Novel Catalytic Etherification Reaction of Glycerol to Short-Chain Polyglycerol

A thesis presented to
the faculty of
the Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

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April 2017
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This thesis titled
Novel Catalytic Etherification Reaction of Glycerol to Short-Chain Polyglycerol

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ABSTRACT

VAHDATZAMAN, MARAL, M.S., April 2017, Chemical and Biomolecular Engineering
Novel Catalytic Etherification Reaction of Glycerol to Short-Chain Polyglycerol (63 pp.)
Director of Thesis: Sunggyu Lee

A study that shows a novel technique to treat and enhance solid catalyst morphological properties that can be used in glycerol polymerization etherification reaction is here reported. More specifically, supercritical (SC) CO$_2$ fluid technology and impregnation treatments have been utilized on zeolite Y sodium (ZYS) to increase available pore volume and average pore size, to maximize surface area for reaction to occur, and to enhance the material catalytic activity. SC-treatment on ZYS was performed in a bolt-closure reactor at $260^\circ$C and 10.34 MPa. Impregnation treatment was performed by immersing the catalyst in solutions with different concentrations of sodium carbonate (Na$_2$CO$_3$). After exposing the catalyst to the Na$_2$CO$_3$, calcination took place. Results indicated that SC-treatment does increase the average pore size by an average of 46.2 Å, which leads to an increase in available pore volume. Glycerol conversion proved to be at its highest when the catalyst was impregnated; glycerol conversions surpassed 90%. The effect on di/triglycerol selectivities were also studied, and these proved to be a function of reaction time, Na$_2$CO$_3$ concentration, and temperature. The solid catalyst physical and performance properties were studied by accelerated surface area porosimetry (ASAP), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and also in an glycerol etherification reaction setup. The best performing catalyst was the SC-treated and impregnated, showing higher meso-to-micro pore distribution, glycerol conversion higher than 90%, and highest di/triglycerol selectivities.
DEDICATION

To my husband Allen A. Rodriguez for his unconditional support throughout my studies and graduate life’s challenges, for always being there for me and helping me towards becoming a better person and professional. I believe that without him this step in my professional life would not be possible. Thank you.

To my mother Maryam Mohammadalipour for believing and encouraging me to become my very best, for loving me, and for always standing next to me regardless of the situation.

To my aunt Shahin Mohammadalipour for being like a mother to me and caring for me as if I was her own daughter; for her emotional, and financial support, and for being not only like a mother, but also a best friend to me.

Finally, I dedicate this work to God, who gave me the health, capacity, and strength to achieve another step in my professional life.
ACKNOWLEDGMENTS

I want to thank my graduate advisor Dr. Sunggyu Lee, and my graduate committee Dr. Monica Burdick, Dr. Douglas Goetz, and Dr. Jixin Chen for their guide throughout the development of my research and this final work. I give thanks to Dr. John Staser for his feedback, help and guidance throughout the writing of my proposal. I also take this opportunity to thank graduate students: Hamed Bateni and Gregory Horne. My gratefulness to Hamed for providing me with information and support that helped polish this final presented work and to Gregory for his technical support and help.

Special thanks goes to my husband Allen A. Rodriguez for his time devoted towards the help and guidance with the writing of this document, the research work hereby presented, my preparation for proposal and oral defense, and overall, for his help on every step of the way until this moment. I would also like to thank Dr. Alberto Santana for helping me in the edition of this document, and for assisting me with research-related questions.

Finally, I would like to thank the Chemical Engineering Department Staff and Faculty especially, Tom Riggs for providing support throughout my time as a graduate student and assisting me in situations encountered throughout.
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CHAPTER 1 INTRODUCTION

1.1 Project Overview

Polyglycerol (PG) is a highly branched polyol that is a biocompatible oxygenated compound. It has highly active functional hydroxyl groups which permit for different functionalization pathways that give birth to certain polymer derivatives. These derivatives can be used in different industries such as food, pharmaceutical and cosmetics. PG is also characterized as a clear, viscous, non-volatile polymer which is soluble in polar solvents at room temperature. These, among other beneficial characteristics of the polymer, are what makes the synthesis of this compound attractive not only from a manufacturer standpoint, but for being environmentally-friendly. Behind the polymeric material success lies the fact that PG can be synthesized starting from glycerol, an over-abundant byproduct from the biodiesel industry.

Estimates indicate that more than 4 billion gallons of crude glycerol are produced per year, with the highest percentage of this compound being considered as waste [1] . On the average, per every ton of biodiesel produced about 100 kg of glycerol byproducts are generated as well [2] . This has been considered a potential problem and drawback in the biodiesel production processes as the applications and uses of glycerol are limited in the current market. Glycerol has found use, mainly, in combustion and heat supply for industrial units such as boilers [3, 4] . Due to a strong demand for biofuel, biodiesel production rapidly increased in the past decade which, indirectly, increased the glycerol generation while leaving its demand relatively constant or flat. Therefore, biodiesel production industries are constantly looking for market options that permit to add values and increase the glycerol demand.

Because of these facts, a great deal of attention has been devoted to the synthesis of PG from glycerol not only to reduce the amount of waste, but to generate value
added chemicals thereby increasing glycerols market value which will in turn improve biodiesels profitability by reducing biodiesel’s production price by as much as 25% [5].

To date, conversion of glycerol to PG has been mainly studied and performed by the use of homogeneous catalysis while less attention has been paid to the heterogeneous-catalytic conversion.

In recent years, conversion of glycerol to short-chain PG has been mostly done by an etherification reaction which uses a sodium carbonate solution as the homogeneous catalyst. Due to the reaction nature, an excessive amount of water is needed in order to filter, neutralize and purify the catalyst products, which is an undesired condition from an environmental and economic standpoint. Besides the need based on the reaction nature, homogeneous catalysts are generally environmental unfriendly and expensive to operate. Due to this concern, attention has been shifted toward the replacement of homogeneous catalysts by efficient heterogeneous catalysts. More specifically, zeolites which are naturally occurring, have shown to be potentially promising solid catalysts and, based on the previous work performed in our research lab, it has also been found that supercritical fluid treatment could enhance the surface activity of such catalytic substance. Although previous published articles have shown that zeolites are good candidates for the PG synthesis [5–7], little has been accomplished in terms of the optimization of the catalytic activity management as well as the investigation of resultant kinetics of the overall process conversion.

1.2 Statement of Objectives

The overall objective of this work was to develop an efficient heterogeneous catalyst that can be effectively used for the PG synthesis with a higher yield and selectivity than the currently available homogeneous catalysts, without sacrificing the overall glycerol conversion to PG. Heterogeneous catalysts inherently surpass homogeneous ones in that
they simplify the catalyst separation and recovery processes. Therefore, the recovered catalysts can be easily washed and reused, thus making the process economically more prudent. Other potential benefits include the enhanced catalyst thermal stability. Therefore, the specific objectives of this work were to: (1) pre-condition selected zeolite for maximizing its available surface area for the desired reaction using supercritical fluid processing, (2) impregnate and embed the pre-conditioned zeolite with sodium carbonate for catalyst activity enhancement, (3) test the synthesized catalyst in etherification reaction of PG from glycerol and quantify the selectivity of each type of PG produced from this reaction in order to evaluate the catalyst performance.

By meeting these objectives, is believed that it is possible to significantly impact the way PG is synthesized commercially. Not only this work demonstrates that it is possible to add value to glycerol and reduce biodiesel’s production costs, but also that it is possible to significantly enhance the way this polymer/oligomer is currently being produced. This project aimed at introducing a novel zeolite catalyst system that not only enhances the active surface area availability, but also helps control the polydispersity of PG, or the chain length of PG product.

The chemical and physical properties of the catalyst were examined using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and accelerated surface and porosity analyzer (ASAP). The catalyst performance in the PG etherification reaction from glycerol was studied in a batch reactor purged with nitrogen. Results on the selectivity and conversion were validated by gas chromatography (GC).

1.3 Project Significance

Homogeneously-based catalysts, as previously mentioned, presents certain drawbacks that can be obviated if these are replaced with heterogeneous catalysts. In general,
homogeneous catalyst itself is more expensive than most heterogeneous catalysts. Furthermore, a massive amount of water and a great deal of efforts would be required to separate the reactor effluent of catalyst-products mixture. Therefore, heterogeneously-based catalysts are considered a more favorable and better alternative in industrial applications for polymerization reactions. Although these catalysts have been used before in industrial applications, their use has been quite limited, mainly due to the lack of successful development and enhancement of these heterogeneous catalysts.

