

# Selective Production of Gasoline Fuel Blendstock from Methanol using a Metal-doped HZSM-5 Zeolite Catalyst

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**Abstract.** The increasing demand for substitutes for petroleum has become a global concern due to the looming petroleum crisis and the need to reduce carbon dioxide emissions. This study seeks a viable approach for converting methanol into petrochemicals and fuel-range hydrocarbons. A ZSM-5 zeolite catalyst was synthesised and modified with 0.5 wt% transition metals (Co and Ni) to improve selectivity towards the desired liquid product (gasoline) in the methanol-to-hydrocarbon (MTH) conversion. The synthesised catalyst was characterised using various techniques. The catalysts were further evaluated for methanol conversion into fuels and petrochemicals (BTX) under varying weight hourly space velocity (WHSV) (7 and 12 h<sup>-1</sup>) at 350 °C. Results showed that the synthesised catalyst exhibited characteristic features of a typical MFI framework of a zeolite catalyst. The catalyst evaluation results revealed that changes in operating conditions affected product distribution. A WHSV of 12 h<sup>-1</sup> favoured the production of gasoline range hydrocarbons (C<sub>5</sub>-C<sub>12</sub>) with a yield of over 80 % for all catalysts. In addition, C<sub>12</sub><sup>+</sup> hydrocarbons were produced with a selectivity of 12.6 %, 0.7 % and 7.5 % for Ni-doped, Co-doped and HZSM-5 catalysts, respectively. In particular, the Co-doped catalyst showed a 7.1 % higher BTX yield under these specific operating conditions (12 h<sup>-1</sup> and 350 °C). Compared to 7 h<sup>-1</sup>, increasing the WHSV to 12 h<sup>-1</sup> favoured the production of liquid hydrocarbons. Incorporating a small amount of transition metal into the parent catalyst improved the selectivity of the target products and overall liquid hydrocarbon yield. The results concluded that the synthesised catalyst is promising for the MTH process, and catalytic performance can be enhanced by metal modification and optimising reaction conditions to improve biofuel production.

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## 1 Introduction

Zeolites are natural aluminosilicates characterised by their crystalline and microporous structure [1, 2]. Their unique structure has facilitated their use in various fascinating applications, including catalysis, adsorption, and water filtration [3-5]. Zeolites, known for their exceptional properties such as high activity, strong acidity, shape specificity, thermal stability, and cation exchange capacity, occupy a prominent position as solid acid catalysts in oil refining and petrochemicals. Zeolites possess remarkable catalytic capabilities in petrochemical processes such as cracking, isomerisation, aromatisation, and alkylation, which has motivated researchers to explore their potential for future catalytic applications [6-8]. The extensive use and successful commercialisation of zeolite catalysts have led to continuous advances in hydrothermal synthesis techniques. Since developing the first zeolite synthesis technology in the 1940s, various microporous and macroporous materials with different frameworks and morphologies have become accessible [9]. These materials have found applications in various fields. In hydrothermal synthesis, the predominant technique for zeolite production, reaction media containing ionic solutions are subjected to non-ideal and non-equilibrium conditions in hermetically sealed vessels at supercritical or near-supercritical temperatures. These conditions effectively activate the reaction media, leading to significant changes in their physicochemical properties and the formation of unique microporous structures [9]. However, most hydrothermal processes for zeolite synthesis require a certain temperature (80-200 °C), pressure (1-100 MPa) and reaction time (1-20 days), which contributes to the high energy requirements of the process [9-12].

