR toward xylose also decreased. Therefore, based on Figure 8a,b, the optimal reaction time for FuR production via the acid catalytic conversion of degraded xylan was 41.2 min. The concentration of sulfuric acid used as the catalyst was optimized to promote FuR production while suppressing subsequent side reactions. Additionally, the intermediates remained stable up to the optimal time, facilitating efficient conversion to FuR.

3.3.4. Overall Process for Optimum Conditions

The entire process of producing FuR from raw RH is illustrated in Figure 9. Initially, to ensure the smooth downstream processing of raw RH, a de-ashing pretreatment was performed to remove silica-based ash. After de-ashing, the solid-remaining fraction was 65.75%, which means that from 100 kg of raw RH, 65.75 kg of solid de-ashed RH was obtained. Specifically, after the selective removal of ash using NaOH, the glucan content was 50.3 wt.%, XMG was 22.0 wt.%, arabinan was 2.5 wt.%, ash was 0.9 wt.%, and lignin was 23.2 wt.%. The ash content decreased from 16.2 to 0.9 wt.%, achieving a reduction of approximately 15.3 wt.%p in the solid content. However, de-ashed RH still contained 23.2 wt.% lignin, which acted as a chemical inhibitor, necessitating delignification pretreatment.

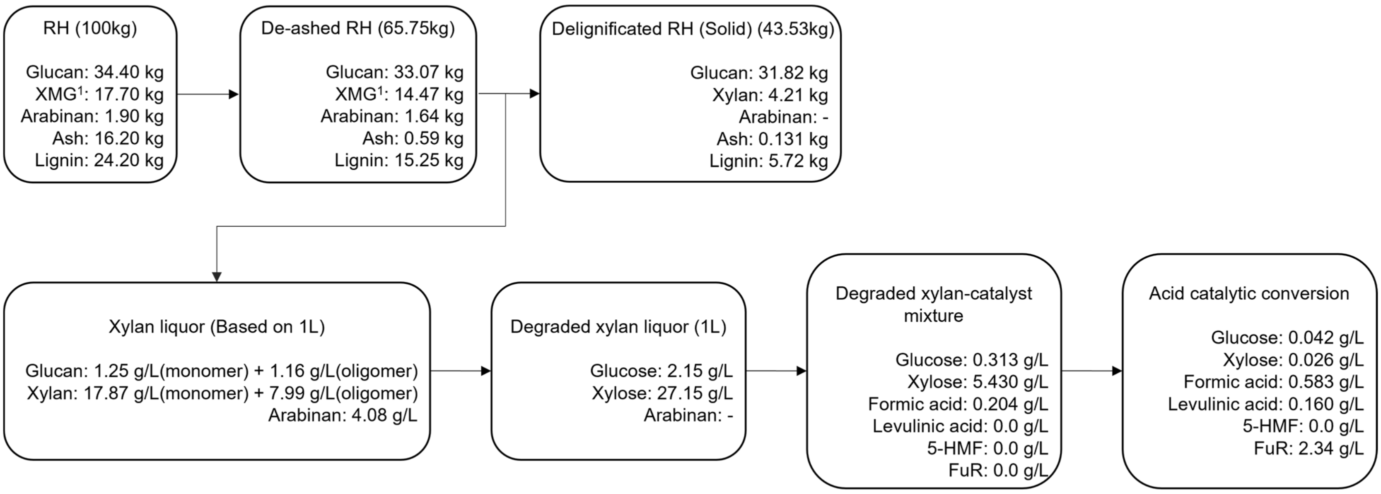


Figure 9. Overall process for optimized FuR production from raw RH. Note: XMG means xylan, mannan, and galactan.

Following the delignification pretreatment using organosolv fractionation based on EtOH, the remaining solid fraction was 66.20%, resulting in a total of 43.53 kg of solids from the de-ashed RH. At this stage, the solid composition is 73.1 wt.% glucan, 9.67 wt.% xylan, 0.3 wt.% ash, and 13.14 wt.% lignin, indicating a reduction in lignin content by approximately 10.06 wt.%p. This demonstrates that, compared with the de-ashed RH, the carbohydrate-to-lignin ratio in the delignificated RH was significantly improved, suggesting that organosolv fractionation is highly effective in removing lignin.

