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ORIGINAL RESEARCH ARTICLE

Catalytic conversion of 5-hydroxymethylfurfural to furan derivatives 2,5-dimethylfuran

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ABSTRACT

This study investigates the catalytic transfer hydrogenolysis of 5-hydroxymethylfurfural (HMF) to produce the valuable biofuel 2,5-dimethylfuran (DMF) using a Ni-Co/C catalyst. HMF conversion into DMF offers a promising alternative to fossil fuels, leveraging biomass-derived feedstocks. Key process parameters—temperature (150–270 °C), reaction time (6–10 hours), hydrogen pressure (0.5–2.5 MPa), and reaction speed (150–750 rpm)—were systematically evaluated for their influence on DMF yield. A central composite design and response surface methodology were utilized to optimize these variables, allowing precise control over the reaction conditions. Findings indicated that temperature and reaction speed significantly impacted DMF yield, with the highest yield of 96.5% achieved at an optimal temperature of 210 °C and a reaction speed of 450 rpm under self-generated pressure, reducing dependency on external hydrogen sources. This study proposes a novel reaction pathway where 5-methylfurfural (5-MF) serves as an intermediate, diverging from conventional methods using 2,5-bis(hydroxymethyl)furan (BHMF). The approach substitutes formic acid as a hydrogen donor instead of H_2, contributing to a more sustainable and efficient conversion process. Additionally, the influence of formic acid dosage on HMF conversion and DMF yield was assessed, further refining the conditions for high-yield DMF production. Beyond HMF, the methodology was effective in converting furfural to 2-methylfuran, expanding its applicability to other biomass-derived chemicals. These findings advance the catalytic hydrogenolysis of HMF, presenting a viable pathway for sustainable biofuel production, reducing reliance on fossil fuels, and contributing to the development of green chemistry solutions.

Keywords: clean energy; biomass conversion; catalysis; hydrogenolysis; 2,5-dimethylfuran; 5-hydroxymethylfurfural

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1. Introduction

The lignocellulosic biomass consists of essential chemical components: cellulose, hemicellulose, and lignin[1]. The tissues of various plant types exhibit distinct structures and chemical compositions. Cellulose, typically surrounded by hemicellulose and lignin, forms closely arranged fibers with covalent bonds between lignin and polysaccharide. The hemicellulose is oriented parallel to cellulose fibers.

The conversion of hemicellulose and cellulose varies based on the intended products, with options for simultaneous or separate processing. Simultaneous methods, such as gasification or pyrolysis, offer simplified separation advantages. In contrast, fractionation enables customized processing for each fraction, leveraging the unique chemical properties and physical of hemicellulose and cellulose.

Biomass compounds are often highly functionalized, offering potential for producing a range of chemicals. However, their complexity makes it challenging to control selectivity during upgrading, as multiple parallel and consecutive reactions may take place. This is especially problematic when desired products or intermediates degrade within the reaction environment[2].

One of the most effective methods for processing lignocellulosic materials involves a series of steps. The first step partially removes oxygen, lowering the reactivity of the raw material. The subsequent step modifies the leftover functional groups to facilitate conversion into more valuable chemicals or fuels[3]. This sequential approach helps manage the intricacies of the biomass composition and reactions, ultimately enhancing control and efficiency in the production of desired end products.

Lignocellulosic biomass is primarily composed of two essential biopolymers: polysaccharides (cellulose and hemicellulose) and lignin. The pretreatment stage plays a pivotal role in the conversion of lignocellulosic biomass into sugars, with its primary objective being the separation of polysaccharides from other components. The pretreatment enhances the accessibility of polysaccharides, and hydrolysis is the subsequent process responsible for converting these polysaccharides into sugars[4]. Hydrolysis is a critical step in the efficient conversion of polysaccharides to sugar, particularly for biofuel and bioproduct production from lignocellulosic biomass. This process can be executed using specific enzymes that target the glycosidic bonds within cellulose, cleaving them and releasing soluble sugars. Alternatively, chemical agents such as acids or bases can be employed for hydrolysis. The summarized representation of the pretreatment and hydrolysis of lignocellulosic biomass is illustrated. The high oxygen content in the molecular structure of sugar poses a limitation in biofuel utilization. Therefore, processes aimed at lowering the oxygen content have been investigated. An innovative biorefinery processing technology was introduced to produce HMF and DMF[5]. The HMF serves as the primary product in biorefinery production, acting as an intermediate compound that is typically further converted into DMF[6].

