# Optimization of 5-HMF production from rice straw using an acid catalyst in a biphasic system

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## 1. Introduction

The global pandemic due to COVID-19, manifested the requirement of global actions on renewable and more sustainable energy projects [1]. Nevertheless, in 2022, fossil fuels accounted for 82% of the overall global energy consumption, indicating a 1% rise from the 2021 data [2]. Fossil fuels pose several issues, including their major role in causing global warming, [3] posing a substantial threat to the health and future of future generations, perpetuating global disparities and environmental injustices, [4] and the continuous depletion of fossil fuel reserves. [5] To encounter these concerns, biomass can be considered as a requisite solution [6].

5-hydroxymethylfurfural (5-HMF) is a versatile intermediary chemical derived from biomass that may effectively connect the chemical energy of biomass to a wide range of businesses [7]. 5-HMF is a member of the class named "Furan". The molecule has two functional groups, one at position 2 and the other at position 5, which are formyl and hydroxymethyl substituents. As a result, the oxidized 5-HMF is a dicarboxylic acid while reduced 5-HMF is a diol. These two chemicals are utilized in polymer synthesis. Moreover, due to the unsaturation of its aromatic structure, 5-HMF can be hydrogenated to fuel compounds. The intrinsic heterocyclic nature of furans, including HMF, is a pivotal substance in copious biologically active molecules, which allows for medicinal uses in a broad spectrum of compounds [8]. Ultimately, it can supersede fossil-derived binders in the wood and foundry sectors, with a more efficient gluey effect than its counterpart [9]. Due to the significant imports mentioned, 5-HMF is becoming a prominent figure in the advancement of renewable energy and the production of biomaterials.

HMF is commonly produced from monosaccharides like fructose and glucose using acid catalysis in aqueous or biphasic solvents. There is an increasing interest in the efficient production of HMF from lignocellulosic materials or other nonedible polysaccharides. These sources are more abundant and cost-effective compared to edible fructose or glucose sources. As a result, notable resources have been utilized by the scientific community to study and improve ecologically friendly procedures, commonly known as "green" processes, for the manufacturing of HMF [10].

Rice, which is a widely available polysaccharide, is a staple food for around 4 billion people worldwide. It contributes 21 percent of the total energy consumed per person globally and provides 15 percent of the protein consumed per person [11]. Rice straw has a lignocellulosic composition with cellulose content of approximately 42.19% ± 2.78, hemicellulose content of around 24.26% ± 5.39, and lignin content comprising roughly 20.83% ± 3.77. Due to this high cellulose content in the composition, rice straw can be considered as a prominent feedstock for HMF synthesis [12]. The overall synthesis of 5-HMF from rice straw involves two major steps: which are, a pretreatment step of rice straw to convert it into cellulose, and a catalytic reaction of cellulose to turn it into 5-HMF. The synthesis paths are diverse, depending on the preceding processes [13].

The overall derivation of Rice straw to 5-HMF consists of two major steps. Transformation of Rice straw into Cellulose, is followed by conversion of Cellulose into 5-HMF. The first step can be completed using several pre-treatment methods [13]. In this study, to obtain cellulose from rice straw, an acidic pretreatment approach was utilized. Acid treatment of straw biomass is a widely adopted method, primarily aimed at disrupting the linkages between hemicellulose, lignin, and cellulose. This disruption enhances hemicellulose hydrolysis efficiency, aids in lignin removal, and expedites the saccharification and fermentation processes. The conversion of cellulose into 5-HMF was achieved through a MIBK-water biphasic system. Here Mineral acids like HCl are often employed for this purpose, as they function as Bronsted acidic catalysts, facilitating the cellulose.

Even though there are some independent studies have been done on pre-treatment methods and derivation of 5-HMF from Cellulose separately, an overall conversion using an acid pre-treatment followed by an acid catalyst in a biphasic system is an important study area. It will enhance the yield of 5-HMF while being an eco-friendly and cost-effective methodology.