To further optimise the catalytic activity of ZSM-5 catalysts, the introduction of metal species has been used to modify ZSM-5 zeolites and increase the specificity of aromatics and liquid fuel hydrocarbons in the reaction of low alcohol to hydrocarbon [13]. The incorporation of metals into the ZSM-5 zeolite framework has improved the catalytic performance during the low alcohol conversion. Metal modification of HZSM-5 catalysts, including through impregnation or ion exchange, alters their acidity and texture, resulting in varying levels of catalytic activity [14-16]. For example, introducing nickel into ZSM-5 catalysts led to an appropriate acid strength and enhanced hydrothermal stability, reducing coking and dealumination during ethanol-to-gasoline conversion (ETG) [15]. Metals contribute actively to the dehydrogenation of alkanes, leading to the formation of olefins. Subsequently, the olefins are protonated on acid sites, forming carbenium ions, which undergo isomerisation, cracking and reverse stages [17]. Calsavara, et al. [18] synthesised Fe/ZSM-5 zeolites through a combination of direct synthesis and post-ion exchange, and regardless of the iron inclusion method, the partial substitution of framework  $Al^{3+}$  by  $Fe^{3+}$  (0.3–0.5 wt% Fe) resulted in prolonged catalyst life and considerable production of liquid hydrocarbons. This is due to the lower acidity of framework  $Fe^{3+}$  compared to framework  $Al^{3+}$  since framework  $Fe^{3+}$  replaces framework  $Al^{3+}$  [18]. Wang, et al. [19] synthesised mesoporous Zn/ZSM-5 zeolite by directly incorporating zinc into the alkali treatment process. The presence of  $ZnOH^+$  species in the material gradually improves the selectivity of benzene, toluene and xylene (BTX) and liquid hydrocarbons as the amount of incorporated zinc increases [19]. Similarly, Ni, et al. [20] synthesised nano-H [Zn, Al] ZSM-5 by a one-step hydrothermal synthesis, resulting in a catalyst with high selectivity for liquid hydrocarbons and robust catalytic stability.

A limitation of zeolites is their limited pore size, which significantly restricts the passage of large molecules, making them unsuitable for the catalysis reactions involving such molecules [21]. The preparation of zeolites with meso/macroporous pore structures represents an optimal solution to overcome this limitation. Some zeolites with larger surface area and porosity have better catalytic performance than normal zeolites [22]. Therefore, this study aims to synthesise a novel ZSM-5 zeolite catalyst with improved

mesoporous structures and modify the catalyst with a transition metal to improve the catalytic performance in methanol conversion to hydrocarbons. Also, the effect of WHSV on methanol conversion to hydrocarbons was evaluated.

## 2 Methods

### 2.1 Catalyst Synthesis, Characterisation and Evaluation

The synthesis and characterisation of the metal-doped HZSM-5 catalyst have provided valuable insights into its potential as a promising catalyst for bioethanol conversion into aromatics and hydrocarbons. The hydrothermal method was used to synthesise the mesoporous ZSM-5 support catalysts using the molar ratio  $10\text{Na}_2\text{O} : 40\text{SiO}_2 : 1.0\text{Al}_2\text{O}_3 : 10.5\text{TPABr} : 3740.6\text{H}_2\text{O}$  by mixing an appropriate amount of TPABr as the organic structure-directing agent, aluminium sulfate, and water glass as the aluminium and silica source. At the same time, the dry impregnation technique was employed to introduce Co and Ni species, which ensured the successful incorporation of metal species without compromising the catalyst framework and crystalline phase of the standard ZSM-5. The resulting catalyst was denoted Co- and Ni-doped for 0.5 wt% Co- and Ni-doped catalysts. The synthesised catalyst was characterised using different methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier transform infrared (FT-IR), and  $\text{N}_2$  adsorption. The pure and metal-modified catalysts' catalytic performance in converting methanol to hydrocarbons was evaluated at temperatures of 350 °C and weight hourly space velocities (WHSV) of 7 and 12  $\text{h}^{-1}$ . Furthermore, gaseous and liquid hydrocarbons were analysed during the catalytic process using a YL6500 gas chromatograph (GC).