HMF is a multifunctional and versatile furanic compound produced through the dehydration of hexose sugars. Characterized by its yellow color and high water solubility, it serves as an important feedstock for manufacturing industrial solvents. Furthermore, HMF is an essential platform chemical for producing precursors for pharmaceuticals, thermally stable polymers, and macrocyclic compounds. Its applications extend to the production of dialdehydes, amino alcohols, ethers and a variety of organic intermediates. This adaptability allows for the creation of a wide range of chemical products, including solvents, surfactants, phytosanitary agents, and resins[7,8]. HMF has garnered considerable attention because of its potential as a precursor for fuel production, facilitating the synthesis of compounds like C9-C15 alkanes, 5-ethoxymethylfurfural (EMF) and 2,5-dimethylfuran (DMF), ethyl levulinate (EL) as well as important chemicals such as 2,5-dihydroxymethylfurfural (DHMF), levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF)[9].

The utilization of biorefinery processing in converting raw biomass to HMF and its subsequent development into biofuel is illustrated. Various pathways for HMF application include oxidation, hydrogenation, etherification, and rehydration. The advancement of biorefinery processing systems has been a focus of development[10-14]. HMF can be synthesized by dehydrating both fructose and glucose using different catalysts, including phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). Studies have shown that the dehydration of glucose results in a slower reaction rate and lower selectivity for HMF than that of fructose[15]. The HCl and H_2SO_4 exhibited increased HMF selectivity. The introduction of NaCl to create biphasic systems with solvents fully miscible with water aimed to elevate the upper critical solubility temperature of certain partially soluble solvents. The impact of the chosen solvent on HMF yield was thoroughly examined. It indicated that biphasic systems involving C4 solvents yielded the highest HMF, particularly tetrahydrofuran showing the most favorable mixture and achieving a substantial HMF selectivity of 83%[16].

The DMF emerges as a promising renewable fuel candidate derived from biomass. Its utilization aims to diminish the reliance on fossil fuels and curb engine emissions. DMF possesses combustion characteristics similar to commercial gasoline and offers sustainable production when derived from lignocellulosic biomass [17]. The incorporation of biofuels, such as methanol and ethanol, into gasoline for use in transportation fuels, has the potential to significantly reduce dependence on conventional fossil fuels. However, the limitations of methanol and ethanol, for instance, their low heating value, which results in increased transportation costs, and their high water solubility that threatens water security, restrict their practical use[18,19]. DMF has gained considerable interest because of its advantageous characteristics, including a high energy density of 30 MJ/L, a high research octane number (RON = 119), a low oxygen content (O/C = 0.17), and an ideal boiling point of 92-94 °C. Furthermore, DMF's limited solubility in water allows for easier blending with gasoline compared to ethanol. Its low latent heat of vaporization (0.30 kJ cm^{-3}) also contributes to lower energy consumption during distillation, enhancing its efficiency for purification relative to bioethanol[20,21].

Traditional approaches to producing upgraded biofuels or chemical platforms rely on homogeneous and heterogeneous catalysts, as well as biological catalysts like enzymes, microorganisms, and yeasts[22]. The conversion of lignocellulose into DMF involves multiple steps.

The process starts with the pretreatment of lignocellulose to generate glucose, which is then converted into HMF through acid-catalyzed dehydration of its isomer, fructose. The last step involves the catalytic hydrodeoxygenation of HMF, leading to the production of DMF[23, 24]. **Figure 1** illustrates the comprehensive reaction pathway for converting lignocellulosic biomass into DMF.