Zeolites have been utilized for glycerol conversion to PG, however, its optimization, surface area enhancement, and catalytic activity has not been further studied nor looked into. In this work zeolites were supercritically pre-treated; technique that prove to be optimum for increasing average pore size and volume. More specifically, zeolites (as retrieved from nature) have small semi-closed pores which are not available for reaction catalysis due to their small size (nanometer-scale 0.52 nm) and blockage; glycerol molecules size is bigger than 0.52 nm so glycerols molecules cannot diffuse into these pores. Furthermore, previous work in our laboratory has demonstrated that supercritical treatment of these catalysts could increase these pore opening sizes, therefore, making them available for reaction catalysis. Literature reports that sodium carbonate has a good catalytic activity (although not selective), which is why it was believed that chemically treating these supercritically pre-treated zeolites with sodium carbonate would enhance its catalytic activity.

Project success demonstrated a novel way to decrease the micropores distribution which limits the catalyst ability to be used in glycerol polymerization industrial applications, and generate a broader distribution of mesopores, which sizes are optimum for this process. Furthermore, catalytic activity of the catalyst was enhanced by the impregnation of sodium carbonate (Na$_2$CO$_3$). Overall, is believed that this work presents
the solid foundation for and easy-fast-selective way to convert glycerol to short-chained polyglycerol.
CHAPTER 2  LITERATURE REVIEW

2.1 Background

2.1.1 Biodiesel & Glycerol

Biodiesel is one of the promising renewable and sustainable energy sources which is a product of the transesterification of animal fat or vegetable oil with alcohols. About 10% of biodiesel production yields a coproduct of crude glycerol which is considered a wasteful or low-value byproduct [8]. Based on the increase of biodiesel production over the last decade, the supply of glycerol exceeds far more than its demand and if a niche sale market can be developed for crude glycerol and its derivatives, the price of biodiesel production would be lowered by approximately 25% [9].

There are three types of glycerol available on the current market, viz., crude glycerol, purified glycerol, and refined glycerol [10]. Crude glycerol has 60 to 80 percent of glycerol content and the rest is composed of impurities such as ash, soap, alcohols, moisture and others, while purified and refined glycerol are close to 100% pure and have less acidity than crude glycerol [11]. Therefore, if glycerol is to be used in sensitive applications such as pharmaceuticals and food industry, it should be purified to a tight specification beforehand. Glycerol that is being obtained from biodiesel industry is crude glycerol and has impurities such as catalyst residues, alcohols and fatty acids that are being used for or formed during biodiesel production. To remove these impurities and enhance the glycerols quality, this byproduct usually goes through a series of separation processes such as filtration, fractionating vacuum distillation and/or chemical additions [5]. Although the aforementioned processes involve high costs, the obtained purified glycerol still claims its relatively low price (roughly 20 to 30 cents per pound). Since refined glycerol will be used in the proposed work, materials costs are not significantly affected.
As for the chemical conversion potential, glycerol’s chemical properties allow it to be a compound that could be readily converted into value-added chemicals [12]. There are several different catalytic reaction pathways to convert glycerol into other higher-valued products, which include oxidation, hydrogenolysis, dehydration, pyrolysis, transesterification, etherification, oligomerization, and polymerization [13, 14].

2.1.2 Etherification Reaction & Polyglycerol

Etherification-type reactions have recently been preferred due to the advantages offered by its reaction mechanisms. For instance, these types of reaction are known to produce chemicals that can be directly used as fuel additives or intermediate compounds which can be utilized in pharmaceutical and agrochemical industries [15]. More specifically, etherification of glycerol to polyglycerol (PG) has been of interest for the fact that PG’s hydrophilic/lipophilic balance (HLB) for surfactant processes can be controlled [7]. Also, the synthesis of PG from glycerol by etherification reaction is a relatively straightforward and economically feasible process which generates a value-added compound, thus making the overall process profitable.

Polyglycerol has been identified as a potentially useful and value-added polymer/oligomer that can be synthesized starting with glycerol and has applications in food industry, personal hygiene products, cosmetics, pharmaceuticals, plastics, fuel additives and others [16, 17]. Certain applications of PG (i.e., cosmetics, pharmaceuticals) are constrained by the synthesis of such polymer with only di, tri-, and tetramers of glycerol. The presence of excess hepta- or bigger oligomers makes the product applications more limited as they can’t be used in the previous mentioned fields [18–20]. Based on these facts, efforts have been devoted to the fabrication of a catalyst that presents high selectivity and specificity to the glycerol polymerization with the highest yield of di-, and triglycerols.
2.2 Current Studies

Previous work in the field has demonstrated that homogeneous acid-catalyzed etherification reaction results in high glycerol conversion rate. This process, however, leads to non-specific synthesis due to glycerols fast depletion which in turn yields a wide variety of secondary or unwanted products such as cyclic glycerol or unsaturated carbonyls, in which short-chain PG exists at very low concentrations [21, 22]. Homogeneous base-catalyzed etherification reactions have also been explored mostly because, although they present smaller reaction conversion rates, their selectivity towards short-chained PGs is higher. An important characteristic that these base-catalysts should have is that they should be soluble in glycerol (i.e., for better conversion rates) and have high basicity for an enhanced catalytic activity.

Sodium carbonate (Na$_2$CO$_3$) has been identified as a good candidate for glycerol conversion to short-chain PGs. Although the basicity of this homogeneous catalyst is not as strong as other bases such as sodium hydroxide, its solubility in glycerol makes it one of the most commonly employed in industrial applications for the synthesis of short-chain PGs [23]. Several scientific articles have been published in which sodium carbonate catalytic performance has been evaluated. Bookong et al. [24] utilized a 3% wt sodium carbonate catalyst at 270°C for glycerol’s etherification reaction for 1 hour; this short time is adjudicated to the used procedure which employed microwave radiation over the sample. Results showed that an overall conversion of 93% was achieved with combined yields of di-, tri-, and tetracyclic glycerols of 70%. Along these lines, Charles and coworkers [25] reported that by using 2% wt sodium carbonate at 260°C for 24 hours, it is possible to obtain an overall glycerol conversion of 96% with a 24% selectivity towards diglycerol. Finally, in another reported work, Clacens et al. [26] demonstrated that with the use of sodium carbonate as a catalyst for 8 hours, an overall glycerol conversion of 94% can be achieved.
Furthermore, they reported that selectivities towards di, tri-, and tetraglycerol were in the range of 27, 31, and 21% respectively.

2.3 Research Gaps

The mechanisms of base-catalyzed etherification reaction of glycerol have been studied and reported by Ruppert et al. [27]. Their study showed that the reaction proceeds in two main steps. As the first step, once basic pH has been stabilized, the hydroxyl ions of catalyst will attack the hydroxyl group of glycerol and protonate it. During the second step, the formed alkoxy anion is ready to attack the hydroxyl group of another glycerol molecule and generate a water molecule (Figure 2.1). Despite the understanding scientists and engineers have acquired of these homogeneously-based catalyzed reactions, the industry is still in the search of better and enhanced catalytic pathways that can make glycerols conversion more efficient and selective.

![Figure 2.1: Mechanisms of base-catalyzed etherification type reaction of glycerol conversion.][27]

The use of homogeneous catalysts in industrial applications has several drawbacks. Among them, once the reaction ends, separation and/or extraction units are needed to recover the catalyst from the products and this separation process significantly increases the operational cost. Therefore, academic and industrial attentions have shifted to the use of heterogeneous catalysts as they surpass homogeneously catalyzed reactions in that the catalysts can be easily reused and separated from the products. Moreover, selectivity
towards desired short-chained PG such as diglycerol is higher with the use of heterogeneous catalysts [28]. Nonetheless, these types of catalysts have not been commercially exploited in the industry mainly because, compared to homogeneous reactions, the overall glycerol conversion obtained is lower [7].

Porous materials are being extensively used for heterogeneous catalysis purposes. These materials have been classified into three main categories by IUPACK notation as; microporous material with pores smaller than 2 nm, mesoporous material with pores ranging between 2-50 nm and macroporous materials with pores bigger than 50 nm [29]. One of the well-known porous material for catalysis is zeolite which lies into the micropores material category. Zeolite catalysts present advantages such as good thermal stability, insolubility in polar solvents, and high selectivity towards desired products [24, 30]. On the downside, portion of these catalysts is composed of very small-sized pores (0.52 nm or smaller) and if they are being used for liquid polymerization reactions, reactant molecules cannot freely diffuse in and out of these pores. Therefore, not all the catalyst surface area is available for catalysis which makes the material’s overall catalytic activity low. This problem can be alleviated if the microporous materials are activated by different methods like impregnation with alkali oxides, activation with alkali oxides and alkali metal exchange, among others [7]. Among the mentioned methods, impregnation, as reported by Clacens et al. [31] has been proved to be the most effective one for enhancing the catalytic activity. In his work, it was shown that, compared to exchange, impregnation of the mesoporous catalyst MCM-41 yielded a more highly active catalyst which presented higher selectivity towards di- and triglycerol. The developed catalysts could be reused without the need of any major treatments or modifications. Similarly, Golami and coworkers [32] reported that by treating MCM-41 with wet impregnation of calcium and lanthanum oxide, it is possible to achieve an overall glycerol conversion of 91% with a diglycerol yield of 43%. The reaction was performed at 250°C for 8 hours.
2.4 Addressing the Gap

The presented work focused on the use and treatment of a zeolite in order to enhance the catalytic activity, and increase the mesoporous catalytic pore volume. Zeolite Y Sodium was selected as the catalytic candidate, this porous material is environmentally compatible, economical, widely available, and reusable upon utilization [33]. Furthermore, based on previous work reported by Ayoub et al. [34] it has demonstrated that this zeolite can be used as the catalytic base porous material. Also, it was been demonstrated that lithium exchange zeolite Y sodium under 240°C and 8 hours of reaction, presents an overall glycerol conversion of 98% and 21% selectivity towards diglycerol.

