INVESTIAGION OF THE ENCPASULATION EFFICIENCY OF HEXANAL IN γ-CYCLODEXTRIN METAL ORGANIC FRAMEWORKS

by

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ABSTRACT

Nanoporous materials have been extensively studied for applications such as drug delivery and organic compound storage. The nanoporous material of this study is a metal organic framework (MOF) which is a coordination of metal ions with organic binders. The structure created by this coordination can be used to absorb organic compounds, such as plant growth regulators, and subsequently release the organic compounds over a prolonged period to extend the storage life of foods. This study is examining the encapsulation efficiency of hexanal in γ-cyclodextrin metal organic frameworks (γ-CDMOFs) as a mechanism for potential active packaging applications. γ-CDMOFs were synthesized by vapor diffusing methanol into a solution of γ-CD and potassium hydroxide (KOH). After synthesis, the γ-CDMOFs were activated in a vacuum oven at 25°C and 50°C at 0.7 bar to remove residual methanol and water. Hexanal was encapsulated within the γ-CDMOFs over a period of 48 hours. The synthesized γ-CDMOFs were characterized both before and after the encapsulation of hexanal using x-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). XRD characterization results matched literature values which confirmed uniform γ-CDMOF crystallinity and a successful synthesis. SEM images were used as an additional confirmation of the γ-CDMOF crystallinity which matched those of previous γ-CDMOF structures. TGA characterization results revealed an encapsulation efficiency of about 5%.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

The food industry is a complex arrangement of businesses across the globe that are responsible for supplying a large percentage of the world's population with food. One of the industry's largest issues is food waste that results from transportation and insufficient shelf life. Food that does not have a long shelf life cannot be transported long distances and the amount of time it can be sold in grocery stores is reduced. On top of this, the amount of time the consumer has before the food degrades in appearance, taste, and/or smell is also reduced.

As a result of the waste that is ever present in the food industry, technologies are being developed to combat this issue. One of these technologies is the utilization of metal organic frameworks (MOFs) to encapsulate molecules like hexanal for active packaging. Hexanal can be used as a synthetic plant growth regulator and the MOFs allow for a controlled release at a specific rate.

1.1 PROJECT GOALS

The goals of this project are to synthesize and confirm a successful synthesis of γ-cyclodextrin metal organic frameworks (γ-CDMOFs) through vapor diffusion as well as to investigate the encapsulation potential of hexanal in γ-CDMOFs. The purpose of the encapsulation of hexanal in γ-CDMOFs is for potential active packaging applications as a method to extend the shelf life of fruits and vegetables.

2. BACKGROUND

2.1 FOOD WASTE

Fruit and vegetable waste is an ever present problem in the modern world that results in a significant portion of the produce grown to never end up on store shelves or in the hands of consumers. The amount of fruit and vegetable waste that occurs in North America and Oceana during distribution is an estimated 28% for fresh fruits and vegetables and 10% for processed fruits and vegetables [1]. Distribution is the time in which the food is being distributed to and sold in supermarkets.

2.1.1 FOOD WASTE MECHANISMS

Fruit and vegetable waste in markets is dependent on the criteria which deems whether the produce can be sold or must be discarded as waste. Some of the most important criteria are physical appearance, taste, and texture, all three of which are affected by natural mechanisms that alter these qualities over time and are the most obvious signs of deterioration to the consumer. Changes in appearance are mostly related to discoloration on the surface of the fruit or vegetable with the most common example of this being the ripening of fruit or the yellowing of vegetables due to production of the hydrocarbon, ethylene (C_2H_4), which is naturally produced by fruits and vegetables (Figure 1) [2]. Ethylene accelerates chlorophyll degradation and metabolically transforms the natural acids present into basic compounds such as sugars which increase the pH and encourage the growth of spoilage microorganisms [3].

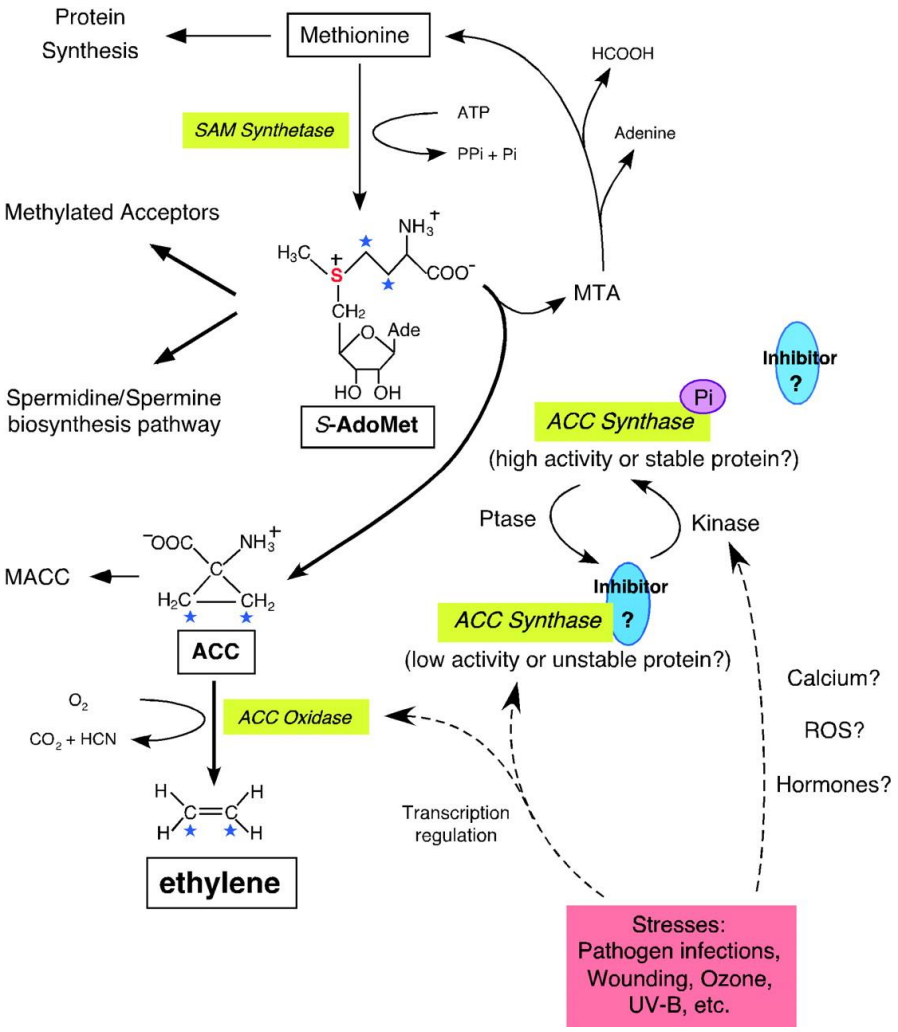

Figure 1 – Biosynthetic pathway and regulation of ethylene in plants [2].