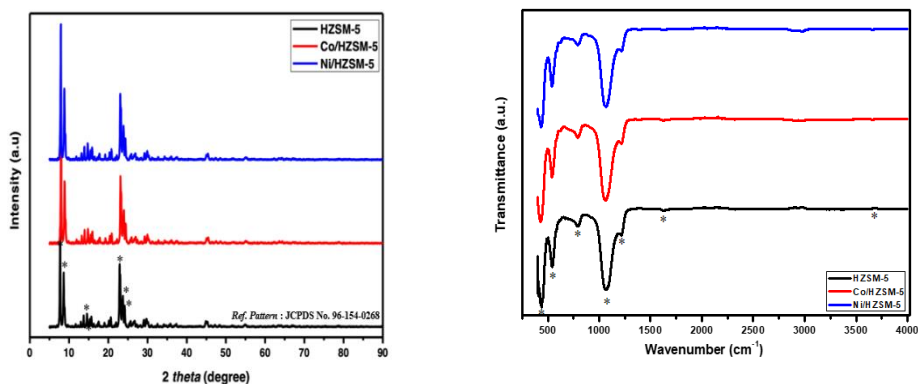
## 3 Results and Discussion

### 3.1 Catalyst Characterisation Results

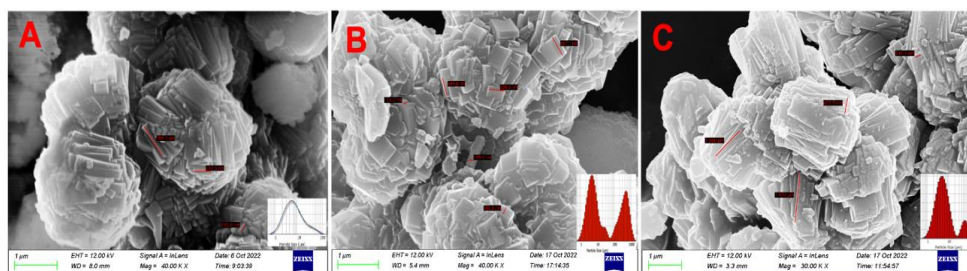
#### 3.1.1. XRD, FTIR and SEM Results

Various characterisation techniques were employed to investigate the properties of the as-synthesised catalysts thoroughly. The crystalline structure of both pure ZSM-5 and Fe-doped ZSM-5 was carefully examined using a Bunker D2 Phase X-ray diffractometer (XRD). Through XRD analysis, we confirmed that the synthesised catalysts maintained the characteristic crystalline phase of standard ZSM-5 after metal doping, displaying distinct peaks at  $2\theta = 7.9^\circ, 8.9^\circ, 14.8^\circ, 23.1^\circ, 23.3^\circ,$  and  $24.0^\circ$ , indicating the successful incorporation of iron species without compromising the overall structure (Fig. 1a). The functional groups in the catalysts were identified using a Perkin Elmer Fourier Transform-Attenuated Total Reflectance-Infrared Spectrometer Sprecum-2. This analysis revealed that the metal-doped catalysts retained their typical functional groups of HZSM-5, providing evidence of preserving essential chemical interactions within the zeolite framework (Fig. 1b). The morphology of the samples was studied using scanning electron microscopy (SEM) with the ZEISS Sigma 300 VP microscope. The high-magnification images showcased the formation of microspheres through the aggregation of nano-sized crystals, hinting at the unique structural properties of the catalyst (Fig. 2). Furthermore, micrographs revealed that the addition of Fe species did not alter the overall morphology of the zeolite, which is crucial for maintaining its catalytic performance. Within the SEM

images, inset graphs depict the particle size distribution (PSD), revealing a particle size range from 0.1 to 100  $\mu\text{m}$ .



**Fig 1.** XRD (a) and FTIR (b) spectra of unmodified and Fe-doped catalysts.



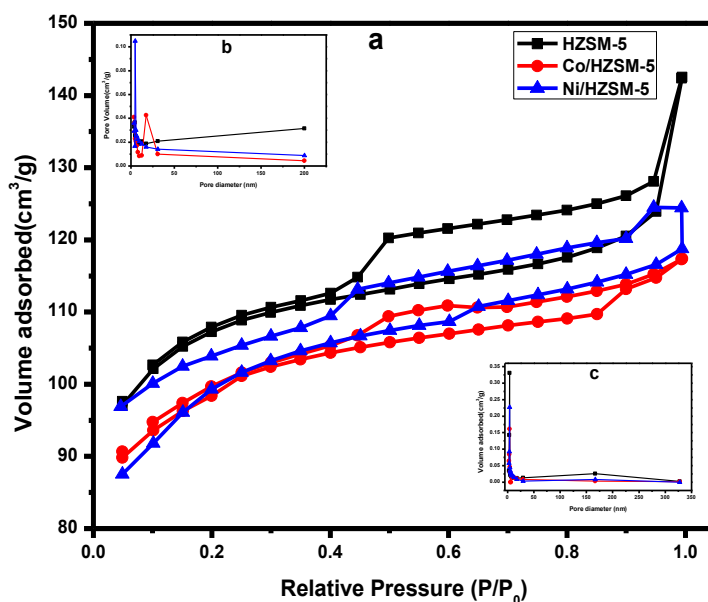
**Fig 2.** SEM images of unmodified (a), Ni-doped (b), and Co-doped (c) catalysts. The inset graph showed the particle size distribution of synthesised catalysts.