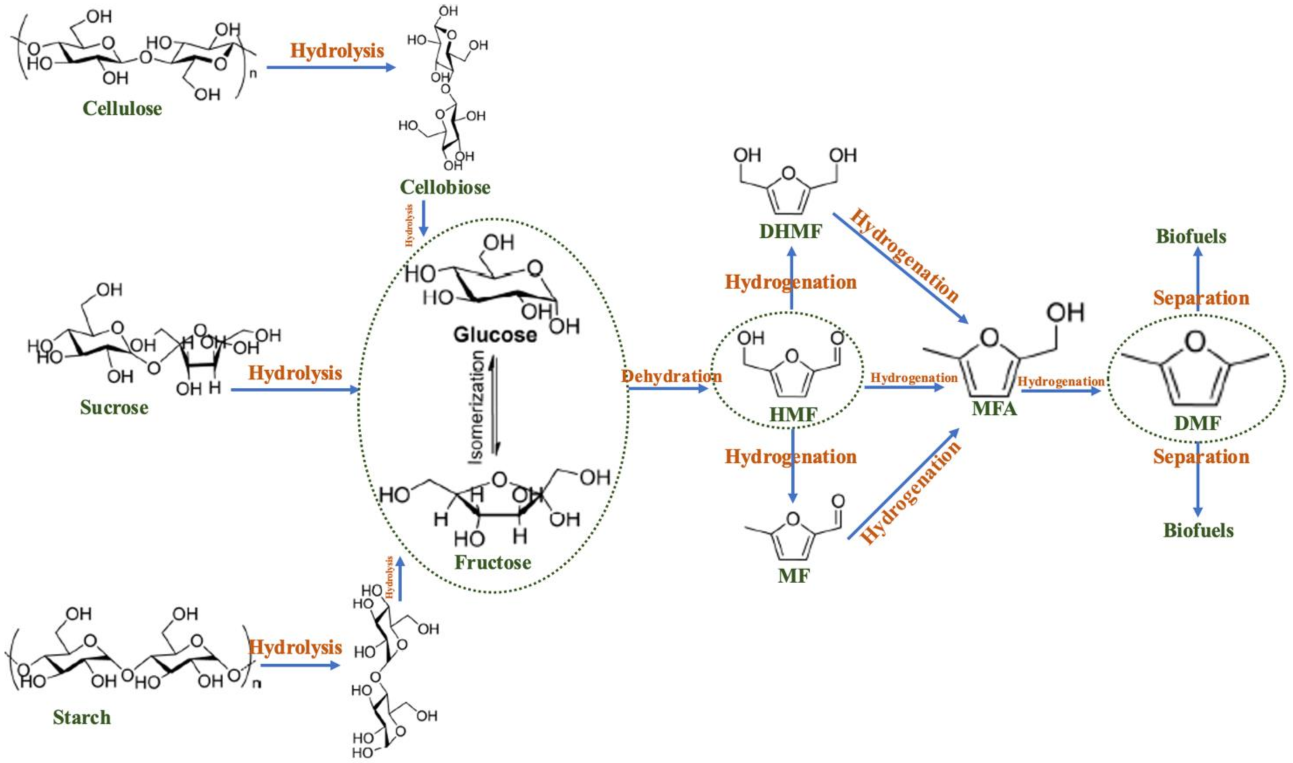

Figure 1. A combined reaction pathway for converting biomass-derived carbohydrates into DMF.

In this work, the catalytic transfer hydrogenolysis of HMF to produce the valuable DMF using a Ni-Co/C catalyst was investigated. The Ni-Co/C catalyst has been known to demonstrate comparable or improved catalytic activity for the hydrogenolysis of biomass-derived furans to DMF. Compared to noble-metal-based catalysts such as Pt, Pd, and Ru, the Ni-Co system exhibited high selectivity while maintaining a reasonable reaction rate, with the metal-support synergy playing a key role in enhancing catalytic performance. Regarding cost, the use of Ni-Co as a bimetallic catalyst provides a cost-effective alternative to noble metals, as both Ni and Co are more abundant and significantly less expensive. The synthesis process also involves relatively inexpensive precursors and scalable techniques, making it more suitable for industrial applications. In terms of sustainability, the non-noble metal-based approach reduces concerns related to resource scarcity and high costs, while the carbon-based support further enhances sustainability due to its renewability and potential for recyclability. Additionally, the catalyst exhibited good stability with minimal metal leaching, which enhances its reusability and reduces waste generation.

2. Materials and methods

2.1. Materials

Nickel 500ml. #A270N00500 (Loba Chemie PVT. Ltd.), Cobalt 500ml. #A130N00500, (Loba Chemie PVT. Ltd.), Carbon 500ml. #A131N00500, (Loba Chemie PVT. Ltd.), 5-Hydroxymethyl furfural 1g. #H40807, Aldrich.

2.1.1. Preparation of catalysts

The Ni-Co/C catalyst was synthesized via a conventional wet impregnation technique. In a typical procedure, 1.976 g of $Co(NO_3)_2{\cdot}6H_2O$ (Sino-Pharm Chemical Reagent Co., Ltd.) and 0.198 g of $Ni(NO_3)_2{\cdot}6H_2O$ (Sinopharm Chemical Reagent Co., Ltd.) were dissolved in 50 mL of deionized water under continuous stirring. Subsequently, 2 g of activated carbon (Aladdin Reagent Limited Company, 40–60 mesh) was added to the mixture. After stirring at ambient temperature for 12 hours, the resulting suspension was dried overnight at 180 °C, followed by reduction under flowing hydrogen at 400 °C for 2 hours in a tubular furnace, with a temperature ramp of 3 °C/min, before being applied as a catalyst[34]. the Ni-Co/C catalyst is expected to exhibit several key properties. A high surface area carbon support is anticipated to promote the uniform dispersion of Ni and Co nanoparticles, thereby increasing the number of accessible active sites. The bimetallic combination of nickel and cobalt is designed to generate a synergistic effect, wherein Ni primarily facilitates hydrogenation reactions, while Co promotes C–O bond cleavage, enhancing the overall hydrogenolysis efficiency. A strong interaction between the Ni-Co alloy and the carbon support is also essential for maintaining catalyst stability by minimizing metal leaching or sintering during the reaction. Furthermore, the catalyst should exhibit good reducibility under mild conditions, ensuring the availability of active metallic sites critical for hydrogen transfer and bond cleavage. High resistance to deactivation is desirable, allowing the catalyst to maintain its performance across multiple reaction cycles without significant loss of activity, particularly in terms of thermal stability and resistance to coke formation or metal oxidation. Finally, the catalyst is expected to be compatible with green chemistry principles by utilizing environmentally benign hydrogen donors such as isopropanol and operating under relatively mild reaction conditions.