Despite its benefits, it has been reported that the stability of such catalysts with alkaline metals, such as Zeolite Y Sodium, on the porous support is low [34]. Also, if activation methods such as impregnation were to be utilized, for the fact that the porous surface of this material is rugged and the pores are small, uneven, and unequally distributed, the activation materials would not be able to distribute homogeneously throughout the catalyst [34].

These issues were solved by the use of supercritical fluid pretreatment technology. By employing supercritical treatment over the microporous catalyst material, it is possible to (and based on previous experiments performed in our laboratory) cleanse the pores and enhance the quality of penetration paths, thus ultimately enhancing the availability of catalytic active sites. Furthermore, by utilizing an activation method over the target catalyst, such as impregnation, is possible to fix a catalytic agent over the surface of this zeolite catalyst which could, in theory, increase the overall catalytic activity and selectivity towards desired short-chained PGs.

In the proposed work, supercritical treatment will be performed by utilizing carbon dioxide as the solvent. Carbon dioxide best serves as the solvent due to its properties, abundance, being non-toxic, inexpensive and non-combustible [35]. The zeolite, before activation, was soaked in the scCO\textsubscript{2} environment in the reactor so that CO\textsubscript{2} diffuses
completely into the zeolites interlayer with its liquid-like density and gas-like diffusivity. As the time passes by, zeolite's platelets go through significant density changes as a result of supercritical saturation, an instant depressurization can cause the carbon dioxide to push the platelets apart, which diminishes van der Waals forces between layers and causes intercalation or delamination [36]. Experiments conducted on cloisite 93A by Horsch et al. shows that due to the supercritical treatment, the outer layer of particles delaminates which results in clay exfoliation and fracturing bigger particles into smaller ones [37].

Glycerol molecules are 0.52nm and for the catalyst to be able to synthesize short-chained PG it should have pore opening bigger than 0.52nm [21]. Based on the experiments conducted in our laboratory on a unique clay, it showed that a good portion of the clay consists of pores smaller than 0.52nm. After supercritical treatment of clay, it was examined again and results showed a good portion of 0.52nm pores were converted to bigger pores. This method will solve the mass diffusion problem with more accessible pores, thus the reaction happens inside the pores rather than the exterior surface of the catalyst and this results in higher selectivity towards the desired products.

This work aimed at introducing a new method for preparing the heterogeneous catalyst with enhanced catalytic activity and overall reaction performance. By utilizing zeolite Y sodium and pretreatment, the catalyst morphological microstructure was altered and it made the catalyst material more suitable for impregnation of sodium carbonate.
CHAPTER 3  METHODOLOGY & SETUP

3.1 Materials

Anhydrous glycerol (>99%), zeolite Y sodium as the porous support material with SiO2:Al2O3 ratio of 5.1:1, sodium carbonate anhydrous (>99.5%), pyridine (>99% grade), silylation reagents; hexamethyldisilazane (>98%), and trimethylchlorosilane (>98%), were purchased from Fisher Scientific. Diglycerol (>80% GC) and triglycerol (>60%, HPLC grade), were used as gas chromatography (GC) standards, and (S)-(−)-1,2,4-Butanetriol (>98%) were used as internal standard, the former was obtained from Fisher Scientific, and the latter was purchased from Sigma Aldrich. Materials were used as received without any further treatment.

All of the utilized chemicals and materials were stored and kept at an optimum environment according to MSDS guidelines and specifications. The zeolites were maintained in a desiccator to avoid moisture contamination. Other utilized chemicals are properly stored and handled as well.

3.2 Experimental Approach

The general methodology used in the performed experiments was as follows.

Zeolite Y sodium (ZYS) was firstly pre-treated with supercritical fluid technology at 260°C and 10.34 MPa pressure conditions. After initial treatment, the supercritically (SC)-treated ZYS was impregnated with sodium carbonate at concentrations of 0.0012M and 0.005M [31]. Catalyst characterization was done before and after the supercritical fluid treatment and before/after the impregnation using accelerated surface area and porosimetry system (ASAP), scanning electron microscope (SEM), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA). Afterwards, the synthesized catalyst was used in etherification reaction of glycerol to polyglycerol (PG) at 230°C for 4, 8, and 12 hours of reaction under atmospheric pressure using nitrogen gas as an inert medium. Products
of this reaction were characterized with gas chromatography (GC) analysis in order to determine the selectivity and glycerol conversion through etherification reaction. The results were compared to the reaction results with non SC-treated / non-impregnated catalysts. Afterwards, based on the results of previous experiments, the best performed catalyst, supercritically-treated and sodium carbonate impregnated 0.0012 M, were selected and polymerization reaction with the chosen catalyst was conducted at 210°C and 250°C in order to study the kinetics of the reaction.

More detailed explanation of the methodology follows in the subsequent sections.

3.2.1 Supercritical Fluid Catalyst Treatment

Supercritical fluid treatment of the ZYS was performed in a stainless steel, custom-built, bolt-closure reactor with a capacity of 300 cm³. After loading the batch reactor with the ZYS catalyst and sealing the compartment, the reactor was pressurized and vented 3 times to remove all entrapped air and moisture from the system. The specified conditions for the supercritical CO₂ treatment was 260°C and 10.34 MPa for a duration of 3 hours over the ZYS. The objective of this treatment, as previously stated, is to convert microporous into mesoporous, and introduce a bigger range of pore distribution to the catalyst. A schematic of the supercritical treatment system is illustrated in Figure 3.1.

![Figure 3.1: CO₂ Supercritical unit system setup scheme.](image_url)
The temperature and pressure of the system was recorded and monitored by Labview®-based data acquisition system. For equipment specifications, please refer to the Material Characterization Techniques section. Once the treatment was finished, ASAP, XRD, TGA, and SEM were used to characterize the treated catalyst and ensure that, in fact, a wider range of pores have been introduced to the catalysts and part of pores smaller than 2 nm have turned to bigger pores in the range of mesoporous area.

3.2.2 Sodium Carbonate Doping on Supercritically Treated ZYS

Once the supercritically treated catalyst was characterized and analyzed, sodium carbonate (Na$_2$CO$_3$) impregnation took place. To this end, 5 g of the treated ZYS was dissolved in 63 mL of a methanol solution, to which sodium carbonate was added. To study the effect of sodium carbonate concentration over the catalytic activity, two different quantities of this chemical were added to the previously mentioned solution: 0.14 g for 0.0012 M or 0.583 g for 0.005 M. The solution was agitated for 6 hours, and then methanol was evaporated via vacuum distillation. Subsequently, the slurry was calcined in an oven at 650°C. Finally, the synthesized catalyst was characterized using ASAP, XRD, TGA, and SEM.

3.2.3 Etherification Reaction

Etherification reaction for glycerol conversion was performed in order to assess the performance of the previously treated and activated ZYS catalyst. For this reaction to occur, 50 g of anhydrous glycerol and 1 g of synthesized catalyst was charged into a three-necked round bottom flask, equipped with a PID temperature controller, a magnetic stirrer and a Dean-Stark apparatus to remove water formed due to the reaction. The reaction was carried out without any solvents and at atmospheric pressure; nitrogen was being constantly blown into the flask to avoid air stagnation which can prevent oxidation and carbonation of the glycerol. Samples were being taken out after 4, 8 and 12 hours of the
reaction. These samples were analyzed to determine the overall conversion of glycerol and selectivity towards di-, tri-glycerol synthesis. A schematic of the reaction system is illustrated in Figure 3.2 [38]

![Figure 3.2: Etherification reaction setup scheme. [38]](image)

The extracted samples were exposed to a silylation-type reaction in which 0.04 g of the sample, 0.2 mL of hexamethyldisilazane, 0.1 mL of trimethylchlorosilane, and 0.5 mL of pyridine were added in a flask and then shaken for 30 seconds. Afterwards, the solution was allowed to stand for 10 minutes followed by centrifugation. Once centrifuged, 1 mL of the top liquid sample was removed and from it 1 µL was injected to the chromatography analysis (approach based on the method that has been reported by Sahasrabudhe [39]). This reaction introduces into the molecule a silyl group, which enhances volatility and decreases surface adsorption, therefore makes the sample suitable for gas chromatography analysis [40, 41].