2.2 HEXANAL

Hexanal is an organic molecule that acts as an inhibitor for the enzyme phospholipase D (PLD) which occurs naturally in plants during lipid peroxidation mediated by lipoxygenase and hydroperoxide lyases [4]. The inhibiting of this enzyme results in decreased ethylene evolution rate, oxidants content, and membrane damage which allows the fruits and vegetables to have a delayed ripening process [4]. This means that hexanal can be used as a synthetic plant growth regulator to extend the shelf life of fruits and vegetables.

2.3 PACKAGING

Packaging is an essential component of food storage and transportation in a modern society. The packaging is responsible for protecting and preserving the food bought and sold by supermarkets to consumers and for improving the transportability of that food such that it gets to the destination as quickly and efficiently as possible to extend the shelf life. Packaging is also responsible for preserving the quality and freshness of fruits and vegetables, and, with an ever-growing world population, demand for more efficient and advanced methods of packaging has led to the introduction and use of active packaging of fruits and vegetables to maintain that quality and freshness.

2.3.1 ACTIVE PACKAGING

Active packaging is defined as a type of packaging that changes the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of the food by deliberately including subsidiary constituents in either the packaging material or packaging headspace. Technologies have been researched, developed, and tested with varying amounts of success to integrate active packaging into fruit and vegetable distribution. Ethylene scavenging is a form of active packaging that aims to adsorb or actively scavenge ethylene produced from fruits and vegetables, though the success of this technology has been relatively limited due to the technical constraints of current adsorbing capacity [5]. Use of hexanal in active packaging for fruits and vegetables is a promising technology due to the way in which it inhibits the enzyme PLD which leads to decreased ethylene evolution rate, oxidants content, and membrane damage.

2.4 POROUS MATERIALS

Porous compounds are defined as solids that contain pores, including cavities, ducts, or interspaces which are filled by fluids (liquid or gas). Porous materials are characterized by their porosity which includes surface area and pore size distribution. The pore sizes of different materials divides them into three distinct categories, those that have pores with free diameter below 2 nm which are microporous, those that have pores with free diameter between 2 to 50 nm which are mesoporous, and those that have pores with a free diameter larger than 50 nm which

are denoted as macroporous [6]. Microporous, mesoporous, and macroporous materials with a uniform pore distribution offer new properties such as absorption, adsorption, exchange separation, and catalysis of different compounds [6]. Microporous, mesoporous, and macroporous materials can be manufactured with substances such as carbon, silicon, silicates, ceramics, minerals, and polymers [6].

2.4.1 Nanoporous Materials

Nanoporous materials are porous frameworks with a cavity size of less than 100 nm. Recent study has found that nanoporous materials can potentially be used for a range of applications including ion-exchange, drug delivery, and catalysis. The relevance of nanoporous materials in this case are their ability to absorb and coordinate with atoms, ions, and molecules on their interior surface and pore space [7].

2.5 Metal Organic Frameworks

Metal organic frameworks (MOFs) are defined as porous structures constructed from the coordinative bonding between metal ions and organic linkers or bridging ligands (Figure 2) [8]. MOFs are formed by anchoring metal-containing units or secondary-building units with organic linkers, by coordination, yielding open frameworks that show the exceptional features of permanent porosity, stable framework, enormous surface area, and pore volume [8]. The shape and size of the pores govern the shape and size selectivity of the guest molecules to be incorporated [8].

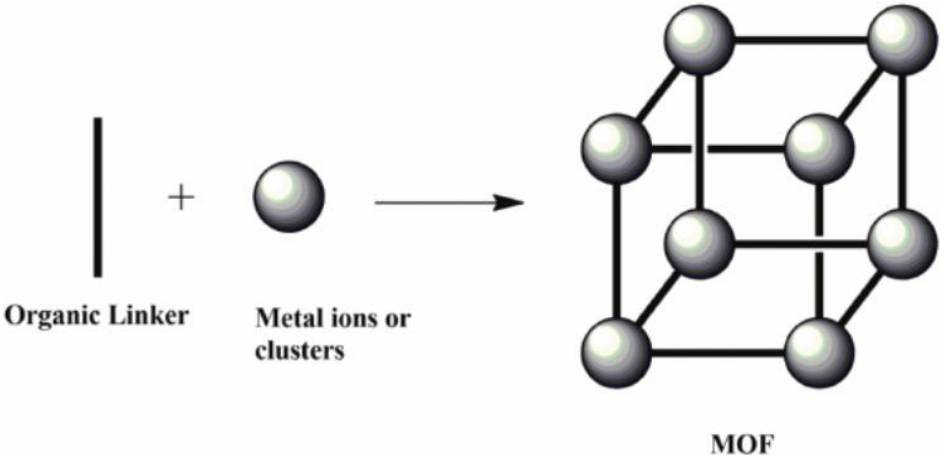

Figure 2 – Structure of metal organic framework [8].

This new field of crystalline porous materials is attracting much attention and investigation because of the large pore sizes, high apparent surface areas, selective uptake of small molecules, and optical or magnetic responses to the inclusion of guests [8]. However, perhaps the most important quality of these new materials is the ability to directly tailor these properties by making changes to their synthesis from the molecular building blocks. Solids labeled as metal organic frameworks must have strong bonding which provides the characteristic robustness of MOFs, linking units that are available for modification by organic synthesis, and a geometrically well-defined structure [8]. This well-defined structure means that the MOFs must be highly crystalline, a feature which establishes precise structure-property relationships.

Metal-containing units and organic linkers can be varied resulting in a variety of MOFs tailored for different applications. MOFs with large spaces can result in the formation of interpenetrating structure, thus it is important to carefully select the organic links used in the MOF to inhibit this interpenetration [8]. The pore size can be tuned, and the spatial cavity controlled by careful selection of metal centers and organic ligands and by adjustment of synthesis conditions (Figure 3) [8]. MOFs have pore openings up to 2 nm which allows the accommodation of small molecules, but rarely allow the accommodation of large molecules like proteins or enzymes [8].

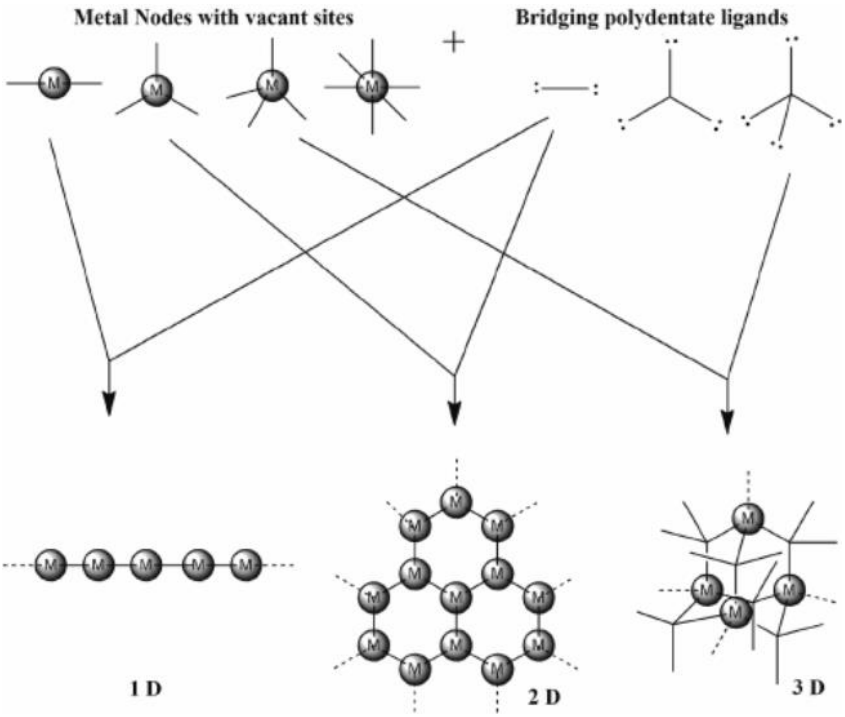

Figure 3 – MOFs resulting from different metal nodes and bridging ligands [8].

