1-2021

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Recommended Citation

Zhou, Yuehan, "Exploring Meerwein-Ponndorf-Verley reactions using metal organic framework catalysts." (2021). *Electronic Theses and Dissertations.* Paper 3910.
https://doi.org/10.18297/etd/3910

Exploring Meerwein-Ponndorf-Verley Reactions Using Metal Organic Framework Catalysts

By

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B.S., University of Louisville, 2020

A Thesis
Submitted to the Faculty of the
University of Louisville
J.B. Speed School of Engineering
as Partial Fulfillment of the Requirements
for the Professional Degree

MASTER OF ENGINEERING

Department of Chemical Engineering

July 2021

Exploring Meerwein-Ponndorf-Verley Reactions Using Metal Organic Framework Catalysts

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A Thesis Approved On

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(Date)

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Lee M. Thompson

ACKNOWLEDGMENT

First and foremost, I would like to express my sincere gratitude to my thesis supervisor, Dr. Noppadon Sathitsuksanoh, Assistant Professor in Chemical Engineering, University of Louisville, for allowing me to work on and for guiding this research. He has taught me how to convey ideas for my thesis and has helped me troubleshoot the errors that had occurred during the experiments.

I would also like to thank the rest of my thesis committee, Dr. Vance W. Jaeger and Dr. Lee M. Thompson, for their insightful comments on my thesis. I also thank my academic advisor, Mrs. Susan Best, for assisting me in my undergraduate and graduate education.

My appreciation also extends to my laboratory colleagues, Anwar Hossain and Shahin Rahaman, for their guidance in performing analytical instrument and experiments.

ABSTRACT

The Meerwein–Ponndorf–Verley (MPV) reaction is a reaction that is used to reduce aldehydes and ketones to the corresponding alcohols with the added use of catalysts. The common metal triflate catalysts used in MPV reduction incur tremendous environmental hazards and high operational costs. The use of Metal-Organic Frameworks (MOFs) as catalysts can be an alternative due to MOFs' extraordinarily high surface areas, ultrahigh porosities, tunable pore sizes, modifiable internal surfaces, and numerous framework structures. Moreover, using MOFs as catalysts for MPV hydrogenation is economically viable due to low operational and material costs. This study involves using MOF-808 (Hf) in the MPV reductions of various aldehyde and ketone compounds, specifically discussing its synthesis techniques. It determines the catalytic activity of MOF-808 in MPV reaction by the calculated conversions, product yields, and product selectivity values of each aldehyde and ketone compound. Its results indicate that MOF-808 (Hf) can reduce various aldehyde and ketone compounds, including cyclohexanone and hydroxymethylfurfural (HMF), to their corresponding alcohol products with high conversions, product yields, and product selectivity values.

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I. INTRODUCTION

1.1 Meerwein–Ponndorf–Verley Reduction Mechanism

The Meerwein-Ponndorf-Verley (MPV) reduction involves reducing ketones and aldehydes to their corresponding alcohols, utilizing a metal alkoxide catalyst and an alcohol solvent as its hydrogen source.[1,2] As shown in Figure 1, the reaction is initiated by a carbonyl group, an alcohol solvent, and a metal alkoxide (A), the catalyst for the reaction. The carbonyl compound transports to the active sites on the catalyst. Then, the reduction process undergoes a six-membered ring transition state. Metal alkoxide coordinates with carbonyl oxygen to attain a tetra-coordinated intermediate. A hydride shift occurs in the coordination from the alkoxy ligand to the carbonyl carbon atom. Then, the newly reduced carbonyl group is separated from the tetra-coordinated intermediate, leaving a tri-coordinated structure. During the hydride shift, the alcohol solvent donates hydrogen atoms and is converted to a carbonyl compound. Moreover, the carbonyl group accepts hydrogen atoms from the alcohol solvent then reduces to alcohol.[2]

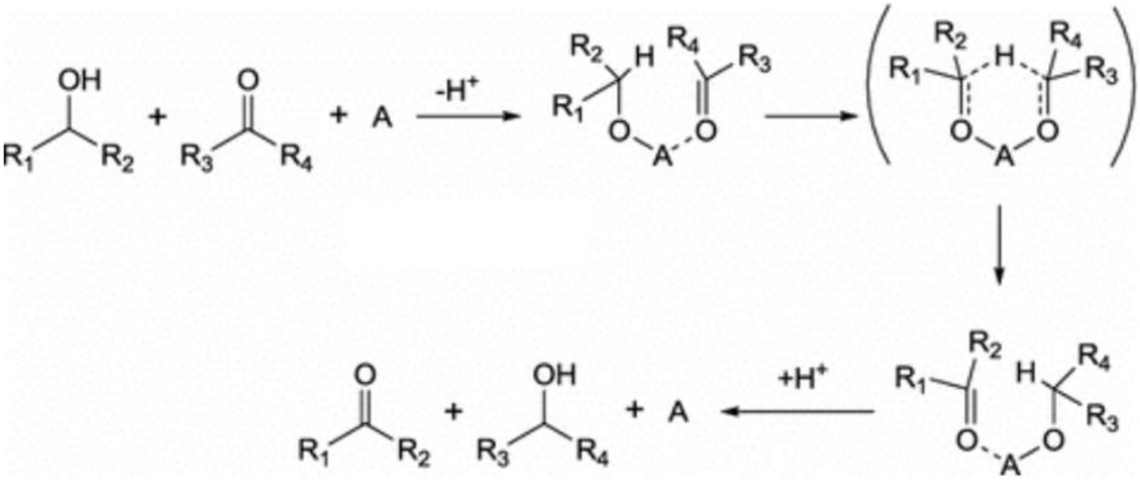


FIGURE 1 – MPV Reduction Mechanism. From Nakagawa, Y., et al. (2018). "Perspective on catalyst development for glycerol reduction to C3 chemicals with molecular hydrogen." *Research on Chemical Intermediates* 44: 1-25.

1.2 Meerwein–Ponndorf–Verley Reduction Catalysis

Most of the catalysts used in MPV reduction are metal triflates, due to the properties of high reactivity, high selectivity, and thermal stability. These solid-phase catalysts are typically used with reactants in the gas or liquid phase. Previous research has found that metal triflates catalysts like hafnium trifluoromethanesulfonate ($Hf(OTf)_4$) and zirconium trifluoromethanesulphonate ($Zr(OTf)_4$), are generally used for the MPV reduction of benzaldehyde[3]. Both catalysts have higher product conversion rate and result in high product yields compared to other metal triflates such as $Al(OTf)_3$, $Ti(OTf)_4$, and $Fe(OTf)_3$.[4] Additionally, an experiment conducted by Chan et al. in 2017 indicated that bismuth trifluoromethanesulfonate ($Bi(OTf)_3$) could be a potential catalyst for the MPV reduction of cinnamyl aldehyde to cinnamyl alcohol.[4] A study by Mollica et al. in 2011 also determined that ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$) had the best catalytic performance among various catalysts in reducing substituted aromatic and aliphatic aldehyde compounds.[5] Additional studies by Uysal et al. in 2010 suggested that boron triethoxide ($B(OEt)_3$) effectively reduces various aliphatic, aromatic, and unsaturated aldehydes to their corresponding alcohols.[6] Although metal triflates provide a vast range of chemical applications, such as valorization of polysaccharides,[7] adsorbents for desulfurization and denitrogenating,[8] and organic compound synthesis, these metal triflate catalysts are not economy- and environment-friendly.[9] Most of the metal triflate catalysts are made up of rare earth metal, which is expensive and can cause severe pollution when processing.[10] Therefore, Metal-Organic Frameworks (MOFs) can be alternative catalysts with significant catalytic performance in MPV reactions.