## 2. Materials and Methods

### 2.1 Materials

Unprocessed rice straw (RS) was sourced from local farmers in Menikhinna, situated in the Central province of Sri Lanka. The raw material underwent cutting into pieces and thorough washing using tap water to eliminate impurities such as dirt and sand. Thereupon, the washed RS was left to air dry at ambient temperature for seven days. The dried RS underwent grinding and sieving through a 0.18 mm mesh to ensure uniformity. The RS powder was further dried for 24 hours at 105°C and subsequently stored in a desiccator until utilized for pretreatment.

### 2.2 Design of Experiments

The experiment comprised two major steps: the conversion of rice straw to cellulose and the subsequent conversion of cellulose to 5-HMF. Literature-based screening of parameters was conducted to identify the most significant factors. For the pretreatment, sulfuric acid was chosen, and the factors related to this pretreatment were maintained constant across all trials. In the second stage, a biphasic system was created using aqueous hydrochloric acid and methyl isobutyl ketone. It was identified that the key parameters influencing 5-HMF yield include acid concentration, reaction temperature, reaction time, and the ratio of Rice straw to acid solution loading. However, in this study, hydrochloric acid concentration and reaction temperature were identified as critical factors based on their direct impact on 5-HMF yield.

### 2.3 Rice straw pretreatment

The RS pretreatment procedure began by pouring 20 ml of 0.1 M sulfuric acid into a Falcon tube. Subsequently, 1 g of rice straw powder was measured and added to the same Falcon tube. The pretreatment process was carried out in a water bath set to 100°C for 40 minutes. Following the specified reaction time, the samples were promptly transferred to a cool bath to halt further reaction. After cooling, filtration was followed to separate the solid residue. The solid residue was then dried inside a desiccator. Eventually, 40 ml of 50% (w/w) ethanol solution was mixed with the dried powder. The resulting solution was placed in a stirred heater and maintained at 50°C for 2 hours. Upon the cooling step followed by the heating procedure, the mixture was filtered, yielding cellulose powder.

### 2.4 Recovery of 5-HMF and characterization

To proceed with the experiment, 100 mg of cellulose powder was accurately measured, followed by the addition of 1 ml of 0.1 M HCl and 24 ml of MIBK. The resulting mixture was then inserted into the reactor (High-Pressure Lab Reactor by "Toption instruments"), and the temperature was adjusted according to the values mentioned in Table 1. Moreover, the reaction time was set to 1 hour for all trials to allow for the desired chemical reaction to occur.

UV spectroscopy was employed to identify and quantify 5-HMF in the final product. According to the study [14], the maximum absorption wavelength for 5-HMF was set to be 284 nm. The relationship between the concentration of 5-HMF, denoted as C (mg/ml), and absorbance (A) can be expressed as follows:

*Equation 1- the relationship of concentration and absorbance*

$$A = 142.1C - 0.01806$$

Software simulations, employing MATLAB, were utilized to estimate the main effects and interaction effects of each independent variable.

## 3. Results and Discussion

The table 1 illustrates the correlation between temperature variations and the resultant yield of 5-HMF, indicating a discernible relationship between temperature modulation and the production efficiency of 5-HMF.

Increasing the temperature of the reactor led to a corresponding increase in the yield of 5-HMF until reaching 180°C, beyond which a decline in yield was observed with further temperature increments. This trend suggests an optimal temperature range between 170°C and 180°C. Utilizing MATLAB software, the optimal temperature was determined to be 178°C.