Due to the complexity and number of prerequisites to construct MOFs, they are usually derived from non-renewable petrochemical feedstocks and transition metals. Derivation of MOFs from natural products has been mostly unsuccessful due to the asymmetry of the building units which results in materials that are low in porosity and not stable. Recently, however, a non-toxic, edible, highly stable and porous MOF has been derived from renewable γ-cyclodextrin (γ-CD) [7].

2.6 γ-CYCLODEXTRIN

Cyclodextrins are natural, symmetric cyclic oligosaccharides produced from starch by enzymatic conversion (Figure 4). γ-CD is metabolized in the human body by α-amylase which is found in saliva and tears. γ-CD is hydrophilic with numerous hydroxy groups on its outer surface, however, its solubility in water is limited due to intermolecular hydrogen bonding in the crystalline state. Random substitution of the hydroxy groups, even by lipophilic methyl moieties, will enhance the solubility of γ-CD in water.

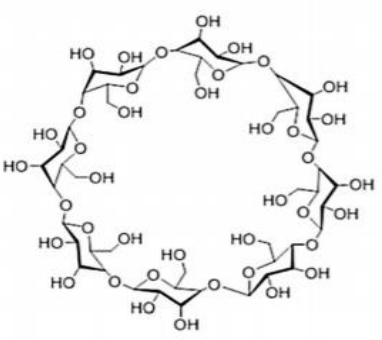

Figure 4 – Structure of γ-cyclodextrin [9].

Compared to the other natural CDs (α-CD, β-CD), γ-CD has the largest hydrophobic cavity, the highest water solubility, and the most favorable toxicological profile (Table I). This means that γ-CD has the highest potential since it can encapsulate the most material and dissolve in water much easier than the other CDs (α-CD solubility in water is 14.5% w/v, β-CD solubility in water is 1.85% w/v). γ-CD's hydrophilic profile means it does not penetrate quickly into the biological membranes of the body and can be quickly digested by the bacteria in the gastrointestinal tract [9].

Table I – Properties of γ-CD [7].

Property	γ-CD
# of Glucopyranose Units	8
Molecular Weight (g/mol)	1297
Solubility in Water at 25°C (%, w/v)	23.2
Outer Diameter (Å)	17.5
Cavity Diameter (Å)	7.5-8.3
Height of Torus (Å)	7.9
Cavity Volume (Å)	427

Encapsulation of hexanal in γ-CD has been mostly unresearched, however, studies have been conducted on encapsulation of 1-MCP in β-CD. Molecular encapsulation agent is defined as a compound that has a lock and key structure similar to an enzyme whereby a substrate selectively fits into the encapsulation site. A lock and key structure refers to one guest molecule or part of the guest molecule that is anchored in the host substrate due to stereometric compatibility of the guest with the host; this is true for 1-MCP in CD (**Error! Reference source not found.**) [11].

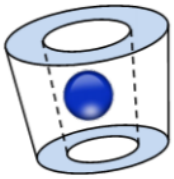

Figure 5 – Encapsulation of 1-MCP in CD [11].

1-MCP adsorption in modified β-CD and zeolite (zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts) materials occur for a group of 1-MCP molecules rather than the lock and key structure where a single guest is anchored in a single host. The pore structure in β-CD can be cage-like and tube-like, and the size of the pore opening determines the type of gas that can be trapped (**Error! Reference source not found.**) [11]. The group of molecules are aligned on the interior of surface of the pore.

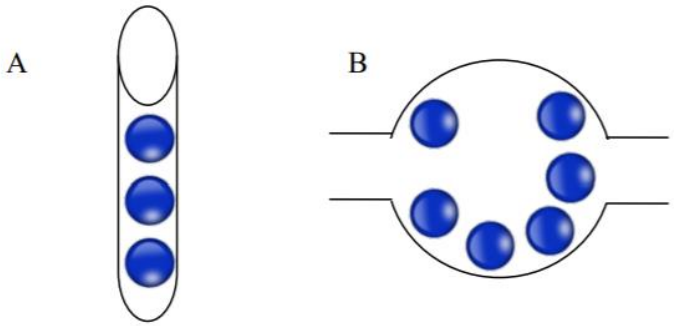

Figure 6 – Adsorption of 1-MCP in zeolites. (a) tube-like structure. (b) cage-like structure.

2.7 γ-Cyclodextrin Metal Organic Frameworks

γ-Cyclodextrin metal organic frameworks (γ-CDMOFs) are highly porous; γ-CDMOF is composed of six γ-CD tori with alternating K^+ cation coordination, resulting in $(\gamma\text{-CD})_6$ cubes. The cubes are also linked together by K^+ cations coordinated on the secondary faces of the γ-CD tori, leading to an extended porous superstructure (Figure 7) [10]. This coordination results in an extended and highly porous structure [7]. This structure results in a high specific surface area (the total surface area of a material per unit of mass or volume). Specific surface area is important when evaluating nanoporous materials since it serves as a method for assessing adsorption potential and porosity. The structural unity of γ-CDMOFs promotes cohesion and

stability so the molecule does not collapse when exposed to certain environments and stresses. The stability, porosity, non-toxicity, bioavailability, and tailorability of γ-CDMOFs make them a viable option for use in active packaging of fruits and vegetables.