A similar procedure, but without the supercritical fluid treatment, was utilized on the zeolite Y sodium catalyst so that samples of reaction could be compared: treated versus non-treated catalyst. Furthermore, etherification reaction with two samples of SC treated and not treated without impregnation was conducted in order to evaluate sodium
carbonate’s catalyst activation performance. After the reaction took place, the samples were prepared for GC analysis as well. Samples from polymerization reaction were taken every 4 hours until reaching 12 hours in order to study the kinematics of the reaction. Furthermore, for the SC treated ZYS and impregnated with 0.0012 M Na$_2$CO$_3$, reactions were conducted at 210°C and 250°C to study the effect of temperature in glycerol conversion and di, tri-glycerol selectivity.

For GC calibration purposes (done before analyzing etherification reaction samples), solutions of diglycerol, triglycerol, and butanetriol were used as standards (methodology concept used based on work found in literature [42]). The specifications of these solutions are stated on Tables 3.1 and 3.2. Table 3.1 shows how the base solutions were prepared; simply, a specified amount of mass of the solutes were taken and added to pyridine, the solution media of sample preparation. Butanetriol was used as the internal standard (for more detailed information please refer to Chapter 4). Once these solutions were prepared, then the solutions with specified volumes used and based on them, GC calibration curves were prepared.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Approx. Mass [mg]</th>
<th>Pyridine Volume [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>Diglycerol</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>Triglycerol</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>Butanetriol (internal standard)</td>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.1 shows the solution volumes selected from the initial solutions referenced by Table 3.1. Once the appropriate volumes of solutions where added to a flask (volumes specified in Table 3.2), 0.2 mL of hexamethyldisilazane and 0.1 mL trimethylchlorosilane
were added to the solution and shaken for 30 seconds. The solutions were then allowed to stand at room temperature for 10 minutes. After the 10 minutes, the solutions were centrifuged and the top 1 µL of the solution was injected and analyzed by GC. The results of calibrations curves are shown and discussed in Chapter 4.

<table>
<thead>
<tr>
<th>Calibration Solution</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol [µL]</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Diglycerol [µL]</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Triglycerol [µL]</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Butanetriol [µL]</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Finally, the catalyst was characterized and analyzed before reaction for both treated and non-treated cases. Pore studies were conducted utilizing ASAP and surface studies were conducted by SEM and XRD. Once GC calibration curves were obtained and the etherification reaction samples were collected and prepared, the glycerol conversion and diglycerol/triglycerol selectivity were calculated from following formulas [32]:

\[
\%\text{Conversion}_{GLY} = \frac{n_{convGLY}}{n_{oGLY}} \times 100
\]

\[
\%\text{Selectivity}_{di-triGLY} = \frac{n_{convdi-triGLY}}{n_{totProducts}} \times 100
\]

Were "GLY" represents glycerol and "n" represents the mole.

### 3.3 Material Characterization Techniques

The analytical equipment that was used for the chemical and physical characterization analysis of the catalyst and the glycerols etherification reaction products were available at our laboratory and meet the following specifications:
- National Instrument’s LabVIEW was used in the supercritical fluid technology system to control and record scCO\textsubscript{2} pressure and temperature.

- Accelerated Surface Area and Porosimetry analyzer (ASAP) was employed for catalyst surface characterization. Model 2020 Micromeritics with BJH method calculator, based on nitrogen adsorption - desorption isotherms at −196°C.

- X-ray diffraction (XRD) was employed for catalyst physical characterization and the spectra was obtained from a Rigaku Model Miniflex 600 system with CuK\textsubscript{\alpha} (40 kV/44 mA) with a goniometer rotation rate of 5° min\textsuperscript{−1}.

- A thermogravimetric analysis (TGA) was employed to study thermal stability of the materials used. The curves were obtained utilizing a Q600 SDT for samples weighing from 12 to 16 mg. Samples were heated from room temperature to 1000°C at a rate of 10°C/min. Analysis was conducted under nitrogen atmosphere with a flow rate of 200 mL/min.

- A Field emission scanning electron microscope (SEM) was also used to study the catalyst surface and impregnation. For this, a JEOL-JSM-6010PLUS/LA was used. Studies used an accelerated voltage of 20kV and the samples were gold coated with a Denton Vacuum prior to SEM picturing.

- An IKA heater (RTC basic model) with an integrated temperature control was used for etherification reaction.

- Finally a Gas chromatography (GC) equipment was used for selectivity and conversion studies. For this, an equipment model Trace 1310 with an inert column HP-5MS (Agilent J& W) with the following dimensions: 30 m length,0.25 mm i.d., and 0.25 µm film thickness was used. The temperature limit of this column is in the range of −60°C to 350°C. The injector temperature was set at 360°C and detector
temperature was kept constant at 380°C. The oven was programmed to heat from 50°C to 320°C with the rate of 10°C/min.
CHAPTER 4 RESULTS & DISCUSSION

In this chapter the project results are presented. First the physico-chemical characterization of the Zeolite Y Sodium will be discussed and finally glycerol conversion and di,tri-glycerol selectivity results will be presented.

4.1 Zeolite Y Sodium Samples Characterization

4.1.1 Accelerated Surface Area Porosimetry

Previous work in our research laboratory with clay and clay-like samples has shown that by employing supercritical fluid treatment over the targeted catalyst, it is possible to alter its morphology [43, 44]. The hypothesis that sustained the work herein was that by employing the same methodology, it is possible to reproduce similar results on a zeolite and zeolite-like material. Based on this approach, the first set of experiments consisted of supercritical treatment of zeolite Y sodium (ZYS). Results of such treatment were studied using an accelerated surface area and porosimetry (ASAP) analyzer. Specific objective of this work was to enhance the catalytic activity and increase average pore diameter. Other published studies reached this goal by means of impregnating catalyst with metal ions. For better enhancement of the catalyst under the study, catalyst impregnation with a catalytic activity enhancer, sodium carbonate, was also performed and studied by means of ASAP. The results of such studies are presented in Figure 4.1.

As mentioned, supercritical treatment over a porous material can potentially alter its morphology, in this case, the pore distribution and sizes [45]. Throughout supercritical treatment, catalyst is exposed to high temperatures and pressures. Therefore, the pore impurities leave the solid matrix and a fraction of the solid matrix collapses, leading to a higher meso/micro pore ratio. As hypothesized, it was believed that supercritical treatment over the ZYS would help obtain the same tendency. Figure 4.1 shows the ASAP results before and after supercritical treatment was performed; these are represented by the curves.
Based on [46, 47] the almost vertical portion of the curve at the left end of the graph represents the extent/amount of micropores (less than 2 nm) in the solid catalyst matrix; the smaller the height of that vertical portion, the smaller the amount of micropores in the material. On the other end, the loop that can be noted in the far right of the curve, at the almost horizontal portion, represent the extent of mesopores (2 - 50 nm) present in the solid matrix. This "loop" behavior in the curve, known as a hysteresis loop, appears on adsorption-desorption curves when a phenomenon named capillary condensation (CC) occurs [48, 49]. First, a monolayer of adsorbate forms over the porous surface of catalyst, and as pressure continues to rise, layers on adsorbate forms over the previous layer. This rise of pressure inside the capillary pores of the catalyst causes an increase in Van der Waals forces between these vapor molecules therefore creating condensation below the vapor pressure of the gas ($P_{vap}$). This phenomena is known as capillary condensation [48, 49].

![Graph showing N₂ adsorption-desorption isotherms and t-Plot for the same curve specifications.](image-url)

**Figure 4.1:** a) N₂ adsorption-desorption isotherms for [a] untreated zeolite Y sodium (zys), [b] zys impregnated with a 0.0012 M solution of Na₂CO₃, [c] supercritically (sc)-treated zys, [d] sc-treated and Na₂CO₃ 0.0012 M impregnated zys, [e] zys impregnated with a 0.005 M solution of Na₂CO₃, and [f] sc-treated and Na₂CO₃ 0.005 M impregnated zys, b) t-Plot for the same curve specifications.
As seen from Figure 4.1, the amount of micropores present in the solid matrix decreases (vertical height at the left side of the curve decreases), and the amount of mesopores increases (hysteresis loop thickness increases). This tendency was expected and is confirmed by using the BJH model, Barrett-Joyner-Halenda analysis, which measures the relative average pore size based on mathematical models from gas vapor adsorption and desorption. These results are presented on Table 4.1. Table 4.1 shows, based on the adsorption model (most commonly used in literature as opposed to the desorption) that the average pore size has increased from 76.32 to 117.624 (Å) once supercritical (SC) treatment is done over the catalyst.