2.2. Methods

2.2.1. Experimental Setup and Procedure

In this experiment, a stainless steel autoclave with a capacity of 50 mL that is equipped with a magnetic stirring bar was charged with 0.200 g of catalyst, 0.252 g of HMF, 0.920 g of formic acid, 10 mL of tetrahydrofuran (THF), and 0.245 mL of tridecane (which served as an internal standard). The reactor underwent several rounds of nitrogen pressurization to remove any air prior to being heated to the desired temperature. Following the reaction, the autoclave was rapidly cooled to room temperature, and the solid catalyst was filtered out from the reaction mixture. The resulting filtrate was analyzed with an Agilent 7890 GC using a FID detector and an HP-5 column, and further structural characterization of the products was performed using GC-MS. The yield of DMF was calculated as follows:

$$Yield = \frac{Moles\ of\ DMF}{Moles\ of\ HMF} \times 100\% \tag{1}$$

The allied study on the NiCo/C catalyst for conversion of furan into DMF was the initial removal of oxygen atoms through acid-catalyzed dehydration, resulting in HMF. The HMF is then extracted in the organic phase of the reactor and further transformed into DMF through hydrogenolysis of C-O bonds facilitated by a NiCo/C catalyst. The effect of process parameters including temperature (150-270 °C), reaction time (6-10 hours), H_2 pressure (0.5-2.5 MPa), and reaction speed (150-750 rpm) in **Figure 2**.

In this study, the use of the NiCo/C catalyst was of interest because The NiCo/C catalyst is highly suitable for the conversion of furan into 2,5-dimethylfuran (DMF) due to the synergistic effects of the bimetallic components—Ni and Co—and the C support. Nickel is particularly effective in hydrogenation reactions, facilitating the addition of hydrogen to the furan ring, which is a critical step in the formation of DMF. Cobalt, on the other hand, enhances the activation of C-O bonds and contributes to the overall reaction kinetics, ensuring efficient conversion. The interaction between Ni and Co improves the catalytic activity compared to using either metal alone, allowing for an optimal balance of hydrogenation and dehydrogenation reactions. The carbon support plays a crucial role in stabilizing the metal nanoparticles, improving their dispersion, and providing a high surface area for reactant interaction. This high surface area facilitates better contact between the catalyst and furan molecules, increasing the reaction efficiency. Additionally, the NiCo/C catalyst operates effectively under mild reaction conditions, which is advantageous for selectively hydrogenating furan to DMF while minimizing side reactions. Together, these features make NiCo/C an ideal catalyst for the efficient and selective conversion of furan into 2,5-dimethylfuran.