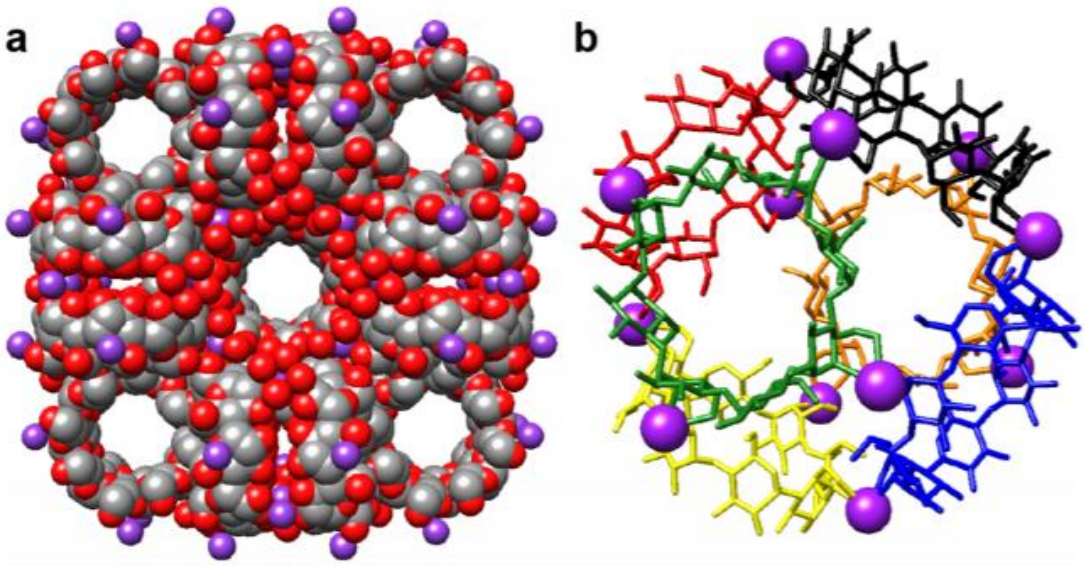

Figure 7 – (a) Space-filled representation of the solid-state extended structure of γ-CDMOF where carbon is gray, oxygen is red, and K^+ is purple. (b) $(\gamma\text{-CD})_6$ cubic unit constructed by coordination of K^+ cations (purple spheres) to the primary face of γ-CD [10].

2.8 Encapsulation of Hexanal in γ-CD MOFs

Encapsulation of hexanal in γ-CDMOFs has been mostly unresearched, however, previous research has been conducted on the encapsulation of ethanol in γ-CDMOFs which achieved an encapsulation efficiency of about 20% [12].

3. MATERIALS AND METHODOLOGY

3.1 MATERIALS

γ-Cyclodextrin (anhydrous, > 99 purity), potassium hydroxide (ACS reagent, ≥ 85% purity) in pellets was provided by Dr. Ajay Kathuria of California Polytechnic State University (San Luis Obispo, CA, USA). Methanol (≥ 99.9% purity) and hexanal (98% purity) were purchased from Sigma Aldrich (Saint Louis, MO, USA).

3.2 OVERVIEW OF METHODOLOGY

γ-CDMOF crystals were synthesized using vapor diffusion of methanol into a solution of γ-CD and KOH. The γ-CDMOF crystals were activated in a low temperature oven to remove residual methanol and water as well as to open up the pores of the γ-CDMOF prior to encapsulation. XRD and SEM were used to characterize the γ-CDMOF crystallinity which was compared against literature results. After activation, hexanal was encapsulated within the γ-CDMOF crystals for 48 hours and characterized using TGA and XRD to determine the encapsulation efficiency.

3.3 VAPOR DIFFUSION SYNTHESIS OF γ -CDMOF

1.30 g of γ-CD and 0.45 g of KOH (1 mol γ-CD:8 mol KOH) were dissolved into a 50 mL beaker containing 20 mL of deionized water. The γ-CD + KOH solution was stirred for 6 hours at 600 rpm and room temperature. Next, the beaker containing the γ-CD + KOH was placed inside a 250 mL beaker containing 50 mL of methanol. The opening of the 250 mL beaker was covered with parafilm to allow for the methanol vapor to diffuse into the γ-CD + KOH solution. The 250 mL beaker containing the methanol and the 50 mL beaker of γ-CD + KOH solution was left for seven days at room temperature to allow for the growth of γ-CDMOF crystals. On the seventh day, the crystals were filtered, covered in methanol, and left for three days to remove any unlinked K+ ions from the structure of the γ-CDMOF crystals.

3.4 ACTIVATION

The crystals were filtered once more and placed into a 50 mL beaker for activation. The 50 mL beaker containing the γ-CDMOF crystals was placed inside of a vacuum oven and left for 10 hours at 25°C and then for 12 hours at 50°C to remove any residual methanol or volatile compounds and to open up the pores of the γ-CDMOF structures. Figure 8 visually describes the synthesis and activation procedures for γ-CDMOFs.

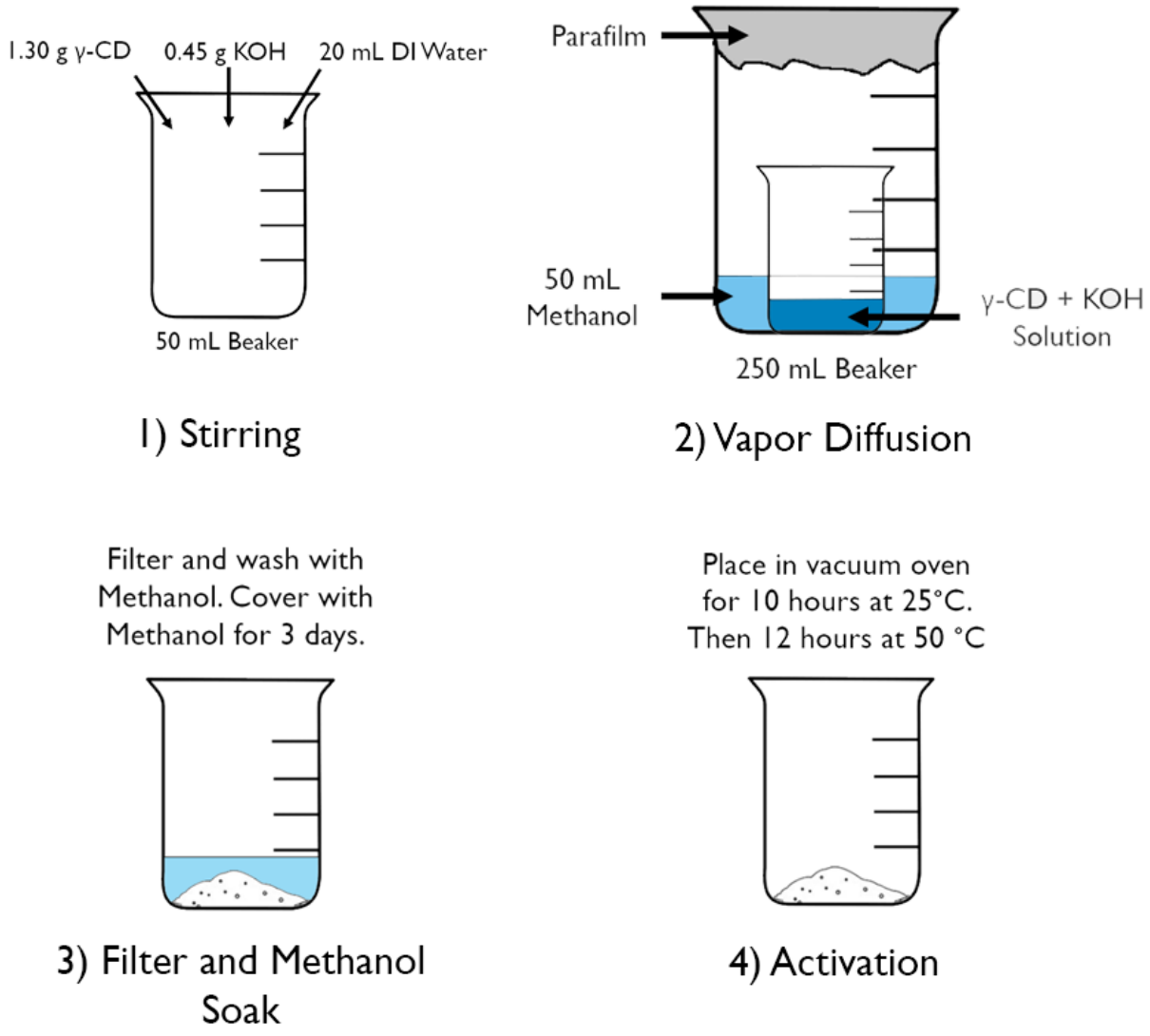

Figure 8 – Synthesis and activation procedure for γ-CDMOFs.