Following the same analysis, based on Figure 4.1 we can see that impregnating the porous catalyst with sodium carbonate (Na$_2$CO$_3$) also causes a decrease in distribution of pores in micropore size range and an increase in meso size range; results shown in Figures a-a and a-b. The decrease in size of pore distribution in micro size range and increase in mesopores range due to impregnation can be attributed to several facts: (1) when impregnated, the pores are subjected to a strong alkaline environment which can causes partial de-alumination of the ZYS structure or cause a reaction between alumina and silica of the ZYS and form secondary pores, and (2) the impregnation of alkaline metals over the porous surface which forms metal silicates therefore forming secondary pores which are bigger than the originals, and (3) partial blockage of micro size pore of ZYS by sodium impregnation. For these reasons, it was expected to see an increase in average pore size once the catalyst was subjected to impregnation.

Based on the fact that both, supercritical treatment and impregnation cause an overall increase in pore size, it was expected that the combination of both would decrease the amount of micropores even more than the individual treatments and cause an increase in average pore size. This result was confirmed and can be seen by comparing the curves a, b, c, d from Figure 4.1. Figure a-d shows that the supercritically treated and impregnated
catalyst has a lower amount of micropores (smaller vertical portion height) and a higher amount of mesopores (bigger hysteresis loop thickness) than the ZYS, the SC-treated ZYS, and the impregnated ZYS with a 0.0012 M solution of Na$_2$CO$_3$, respectively. Curves with higher impregnation concentration (Figure a-e) plus SC-treatment follow the same trend as the ones explained.

All of the discussed results can be confirmed by looking at the BJH adsorption model results presented in Table 4.1. Figure 4.1 - b, shows a t-Plot which demonstrates thickness of adsorbed gas over porous catalyst versus volume of adsorbed gas on the catalyst and from it, the same information that Figure 4.1-a shows, can be obtained. Similar to Table 4.1, this t-Plot confirms by another method that the results are consistent and in agreement with one another and that these are in agreement to what it was originally hypothesized for this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BJH Adsorption Avg. Pore D (Å)</th>
<th>BJH Desorption Avg. Pore D (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZYS</td>
<td>76.32</td>
<td>53.53</td>
</tr>
<tr>
<td>SC</td>
<td>117.62</td>
<td>74.51</td>
</tr>
<tr>
<td>SC-0.13</td>
<td>151.16</td>
<td>88.86</td>
</tr>
<tr>
<td>ZYS-0.13</td>
<td>105.68</td>
<td>62.38</td>
</tr>
<tr>
<td>SC-0.53</td>
<td>131.71</td>
<td>147.03</td>
</tr>
<tr>
<td>ZYS-0.53</td>
<td>107.84</td>
<td>122.10</td>
</tr>
</tbody>
</table>

4.1.2 X-Ray Diffraction

Figure 4.2 shows the XRD spectra obtained for the different samples prepared based on ZYS. A glance at all the curves presented in the figure, clearly exhibits the diffraction pattern expected for ZYS catalyst. The characteristic peaks are at the angles (θ): 5.97,
15.25, 23.29, 26.48, and 30.90. These peaks correspond to the crystal reflection of (111), (331), (533), (642), and (555) [50]. It can be observed that despite supercritical, impregnation, or both treatments, the crystalline pattern, its framework, has been preserved. Simply, the major noted differences are a decrease in peak intensity as supercritical treatment and/or impregnation takes place.

![XRD spectra of non-treated/treated zys samples.](image)

**Figure 4.2:** XRD spectra of non-treated/treated zys samples. [a] zys, [b] sc-treated zys, [c] zys impregnated with Na$_2$CO$_3$ at a concentration of 0.0012 M, [d] sc-treated and Na$_2$CO$_3$ impregnated zys at a concentration of 0.0012 M, [e] zys impregnated with Na$_2$CO$_3$ at a concentration of 0.005 M, and [f] sc-treated and Na$_2$CO$_3$ impregnated zys at a concentration of 0.005 M.

By comparing the diffraction pattern of ZYS versus sc-treated ZYS, curves [a] and [b] in Figure 4.2, it can be easily noticed that the overall peak’s intensity has decreased once it has been sc-treated. This behavior suggests that after sc-treatment solid matrix’s crystal size decreases. Also, by closely looking at the peak at 5.97$\theta$, which corresponds to the micro/meso parts of the material [51], it is observed that the peak for the sc-treated
ZYS (Figure 4.2 [b]) has broadened and its intensity has decreased. This peak change is associated with the increase in pore distribution in the micro/meso parts of the catalyst which were not there before the treatment was performed. The long and narrow peak exhibited by the untreated ZYS at 5.97θ merely indicates a narrow distribution of pores.

In a similar manner, the impregnation of Na₂CO₃ shows in the XRD spectra a behavior that resembles to when sc-treatment is performed. In this case, this behavior is attributed to the fact that sodium carbonate particles impregnate inside the pores and partially fill the solid matrix. As expected, then, an increase in the concentration of Na₂CO₃ fills more of those pores therefore reducing even more the intensity of the noticeable peaks present in the untreated ZYS spectra. This phenomena, behavior, has been previously noted and reported in literature [52, 53]. In these articles, it is described that impregnation treatment over the catalyst causes a scattered contrast between pore walls (the pores are filled with the impregnated particles), therefore a decrease in peak intensity comes as a consequence. Literature also acknowledges that this decrease of peak intensity can be associates with a lesser degree of pore order distribution and smaller crystal size [54, 55]. With both/either, supercritical treatment and impregnation, the pore distribution becomes more disorganized and disordered.

Finally, as it is seen from Figure 4.2, the catalyst samples that have undergone impregnation procedures present a slight shift to the left of the peak that corresponds to (111) which reflection has happened. Literature reports this small shift to be associated with the successful impregnation of the metal oxide over the catalyst. Table 3.1 also provides some insight of the successful impregnation of the Na₂CO₃. The table reports the average pore size increases when impregnation takes place. This correlation has been identified and explained in literature [56] which reports that an increase in average pore diameter is consequence of successful impregnation. Once sodium impregnates over porous catalyst, Van der Waals forces between metal ions and functional group of catalyst forms and results
in formation of secondary pores with bigger diameter sizes than the original ones [34]. Ion clustering can be also a major trigger for bigger size pore formation.

### 4.1.3 Thermogravimetric Analysis

A fast analysis at Figure 4.3 suggests that thermal stability in the catalytic material increases with the strength of treatment. The least stable sample is pure ZYS and the most stable sample is sc-treated and Na$_2$CO$_3$ impregnated (at the high concentration of 0.005 M) one. This result follows the same order pattern that the previously discussed studies of ASAP and XRD showed.

![Figure 4.3: TGA curves of non-treated/treated zys samples.](image)

A more in depth analysis of Figure 4.3 demonstrates that all the curves have their most significant weight loss step at temperatures below 200°C. More specifically, weight loss steps at temperatures below and up to 100°C are commonly associated in literature to moisture evaporation from the sample and weight loss steps at temperatures between 100°C
and 200°C are reported to be associated with some water elimination from the interlayer structure of the catalyst and to dehydroxylation processes [57, 58]. By comparing ZYS with sc-treated ZYS (curves [a] and [c] respectively) it can be noted easily that sc-treated ZYS is more thermally stable than pure ZYS. This thermal stability enhancement is attributed to the fact that when catalyst undergoes sc treatment, it is exposed to supercritical conditions (high P and T), therefore catalyst loses its moisture. Because of this, once the catalyst has been sc-treated and then studied by TGA, the water/moisture weight loss step is not as significant as the untreated zys, given that fragment of water has already left the material. The weight loss step in the sc-treated curve [c] at temperatures between 100°C and 200°C is mostly attributed to dehydroxylation processes.

On the other hand, impregnation seems to enhance thermal stability as well. This thermal stability enhancement that is seen by comparing curves [a], [b], and [e] in Figure 4.3 is explained in a similar fashion than that when the material is sc-treated. In this case, when impregnation takes place, as part of the whole process the material undergoes a calcination process which exposes the catalyst to really high temperatures, therefore crystallization happens and forces the water moist to leave the sample. ZYS is known to be a hygroscopic material (absorbs moist from the air), so it is possible that it re-absorbs some of the lost moist due to environment exposing. Although hygroscopic, impregnation causes the material to have sodium carbonate in the solid catalyst matrix which prevents to some degree the absorption of all the moisture/water lost after it was exposed to calcination.