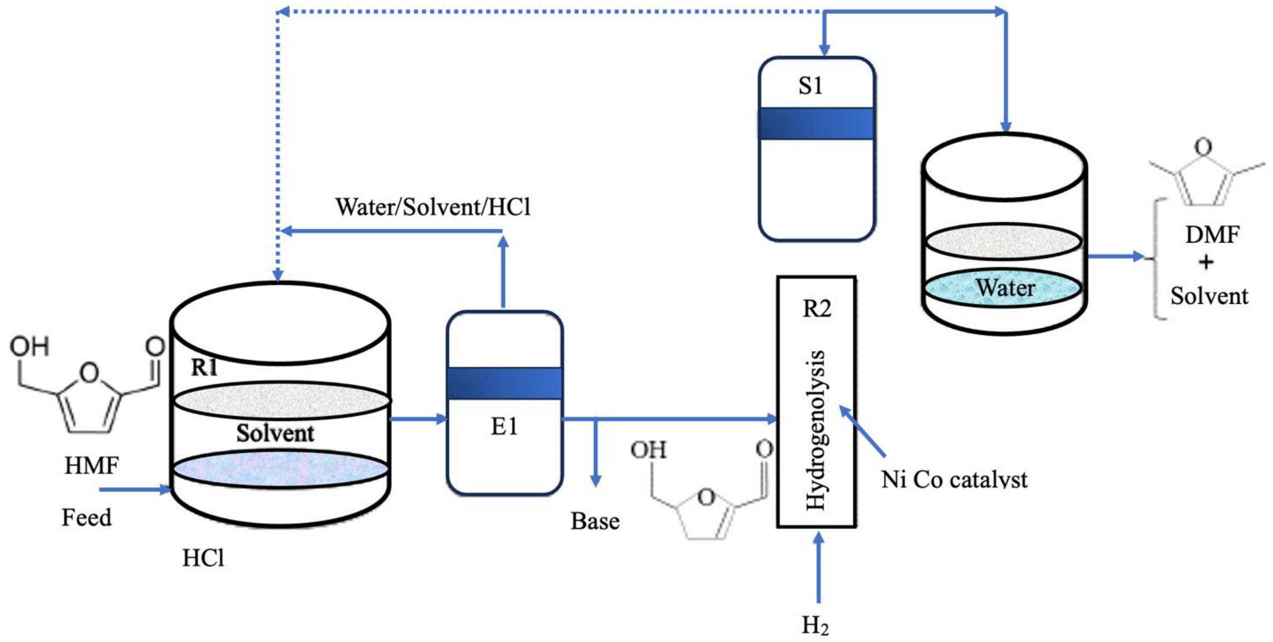

Figure 2. The process of producing DMF from different feedstocks using a carbon-supported Ni/Co catalyst system.

2.2.2. The Design of Experiments

The experiments were conducted with temperature ranging from 150 to 270 °C, time from 6 to 10 h, H_2 pressures between 0.5 and 2.5 MPa and the reaction speed varying from 150 to 750 rpm. The objective was to examine the connection between these process parameters and optimize the DMF yield using response surface methodology (RSM) and central composite design (CCD). For the generation of experimental conditions, statistical analysis, and the creation of regression models, Minitab software (Minitab Inc., USA) version 16 was employed. The study focused on four numerical factors: reaction temperature (X_1), reaction time (X_2), H_2 pressure (X_3) and reaction speed (X_4). The spectrum of independent variables and the corresponding experimental levels is detailed in **Table 1**. The required number of runs was determined by CCD and RSM to produce reliable measurements of the target response for optimization [25,26]. The study involved 31 experimental runs, comprising sixteen factorial points, eight axial points, and seven center points. The two axial points on each design variable axis were positioned at a distance α of 2. Each of the 31 tests was conducted, and every condition was repeated a minimum of three times, resulting in a total of 91 experimental runs for DMF yield analysis.

Equations for the models and response surface plots were developed based on the experimental data. The models were validated through a comparison of the outcomes. with those achieved in the experiments and refined to identify the conditions that yielded the maximum DMF conversion. The collaboration between CCD and RSM facilitated the determination of the effect of temperature, reaction time, H_2 pressure and speed of DMF conversion. The data for each DMF yield were plotted using the subsequent second-order polynomial equation.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k} \beta_{ii} x_j + \varepsilon \tag{2}$$

where Y represents the response variable (Conversion of HMF); X_i and X_j are variables (interpreted as independent process factors); β_0, β_i, β_{ii}, and β_{ij} (i = 1, 2, i < j and k > j) are the regression coefficients, respectively.

Table 1. The range and coded levels of the process variables applied in the CCD.

Factor	Symbol	The range and coded levels of the process parameters -α = -2	-1	0	+1	+α =+2
Temperature (°C)	X_1	150	180	210	240	270
Time (hour)	X_2	6	7	8	9	10
H_2 Pressure (MPa)	X_3	0.5	1.0	1.5	2.0	2.5
Speed (rpm)	X_4	150	300	450	600	750

3. Results and discussion

The experimental findings from trials 31 scenarios for the statistical design of DMF production from HMF are detailed in **Table 2**. DMF conversion ranged from 62.8% to 96.5%, depending on the experimental conditions. To evaluate the model's adequacy and the importance of the process parameters affecting DMF conversion, an analysis of variance (ANOVA) [27] was performed, with results presented in **Table 3**. The R^2 value for the DMF conversion model was 0.7965, indicating a strong correlation between the experimental and predicted outcomes, where an R^2 value of 1 signifies complete agreement [28,29]. The significance of each term was assessed by analyzing the p-value and f-value at the specified confidence level. The p-value is essential for determining whether to reject the null hypothesis, with a smaller p-value indicating a greater contribution to the outcome variable and its associated coefficient. A high F-value denotes a highly significant variable [30,31]. In this study, ANOVA was conducted at a 95% confidence threshold, revealing that variables with significant importance and significant impacts on the outcome were associated with elevated f-values and reduced p-values (<0.05) [32,33], as demonstrated as indicated in **Table 3**. In the statistical evaluation, two linear terms (X_1, X_4) and two quadratic terms (X_1^2, X_4^2) were identified as statistically significant for DMF yield at the 95% confidence level. The order of importance for each model term was as follows: X_1^2 (temperature squared), X_4^2 (reaction speed squared), X_4 (reaction speed), X_1 (reaction temperature). The regressive polynomial model for DMF yield (Y_{DMF}) is provided as follows:

$$Y_{HMF} = -275.7 + 2.938x_1 + 0.2168x_4 - 0.00687x_1^2 - 0.000218x_4^2 \tag{3}$$

where, Y_{DMF} = DMF yield (%), X_1 = reaction temperature °C), X_4 = reaction speed (rpm).