### 3.1.2. Textural Properties and $\text{NH}_3$ -TPD Results

The ZSM-5 zeolites' surface area and porous properties were determined using  $\text{N}_2$  adsorption-desorption analyser, allowing for an in-depth assessment of their porosity and surface characteristics. Notably, the presence of mesopores in the zeolite structure was observed, and the introduction of metal species appeared to impact the pore structure, suggesting potential changes in the catalyst's textural properties due to the presence of metal species. A decrease in surface area (from 398  $\text{m}^2/\text{g}$  (HZSM-5) to 381 and 363  $\text{m}^2/\text{g}$ ), total pore volume (from 0.71 to 0.59 and 0.46  $\text{cm}^3/\text{g}$  for 0.5wt% Ni and Co, respectively) and also a reduction in mesopores volumes was observed with the introduction of the metal species by 0.10 and 0.22  $\text{cm}^3/\text{g}$  respectively (Table 1). This can be due to the metal accumulation and blockage of the surface of zeolite channels by the metal species. The catalysts showed a type IV isotherm with a hysteresis loop, revealing a mesoporous structure in the catalyst's framework (Fig. 3). The diagram shows that both the pure ZSM-5 zeolite and the metal-doped ZSM-5 zeolites exhibited similar  $\text{N}_2$  adsorption-desorption isotherms. Moreover, the adsorption and desorption curves nearly overlapped at relatively low pressure, indicating that the macro-mesoporous structures were well preserved after the metal was incorporated. The inset Figures (3b and c) show the BJH pore size distribution for adsorption and desorption of the synthesised catalysts, revealing the presence of considerable mesopores. The presence of mesopores in the zeolite structure was evident

from the isotherms, and intriguingly, the adsorbed volume decreased with metal incorporation, indicating possible changes in pore structure due to the presence of metal species. The adsorbed volume for the Ni-doped catalyst was notably higher when compared to that of the Co-doped catalyst. This observed difference in adsorption volume directly correlates with the respective surface areas of these catalysts. The appreciable adsorption capacity of these catalysts suggests that they possess a sufficient accessible surface area for reactant molecules to interact with, potentially leading to enhanced catalytic performance and specificity in the reaction system [23-25]. This underscores the significance of surface area in catalyst performance and offers valuable insights into optimising catalytic processes.

Table 2 shows the NH<sub>3</sub>-TPD results indicating the presence of three different peaks at different temperatures. The release of ammonia at lower temperatures, indicating weak acid sites, increased from 950 μmol g<sup>-1</sup> NH<sub>3</sub> in HZSM-5 to 1050 μmol g<sup>-1</sup> (for Co/HZSM-5) and 1060 μmol g<sup>-1</sup> (for Ni/HZSM-5). These metal inclusions also resulted in a shift in desorption temperatures for the metal-doped samples. The desorption peaks at intermediate temperatures associated with moderately strong acids decreased slightly with the incorporation of transition metals. NH<sub>3</sub> desorption decreased to 690 and 680 μmol g<sup>-1</sup>, in contrast to HZSM-5, which registered 740 μmol g<sup>-1</sup>. Conversely, there was a significant decrease in the strong acid sites, especially the Brønsted acid sites. The amount of ammonia released decreased from 24 μmol g<sup>-1</sup> in HZSM-5 to 15 and 14 μmol g<sup>-1</sup>, respectively. It is noteworthy that in the course of the dry impregnation process, some of the acidic protons responsible for the Brønsted acid in the crystalline ZSM-5 zeolite may have undergone ion exchange with Co or Ni ions. Overall, the incorporation of metal species increased the total acid sites of the catalysts [26].