MOFs are multi-dimensional hybrid crystalline porous materials comprised of organic and inorganic components. MOFs are composed of a regular array of positively charged metal ions surrounded by organic ligand molecules forming a cage-like structure.[11] Organic ligands are ions that are attached to metals via a coordinate bond. Since MOFs are constructed from a vast range of metal ions and organic ligands, there are numerous possible structures of metal-organic combinations.[12] MOFs' use has become popular over the past two decades due to their endless possible structural configuration. The fast-growing market of MOFs has led to a significant interest in their applications, such as energy storage, separation, and catalysis.[13] Additionally, MOFs can alter the structure, surface area, porosity, and diversity in metal clusters and organic struts to suit desired reactions. MOFs' porosity allows better stability and higher catalytic performance with various pH and temperature ranges.[14] MOFs' tunable properties lead to various potential applications, including two-dimensional nanosheets for catalysis[15] and synthesis of microporous materials by ultrasonic means.[16] Furthermore, MOFs are applicable in various processes such as drug delivery, sensing, conductivity, degradation of chemical warfare agents, clean-energy electrocatalysis, Knoevenagel condensation reactions, olefin oxidation, alkylation of aldehydes, nanocomposite synthesis, continuous flow catalysis, ethylene and carbon dioxide separation, hydrogen and carbon dioxide storage, photocatalysis, renewable energy and other environmental applications, and porosity and dye adsorption enhancement.[17–28]

MOFs are also applicable in MPV hydrogenation reactions as potential catalysts. As mentioned, MOFs do not only have tunable properties but are also recyclable, making them environment-friendly.[29] MOFs are synthesized from metal salts, referring to metal-based Lewis acid as an electron acceptor to increase the reactivity of the overall reaction. Common metal salts are based on reagents, including aluminum (Al), silicon (Si), tin (Sn), zirconium (Zr), titanium (Ti), iron (Fe), and hafnium (Hf), all of which are easily obtainable.[30] Additionally, compared to rare-earth metal catalysts, metal salts used for MOFs synthesis are less expensive. Moreover, a previous study by Rimoldi et al. suggested that commonly used catalysts processed from metal oxides lack structural uniformity and active sites. Thus, the use of highly porous and uniformed MOFs as catalysts can significantly enhance catalysis reactivity and selectivity.[29]

Since MOFs are synthesized from various metal salts, different metal salts can influence MOFs' properties and catalytic behaviors. Early research by Bai et al. in 2016 indicated that among various MOFs, Zr-based ones exhibit rich structural types and offer higher stability and are considered one of the most promising catalysts.[31] Meanwhile, several studies have found that MOFs with Hf metal centers have similar stability and catalytic performance in various processes. Early research determined that the Hf-O bond had higher oxophilicity than the Zr-O bond, implying that the tendency of Hf-based MOFs to form or extract oxygen is higher than Zr-based ones. This finding suggested that Hf-based MOFs had better catalytic performance than Zr-based ones. The said research further assessed the absorption and desorption for both Hf-based and Zr-based MOFs, finding that Hf-based MOFs demonstrated slightly higher catalytic activity than Zr-based ones.[32] Based on comparing catalytic activity between Zr-based and Hf-based MOFs from early studies, Hf-based MOFs tend to have more promising catalytic performance. Thus, MOFs with Hf metal centers are synthesized and tested in this study.

1.3 Research Purpose

Most MPV hydrogenation studies with MOFs as catalysts focus on using MOFs to reduce individual aldehyde compounds. Some studies have compared MOFs' catalyst performance of reducing one type of aldehyde compound through various specific properties, including flexibility, porosity, and surface area. However, the scope of these studies focuses only on reducing few aldehyde compounds. Hf-based MOFs demonstrate the most promising catalytic performance by comparing the catalytic activity of various metal-based MOFs from early studies. Therefore, this study aims to explore Hf-based MOFs' catalytic activities and to compare the catalytic performance of Hf-based MOFs for reducing various aldehyde and ketone compounds.

1.4 Research Scope

This study synthesized Hf-based MOF-808 and compared its catalytic activity for the MPV reduction of various aldehyde and ketone compounds to their respective alcohol products. The reaction time and temperature for the said reductions were kept constant. This study assessed the following aldehyde and ketone compounds: 2-furaldehyde, 5-methyl-2-furaldehyde, cyclohexanone, ethyl levulinate, methyl levulinate, hydroxymethylfurfural (HMF), acetophenone, and 4-hydroxybenzaldehyde. It compared the compound conversions, product yields, and product selectivity values of various alcohols.

II. MATERIALS AND INSTRUMENTATION

2.1 Chemicals

Hafnium (IV) chloride ($HfCl_4$) was obtained from Sigma-Aldrich (St. Louis, MO, USA) with molecular weights of 320.30 g/mol and 98% purity. The 1,3,5-benzenetricarboxylic acid was purchased from Beantown Chemical Corporation (Hudson, NH, USA with a molecular weight of 210.14 g/mol and 98% purity. The N-dimethylformamide (DMF) solvent was obtained from Chem-Impex Int'l. Inc. (Wood Dale, IL, USA) with a molecular weight of 73.09 g/mol and 100% purity. Formic acid was purchased from Beantown Chemical Corporation (Hudson, NH, USA with a molecular weight of 46.03 g/mol and 97% purity.

The following chemicals used for MPV hydrogenation reactions were obtained from Alfa Aesar (Ward Hill, MAUSA, ethyl levulinate, 5-methyl-2-furaldehyde, 2-furaldehyde, and n-hexadecane. Methyl levulinate was purchased from TCI (Portland, OR, USA) with 99% purity. Cyclohexanone was purchased from Beantown Chemical Corporation (Hudson, NH, USA) with 99% purity. Acetophenone was obtained from Chem-Impex Int'l. Inc. with 99% purity. 5-Hydroxymethylfurfural was purchased from Ark Pharm

(Libertyville, IL, USA with 98% purity. A list of chemicals/reagents used in this study was shown below in Table 1.

TABLE 1.

LIST OF CHEMICALS/REAGENTS USED IN THIS STUDY

Material/Chemical	Supplier	Purity	CAS Number
Cyclohexanone	Beantown Chemical Corporation (Hudson, NH,USA)	99%	108-94-1
Ethyl Levulinate	Alfa Aesar (Ward Hill, MA, USA)	98%	539-88-8
Methyl Levulinate	TCI(Portland, OR, USA)	99%	624-45-3
5-Methyl-2-furaldehyde	Alfa Aesar (Ward Hill, MA, USA)	98%	620-02-0
2-Furaldehyde	Alfa Aesar (Ward Hill, MA, USA)	98%	98-01-1
Acetophenone	Chem-Impex Int'l. Inc.	99%	98-86-2
5-Hydroxymethylfurfural	Ark Pharm (Libertyville, IL, USA)	98%	67-47-0
n-Hexadecane	Alfa Aesar (Ward Hill, MA, USA)	99%	544-76-3
Hafnium(IV) chloride	Sigma-Aldrich (St. Louis, MO, USA)	98%	13499-05-3
1,3,5-benzenetricarboxylic acid	Beantown Chemical Corporation (Hudson, NH, USA)	98%	554-95-0
Formic Acid	Beantown Chemical Corporation (Hudson, NH, USA)	97%	64-18-6
Acetone	Jasco (Memphis, TN, USA)	100%	100-41-4
N,N-dimethylformamide	Chem-Impex Int'l. Inc. (Wood Dale, IL, USA)	100%	68-12-2

2.2 Instrumentations

In this study, a gas chromatograph was used to analyze the liquid product. The gas chromatograph was purchased (7890B GC) from Agilent Technologies (Santa Clara, CA, USA) and was equipped with a mass spectrometer and flame ionization detector (FID) for product identification and quantification, respectively. A DB-1701 column (30m x 0.25 mm x 0.25 μm, Agilent Technologies, Santa Clara, CA, USA) was used for product separation with the following parameters: injection temperature 275 °C and FID detector temperature 300 °C; split ratio 1:50. The temperature profile started at 50 °C with a heating rate of 8°C/min to 200 °C.