Table 2. Experimental design and response of DMF yield.

Run No.	Variable (Uncoded)				DMF yield (%)
	Temperature (°C), X_1	Time (hour), X_2	H_2 Pressure (MPa), X_3	Speed (rpm), X_4	
1	180	7	1	300	62.8
2	240	7	1	300	78.5
3	180	9	1	300	70.8
4	240	9	1	300	74.3
5	180	7	2	300	65.4
6	240	7	2	300	72.9
7	180	9	2	300	77.3
8	240	9	2	300	86.7
9	180	7	1	600	73.5
10	240	7	1	600	69.5
11	180	9	1	600	72.8
12	240	9	1	600	80.9
13	180	7	2	600	87.2
14	240	7	2	600	85.5
15	180	9	2	600	84.7
16	240	9	2	600	79.8
17	150	8	1.5	450	74.3
18	270	8	1.5	450	76.4
19	210	6	1.5	450	90.8
20	210	10	1.5	450	92.5
21	210	8	0.5	450	93.7
22	210	8	2.5	450	89.7
23	210	8	1.5	150	73.3
24	210	8	1.5	750	87.6
25	210	8	1.5	450	96.5
26	210	8	1.5	450	95.5
27	210	8	1.5	450	97.5
28	210	8	1.5	450	96.5
29	210	8	1.5	450	94.5
30	210	8	1.5	450	96.5
31	210	8	1.5	450	98.5

Table 3. Experimental design and results for DMF yield.

Origin	Sum of squares	Mean square	f-value	p-value
Models	2650.74	189.34	4.34	0.0038
X_1	59.53	59.53	1.36	0.260
X_2	52.21	52.21	1.20	0.290
X_3	97.61	97.61	2.24	0.154
X_4	226.94	226.94	5.20	0.037

Origin	Sum of squares	Mean square	f-value	p-value
X_1^2	1277.28	1277.28	29.26	0.000
X_2^2	194.55	194.55	4.46	0.051
X_3^2	192.69	192.69	4.41	0.052
X_4^2	836.43	836.43	19.16	0.000
$X_1 X_2$	0.12	0.12	0.00	0.958
$X_1 X_3$	10.56	10.56	0.24	0.629
$X_1 X_4$	93.12	93.12	2.13	0.163
$X_2 X_3$	0.56	0.56	0.01	0.911
$X_2 X_4$	45.56	45.56	1.04	0.322
$X_3 X_4$	37.82	37.82	0.87	0.366
R^2	0.7915	Adj. $R^2 = 0.6090$		

Table 3. (*Continued*)

The predicted and experimental values exhibited minor discrepancies, underscoring the model's performance. The optimization process targeted achieving the highest DMF yield from HMF utilizing RSM. The polynomial model equation was solved using Minitab software to identify the optimum conditions. The optimal conditions were found to be a reaction temperature (X1) of 210 °C and a reaction speed (X4) of 450 rpm. These conditions resulted in a DMF yield of 96.5%, as illustrated in **Figure 3**.

Reaction temperature and reaction speed are critical factors in optimizing the process to achieve the highest DMF yield from HMF due to their influence on the chemical reaction kinetics and overall efficiency. The reaction temperature plays a significant role by affecting the activation energy required for the reaction to proceed. A higher temperature increases the rate of reaction by providing more energy to the molecules, helping them overcome the activation barrier more easily, which can lead to higher DMF yields. However, temperature must be carefully controlled, as temperatures that are too high can cause undesirable side reactions or degradation of HMF or DMF, ultimately reducing the yield. On the other hand, reaction speed, or stirring rate, influences the efficiency of mass transfer and the interaction between reactants and catalysts. Faster stirring ensures more uniform mixing of HMF and the catalyst, improving conversion efficiency. At optimal reaction speeds, the catalyst is more effective, leading to a more complete conversion of HMF to DMF. If the reaction speed is too slow, the catalyst may become less efficient, and the reaction may not proceed to completion, which can lower the DMF yield. Therefore, both temperature and reaction speed must be optimized to balance reaction efficiency and selectivity, ensuring the highest possible yield of DMF while minimizing byproducts or degradation.