It is interesting to notice that curve [e] on Figure 4.3 exhibits a slight weight loss step at temperatures around 850°C. Interestingly, the melting temperature of sodium carbonate lies within that range, being 851°C. This particular weight loss step in this curve is attributed to partial evaporation/decomposition of the excess sodium carbonate in the ZYS catalyst. Throughout impregnation process, once the catalyst has been exposed to a concentration solution of Na₂CO₃, calcination follows. During this step, it is expected that sodium
carbonate converts to sodium oxide, if, by any means, this step was unsuccessful or not have a 100% conversion, this remaining excess of sodium carbonate will then decompose at around 850°C, which is observed in curve [e]. Sodium oxide, on the other hand, has a melting temperature around 1,125°C. Because the TGA was set to target a maximum temperature of 1,000°C, there is no weight loss step in the curves at high temperatures shown that can be attributed to the decomposition of sodium oxide.

In general, and finally, it can be concluded that both sc-treatment and impregnation enhances the thermal stability of the catalyst material. Given that both enhance the thermal stability, it can be assumed that the combination of both treatments will enhance the thermal stability at a higher degree. A comparison between curves [b], [c], and [d] & [c], [e], and [f] confirms this trend. The most thermally stable sample is that with sc-treatment and impregnated with the highest concentration of Na₂CO₃ as represented by curve [f].

4.1.4 Scanning Electron Microscopy

In order to better understand and study the overall shape, morphology, size, and appearance of the treated/non-treated ZYS, a Scanning Electron Microscope (SEM) was used. Figure 4.4 shows the SEM pictures obtained for each individual sample. Generally, it can be observed that the ZYS catalyst matrix is composed of spherical particles and that their arrangement/distribution changes as the catalyst is treated by either SC, impregnation, or both.

Figure 4.4, [a] and [b], show the images retrieved when the ZYS was left untreated and when it was exposed to SC treatment. It can be easily noticed that the overall distribution of the catalyst once is SC-treated is much higher. The untreated ZYS exhibits, Figure 4.4 [a] conglomeration of particles which makes difficult noticing pore areas (at magnification - 4,500x) which, at a micro-scale, will make internal pore area and available catalytic area harder to reach or simply unreachable. Opposed to this, once SC-treatment is done over the
ZYS matrix it was noticed that the spherical particles that compose ZYS are much more distributed/dispersed, which not only indicates pore size increase but enhanced access to its internal pore area available for catalysis. This result confirms the results obtained from ASAP and XRD.

Following the same tendency, it is possible to see similar results when impregnation, SC treatment, or both are performed over the catalyst. Clearly SC-treatment disperses and breaks down the ZYS conglomerated structure present when the material is untreated.
Because of this, similar results were expected when the material was only treated with impregnation (which conditions are less strong than SC). Figures 4.4 [c] to [f] confirms this expectation; red arrows indicate the presence of impregnated Na$_2$CO$_3$. Figure 4.4 [c] shows the impregnation of ZYS with Na$_2$CO$_3$ 0.0012 M and [d] shows the same sample but also SC-treated. When comparing these two images we see that [c] shows impregnated Na$_2$CO$_3$, and although it shows that the material has been partially de-conglomerated compared to [a], the degree of it is much less than when comparing to [d]. It can be easily noticed than when SC-treatment is performed ([d]) over the impregnated sample, the material still shows the presence of impregnated Na$_2$CO$_3$ but this time it is significantly more disperse and more de-conglomerated as opposed to either the untreated ZYS or the impregnated ZYS with 0.0012 M Na$_2$CO$_3$.

A comparison between [e] and [f] shows the exact same tendency as a comparison between [c] and [d]; impregnation attached the Na$_2$CO$_3$ to the ZYS and partially deconglomerate the ZYS, while when SC-treatment is added to the sample, the catalytic matrix looks much more deconglomerated and still exhibits the presence of impregnated sodium carbonate. As before, these results suggest that the pores have increased as SC-treatment is done and/or a combination of SC/impregnation is done, results that have been confirmed by ASAP and XRD studies.

Figure 4.4 [g] simply shows the SEM image of Na$_2$CO$_3$. As seen in the referenced figure, light sodium carbonate particles have an average 100 $\mu$m size in diameter and dense sodium carbonate particles have diameter size in the range of 300 to 500 $\mu$m. This image has been inserted to compare and identify the presence of these particles when an impregnation step has been done over the material.
4.2 Etherification Reaction Validation

Gas chromatography (GC) was employed to analyze etherification reaction results. The obtained results were used to quantify the catalyst performance as to produced products, conversion and selectivity.

4.2.1 Gas Chromatography Calibration

Before GC could be used to evaluate the catalyst performance, a calibration needed to be made. Figure 4.5 shows the calibration curve obtained. Please note, the data points collected in the figures mentioned were measured in triplicates and they showed a standard deviation of ± 8%.

![Calibration Curves](image)

Figure 4.5: Calibrations curves obtained from standard solutions. [a] calibration curve for glycerol, [b] calibration curve for diglycerol, and [c] calibration curve for triglycerol.
For results quantification to be reliable, standardized, and to cancel performance error, an internal standard, in this case butanetriol, was used [59]. Calibrations curves were also made for glycerol, diglycerol, and triglycerol for procedure standardization. The solutions and volumes used for calibration purposes, along with the calibration samples preparation steps, are outlined in Chapter 3 and tables 3.1 and 3.2.

Once these steps were completed and the solutions were prepared, they were ran through GC for calibration curves preparation. The calibration curves obtained from GC studies are shown in Figure 4.5. These calibrations curves were graphed based on the sample peak area over the calculated area for internal standard versus sample concentration over concentration of the internal standard. The results closely resemble linear behavior and all of them have an $R^2$ value higher than 0.99.

### 4.2.2 Gas Chromatography Analysis on Etherification Reaction - Time Studies

After calibration curves and results were obtained, the different prepared catalysts were used in etherification reaction processes in order to evaluate and determine the glycerol conversion and di/triglycerol selectivity. The first study performed was at a fixed temperature of 230°C and the only changed variable was reaction time which were set to 4, 8, and 12 hours at which samples were collected and analyzed by GC to determine desired conversion and selectivity. Results of these experiments are shown in Figure 4.6. Please note that the data point collected for all the referenced figures were taken in quadruplicates. The obtained values were averaged and the percent error, or standard deviation, lied in between ± 11%.

Figures 4.6 [a], [b], and [c] (red and light blue lines) show the results obtained for untreated and SC-treated ZYS. By specifically looking at Figure 4.6 [a] we can see that at a reaction time of 4 hours, the conversion of both SC-treated and untreated ZYS is about the same being 20.8% for ZYS and 20.6% for SC-treated ZYS. The same does not holds
true at higher reaction times, it can be seen that as reaction time increases, SC-treated starts showing higher glycerol conversions reaching a maximum of 52.7% while untreated ZYS reaches a maximum of 40.3% at a reaction time of 12 hours. Higher conversions obtained for SC-treated ZYS are attributed to the increase in average pore size (mesopores) and removal of impurities due to supercritical conditions exposure [60]. When looking at Figure 4.6 [b], same case (untreated and SC-treated ZYS), we see the results obtained for diglycerol selectivity. At all analyzed reaction times we see that the diglycerol selectivity remains higher for the SC-treated ZYS as opposed to the untreated. At 12 hours reaction the maximum diglycerol selectivities obtained were 15.4% for untreated ZYS and 20.3% for SC-treated ZYS. Similar tendency was obtained for triglycerol selectivity, at all studied
reaction times the selectivity of the SC-treated ZYS remained higher than the selectivity for the untreated ZYS. As before, this tendency of conversion and selectivity increase when SC-treating the ZYS is attributed to the fact that the average pore sizes have increased and due to impurities removal by high temperatures and pressures.