3.5 Encapsulation of Hexanal in γ -CDMOFs

Encapsulation of the hexanal was performed after activation of the γ-CDMOFs. 1 g of the γ-CDMOFs was placed into a 50 mL beaker. That 50 mL beaker was then placed inside of a 250 mL beaker which contained 5 mL of hexanal. The 250 mL beaker was covered with parafilm to allow hexanal encapsulation within the γ-CDMOFs over 48 hours. Figure 9 shows the encapsulation process used.

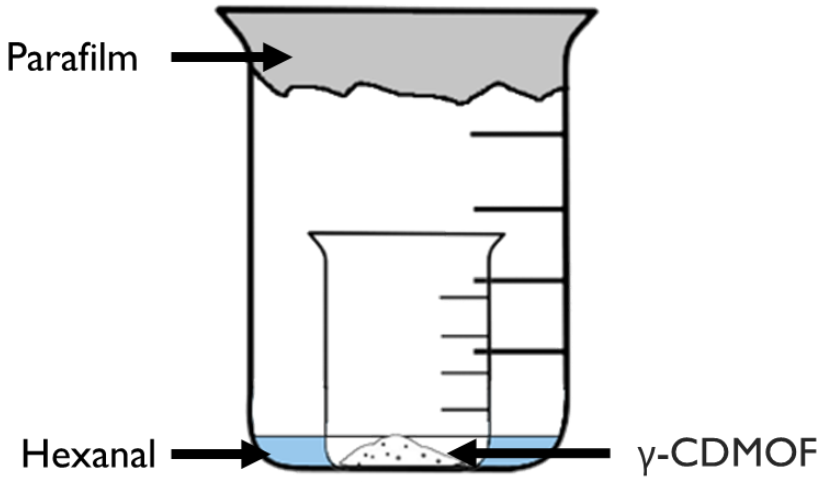

Figure 9 – Procedure for encapsulation of hexanal in γ-CDMOFs.

3.6 Characterization of γ-CDMOFs

The γ-CDMOFs were characterized prior to encapsulation with hexanal using X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). XRD was performed to evaluate the crystallinity of the γ-CDMOFs and to determine if a successful synthesis had taken place. SEM images were captured to examine the physical appearance, shape, and size of the γ-CDMOF crystals to confirm the results of XRD. TGA was performed after confirmation that a successful synthesis of the γ-CDMOFs had taken place to establish a baseline of the degradation of the γ-CDMOFs with increasing temperature.

The γ-CDMOFs were characterized again after encapsulation of hexanal using XRD and TGA. XRD was performed to evaluate whether a change in crystallinity had occurred after encapsulation. TGA was used to examine the degradation of the hexanal encapsulated γ-CDMOFs.

3.6.1 XRD Characterization

XRD characterization of the γ-CDMOFs before and after encapsulation of hexanal was performed with a Siemens Diffractometer D5000 with CuK_α radiation (k = 1.5418 Å, λ = 0.154 nm) at 40 kV and 30 mA using a divergence and antiscatter slit of 2 mm and a detector slit of 0.6 mm. XRD scans were taken from 2-40° at 0.02 increments at a scan speed of 0.1 $sec \cdot step^{-1}$. All XRD tests were performed using the powder sample holder.

3.6.2 SEM Characterization

SEM characterization of the γ-CDMOFs before encapsulation of hexanal was performed with a FEI Quanta 200 scanning electron microscope using the low vacuum mode with an internal pressure of 130 Pa using water as the gas. The γ-CDMOF crystals were adhered to carbon black tape which had been mounted onto a sample stage. The acceleration voltage was set to 12.5 kV, the spot size to 4, and the working distance to 5 mm.

3.6.3 TGA Characterization

TGA characterization of the γ-CDMOFs before and after encapsulation of hexanal was performed with a Mettler Toledo thermogravimetric analyzer with nitrogen as the purge gas with a balance purge flow of 40 $mL \cdot min^{-1}$ and a sample purge flow of 60 $mL \cdot min^{-1}$. The γ-CDMOF crystals were heated from 25-600°C at a rate of 10°$C \cdot min^{-1}$ using a ceramic pan.

4. Results and Discussion

4.1 X-Ray Diffraction

Figure 10 shows the diffractogram produced by the γ-CDMOFs prior to encapsulation. Three distinct peaks are seen at 3.96°, 5.68°, and 6.96° which are similar to the peaks of those found in literature but at different intensities [12] [13]. Intensities of the γ-CDMOFs characterized by XRD can vary depending on crystal size or differences in instrumentation so the most significant results obtained by this diffractogram are the similarities of 2θ angles to those found in literature. The peak angles had corresponding crystallographic planes of (110), (200), and (211), respectively [13].

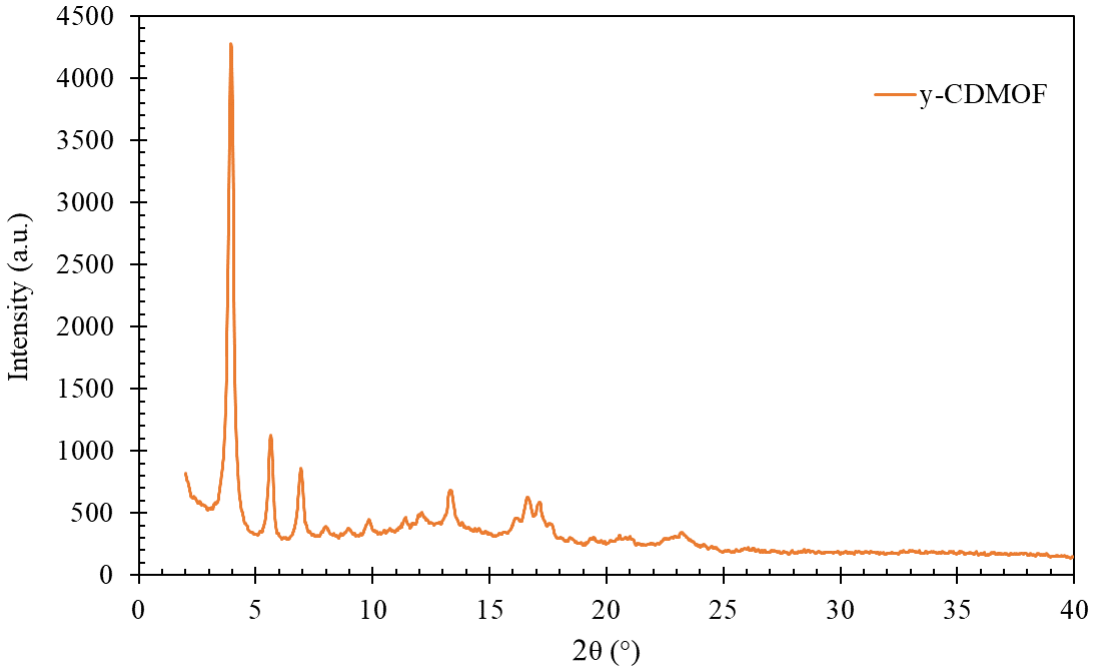

Figure 10 – XRD diffractogram of the γ-CDMOFs prior to encapsulation of hexanal.