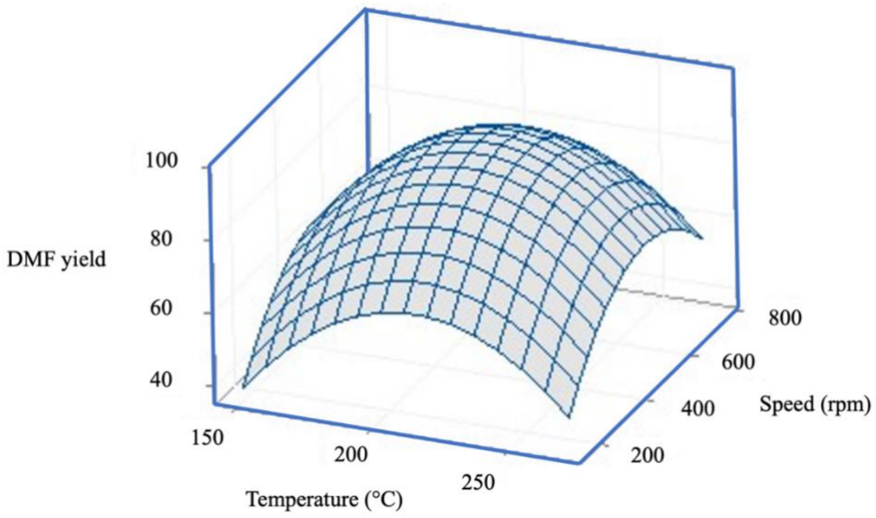

Figure 3. Response surface plot illustrating the effect of reaction temperature and reaction speed on DMF yield.

To scale the findings from this study to large-scale biofuel production, several factors need to be considered. First, the catalyst system (Ni-Co/C) must be evaluated for cost-effectiveness, availability, and efficiency at a larger scale. Alternative catalysts could be explored to improve scalability. Operational parameters like temperature, reaction speed, and hydrogen pressure, which were optimized for high yields in the study, need to be tested in larger systems to ensure energy efficiency and cost-effectiveness. Additionally, the energy requirements for heating, maintaining pressure, and mixing during the reaction must be optimized. Finally, reactor design and reaction kinetics should be further refined to ensure the process can be integrated effectively into existing biofuel production systems while maintaining high yields and efficiency.

The stability of the Ni-Co/C catalyst was studied to determine its durability and effectiveness during the hydrogenolysis of 5-HMF to DMF. After the reaction, potential changes in the physical and chemical properties of the catalyst were assessed. These changes may include particle sintering, metal oxidation, or alterations in the metal-support interaction, which could influence catalytic performance. A reduction in active metal dispersion or an increase in particle size could lead to decreased catalytic activity and selectivity. Additionally, potential leaching of Ni and Co species into the reaction medium was considered, as this could reduce catalyst stability and long-term usability. Characterization techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and inductively coupled plasma optical emission spectroscopy (ICP-OES) were employed to analyze these changes. If significant metal leaching occurred, it could indicate weak metal-support interactions, leading to reduced catalytic efficiency over multiple reaction cycles. Overall, the stability of the Ni-Co/C catalyst is crucial for maintaining high selectivity and activity, and further optimization may be necessary to enhance its resistance to deactivation.

The proposed reaction pathway, which involves 5-HMF as an intermediate, offers a unique approach compared to traditional routes for the production of DMF. Conventional methods typically rely on direct hydrogenation of furfural or 5-HMF using noble-metal catalysts such as Pd, Pt, and Ru. While these methods often achieve high DMF yields, they may require harsher reaction conditions or expensive catalysts, which limit their scalability. In contrast, the pathway investigated in this study leverages the selective hydrogenolysis of 5-HMF over a Ni-Co/C catalyst, which promotes high selectivity toward DMF while avoiding excessive hydrogenation of the furan ring. This approach enhances efficiency by optimizing reaction steps and minimizing undesired side reactions. Furthermore, the bimetallic synergy between Ni and Co facilitates effective C–O bond cleavage, leading to improved catalytic performance under milder conditions. Regarding yield, the study demonstrates that the proposed pathway achieves a competitive DMF yield compared to conventional methods. Additionally, the catalyst exhibits good stability and reusability, contributing to overall process efficiency. A comparison of key reaction parameters, such as temperature, pressure, solvent, and catalyst performance, would further highlight the advantages of this novel approach over traditional routes.

The reaction parameters examined in this study include temperature, hydrogen pressure, reaction time, and reaction speed. These parameters were selected based on their significant influence on the catalytic hydrogenolysis of 5-HMF to DMF.

Temperature is a crucial reaction parameter that significantly influences the catalytic hydrogenolysis of 5-HMF to DMF. In this study, the reaction temperature was carefully selected based on its impact on catalyst activity, reaction kinetics, and product selectivity. Temperature affects both the reaction rate and product distribution. Higher temperatures generally enhance reaction kinetics and facilitate hydrogen activation, but excessively high temperatures may lead to undesirable side reactions, such as coke formation or further hydrogenation of DMF. On the other hand, lower temperatures may result in incomplete conversion due to insufficient activation energy. The selected temperature range was based on previous literature and preliminary experiments that demonstrated optimal catalytic performance for Ni-Co/C. The chosen temperature ensures a balance between high DMF yield and minimal byproduct formation, while also maintaining catalyst stability over prolonged reactions.