After comparing the untreated and SC-treated ZYS, it is important to analyze the behavior that occurs when the catalytic matrix is exposed to an impregnation step. For this, Figures 4.6 [a], [b], and [c] will be compared, specifically the light blue, black and grey lines which correspond to untreated, 0.13 g Na$_2$CO$_3$ impregnation, and 0.53 g Na$_2$CO$_3$ impregnation respectively. Figure 4.6 [a] shows that at 4 hours reaction, the glycerol conversion of the impregnated ZYS samples is significantly higher than for the untreated ZYS. Also, at 4 hours reaction time is noted that the glycerol conversion of both impregnated samples (with 0.13 g and 0.53 g) is the same, being 40.1% for both samples. The same does not hold true at higher reaction times. At higher reaction times the catalyst impregnated with 0.53 g Na$_2$CO$_3$ presents a slightly higher glycerol conversion than the catalyst impregnated with less molarity of Na$_2$CO$_3$, 0.13 g. When comparing the untreated ZYS with both impregnation-treated samples, as discussed, the impregnated samples show remarkably higher conversion and this is attributed to the fact that sodium carbonate is known to be a catalytic activity enhancer ([61]), therefore the sole presence of this catalytic activity enhancer will cause a higher conversion than the sample without it. Also, it is known that impregnation process has a calcination step which exposes the sample to high temperatures that can potentially increase the average pore size, therefore increasing the average catalytic available volume (proved by ASAP/XRD), and can remove impurities from the sample (proved by TGA). The difference in glycerol conversion between both impregnated samples (0.13 and 0.53 g) is attributed to the fact that the 0.53 g Na$_2$CO$_3$ impregnated sample, can potentially dope more sodium oxides into the material per unit area, therefore making the material more catalytically active.
Figure 4.6 [b] shows the results for diglycerol selectivity. When comparing the mentioned curves (light blue, black, and grey) it can be noticed that at all reaction times the selectivity towards diglycerol is higher in the impregnated samples as opposed to the untreated; behavior expected given an increase in catalytic activity due to sodium carbonate. Furthermore, the 0.13 g Na$_2$CO$_3$ impregnated (black curve) exhibits higher selectivity towards diglycerol than the 0.53 g (grey) Na$_2$CO$_3$ impregnated. This behavior is attributed due to the fact that 0.53 g impregnated ZYS has a lower degree of micropores than the 0.13 g impregnated ZYS sample (refer to ASAP studies), in other words, 0.53 g impregnated ZYS has bigger pores. Glycerol polymerization is a chain reaction, meaning that from glycerol we obtain diglycerol and from it we obtain triglycerol and so on to higher polyglycerol degrees. When glycerol polymerizes in a small pore, if the pore is not big enough for it to handle another polymerization step, after diglycerol formation reaction stops in that pore. While if the reaction occurs in a bigger pore, diglycerol may potentially continue to react to higher order polyglycerol chains ([62]). Because of this, we expect that the selectivity towards diglycerol is higher in the 0.13 g impregnated ZYS which contains a higher amount of micropores. Finally, the opposite is true when we compared this curves from a triglycerol selectivity perspective as showed in Figure 4.6 [c]. As explained, the 0.53 g impregnates ZYS has bigger pores, therefore the material’s pore has enough space to allow for the possibility of diglycerol to convert to triglycerol and higher order polyglycerol chains. Because of this, at 12 hours reaction time the 0.13 g Na$_2$CO$_3$ impregnated sample presented a triglycerol selectivity of 23.1% and the 0.53 g Na$_2$CO$_3$ impregnated sample a 28.2% triglycerol selectivity.

Finally, the effect of both impregnation and SC-treatment must be addressed. To this end, Figure 4.6 [a], [b], and [c] are compared, especially dark blue and purple curves which represent the SC-treated / 0.13 g Na$_2$CO$_3$ impregnated and the SC-treated / 0.53 g Na$_2$CO$_3$ impregnated sample respectively. Glycerol conversion effect can be observed in
Generally, given that SC-treatment increases the glycerol conversion, and impregnation increases the conversion as well, it is expected that the combined treatment would surpass the conversion of the individual treatments. This expected behavior is confirmed in 4.6 [a]. As it can be seen, the glycerol conversion at a reaction time of 4 hours for both (SC/0.13 and SC/0.53) is higher than all other samples. Furthermore, glycerol conversion for the SC/0.53 surpasses the SC/0.13 catalyst. This expected behavior of SC/0.53 surpassing SC/0.13 conversion is not met at higher reaction times of 8 and 12 hours. At 8 and 12 hours SC/0.13 surpasses SC/0.53 and these achieve a maximum glycerol conversion of 93.1% and 90.9% respectively. Based on literature [32], this unexpected behavior can occur due to the fact that the 0.53 g Na₂CO₃ impregnated sample was exposed to higher basic solution concentration, therefore, an alkali-silica reaction could have occur and partially weaken the solid matrix structure which results in a partial structure collapse. This would make certain pores to be sealed so no reaction would occur in those. This phenomenon along with the mechanical solution agitation, could have been the reason why the SC/0.53 catalyst did not consistently demonstrate a higher glycerol conversion.

The results obtained for diglycerol and triglycerol selectivity for the same curves (dark blue and purple) are shown in Figures 4.6 [b] and [c]. Figure [b] shows that the diglycerol selectivity of the SC/0.53 is lower than that of SC/0.13 which, as before, can be explained to the fact that based on ASAP, this catalyst sample had the higher amount of mesopores, therefore the pores in this material are too big for the polymerization reaction to stop at diglycerol, so the reaction produces diglycerol but this is further polymerized to higher order polyglycerols and other oxygenated compounds. The SC/0.13 exhibits the opposite, this material showed the highest diglycerol selectivity. Although based on ASAP, this material has, in general, bigger pores than the impregnated-only ZYS (0.13 g), which would refute the conclusion that higher extent of smaller pores is better, is important to recall that although a higher number of bigger pores, these bigger pores are now filled with Na₂CO₃.
particles, which would, in theory reduce the internal pore size, therefore still leading to higher diglycerol selectivities.

Finally, is important to discuss the triglycerol selectivity of the aforementioned curves, the results for this case are shown in Figure 4.6 [c]. As can be seen, the triglycerol selectivity of SC/0.13 is very close to that of SC/0.53 up to 4 hours of reaction time, afterwards, the selectivity for triglycerol of SC/0.53 is lower than that of SC/0.13. This can be explained as before. SC/0.53, based on ASAP, exhibits the lower amount of micropores and the highest amount of mesopores, this, in turn, allows for pores big enough that permits the conversion of triglycerol to higher order chains, and secondary products such as oxygenated compounds, unstable polyglycerol chains, and acrolein. On the other hand, the SC/0.13 exhibits higher triglycerol selectivity mostly due to its higher degree of micropores present in the solid matrix.

4.2.3 Gas Chromatography Analysis on Etherification Reaction - Temperature Studies

From the previous section discussion, it can be noticed that the "best" catalytic sample is the SC-treated and 0.13 g Na₂CO₃ impregnated ZYS. Because this catalyst showed the best performance overall, it was decided that temperature studies were to be performed with this catalyst sample. The previous section’s results were obtained at a reaction fixed temperature of 230°C. For the studies discussed in this section, the catalyst sample was used in etherification reactions that ran at 210°C and at 250°C. The results of this study for glycerol conversion, di/triglycerol selectivity are shown in Figure 4.7 [a], [b], and [c]. Please note that the data point collected for all the referenced figures were taken in quadruplicates. The obtained values were averaged and the percent error, or standard deviation, lied in between ± 11%.
First, it is important to discuss the temperature effect over glycerol conversion. Based on literature, it is expected that glycerol conversion increases with temperature increase. This behavior is confirmed and presented in Figure 4.7 [a]. As seen in [a], the glycerol conversion is at its highest when the etherification reaction temperature is set to 250°C and is at its lowest when the temperature is set to 210°C. The reaction set to 250°C reached a maximum at around 8 hours, as the change from 8 hours to 12 hours is slight. The reaction at 250°C reached a conversion of 95.2% after 12 hours, while the reaction at 210°C reached a maximum conversion of 30%.

Figure 4.7: GC analysis results on etherification reaction with SC/0.13 catalyst conversion and selectivity at different temperatures. [a] glycerol conversion, [b] diglycerol selectivity, and [c] triglycerol selectivity.
Diglycerol selectivity curves at different temperatures are shown in Figure 4.7 [b]. At 210°C, as discussed, the glycerol conversion is very low throughout the reaction time. Therefore, it is expected to see a low diglycerol conversion given that the reaction rate is so low, that etherification is not the favored reaction at this temperature. Other by-reactions happen as well, and this results in production of secondary products and low diglycerol selectivity. At 250°C, the behavior is not the same. In this case, it presents a higher selectivity than at 210°C (expected due to faster reaction rate), but not as high as when the reaction takes place at 230°C. When graph [a] is observed it can be noticed that the highest slope change occurs between 0 and 4 hours, which coincides with the increase in diglycerol selectivity observed on [b]. The rapid glycerol conversion, indicates that at 250°C the reaction is rapidly occurring which, given this catalytic sample pore size distribution (refer to ASAP), sustains that diglycerol could be rapidly converting to other higher order polyglycerol chains. As observed from [b], 230°C is the optimum temperature studied for diglycerol selectivity. In this case, it is seen that the rapid increase in selectivity up to 8 hours reaction time coincides with the increase in glycerol conversion seen in 4.7 [a]. This, and the fact that the diglycerol selectivity is higher at 230°C than that of reaction at 210°C or 250°C, indicates that the reaction rate is at its optimum to allow diglycerol to diffuse out of the pores for new glycerol to polymerize. After 8 hours, enough glycerol has been converted as seen in [a] (at 230°C), 91.2% conversion, and there is a decrease in slope from 8 to 12 hours. This behavior in [a] coincides with the decrease in diglycerol conversion from 8 to 12 hours at 230°C in [b]. This means that the reaction is now taking place with the diglycerol available in the solution to be polymerized into higher order chains.