Figure 11 shows the diffractogram produced by the hexanal encapsulated γ-CDMOFs. The peaks observed from the previous diffractogram of the γ-CDMOFs prior to hexanal encapsulation were significantly decreased which suggests the possibility of a reduction in crystallinity of the γ-CDMOFs after encapsulation with hexanal. While the intensities of the diffractogram peaks were significantly reduced after the encapsulation of hexanal, the behavior of this reduction was also

seen with encapsulation results of previous literature which suggests that there was not a decrease in crystallinity after encapsulation [7] [12]. Figure 12 compares the diffractograms produced before and after encapsulation of hexanal.

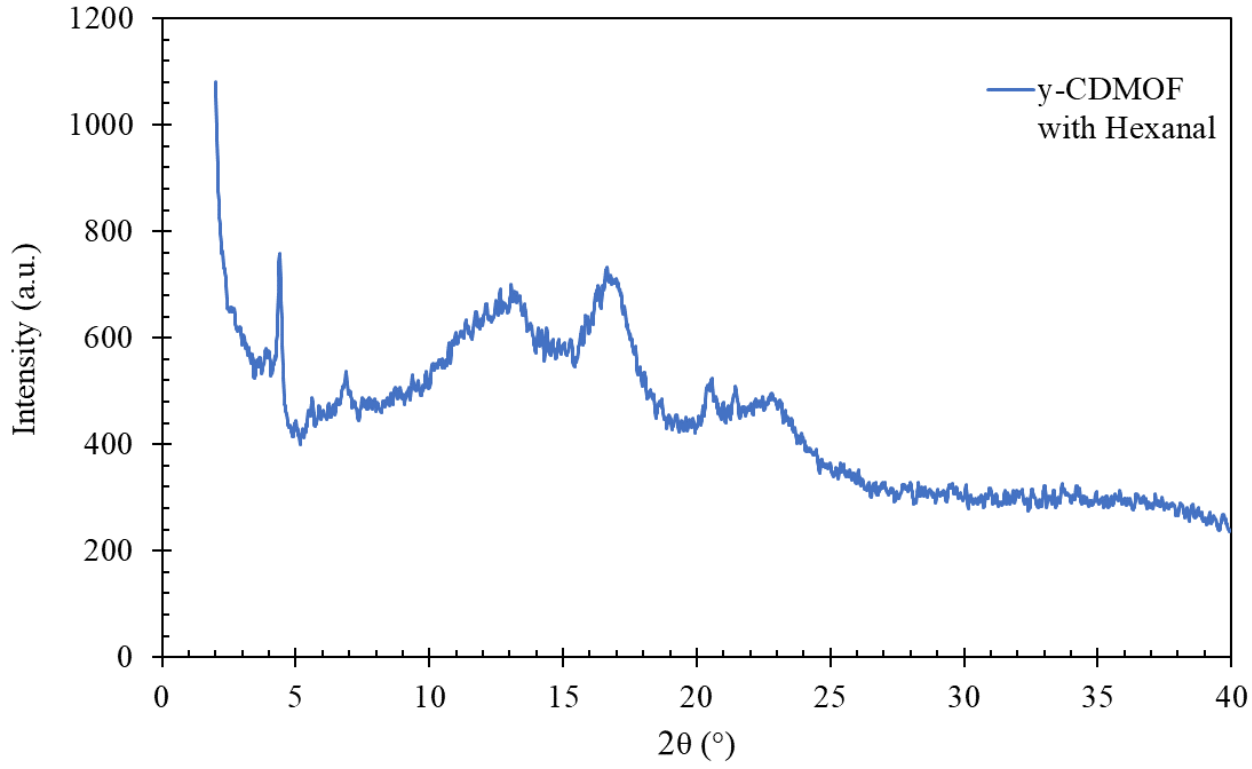

Figure 11 – XRD diffractogram of the γ-CDMOFs after encapsulation of hexanal.

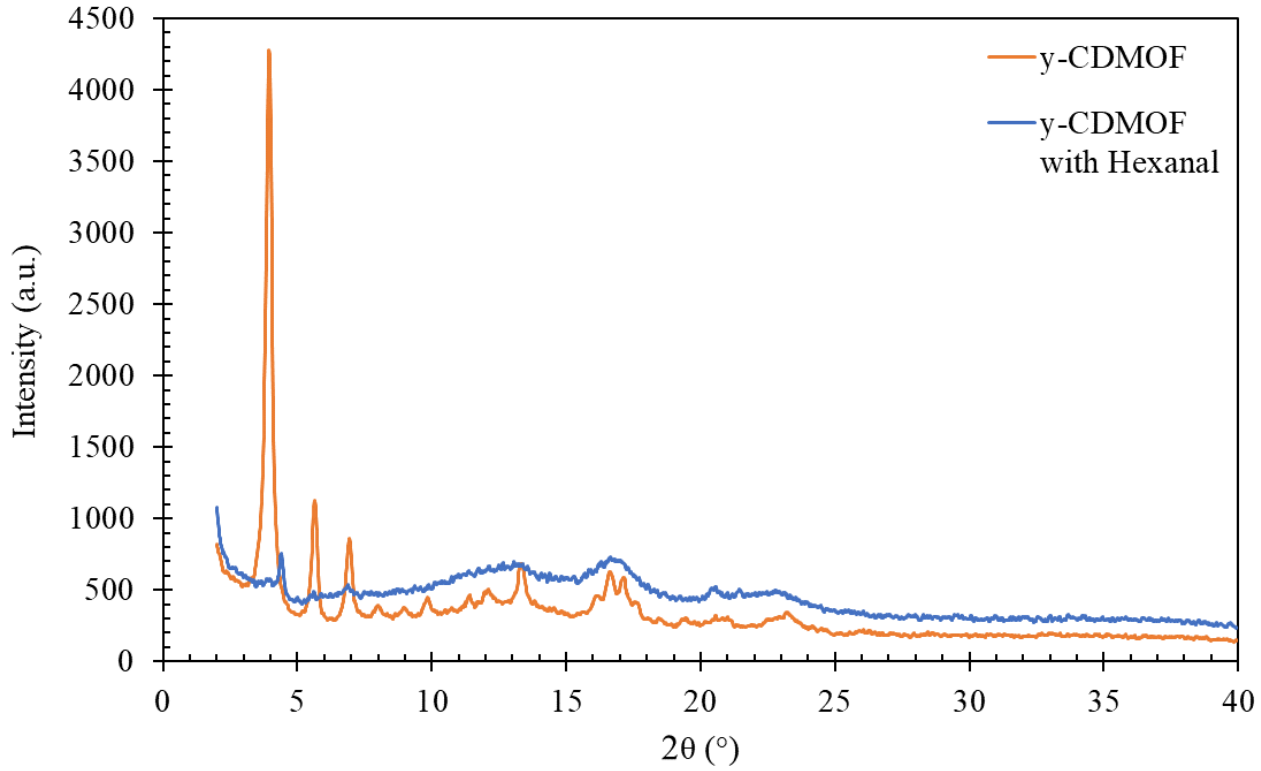

Figure 12 – XRD diffractograms of γ-CDMOFs before and after encapsulation of hexanal.