III. PROCEDURE AND METHODS

3.1. Catalysts Preparation

MOFs were synthesized by mixing metal salts with organic ligands in their respective solvents at high temperatures. MOF-808 Hf was prepared by mixing 160 mg (or 0.5 mmol) of hafnium (IV) chloride ($HfCl_4$) with 110mg (or 0.5 mmol) 1,3,5-benzenetricarboxylic acid. Then, 20 mL N-dimethylformamide (DMF) and 20 mL formic acid were added to the mixture. After adding the solvents, the MOF mixture was sonicated for 30 minutes. Sonication allowed the mixture to dissolve in the solution completely. Afterward, the mixture was transferred in an autoclave and placed in the oven at 100°C for 72 hours. The autoclave was removed from the oven afterward and cooled at room temperature for another three to four hours. After the mixture was completely cooled, a solid white product could be easily seen at the bottom of the autoclave. The MOF mixture was transferred into 40mL centrifuge tubes for post-processing.

For the post-processing of MOF synthesis, solvent exchange activated the MOFs.[33] The MOF mixtures were initially washed thoroughly with 20mL of DMF in centrifuge tubes to remove impurities. Then, the MOFs were centrifuged and repeatedly washed with

20mL of DMF thrice. Then, DMF was removed from the MOFs by exchanging with a lower boiling point solvent to avoid framework collapse. Afterward, the MOFs were soaked, washed, and centrifuged in 20mL acetone thrice. Finally, the MOF-808 products were dried and activated in a vacuum oven at 120°C for 12 hours.[34]

3.2. MPV Hydrogenation of Various Compounds

Eight aldehyde and ketone compounds were individually tested with MOF-808 (Hf) as catalysts in MPV reactions: 2-furaldehyde, 5-methyl-2-furaldehyde, cyclohexanone, ethyl levulinate, methyl levulinate, hydroxymethylfurfural (HMF), acetophenone, and 4-hydroxybenzaldehyde. For each experiment, 3 mol% of the MOF catalyst and 1 wt.% of the corresponding aldehyde compound were placed in a reactor vessel. Each reactor vessel was labeled with the feedstock name. Then, 13.26 g of isopropanol was added to the MOF mixtures, with the addition of 0.25 wt.% of hexadecane as an internal standard for the reaction. The reactor vessel was capped with a rubber stopper to prevent leaks and evaporation. After mixing each reactor vessel for 30 seconds, the vessel was placed in an oil bath at 100°C for one hour. It was then quenched in a water bath for the given reaction time to prevent lingering reactions.

After the vessel was cooled completely, 1.5 mL ethyl-acetate was added, then it was placed in a mixer for vortex for 30 seconds. Afterward, 1.5 mL of the solution from the reactor vessel was transferred to a small centrifuge tube by a 3 mL plastic transfer pipette. After centrifugation for two to three minutes, the liquid products were separated from the solids. A volumetric pipette measured 200μL of the liquid solution and mixed it with 800μL of ethyl-acetate in a glass tube, followed by a vortex for 30 seconds. Finally, the final product was analyzed by a gas chromatograph, equipped with a mass spectrometer and flame ionization detector (FID), for product identification and quantification, respectively.

IV. CALCULATIONS

In this study, the conversion, yield, and selectivity of aldehyde and ketone functional group products were calculated by utilizing Equations 4.1 to 4.3:

$$\text{Conversion (\%)} = \frac{\text{Aldehyde reacted (mol)}}{\text{Initial aldehyde (mol)}} \tag{4.1}$$

$$\text{Product yield (\%)} = \frac{\text{Product formed (mol)}}{\text{Initial aldehyde (mol)}} * 100 \tag{4.2}$$

$$\text{Product selectivity (\%)} = \frac{\text{Product yield (\%)}}{\text{Conversion (\%)}} * 100 \tag{4.3}$$

To calculate the conversions, yields, and selectivity values of the products, the amounts of aldehyde reacted in moles, and the amounts of product formed in moles must be determined from the percent areas of the peaks detected by GC-MS with hexadecane, the internal standard. As discussed in the previous section, hexadecane is an internal standard of the reaction. Its concentration is assumed to be constant during the reaction;

therefore, relative changes in peak areas of reactants and products correspond to the amount of loss or gain of a reactant or product throughout the reaction. In comparison with the internal standard, the conversion of aldehyde and ketone compounds can be determined by Equation 4.4:

$$\text{Conversion (\%)} = \frac{\left[100 - \left(\frac{\text{peak \% area of aldehyde after reaction}}{\text{peak \% area of hexadecane after reaction}}\right) * 100\right]}{\left(\frac{\text{peak \% area of aldehyde before reaction}}{\text{peak \% area of hexadecane before reaction}}\right)} * 100 \tag{4.4}$$

After calculating the conversion by comparing the relative percent peak areas between aldehyde and hexadecane, the product formed can be calculated using the same relative percent peak areas. The relative response factor (RRF) calculates the amounts of product formed in the reaction. It is an analytical parameter commonly applied in gas chromatography to correct the differences in detector response with the analyte peak. Equation 4.5 can determine the RRF from the correlation between the product and the internal standard:[42]

$$\text{RRF of product (unitless)} = \frac{\text{Response factor of product } (\text{g}^{-1})}{\text{Response factor of hexadecane } (\text{g}^{-1})} \tag{4.5}$$

There are two ways to calculate the RRF of a product. One way is by sampling a known concentration of analytes with gas chromatography. Then, the RRF value can be calculated using Equation 4.6:

$$\text{RRF of product } (\text{g}^{-1}) = \frac{\text{peak \% area of product (unitless)}}{\text{concentration of product (g)}} \tag{4.6}$$

If the alcohol product cannot be found in the laboratory or is not locally available, then the RRF of the estimated product can be determined using the effective carbon number (ECN).[43] The ECNs used in this study were determined from Microsoft Excel using Equation 4.7. The ECN is an approach for approximating response factors for compounds that have no reliable and authentic standards. The estimation considers the amount and various types of carbon and oxygen atoms and their respective bonds. As shown in Equation 4.7, the number of aliphatic carbon atoms, aromatic carbon atoms, olefinic carbon atoms, acetylenic carbon atoms, carbonyl carbon atoms, ether oxygen atoms, 1° alcohol oxygen atoms, 2° alcohol oxygen atoms, and 3° alcohol atoms were used to calculate the ECN of a product.

$$\text{ECN (unitless)} = (\#\text{ aliphatic C} * 1) + (\#\text{ armoatic C} * 1) + (\#\text{ olefinic C} * 0.95) + (\#\text{ aacetylinic C} * 1.3) + (\#\text{ carbonyl C} * 0) + (\#\text{ether O} * -1) + (\#\text{ 1° alcohol O} * -0.6) + (\#\text{ 2° alcohol O} * -0.75) + (\#\text{ 3° alcohol O} * -0.25) \tag{4.7}$$

After the ECN of the product is determined, the RRF of the product can be calculated using Equation 4.8:

$$\text{RRF of product} = \frac{\text{ECN}_{\text{product}}(\text{unitless}) * \text{MW}_{\text{I.S.}}(\frac{\text{g}}{\text{mol}})}{\text{MW}_{\text{product}}\left(\frac{\text{g}}{\text{mol}}\right) * \text{ECN}_{\text{I.S.}}(\text{unitless})} \qquad (4.8)$$

In Equation 4.8, I.S. indicates the internal standard (hexadecane) used in the reaction. MW signifies the molecular weight of the product or internal standard in g/mol. Since most of the products in this study were not locally available, Table 2 lists the RRFs calculated using ECN.

TABLE 2.

LISTS OF CHEMICALS WITH ECN AND RRF IN THIS STUDY

Chemicals	**ECN**	**MW**	**RRF**
Hexadecane - standard compound	16.00	226.41	1.00
2-Furanmethanol	3.40	98.1	0.49
5-methyl 2-furyl methanol	4.40	112.13	0.56
Cyclohexanol	5.40	100.158	0.76
2(3H)-Furanone/ dihydro-5-methyl-	3.75	100.12	0.53
2-Fueancarboxaldehyde/ 5-methyl-	3.75	110.112	0.48
Benzenemethanol	7.40	122.164	0.86
2,5-diformylfuran	3.80	124.09	0.43
1,3,5,7-cyclooctatetraene	8.00	104.06	1.09

After the above calculations determine the RRF, the mass of the product can be determined by Equation 4.9:

$$\text{Mass of product (g)} = \frac{\left(\frac{\text{peak \% area of product after reaction (\%)}}{\text{peak \% area of hexadecane after reaction (\%)}}\right)}{\text{RRF of product (unitless)}} * \text{ weight of hexadecane (g)} \tag{4.9}$$

After the mass of the product is determined by the percent peak areas, RRF of the product, and the initial weight of the internal standard, percent product yield and percent product selectivity can be determined by Equations 4.2 and 4.3.