**Fig. 3.** N<sub>2</sub> adsorption-desorption isotherm results for the HZSM-5 and metal-doped HZSM-5 zeolites. Inset Figures (b) BJH pore size distribution for adsorption & (c) desorption of synthesised catalysts.

**Table 1.** Textural Properties of Synthesised Catalysts.

Catalysts (Si/Al)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>macro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	Avg pore dia. (nm)
<b>HZSM-5 (40)</b>	398	0.71	0.68	0.029	2.2
<b>Co/HZSM-5</b>	363	0.46	0.46	0.006	2.0
<b>Ni/HZSM-5</b>	381	0.59	0.58	0.008	2.0

**Table 2.** NH<sub>3</sub>-TPD results of synthesised catalysts.

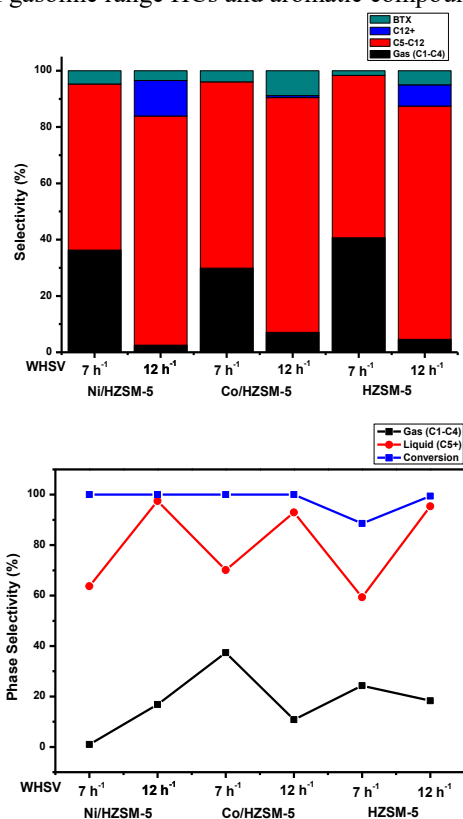
Catalysts	Acidity conc. (μmol NH <sub>3</sub> /g)			Total acidity
	Weak (T=100-300 °C)	Moderate (T=300-500 °C)	Strong (T=500-700 °C)	
<b>HZSM-5</b>	950	740	24	1714
<b>Co/HZSM-5</b>	1050	690	15	1755
<b>Ni/HZSM-5</b>	1060	680	14	1754

### 3.2 Catalytic Performance

MTH conversion was performed to investigate the effects of WHSV and transition metal doping on product selectivity (gasoline range hydrocarbons, GRHs) and methanol conversion. The result showed that at an operating condition of 350 °C and a WHSV of 7 h<sup>-1</sup>, unmodified (HZSM-5) catalysts exhibited a preference for gaseous hydrocarbons (C<sub>1</sub>-C<sub>4</sub>), with a selectivity of over 40.6 % at this condition compared to modified catalysts. However, the modified, unmodified catalysts showed significant selectivity towards gasoline range HCs (C<sub>5</sub>-C<sub>12</sub>), reaching 59.0 and 66.2% for Ni- and Co-doped catalysts, respectively, while HZSM-5 showed a selectivity of 57.7 % for this HC range (Fig. 4a). The results also showed that doping with transition metals improved methanol conversion and BTX selectivity (benzene, toluene, and xylene), with the doped catalysts achieving 100 % conversion at these operating conditions compared to 88% for the unmodified catalyst (Fig. 4a). BTX selectivity also increased from 1.7 % for HZSM-5 to 3.9 and 4.7 % with Co- and Ni-doped HZSM-5, respectively. While this operating condition (7 h<sup>-1</sup>, 350 °C) did not favour the production of C<sub>12</sub>+ HC, increasing the WHSV to 12 h<sup>-1</sup> at the same temperature (350 °C) showed a selectivity for this HC fraction that was 12.6, 0.7, and 7.5 % for Ni-, Co-doped, and HZSM-5 catalysts, respectively. Moreover, the WHSV of 12 h<sup>-1</sup> gave methanol conversion of 100 % and 99.4% for metal-modified and unmodified catalysts, respectively. While all catalysts showed considerable selectivity to gasoline range HCs (> 80 %) compared to the previous operating condition, the Co-doped catalyst showed a considerable increase in BTX production with 8.8 % selectivity compared to the other catalysts. Overall, the result showed that the MTH conversion at 12 h<sup>-1</sup> and 350 °C yielded a significant amount of hydrocarbons from the gasoline range, while the metal doping improved the production of liquid hydrocarbons (Fig. 4b). Table 3 shows the comparative evaluation of average selectivity and liquid hydrocarbon yield for all catalysts studied.