4.2 Scanning Electron Microscopy

Figure 13 shows the SEM micrograph produced by the γ-CDMOFs prior to encapsulation of hexanal. The image was used to evaluate the crystallinity of the γ-CDMOFs to confirm the results of XRD and that a successful synthesis had taken place. The size, shape, and physical appearance of the γ-CDMOFs were comparable to micrographs found in previous literature [7] [12] [13].

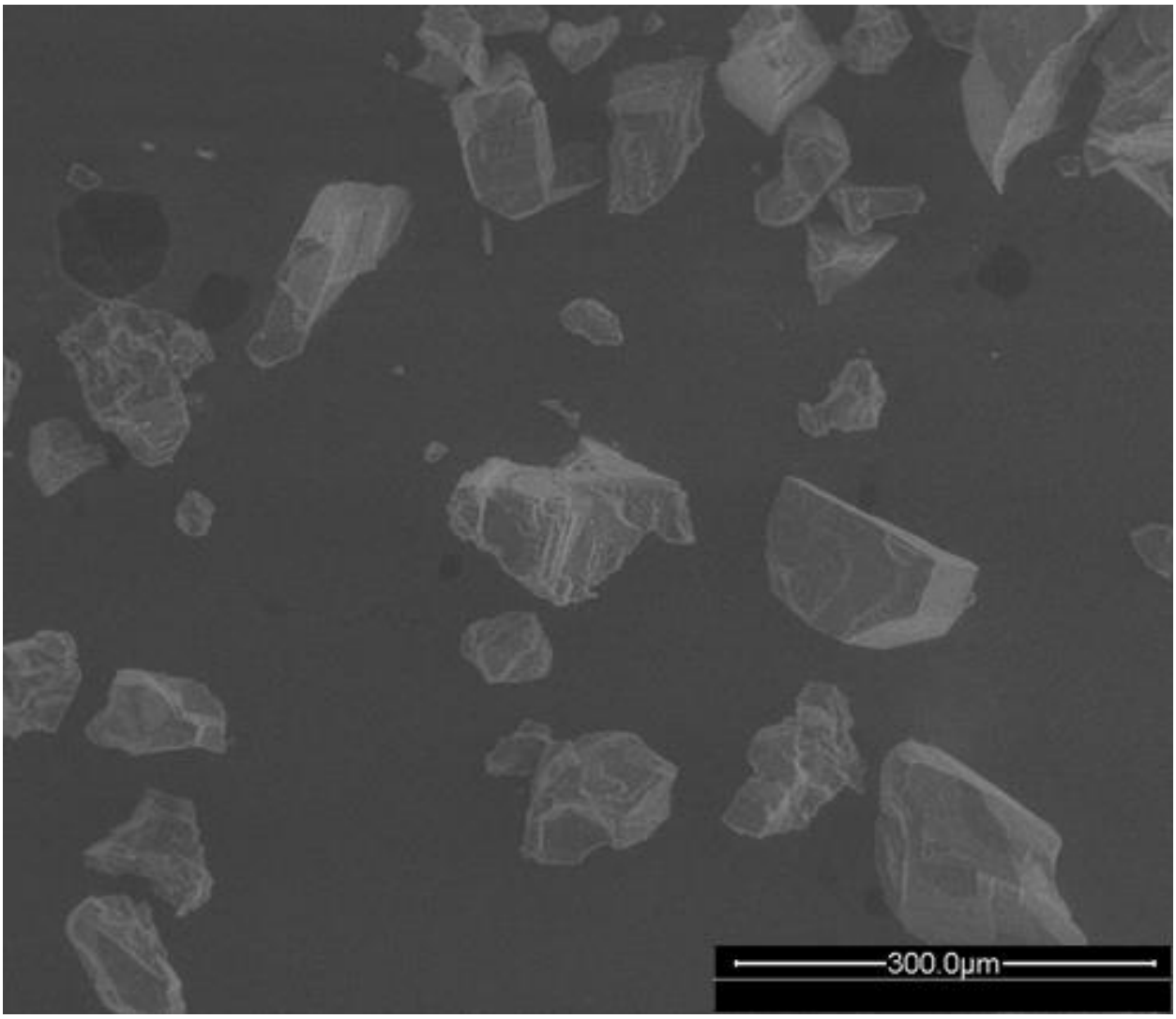

Figure 13 – SEM micrograph of γ-CDMOFs prior to encapsulation of hexanal.

4.3 THERMOGRAVIMETRIC ANALYSIS

Figure 14 shows the TGA thermograms of the γ-CDMOFs before and after the encapsulation of hexanal. The curves of the thermograms indicate two pronounced regions of degradation of the γ-CDMOFs. Derivative slops were calculated for the thermogram curves to identify significant regions of degradation.