V. RESULTS

The following eight aldehyde and ketone functional groups were tested with MOF-808 Hf: 2-furaldehyde, 5-methyl-2-furaldehyde, cyclohexanone, ethyl levulinate, methyl levulinate, hydroxymethylfurfural (HMF), acetophenone, and 4-hydroxybenzaldehyde. The experiments with these compounds were repeated to obtain significant results. The experiments were conducted with constant reaction time and process temperature. Tables 3 and 4 indicate each feedstock's number, starting aldehyde and ketone molecules, detected alcohol products, conversion, product yield, and product selectivity. In the Appendix, Figure 2-9 shows the gas chromatography plots for each aldehyde and ketone feed for the MPV reactions. The GC plots for the MPV reactions with 2-furaldehyde are shown in Figure 2, and the GC plots for 5-methyl-2-furaldehyde as feedstock are shown in Figure 3. For the reactions with cyclohexanone, ethyl levulinate, and methyl levulinate as feedstocks, the GC plots are shown in Figure 4, 5, and 6. The GC plots for the reactions with HMF are shown in Figure 7, and the GC plots for acetophenone as feedstock are shown in Figure 8. The GC plots for the reactions with 4-hydroxybenzaldehyde are shown in Figure 9.

TABLE 3. LISTS OF ADDITIONAL ALDEHYDE FEEDSTOCKS FOR EXPERIMENT ONE OF MPV REACTION WITH MOF-808 (Hf)

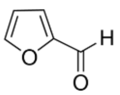
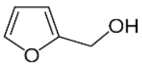
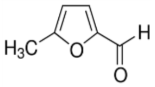
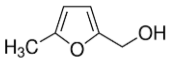
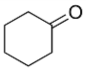
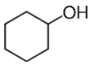
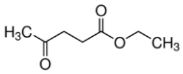
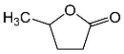
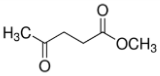
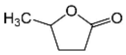
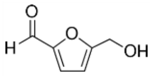
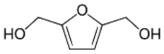
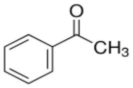
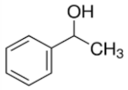
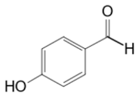
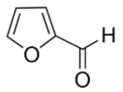
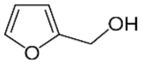
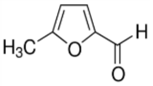
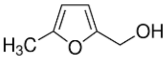
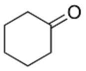
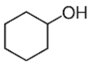
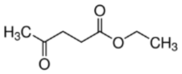
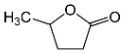
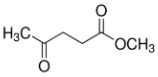
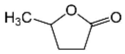
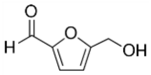
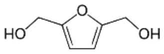
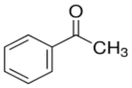
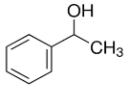
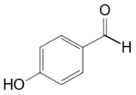
Feedstock	Starting Material	Product(s)	Conversion (%)	Yield (%)	Selectivity (%)	GC Plot
2-Furaldehyde			80.10	26.61	32.22	Fig 2 A, C
5-Methyl-2-furaldehyde			87.30	0.61	0.70	Fig 3 A, C
Cyclohexanone			100.00	22.80	22.80	Fig 4 A, C
Ethyl levulinate			72.93	2.07	2.84	Fig 5 A, C
Methyl Levulinate			50.10	7.20	14.37	Fig 6 A, C
HMF			50.08	7.19	14.37	Fig 7 A, C
Acetophenone			99.99	22.87	22.87	Fig 8 A, C
4-Hydroxybenzaldehyde		no detected products	63.14	N/A		Fig 9 A, C

TABLE 4. LISTS OF ADDITIONAL ALDEHYDE FEEDSTOCKS FOR EXPERIMENT TWO OF MPV REACTION WITH MOF-808 (Hf)

Feedstock	**Starting Material**	**Product(s)**	**Conversion (%)**	**Yield (%)**	**Selectivity (%)**	**GC Plot**
2-Furaldehyde			80.09	18.65	23.28	Fig 2 B, D
5-Methyl-2-furaldehyde			87.32	0.61	0.70	Fig 3 B, D
Cyclohexanone			99.87	82.31	82.42	Fig 4 B, D
Ethyl levulinate			72.92	2.27	3.11	Fig 5 B, D
Methyl Levulinate			50.08	6.13	12.25	Fig 6 B, D
HMF			99.90	58.16	58.21	Fig 7 B, D
Acetophenone			99.98	21.86	21.86	Fig 8 B, D
			99.98	26.94	26.94	Fig 8 B, D
4-hydroxybenzaldehyde		no detected products	63.14	N/A		Fig 9 B, D

VI. DISCUSSION

The results indicate that the aldehyde and ketone conversions, product yields, and product selectivity values determined MPV reaction with MOF-808 (Hf). Five runs of experiments were conducted to obtain significant results. In Table 3, the reaction with 1-furaldehyde produced 2-furanmethanol with the conversion of 80.10%, product yield of 26.61%, and product selectivity of 32.22%. When utilizing 5-methyl-2-furaldehyde as the feedstock, the resulting alcohol was 5-methyl 2-furyl methanol with the conversion of 87.30%, product yield of 0.61%, and product selectivity of 0.70%. The reaction with cyclohexanone as feedstock produced cyclohexanol with 100% conversion, 22.80% product yield, and 22.80% product selectivity. Reactions with ethyl levulinate and methyl levulinate produced 2(3H) furanone, dihydro-5-methyl, with the conversion values of 72.93% and 50.10%, product yield values of 2.07% and 7.20%, and product selectivity values of 2.84% and 14.37%, respectively. The reaction with hydroxymethylfurfural (HMF) as feedstock produced 2,5-dihydroxymethylfuran, with the conversion of 50.08%, product yield of 7.19%, and product selectivity of 14.37%. The reaction with acetophenone produced 1-phenylethanol, with the conversion of 99.99%, product yield of 22.87%, and product selectivity of 22.87%. For the reaction with 4-hydroxybenzaldehyde, no significant product was detected by GC-MS while the reactant feed compound was still diminished, resulting in a conversion of 63.14%.

Gas chromatography detected no significant products for the second, third, and fourth runs of the experiments. However, the conversions were still determined from the feed compounds for each experiment run. In Table 4, the results for the last experiment run were calculated. The reaction with 2-furaldehyde as feedstock produced 2-furanmethanol with the conversion of 80.09%, product yield of 18.65%, and product selectivity of 23.28%. For the second reaction, 5-methyl-2-furaldehyde was used as feed; it produced 5-methyl 2-furyl methanol with 87.32% conversion. However, yield (0.61%) and selectivity (0.70%) were significantly low. The reaction with cyclohexanone as feedstock produced cyclohexanol with 99.87% conversion, 82.31% product yield, and 82.42% product selectivity. Reactions with ethyl levulinate and methyl levulinate produced 2(3H) furanone, dihydro-5-methyl with the conversion values of 72.93% and 50.08%, product yield values of 2.27% and 6.13%, and product selectivity values of 3.11% and 12.25%, respectively. The reaction with hydroxymethylfurfural (HMF) produced 2,5-dihydroxymethylfuran with the conversion of 99.9%, product yield of 58.16%, and product selectivity of 58.21%. The reaction with acetophenone produced two products detected by gas chromatography. 1-phenylethanol with the conversion of 99.98%, product yield of 21.86%, and product selectivity of 21.86%. Meanwhile, GC-MS detected 1,3,5,7-cyclooctatetraene, an additional product, with the conversion of 99.98%, product yield of 26.94%, and product selectivity of 26.94%. For the reaction with 4-hydroxybenzaldehyde, no significant product was detected by GC-MS while the reactant feed compound was still diminished, resulting in a conversion of 63.14%.