Schulz and Bandermann [27] have suggested that changes in operating conditions during the catalytic reaction may cause gaseous products such as ethylene or diethyl ether to be integrated into an ethanol molecule chemisorbed on the catalyst's surface. This

phenomenon can lead to longer aliphatic chains, some of which can rapidly transform into aromatic compounds depending on the operating conditions. Our results support the hypothesis that at WHSV of 7 h<sup>-1</sup>, the primary gaseous products resulting from ethanol conversion are likely to be ethylene and diethyl ether. However, at higher WHSV of 12 h<sup>-1</sup>, additional reactions are expected to lead to the synthesis of liquid hydrocarbon compounds. These liquid products will contain molecules with C<sub>5</sub>+ aliphatic chains and aromatic chemicals. This concept is consistent with the hypothesis put forward by Wu, et al. [28] that increasing the reaction temperature to > 300 °C on TiO<sub>2</sub>/zeolite catalysts would enhance ethanol conversion to liquid HCs. In agreement with their results, our observations indicate that at the operating conditions of 12 h<sup>-1</sup> and 350 °C, the activity of the reaction shifts toward the synthesis of gasoline range HCs and aromatic compounds.



**Fig. 4.** (a) Hydrocarbon product distribution and (b) phase selectivity for unmodified and transition metal-doped HZSM-5 at T=350 °C and WHSV= 7 & 12 h<sup>-1</sup>.

**Table 3.** Comparative evaluation of (average) product distribution for all catalysts.

Catalysts	Gas (C1-C4)	C5-C12 (Gasoline HC)	C12+	Aromatics (BTX)	Conversion	Liquid HC
HZSM-5	22.6	<b>70.2</b>	3.8	<b>3.4</b>	94.1	77.4
Co/HZSM-5	18.5	<b>74.8</b>	0.36	<b>6.4</b>	100	81.5
Ni/HZSM-5	19.4	<b>70.2</b>	6.3	<b>4.1</b>	100	80.6

## 4 Conclusion

Mesoporous ZSM-5 zeolites were hydrothermally synthesised and doped with Ni and Co metal species. Optimised operating conditions employed during the synthesis process resulted in improved mesoporous HZSM-5, while the incorporation of metal species into the zeolite framework was effectively achieved by dry impregnation. Characterisation techniques provided valuable insights into the properties of the synthesised catalysts, revealing characteristic peaks and functional groups associated with a typical MFI zeolite framework. Catalyst evaluation demonstrated that incorporating metal species improved the catalytic performance and product selectivity. Varying operating conditions affected the product distribution as WHSV of  $12 \text{ h}^{-1}$  favoured gasoline range HC ( $\text{C}_5\text{-C}_{12}$ ) product yield ( $> 80 \%$ ) for all catalysts, and  $\text{C}_{12+}$  with 12.6, 0.7, and 7.5 % selectivity for Ni-, Co-doped, and HZSM-5 catalysts. However, the Co-doped catalyst showed 7.1 % increase in BTX yield at this operating condition. This study demonstrates the effect of WHSV on product distribution and selectivity during methanol conversion with HZSM-5 modified zeolite catalysts. Understanding these WHSV-dependent effects is critical for optimising the catalytic process and developing efficient and selective strategies for biofuel production. By fine-tuning the metal loading and optimising reaction conditions, the catalytic performance of metal-doped catalysts can be further enhanced to achieve higher selectivity towards desired liquid products, which is crucial for successfully implementing methanol as a sustainable petrochemicals and fuel source. The successful synthesis and catalytic performance showed that these catalyst holds promise in methanol conversion and application as a viable alternative fuel and underscore the significance of catalyst development in advancing the renewable energy and green chemistry field. Future research in this direction is expected to unlock even greater potential in biofuel production and accelerate the transition towards a more sustainable energy landscape.

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