Using organosolv fractionation for delignification pretreatment, an EtOH-based C5-rich xylan liquor was obtained. In 1 L of xylan liquor, approximately 17.87 g/L of monomeric xylose and 7.99 g/L of oligomeric xylose were present. As oligomeric xylan could obscure the initial concentration of xylose and the yield of FuR in the experiments, a degradation reaction from xylan to xylose was performed. After the reaction, the xylose increased to 27.15 g/L. Thus, the initial concentration of xylose for the acid catalytic conversion process was consistently found to be approximately 5.5 g/L. Subsequently, by applying the optimized variables (reaction temperature of 169 °C, catalyst concentration of 1.9 wt.%, reaction time of 41.2 min) determined through RSM, FuR was produced at a concentration of 2.34 g/L from an initial xylose concentration of 5.430 g/L.

4. Conclusions

This study was conducted to optimize the production of FuR from liquid xylan obtained through the pretreatment of raw RH. To efficiently produce a large amount of FuR, appropriate pretreatment methods and chemical conversion techniques were considered based on the characteristics of the raw biomass. Delignification pretreatment using ethanol allowed the separation of significant amounts of xylan and lignin in the liquor form. Methods for securing xylose from xylan liquor obtained through pretreatment were proposed, and acid catalytic conversion using sulfuric acid was optimized using RSM. Finally, strategies to achieve a high FuR yield and selectivity by utilizing the optimized process variables are discussed in this paper.

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References

1. Perea-Moreno, M.; Samerón-Manzano, E.; Perea-Moreno, A. Biomass as Renewable Energy: Worldwide Research Trends. *Sustainability* **2019**, *11*, 863. [CrossRef]
2. Saleem, M. Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source. *Heliyon* **2022**, *8*, e08905. [CrossRef] [PubMed]
3. Zhou, Q.; Le, Q.V.; Yang, H.; Gu, H.; Yang, Y.; Sonne, C.; Tabatabaei, M.; Lam, S.S.; Li, C.; Chen, X.; et al. Sustainable conversion of agricultural biomass into renewable energy products: A Discussion. *BioRes* **2022**, *17*, 3489. [CrossRef]
4. Sarkar, N.; Ghosh, S.K.; Bannerjee, S.; Aikat, K. Bioethanol production from agricultural wastes: An overview. *Renew. Energy* **2011**, *37*, 19. [CrossRef]
5. Holechek, J.L.; Geli, H.M.E.; Sawalhah, M.N.; Valdez, R. A Global Assessment: Can Renewable Energy Replace Fossil Fuels by 2050? *Sustainability* **2022**, *14*, 4792. [CrossRef]
6. Kadhim, A. Applications of nanotechnology in renewable energies—A comprehensive overview and understanding. *Renew. Sustain. Energy Rev.* **2014**, *42*, 460. [CrossRef]
7. Demirbaş, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manag.* **2001**, *42*, 1357–1378. [CrossRef]
8. Bridgwater, T. Biomass for energy. *J. Sci. Food Agric.* **2006**, *86*, 1755. [CrossRef]
9. Bar-On, Y.M.; Phillips, R.; Milo, R. The biomass distribution on Earth. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 6506. [CrossRef]
10. Ramprakash, B.; Lindblad, P.; Eaton-Rye, J.J.; Incharoensakdi, A. Current strategies and future perspectives in biological hydrogen production: A review. *Renew. Sustain. Energy Rev.* **2022**, *168*, 112773. [CrossRef]
11. Mujtaba, M.; Fernandes Fraceto, L.; Fazeli, M.; Mukherjee, S.; Savassa, S.M.; Araujo De Medeiros, G.; Do Espírito Santo Pereira, A.; Mancini, S.D.; Lipponen, J.; Vilaplana, F. Lignocellulosic biomass from agricultural waste to the circular economy: A review with focus on biofuels, biocomposites and bioplastics. *J. Clean. Prod.* **2023**, *402*, 136815. [CrossRef]
12. Lee, R.A.; Lavoie, J. From first- to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. *Anim. Front.* **2013**, *3*, 6. [CrossRef]
13. Maliha, A.; Abu-Hijleh, B. A review on the current status and post-pandemic prospects of third-generation biofuels. *Energy Syst.* **2022**, *14*, 1185. [CrossRef]
14. Park, Y.C.; Kim, J.S. Comparison of various alkaline pretreatment methods of lignocellulosic biomass. *Energy* **2012**, *47*, 31–35. [CrossRef]
15. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* **2009**, *100*, 10–18. [CrossRef]
16. Mika, L.T.; Cséfalvay, E.; Németh, Á. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. *Chem. Rev.* **2017**, *118*, 505. [CrossRef]
17. Putro, J.N.; Soetaredjo, F.E.; Lin, S.; Ju, Y.; Ismadji, S. Pretreatment and conversion of lignocellulose biomass into valuable chemicals. *RSC Adv.* **2016**, *6*, 46834. [CrossRef]
18. Zhang, M.; Wang, N.; Liu, J.; Wang, C.; Xu, Y.; Ma, L. A review on biomass-derived levulinic acid for application in drug synthesis. *Crit. Rev. Biotechnol.* **2021**, *42*, 220. [CrossRef]
19. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; López Granados, M. Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energy Environ. Sci.* **2016**, *9*, 1144. [CrossRef]
20. Lange, J.; Van der Heide, E.; Van buijtenen, J.; Price, R. Furfural—A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem* **2011**, *5*, 150. [CrossRef]