For Experiments 1 and 2, no byproducts were detected by GC-MS. Except for Experiment 2, GC-MS detected the byproduct of 1,3,5,7-cyclooctatetraene with 99.98% conversion, 26.94% product yield, and 26.94% product selectivity. Comparing the results between Experiments 1 and 2, 2-furanmethanol, cyclohexanol, and 2,5-dihydroxymethylfuran exhibited high conversions, product yields, and product selectivity values. However, the product yields and selectivity values were relatively low when using 5-methyl-2-furaldehyde, ethyl levulinate, and methyl levulinate as feedstocks, which might have resulted from human error during the experiment. Another possible explanation is that gas chromatography detected some of the products. As mentioned in the literature, the high catalytic activity of MOF-808 (Hf) is attributed to its crystal-like structure and the large amounts of defect sites in the MOFs. The exposed Hf-O bond in the said defect sites can be used as Lewis acid sites, promoting catalytic reactions.[35] Such large amounts of defect sites indicate a high Lewis acidity of the MOF-808 (Hf). An early study by Lin et al. proved this theory by density functional theory (DFT) calculations, which indicated that the large defect formation of MOF-808 (Hf) was due to a greater surface area and more Lewis acidity metal center. The said study further suggested that MOF-808 (Hf) has a high Lewis acidity;[36] therefore, it is more likely to accept electrons and is willing to form partial bonds with very electronegative atoms such as aldehyde oxygen in the initial step of the MPV process. Such a high Lewis acidity can cause electronegative atoms in the product molecules to be easily attracted to MOF-808. Furthermore, these molecules are likely to absorb onto the MOFs.[37] One consequence of these interactions is an increased difficulty of product separation from the MOFs for analysis. Additionally, the experiments conducted by Jiang et al. determined that MOF-808 has a relatively high acidity, using a designed catalytic acid/base test reaction. The reaction showed traces of solvent molecules, DMF, and water, filling the gaps in the framework from the defect sites in highly Lewis acidic MOF-808 structures. Moreover, Jiang et al. suggested that MOF-808's acidity can lead to decreased product selectivity.[38]

For Experiments 1 and 2, the conversions for each feedstock were compared. The process procedure, reaction time, and process temperature remained constant throughout the experiments. For each feedstock, the conversions for the Experiment 1 and Experiment 2 were highly similar, with a difference of less than 5%. Such relatively similar conversion results indicate the consistency of the results. Additionally, the conversion, product yield, and product selectivity values of cyclohexanone were compared with those from previous research. In the latter, MOF-808 (Hf) was used for the MPV hydrogenation of cyclohexanone, resulting in 98.1% conversion, 87.1% product yield, and 88.8% product selectivity. The conversion for Experiments 1 and 2 was consistent with the previous results. However, product yield and selectivity in the first run were lower than those in the previous results. It could be explained by human error during the experiments, or that some products were absorbed onto the highly acidic MOF, which could not be separated and analyzed by GC-MS.

VII. FUTURE RECOMMENDATIONS

The second, third, and fourth experiment runs applied the same procedure, reaction time, and process temperature. However, there were no significant products due to the use of inactive MOFs. The MOF-808 (Hf) used for those runs was synthesized separately from the first run, which was inactive due to possible human errors during MOF synthesis and activation. During synthesis, the MOF mixtures were placed in the autoclave for heating. The autoclave was reusable for synthesizing different MOFs. Some undesired residues might have remained inside the autoclave, which could affect the structure and catalytic activity of the MOFs. This error can be mitigated by soaking the autoclave with dimethyl sulfoxide (DMSO) and sonicate it for 30 minutes to ensure the complete dissolution of all undesirable residue.

Another possible human error that can occur during MOF-808 synthesis is the lack of cooling time. After the MOFs are removed from the oven after 72 hours, it is crucial to ensure a wholly cooled autoclave before further post-processing. Depending on the room temperature, the cooling process can take approximately three to four hours. The MOFs' crystal size and phase purity become affected if the autoclave is not completely cooled.[12] Furthermore, errors may occur during the solvent exchange, which can primarily affect the MOFs' catalytic activity. During MOFs synthesis, the reaction solvent molecules are inevitably trapped in the framework pores. The trapped solvent molecules' high surface tension and capillary on the MOF structure can cause framework collapse. Consequently, the reaction solvent molecules (DMF) must be removed by a low boiling point solvent (acetone). Indeed, it is necessary to ensure the complete removal of the DMF solvent from the MOF mixtures; otherwise, the formed MOFs’ catalytic activity reduces significantly. This error is avoidable in future experiments by washing the MOFs thoroughly with acetone, followed by vortex and centrifugation more than thrice to ensure a wholly removed reaction solvent.

VIII. CONCLUSION

In this study, the MOF-808 (Hf) was synthesized and tested in the MPV hydrogenation reaction of various aldehyde and ketone compounds at 100°C for one hour. The following eight compounds were tested individually with MOF-808 (Hf), including 2-furaldehyde, 5-methyl-2-furaldehyde, cyclohexanone, ethyl levulinate, methyl levulinate, hydroxymethylfurfural (HMF), acetophenone, and 4-hydroxybenzaldehyde. The catalytic activity of the MOF was determined by calculating the conversions, alcohol product yields, and alcohol product selectivity values for each reaction. In comparing the catalytic performances of the eight different functional groups, MOF-808 (Hf) has better catalytic performance with 2-furaldehyde, cyclohexanone, and HMF. MOF-808 (Hf) has the highest conversions, yields, and selectivity values with cyclohexanone among the eight aldehyde and ketone feedstocks. This finding can assist in clarifying the MPV hydrogenation mechanism on MOF-808 (Hf) and influence the development of more catalytically active and product selective MOF catalysts. In the future, more studies are necessary to investigate further the catalytic performance of MOF-808 (Hf) with different aldehyde compounds.