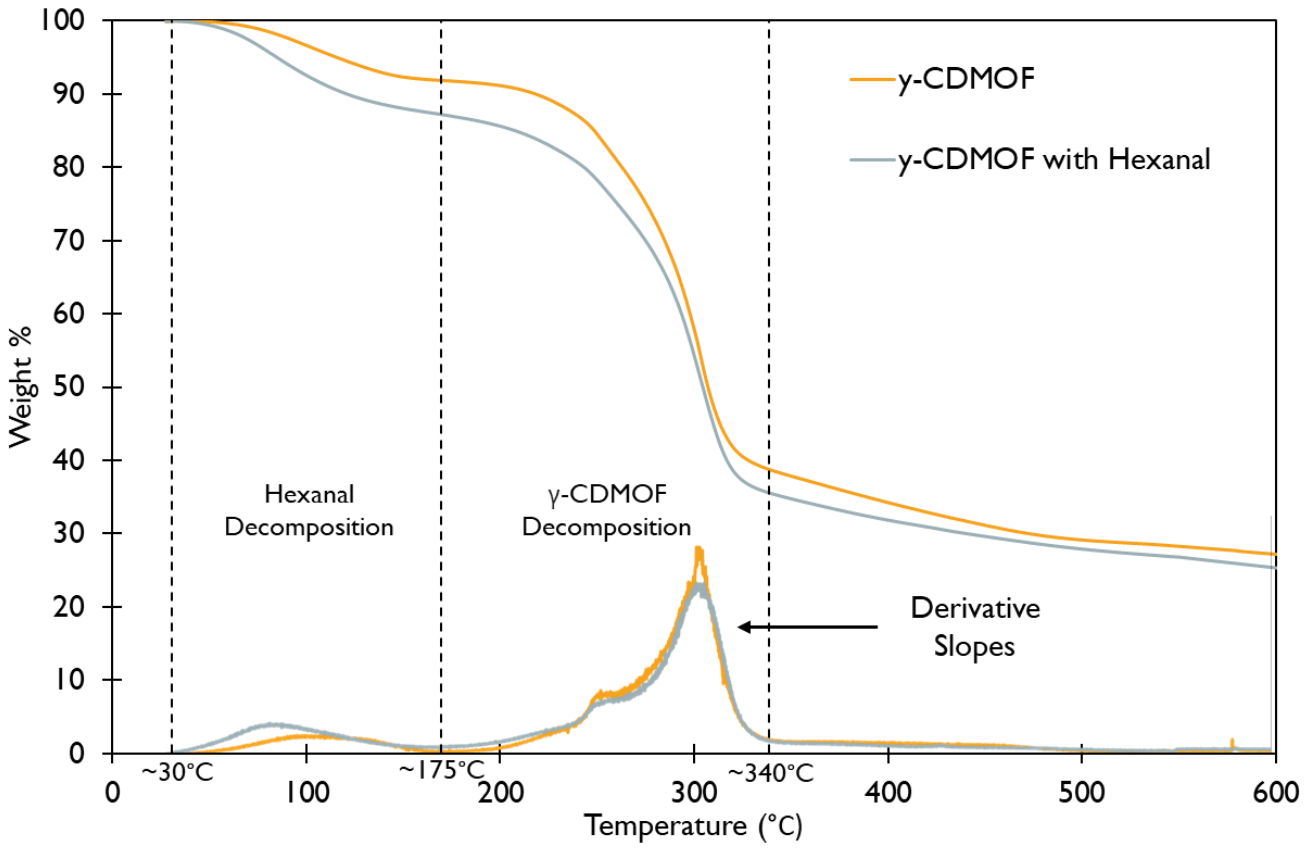

Figure 14 – TGA thermograms of γ-CDMOFs before and after encapsulation of hexanal.

The first region is associated with a decomposition of hexanal and other residual compounds such as methanol and water which comprised a weight loss of about 8% for the γ-CDMOFs without hexanal and about 13% for the γ-CDMOFs with hexanal. It should be noted that the γ-CDMOFs prior to encapsulation still show a significant weight loss in this region which suggests that the activation procedure did not completely remove all the residual compounds from within the structure of the γ-CDMOFs. The second region is associated with a decomposition of the γ-CDMOFs themselves and comprised a weight loss of about 53% without hexanal and about 51% with hexanal. Using the weight % of the thermogram curves in conjunction with the border of the hexanal and γ-CDMOF degradation range it can be concluded, based on the difference in weight % of the curves, that the hexanal had an encapsulation efficiency in the γ-CDMOFs of about 5%. This appears to be a low encapsulation efficiency, however, in comparison to previous research on the encapsulation efficiency of ethanal in γ-CDMOFs which was about 20%, it is more evident on why it is so low since the size of hexanal is about 4x that of ethanol.

5. CONCLUSIONS

1. Based on the results obtained through XRD and SEM characterization of the γ-CDMOFs prior to encapsulation, it is evident that the γ-CDMOFs were successfully synthesized through vapor diffusion.

2. The results obtained by TGA characterization of the γ-CDMOFs before and after encapsulation of hexanal yield an encapsulation efficiency of about 5%.

6. FUTURE WORK

The research conducted throughout this report stands as an initial investigation into the possibilities of encapsulating hexanal within γ-CDMOFs for active packaging purposes. One area of study to investigate in the future would be to incorporate the hexanal encapsulated γ-CDMOFs into active packaging and investigate the effects on shelf life of fruits and vegetables against a packaging that does not contain the hexanal encapsulated γ-CDMOFs. Expanding on this, a study could be conducted on an optimization or control of the release rate of the hexanal from the γ-CDMOFs to further extend the shelf life of the fruits and vegetables.

Another area of study to consider is to investigate the unremoved residual compounds present in the γ-CDMOFs after activation and whether a larger amount of those compounds can be removed by altering the activation procedure. By pursuing this area of investigation, it may be possible to increase the encapsulation efficiency of hexanal in the γ-CDMOFs. A related investigation could be performed to optimize the γ-CDMOF synthesis procedure to further increase the encapsulation efficiency of hexanal within the γ-CDMOFs.

REFERENCES

[1] J. C. Buzby, H. F. Wells, B. Axtman and J. Mickey, *Supermarket Loss Estimates for Fresh Fruit, Vegetables, Meat, Poultry, and SeaFood and their Use in the ERS Loss-Adjusted Food Availability Data,* 2009.

[2] K. L.-C. Wang, H. Li and J. R. Ecker, *Ethylene Biosynthesis and Signaling Networks,* 2002.

[3] J. P. Kerry, *New Packaging Technologies, Materials and Formats for Fast-Moving Consumer Products,* Elsevier Ltd., 2014.

[4] M. Jincy, M. Djanaguiraman, J. P, K. Subramanian, S. Jayasankar and G. Paliyath, "Inhibition of phospholipase D enzyme activity through hexanal leads to delayed mango (Mangifera indica L.) fruit ripening through changes in oxidants and antioxidant enzymes activity," *Scientia Horticulturae,* vol. 218, pp. 316-325, 2017.

[5] L. Vermeiren, F. Devlieghere, M. v. Beest, N. d. Kruijf and J. Debevere, *Developments in the active packaging of foods,* Elsevier, 1999.

[6] V. Solano-Umaña and J. R. Vega-Baudrit, *Micro, Meso and Macro Porous Materials on Medicine,* 2015.

[7] R. Harden and E. Sommerville, *Synthesis of ɣ-Cyclodextrin Metal Organic Frameworks and the Encapsulation of Caffeine and Theophylline,* 2018.

[8] E. Sharmin and F. Zafar, *Introductory Chapter: Metal Organic Frameworks (MOFs),* 2016.

[9] P. Saokham and T. Loftsson, *γ-Cyclodextrin,* Elsevier, 2017.

[10] K. J. Hartlieb, D. P. Ferris, J. M. Holcroft, I. Kandela, C. L. Stern, M. S. Nassar, Y. Y. Botros and J. F. Stoddart, *Encapsulation of Ibuprofen in CD-MOF and Related Bioavailability Studies,* 2017.

[11] X. Chen, *Development of 1-Methylcyclopropene Delivery Formulations for Modifying Response of Fresh Produce,* 2015.

[12] A.-K. Pauwels and A. Kathuria, "Masters Thesis," 2019.

[13] S. Al-Ghamdi, "SYNTHESIS OF NANOPOROUS CARBOHYDRATE METAL-ORGANIC FRAMEWORK AND ENCAPSULATION OF SELECTED ORGANIC COMPOUNDS," 2014.