21. Victor, A.; Sharma, P.; Pulidindi, I.N.; Gedanken, A. Levulinic Acid Is a Key Strategic Chemical from Biomass. *Catalysts* **2022**, *12*, 909. [CrossRef]
22. Hayes, D.J.; Ross, J.; Hayes, H.B.; Fitzpatrick, S. The Biofine Process: Production of Levulinic Acid, Furfural and Formic Acid from Lignocellulosic Feedstocks. *Biorefineries–Ind. Process. Prod.* **2006**, *1*, 139–164.
23. Eseyin, A.E.; Steele, P.H. An overview of the applications of furfural and its derivatives. *IJAC* **2015**, *3*, 42. [CrossRef]
24. Peleteiro, S.; Rivas, S.; Alonso, J.L.; Santos, V.; Parajó, J.C. Furfural production using ionic liquids: A review. *Bioresour. Technol.* **2015**, *202*, 181. [CrossRef] [PubMed]
25. Yong, K.J.; Wu, T.Y.; Lee, C.B.T.L.; Lee, Z.J.; Liu, Q.; Jahim, J.M.; Zhou, Q.; Zhang, L. Furfural production from biomass residues: Current technologies, challenges and future prospects. *Biomass Bioenergy* **2022**, *161*, 106458. [CrossRef]
26. Hoydonckx, H.E.; Van Rhijn, W.M.; Van Rhijn, W.; De Vos, D.E.; Jacobs, P.A. Furfural and Derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library: New York, NY, USA, 2007. [CrossRef]
27. Food and Agriculture Organization of the United Nations. Available online: https://www.fao.org/faostat/en/ (accessed on 27 September 2024).
28. Mosier, N.; Wyman, C.; Dale, B.; Elander, R.; Lee, Y.Y.; Holtzapple, M.; Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2004**, *96*, 673. [CrossRef]
29. Brodeur, G.; Yau, E.; Badal, K.; Collier, J.; Ramachandran, K.B.; Ramakrishnan, S. Chemical and Physicochemical Pretreatment of Lignocellulosic Biomass: A Review. *Enzym. Res.* **2011**, *2011*, 787532. [CrossRef]
30. Mor, D.R. Utilization of Rice Husk and Their Ash: A Review. *Res. J. Chem. Env. Sci.* **2013**, *1*, 126–129.
31. Tsai, C.; Shen, Y.; Tsai, W. Effect of Alkaline Pretreatment on the Fuel Properties of Torrefied Biomass from Rice Husk. *Energies* **2023**, *16*, 679. [CrossRef]
32. Khat-Udomkiri, N.; Sivamaruthi, B.S.; Sirilun, S.; Lailerd, N.; Peerajan, S.; Chaiyasut, C. Optimization of alkaline pretreatment and enzymatic hydrolysis for the extraction of xylooligosaccharide from rice husk. *AMB Expr.* **2018**, *8*, 115. [CrossRef]
33. Dagnino, E.P.; Chamorro, E.R.; Romano, S.D.; Felissia, F.E.; Area, M.C. Optimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol production. *Ind. Crops Prod.* **2013**, *42*, 363. [CrossRef]
34. Bazargan, A.; Bazargan, M.; Mckay, G. Optimization of rice husk pretreatment for energy production. *Renew. Energy* **2015**, *77*, 512. [CrossRef]
35. Kim, T.H.; Kwak, H.; Kim, T.H.; Oh, K.K. Reaction Characteristics of Organosolv-Fractionation Process for Selective Extraction of Carbohydrates and Lignin from Rice Husks. *Energies* **2021**, *14*, 686. [CrossRef]