APPENDIX

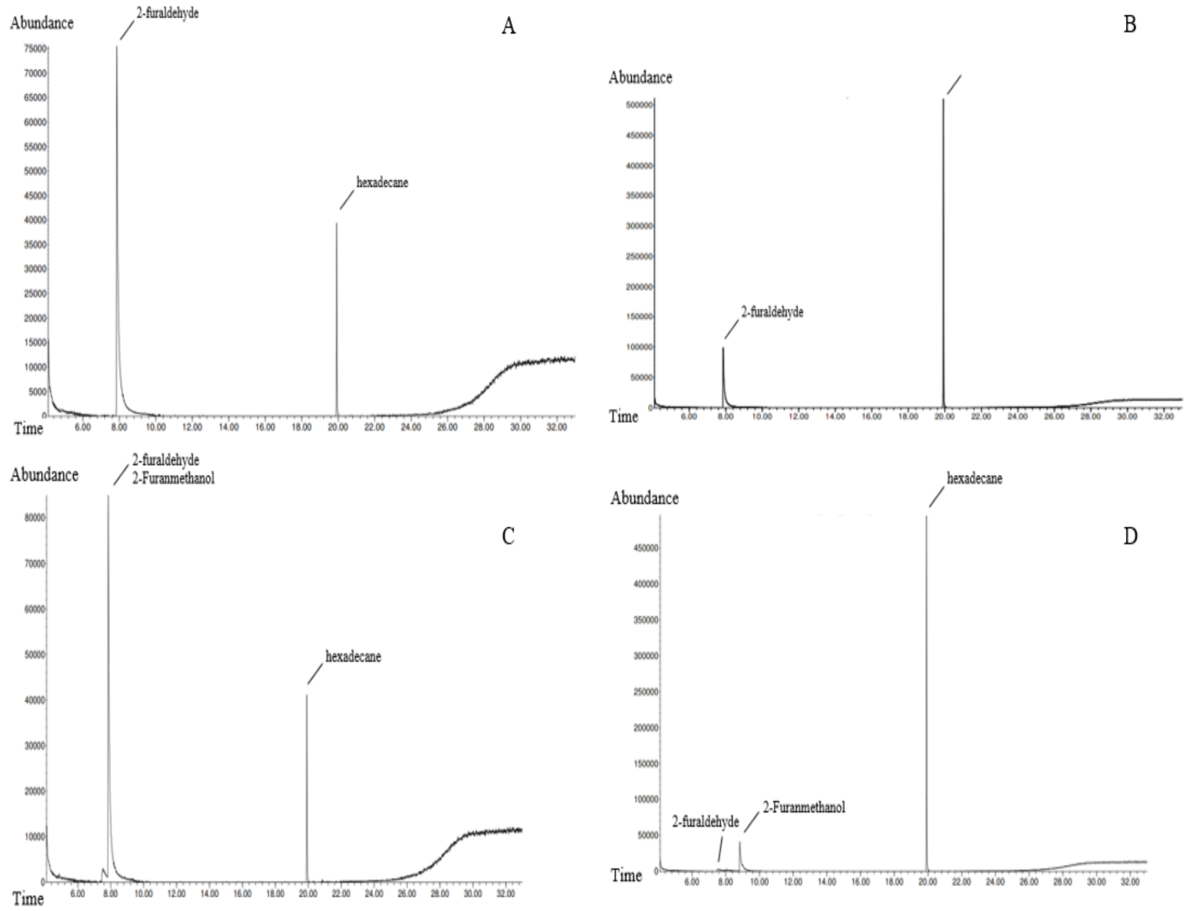


FIGURE 2 — Gas Chromatography Plots for the 2-Furaldehyde Experiments

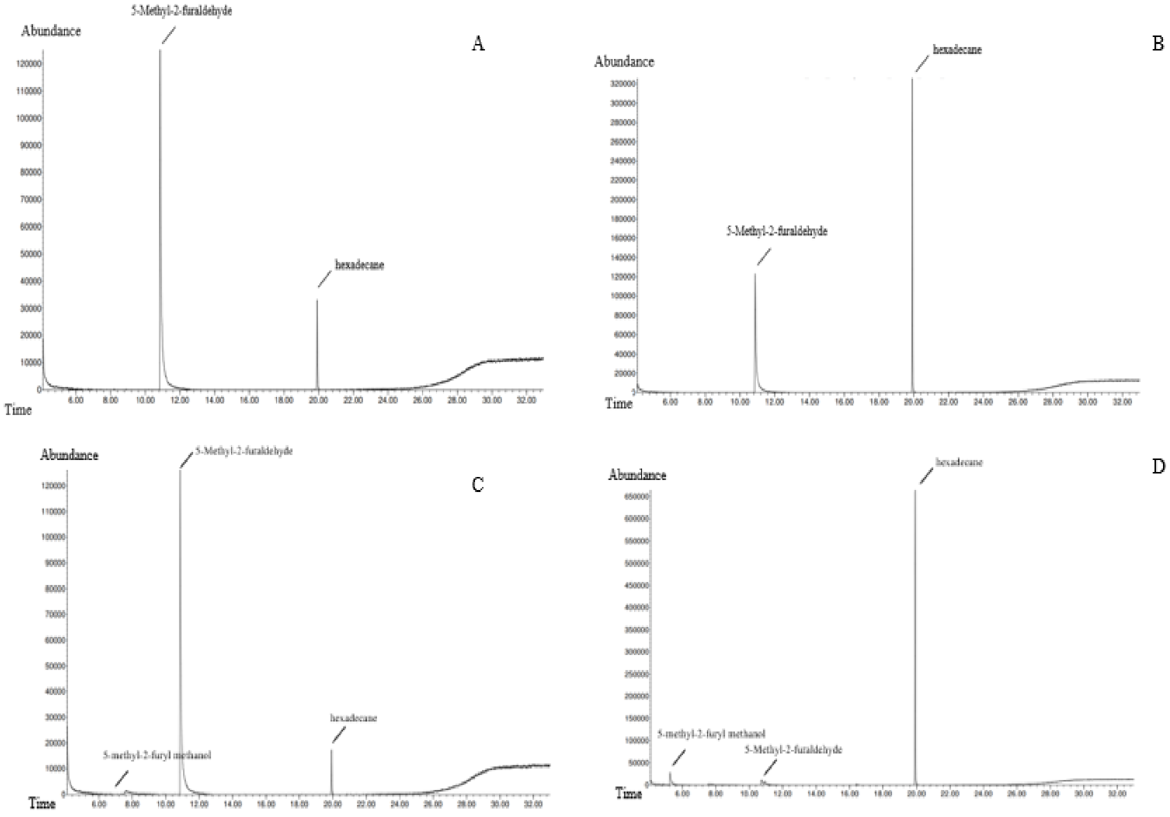


FIGURE 3 — Gas Chromatography Plots for the 5-Methyl-2-furaldehyde Experiments

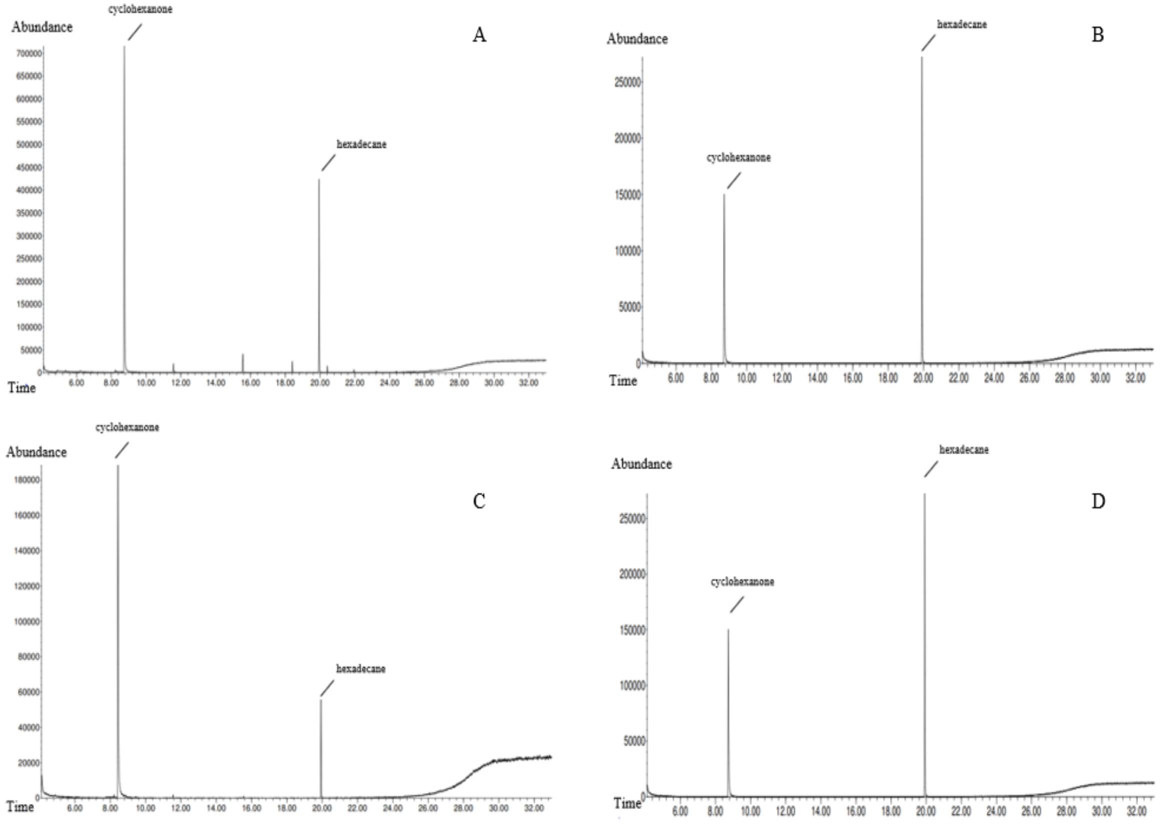


FIGURE 4 — Gas Chromatography Plots for the Cyclohexanone Experiments