*Table 1- results summary of temperature changes*

| Temperature (°C) | No | Weight Of 5-HMF (mg) | Final Weight (mg) |
|---|---|---|---|
| 160 | 1 | 0.0952 | 0.090 |
| | 2 | 0.0825 | |
| | 3 | 0.0925 | |
| 170 | 1 | 2.319 | 2.435 |
| | 2 | 2.488 | |
| | 3 | 2.498 | |
| 180 | 1 | 3.299 | 3.407 |
| | 2 | 3.398 | |
| | 3 | 3.523 | |
| 190 | 1 | 1.612 | 1.565 |
| | 2 | 1.582 | |
| | 3 | 1.502 | |
| 200 | 1 | 0.298 | 0.280 |
| | 2 | 0.276 | |
| | 3 | 0.266 | |

Upon plotting the data, it was observed that a temperature of 178°C yielded the highest 5-HMF production, reaching 3.45% under 0.1M HCl concentration. This was founded by interpolating the data using MATLAB.

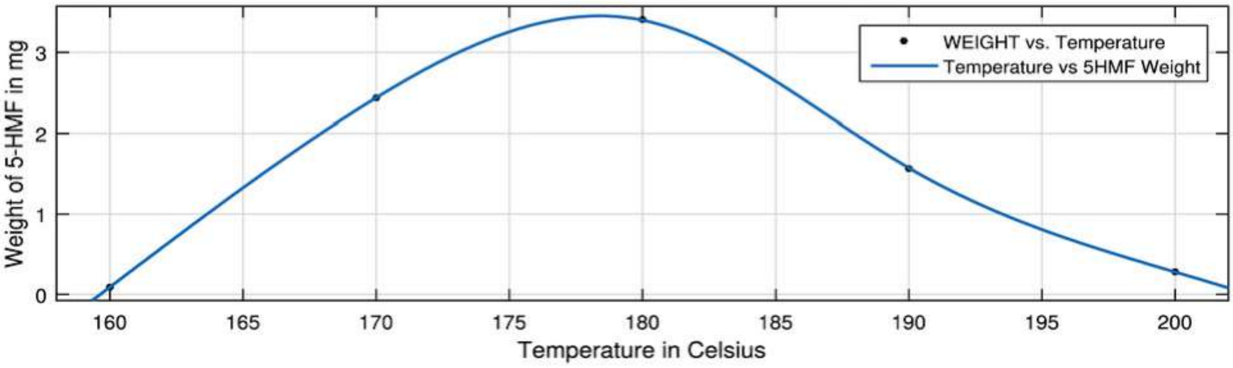

*Figure 1- results summary of temperature vs weight of 5 HMF*

Subsequently, varying the concentration of the HCl solution at 178 °Callowed for the determination of the optimal value, maximizing the yield of 5-HMF.

Analysis of the experimental data indicates a positive correlation between the molarity of HCl and the yield of 5-HMF, with increasing concentrations leading to higher yields up to 0.4M HCl. However, beyond this concentration, the yield of 5-HMF exhibits a diminishing trend as the HCl concentration further increases.

*Table 2- results summary of concentration changes*

| Sulfuric Molarity | 5-HMF weight (mg) |
|---|---|
| 0.1M | 3.505 |
| 0.2 M | 7.818 |
| 0.3M | 21.722 |
| 0.4M | 31.049 |
| 0.5M | 11.716 |

After plotting the data points and analyzing the corresponding graph, it was revealed that the most optimal concentration of HCl solution is 0.3891M, resulting in a remarkable 31.34% yield of 5-HMF.