Hydrogen pressure is a key reaction parameter that directly influences the hydrogenolysis of 5-hydroxymethylfurfural (5-HMF) to 2,5-dimethylfuran (DMF). The hydrogen pressure determines the availability of hydrogen species for catalytic conversion and affects both reaction kinetics and product selectivity. Hydrogen pressure plays a crucial role in the hydrogenation and hydrogenolysis steps. Insufficient hydrogen pressure may lead to incomplete conversion of 5-HMF, resulting in intermediate products or byproduct formation. Conversely, excessively high hydrogen pressure can promote over-hydrogenation, leading to unwanted side products such as tetrahydrofuran derivatives. The selected pressure range was based on literature reports and preliminary experiments to optimize the yield of DMF while minimizing side reactions. The chosen pressure ensures efficient hydrogenation of the furan ring while maintaining selectivity toward DMF rather than further hydrogenation to over-reduced products.

Reaction time is a crucial parameter in the hydrogenolysis of 5-hydroxymethylfurfural (5-HMF) to 2,5-dimethylfuran (DMF), as it influences both conversion efficiency and product selectivity. The duration of the reaction affects the extent of hydrogenolysis, determining whether 5-HMF is fully converted into DMF or whether intermediate products, such as 2,5-bis(hydroxymethyl)furan (BHMF) and 2-methylfuran (MF), accumulate. Longer reaction times may also lead to catalyst deactivation due to carbon deposition (coking) or undesired side reactions. The chosen reaction time was based on preliminary optimization experiments and literature reports, ensuring sufficient time for high DMF yield while minimizing side product formation. A balance was sought between maximizing efficiency and preventing over-hydrogenation or catalyst degradation.

Reaction speed is another critical reaction parameter that influences mass transfer and catalyst-substrate interaction. In this study, the stirring speed was carefully selected to ensure efficient mixing and uniform dispersion of reactants while minimizing mass transfer limitations. Stirring speed affects the diffusion of reactants to the catalyst surface and the removal of products from active sites. Insufficient stirring may lead to mass transfer limitations, reducing reaction efficiency, while excessive stirring could lead to catalyst attrition or mechanical degradation. The selected rpm ensures optimal interaction between the catalyst and reactants, preventing sedimentation and improving hydrogen gas dissolution in the reaction medium. The chosen value balances reaction efficiency and catalyst stability based on previous studies and experimental optimization.

To enhance the catalytic activity and improve the yield of DMF, future works should focus on catalysts with the following key properties:

1. High hydrogenation and hydrogenolysis activity – The catalysts should facilitate efficient hydrodeoxygenation while minimizing undesired side reactions. The optimization of metal composition and electronic properties could enhance selective C–O bond cleavage.
2. Strong metal-support interaction – Enhanced interaction between active metal species (e.g., Ni, Co, or other transition metals) and the support material can improve stability, prevent metal leaching, and maintain catalytic activity over multiple cycles.
3. Acid-base balance – Proper tuning of acidic and basic sites on the catalyst surface can influence reaction selectivity and minimize side reactions leading to coke formation or over-hydrogenation.
4. Thermal and chemical stability – Resistance to sintering and deactivation under reaction conditions is crucial for long-term usability.
5. Porosity and surface area – A high surface area and well-defined porosity can enhance reactant accessibility to active sites, improving conversion efficiency.

4. Conclusion

This study explores the potential of biomass as a sustainable resource for biofuel production through the HMF pathway. HMF, a key intermediate, can be synthesized using Ni-Co/C catalysts or via hydrogenation. The research focuses on evaluating the effects of reaction parameters, including temperature, time, hydrogen pressure, and reaction speed, on the yield of DMF. A fixed amount of Ni-Co/C catalyst (1.976 g of $Co(NO_3)_2 \cdot 6H_2O$) was utilized, with experimental design and analysis conducted using CCD and RSM. The study achieved a maximum DMF yield of 96.5% under optimal conditions: a reaction temperature of 210 °C and a reaction speed of 450 rpm. This result underscores the efficiency of the process and its potential for scalability in biofuel production. The findings emphasize the importance of optimizing operational parameters to maximize yield and highlight the promise of the HMF-based method for further exploration. Future investigations should focus on employing alternative catalysts to enhance the versatility and efficiency of the process.

Author contributions

NC: Data Curation, Formal Analysis, Visualization & Writing – Original Draft, **PP:** Formal Analysis, Methodology & Writing – Original Draft, **NT:** Conceptualization, Supervision, Funding Acquisition, Methodology, Supervision & Writing – Review & Editing.

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Conflict of interest

The authors declare no conflict of interest.

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