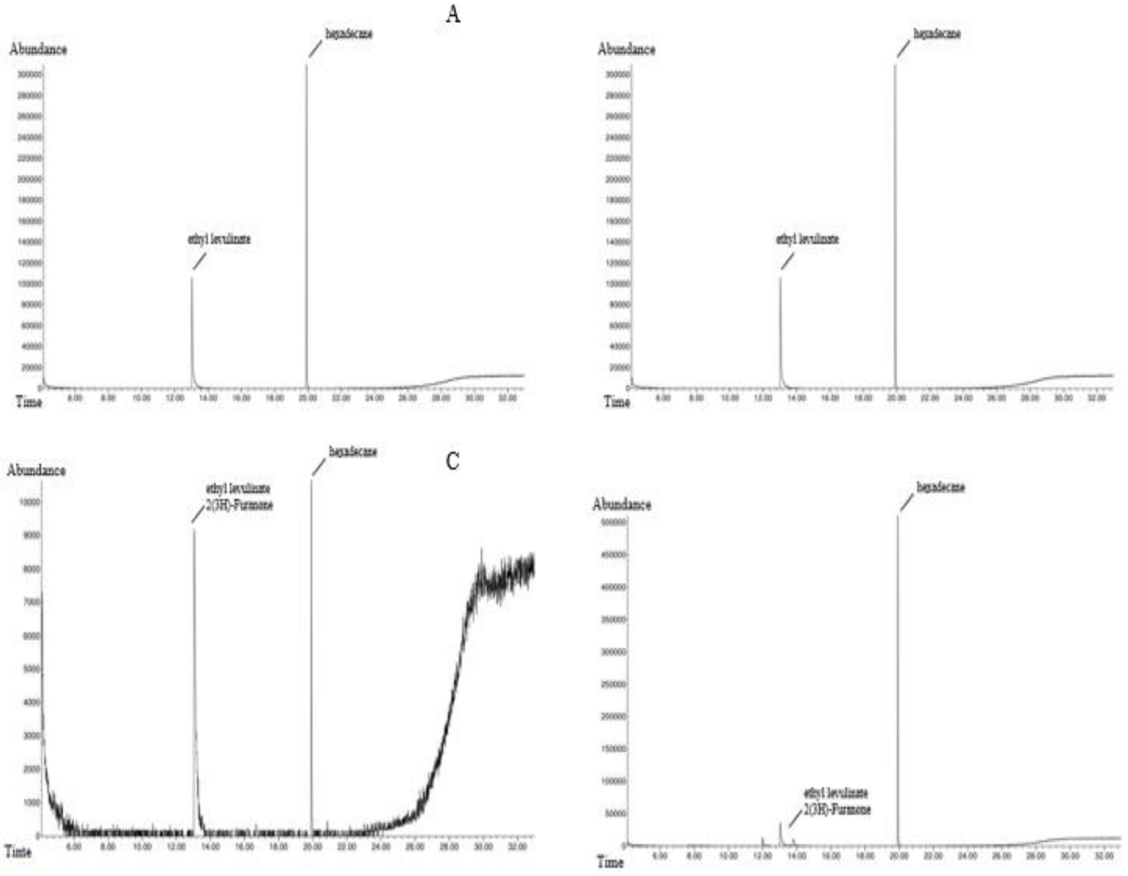


FIGURE 5 — Gas Chromatography Plots for Ethyl Levulinate Experiment

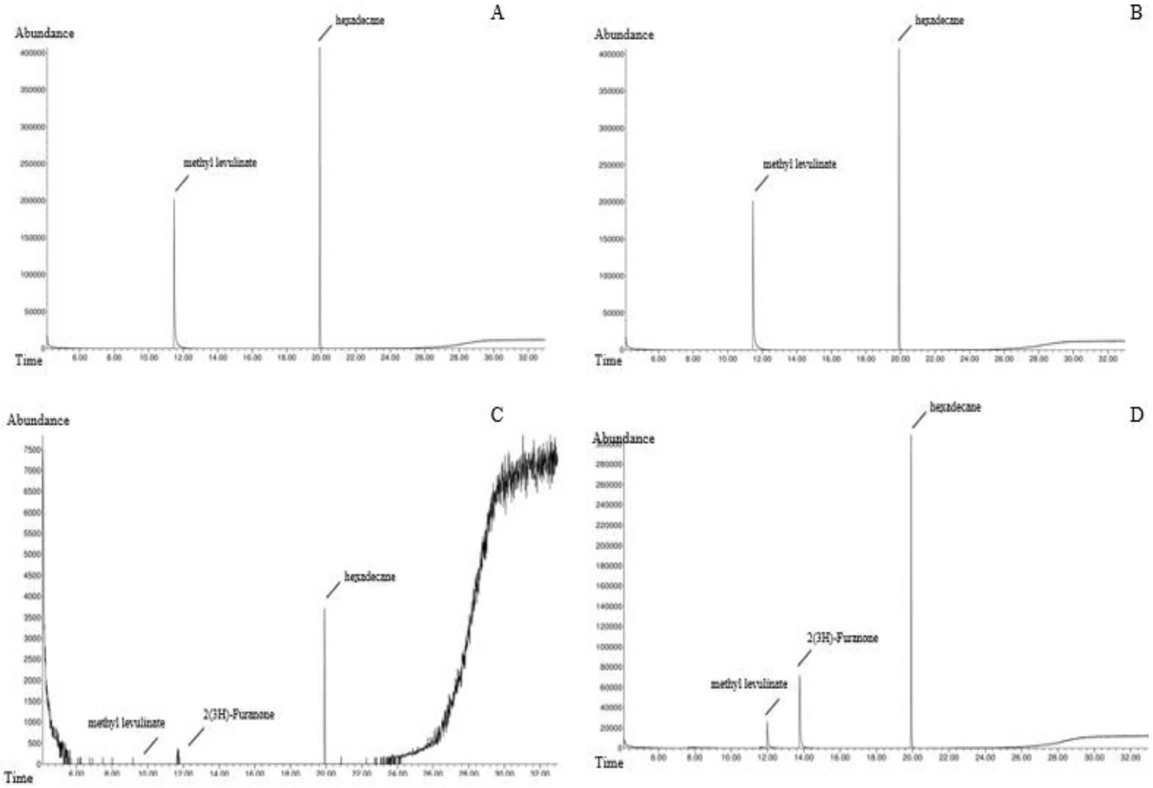


FIGURE 6 — Gas Chromatography Plots for the Methyl Levulinate Experiments

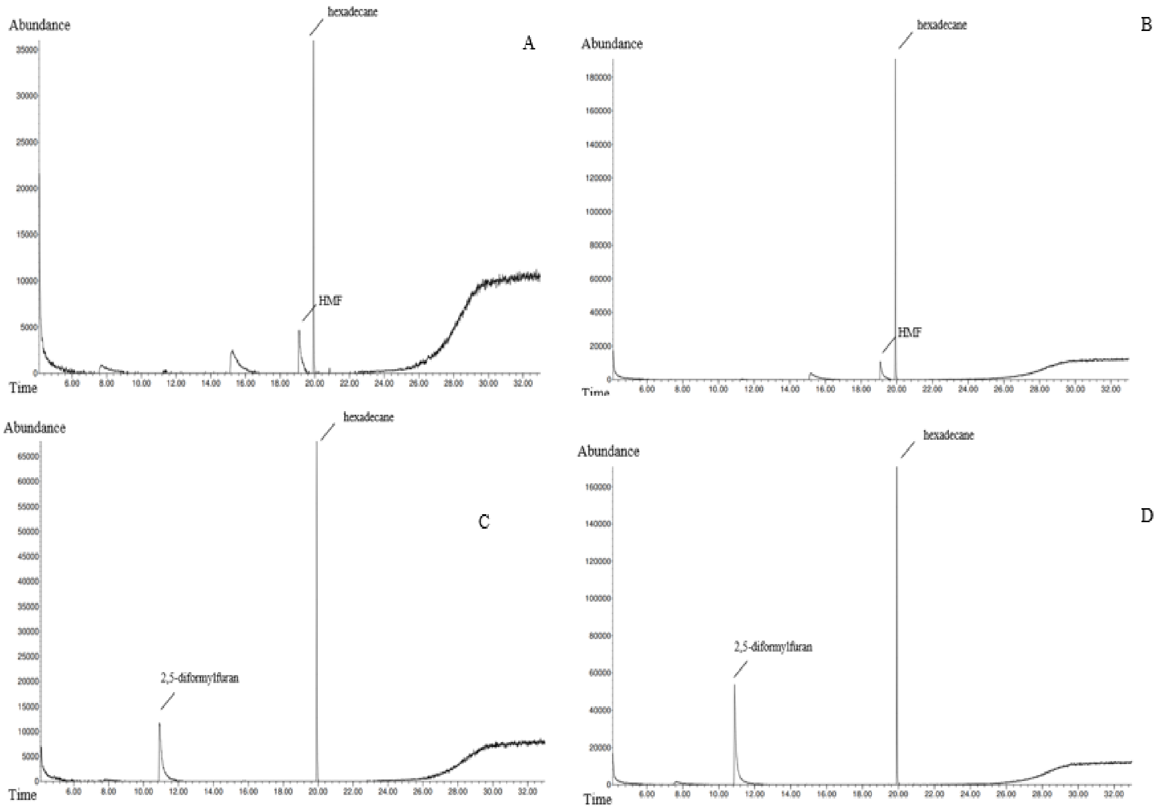