36. Jung, H.J.; Oh, K.K. NaOH-Catalyzed Fractionation of Rice Husk Followed by Concomitant Production of Bioethanol and Furfural for Improving Profitability in Biorefinery. *Appl. Sci.* **2021**, *11*, 7508. [CrossRef]
37. 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. [CrossRef]
38. Zhang, K.; Pei, Z.; Wang, D. Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review. *Bioresour. Technol.* **2015**, *199*, 21. [CrossRef]
39. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. Determination of sugars, byproducts, and degradation products in liquid fraction process samples. *Gold. Natl. Renew. Energy Lab.* **2006**, *11*, 65–71.
40. Ao, S.; Gouda, S.P.; Selvaraj, M.; Boddula, R.; Al-Qahtani, N.; Mohan, S.; Rokhum, S.L. Active sites engineered biomass-carbon as a catalyst for biodiesel production: Process optimization using RSM and life cycle assessment. *Energy Convers. Manag.* **2024**, *300*, 117956. [CrossRef]
41. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. Determination of structural carbohydrates and lignin in biomass. *Lab. Anal. Proced.* **2008**, *1617*, 1–16.
42. Park, Y.C.; Yoon, J.; Kim, S.; Kim, T.H.; Kim, J.S. Two-stage flow-through pretreatment of helianthus tuberosus residue for enzymatic production of fermentable sugar by alkaline and acidic solutions. *Bioresources* **2017**, *12*, 6504–6517. [CrossRef]
43. Kim, K.; Kim, J.S. Optimization of ammonia percolation process for ethanol production from Miscanthus sinensis. *Korean Chem. Eng. Res.* **2010**, *48*, 704–711.
44. Sun, Y.; Liang, C.; Qi, W.; Wang, Q.; Zhan, L.; Tong, J.; Jiang, J.; Yao, Z. One-pot catalytic hydrolysis of sugarcane bagasse into furfural using a pressurized phosphoric acid/acetone/water system. *Biomass Bioenergy* **2024**, *185*, 107242. [CrossRef]
45. Delbecq, F.; Wang, Y.; Len, C. Conversion of xylose, xylan and rice husk into furfural via betaine and formic acid mixture as novel homogeneous catalyst in biphasic system by microwave-assisted dehydration. *J. Mol. Catal. A Chem.* **2016**, *423*, 520. [CrossRef]
46. Hu, X.; Westerhof, R.J.M.; Dong, D.; Wu, L.; Li, C. Acid-Catalyzed Conversion of Xylose in 20 Solvents: Insight into Interactions of the Solvents with Xylose, Furfural, and the Acid Catalyst. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2562. [CrossRef]
47. Li, X.; Liu, Q.; Luo, C.; Gu, X.; Lu, L.; Lu, X. Kinetics of Furfural Production from Corn Cob in γ-Valerolactone Using Dilute Sulfuric Acid as Catalyst. *ACS Sustain. Chem. Eng.* **2017**, *5*, 8587. [CrossRef]
48. Lee, S.; Kim, J.S. Furfural Production From Xylose by Using Formic Acid and Sulfuric Acid. *Korean Chem. Eng. Res.* **2023**, *61*, 561–569. [CrossRef]