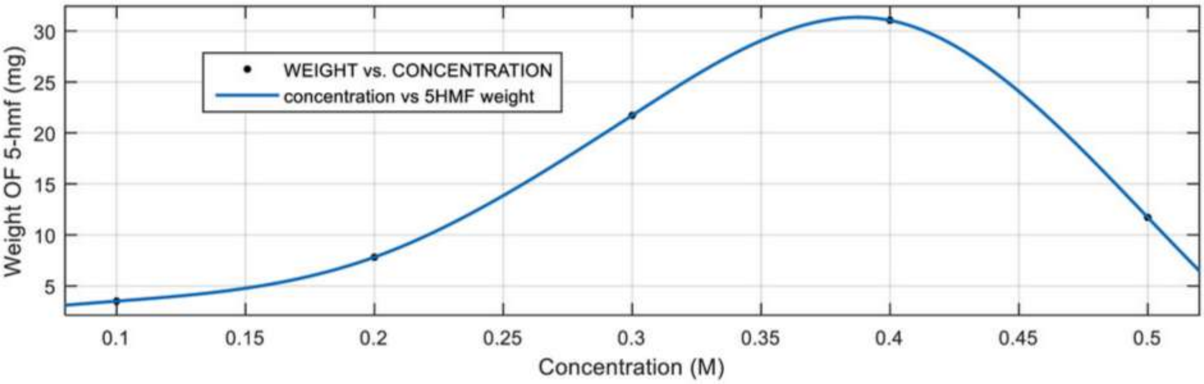

*Figure 2- results distribution of concentration vs weight of 5-HMF at 178* ℃

After carefully referring to all the data that we have collected, we can say that the optimum temperature is 178 ℃ and relevant optimum concentration is 0.3891M for a maximum yield of 5-HMF.

To further enhance the yield of 5-HMF, additional optimization strategies can be explored beyond varying only the temperature and concentration of the secondary reaction process.

1. Variate the concentration of $H_2S0_4$ in the pre-treatment process.

One such approach involves adjusting the concentration of $H_2SO_4$ in the pre-treatment process. While the initial concentration of $H_2SO_4$ was set at 0.1M, determining the optimum concentration can be achieved by conducting the entire reaction system under previously established conditions.

In this optimization process, a choice between concentrated and dilute acid is presented. While concentrated acid may yield higher reaction rates, it carries the risk of equipment degradation and increased operational costs. Moreover, concentrated acid can produce compounds that may inhibit downstream reactions, thereby compromising overall yield. Consequently, the use of diluted $H_2SO_4$ is recommended. Not only is it more cost-effective and less corrosive to equipment, but it also mitigates the risk of unwanted byproducts, making it a more favorable option for scaled-up production of 5-HMF in industrial settings [15].

Then using a diluted acid solution, we can find the optimum concentration values. We can also variate the temperature and time of the $H_2SO_4$ pretreatment process.

The pretreatment of this research was carried out for 40 minutes at 100°C. On the other hand, alternate pretreatment strategies are used either at higher temperatures for a shorter time or lower temperatures for a longer time. Higher temperatures have been shown to have the ability to damage cellulose's structural integrity, which could have a negative impact on the amount of 5-HMF produced [15]. Therefore, have to determine the ideal temperatures for achieving the highest 5-HMF yield.

2. Variate the concentration of ethanol in the cellulose-converting reaction.

Variations in the amount of cellulose extracted throughout the ethanol treatment process have been found to have an impact on the yield of 5-HMF when there are variations in the ethanol concentration. Research has shown that increasing the ethanol concentration causes the yield of lignin to decrease, which then increases the yield of cellulose [16]. It has been found that in comparison to other concentrations, 90% ethanol yielded the least amount of lignin [16]. This result implies that the cellulose yield achieves its maximum value at 90% ethanol concentration, suggesting a possible way to increase the yield of 5-HMF.

## Conclusion

This study has clarified the synthesis of 5-hydroxymethylfurfural (5-HMF) from RS, showcasing its potential as a renewable and sustainable precursor for various industrial applications. The ideal temperature and HCl concentration for the formation of 5-HMF in the secondary reaction were found to be 178°C and 0.3891M respectively, by methodical experimentation and analysis. More optimization techniques were also suggested, such as varying the concentration of sulfuric acid, the temperature and duration of pretreatment, and varying the concentration of ethanol. By investigating these approaches, 5-HMF production can be made as sustainable and efficient as possible, which will progress the development of biomaterials and renewable energy sources. In conclusion, using rice straw as a feedstock for 5-HMF synthesis is a viable way to reduce the reliance on fossil fuels, reduce the environmental impact, and foster the transition towards a more sustainable future.

**Keywords**: 5-Hydroxymethylfurfural (5-HMF), RS , Biphasic system, Sustainable energy, biomass

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