FIGURE 7 — Gas Chromatography Plots for the HMF Experiments

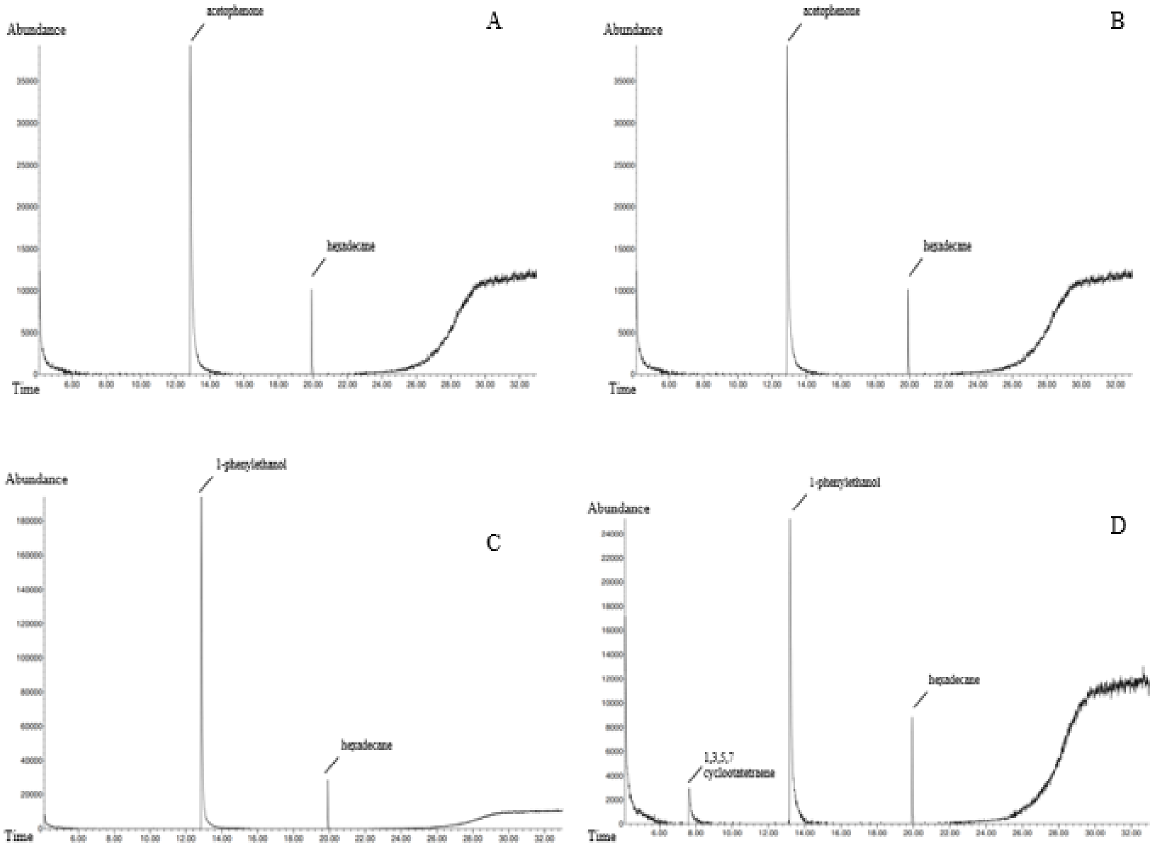


FIGURE 8 — Gas Chromatography Plots for the Acetophenone Experiments

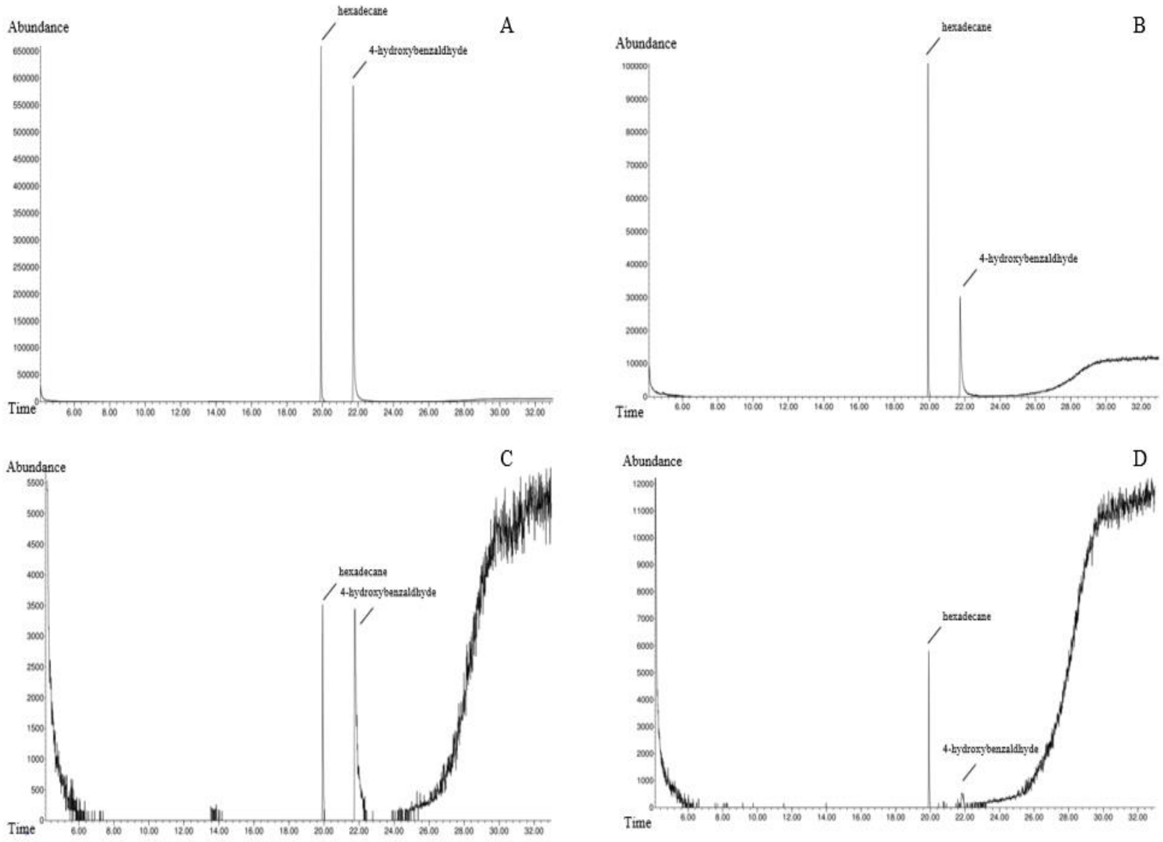


FIGURE 9 — Gas Chromatography Plots for the 4-Hydroxybenzaldehyde Experiments

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