Finally, triglycerol selectivity as reaction temperature changes is shown in Figure 4.7 [c]. Once again, it is seen that the low glycerol conversion shown in [a] for 210°C, coincides with the slow diglycerol selectivity shown in 4.7 [b], and now with the slow
triglycerol selectivity shown in 4.7 [c]. This results are attributed to the slow reaction rate and conversion. For the reaction occurring at 230°C, it is observed that this shows a higher triglycerol selectivity than the reaction occurring at 210°C which is easily explained by the fact that at higher temperatures, the reaction rate is much faster, therefore it permits for triglycerol to be formed in the pores and diffused out for new glycerol to polymerize. The decrease in slope after 8 hours of reaction for triglycerol selectivity at 230°C suggests that, and according to [a] which shows close glycerol depletion, triglycerol is now being polymerized to higher order chains and/or the triglycerol formed was unstable and now is converting to secondary products. The results obtained for the reaction occurring at 250°C, can be explained in a similar way to the ones obtained at 230°C. In this case, we can say that the pore size in this catalyst material is optimum for diglycerol conversion to triglycerol (which explains why diglycerol selectivity is low as opposed to triglycerol), but once triglycerol is formed, it leaves the active catalytic area and more glycerol enters to be converted. After 8 hours reaction time, enough glycerol has been converted, therefore, triglycerol can be converted to higher order chains; this explains the decrease in triglycerol selectivity at 12 hours reaction time.

4.3 Conclusions

4.3.1 Zeolite Y Sodium Samples Characterization

As confirmed by the results presented, in general, the use of supercritical fluid treatment over ZYS increases the average pore size (increases the amount of mesopores) and the distribution of the spherical particles that forms the ZYS (deconglomerates the material), while decreasing the amount and extent of micropores in the material. These tendencies(changes are attributed to the strong temperature/pressure environments used to expose the catalytic material at which, among others, material collapse occurs and the material impurities leave. Results were confirmed by ASAP, XRD, and SEM.
Although not as notable as when SC-treatment is performed, impregnation of sodium carbonate also helped introduce a degree of material deconglomeration and a larger number of mesopores, while decreased the amount of micropores in the material. These changes were attributed mostly to the presence of van der Waals forces between the sodium ions and the silica structure of the ZYS framework. Results were confirmed by ASAP, XRD, and SEM. Also, impregnation itself prove to be successful after confirming the presence of Na$_2$CO$_3$ by means of SEM images after treatment was completed. Similar to supercritical treatment, impregnated samples shown less weight loss during TGA studies, mostly due to the high temperature exposure and impurities removal.

Given an increase in pore volume, increase in average pore size, successful impregnation of Na$_2$CO$_3$, decrease in micropores, and material deconglomeration, it was concluded that the ZYS material samples were ready to be used as tested in an etherification reaction process. The reaction was aimed to polymerize glycerol to short-chained polyglycerol with a scope of evaluating catalyst performances in the conversion of glycerol to di, tri-glycerol and its selectivity.

4.3.2 Etherification Reaction Validation

Etherification reaction results analyzed by GC showed that glycerol conversion and di/triglycerol selectivity are all affected by all 3 studied variables: catalyst pre-treatment, reaction time, and temperature. The prepared catalyst samples were exposed to an etherification reaction setup at a fixed temperature of 230°C. In general, it was shown that the highest conversion of glycerol can be obtained when combining the two treatment methods: SC-treatment and impregnation. The di/triglycerol selectivities were mostly dependent on average pore volume and pore distribution.

Out of all the catalyst samples prepared and treated, SC-treated and 0.13 g Na$_2$CO$_3$ impregnated ZYS turned out to give the better results in terms of glycerol conversion,
and di/triglycerol selectivities when used. Given its performance, it was selected to perform temperature studies. To this end, the catalyst sample was used in another two etherification reaction setups, one at 210°C and another at 250°C. Results indicate that glycerol conversion, as reported in literature, is affected by temperature. The higher the temperature, the better/higher the conversion. The same tendency does not hold true when looking at the di/triglycerol selectivities. It is concluded that low temperatures will not only give low conversions and selectivities, but that high temperatures will affect the selectivities depending, mostly, of reactant availability and average pore size.
CHAPTER 5  CONCLUSIONS & FUTURE WORK

5.1 Conclusions

5.1.1 Overview

In recent years, energy demands have increased along with fossil fuel needs. However, fossil fuel availability has been decaying in the past years and its non-renewability has caused the search for new and alternate ways to generate useful energy. Biodiesel has been identified as one of the most promising alternatives to alleviate the demand of fossil fuels, however, in the process of generating biodiesel by transesterification, the excess generation of glycerol, a by-product, has become a problem. Glycerol’s production surpasses its demand, therefore making this chemical compound relatively cheap as it is considered, mostly, a chemical waste which has ended up increasing biodiesel’s price. The need to find commercial use for glycerol is therefore apparent.

Scientists have been focusing on new ways to produce high value-added compounds departing from glycerol through relatively easy catalytic pathways. If promising, reliable ways of achieving this could be found, not only the process economics could be enhanced, which can aid the process of substituting fossil fuels, but glycerol disposal would significantly diminish or avoided.

Industries have found that through the use of homogeneous catalysts, glycerol can be polymerized to give value-added products, but the use of these homogeneous catalyst have economic limitations as the process of separating the catalyst from the polymer becomes a challenging and expensive process. Also, due to the nature of the separation process, excessive amounts of water are used in the process which ultimately affects the environment. The industry is currently in search of alternate, reliable, heterogeneous catalysts. These heterogeneous catalysts as found in the nature, although good and stable, they exhibit low catalytic activity.
To date, the use of supercritical treatment technology on these solid catalysts has not been exploited and could potentially contain the answer to overcome homogeneous catalysts and open a new door of opportunities.

5.1.2 Zeolite Y Sodium Treatments & Characterization

As originally hypothesized, the supercritical (SC) treatment of zeolite Y sodium (ZYS) did enhance the solid matrix catalyst performance by increasing the overall available pore volume, available areas for catalysis to occur, average pore volume, and by dispersing/deconglomerating the solid compact ZYS matrix. This results were confirmed by studies performed employing ASAP, XRD, and SEM. Furthermore, the impregnation step, as originally intended, proved to be an enhancer for catalytic activity as well as aided the process of average pore size increase and overall available pore volume. Performed tests suggest that the combination of both treatments, supercritical and impregnation, have an additional effect which shows that when combined, the catalyst performance surpasses the performance when the samples are treated by either individually. As with SC-treatment, these results were confirmed by using ASAP, XRD, and SEM.

Simplicity, reliability, and ease of process of the employed methods for catalyst activity enhancements, SC-treatment and impregnation, suggests that these could potentially guide the way heterogeneous catalysts are treated in the future for better, easier, more economical ways to perform industrial polymerization processes.

5.1.3 Gas Chromatography & Etherification Reaction Results

As previously stated, gas chromatography (GC) studies and results demonstrate that catalyst treatment, reaction time, and temperature (the three studied variables), significantly influence the glycerol conversion, and di/triglycerol selectivity. As was originally hypothesized in this work, supercritical treatment and impregnation not only
enhanced physical properties of the catalyst matrix, but catalytic properties as well; this was confirmed by reaction and GC studies.

Initially, all the ZYS samples were prepared and treated accordingly. Glycerol conversion results showed that the untreated and only SC-treated samples have the lowest conversion percentages while the SC-treated and impregnated samples show the highest conversion percentages; these surpass 90% conversion. As with the physical/morphological properties, the catalyst’s ability to convert glycerol tended to add up with treatment combination, being the combination of both treatments, SC and impregnation, the ones giving the highest conversions. The same results did not hold true when studying selectivities. It was concluded, based on results and previous literature reports, that selectivity is mainly driven by the zeolite’s shape selectivity, average pore size, overall available pore volume, and catalytic activity. Simply, bigger available and active pores in the solid matrix allows for formation of high order polyglycerol chains due to space unconstraint. While small pores limit the formation of high order chains, therefore increasing the selectivity of small oligomers, namely, diglycerol and triglycerol.

A careful evaluation of the catalyst samples suggested that the SC-treated and 0.13 g Na$_2$CO$_3$ impregnated ZYS proved to give the best results when used for glycerol polymerization in an etherification reaction setup. Given its performance, it was then selected to be used in etherification reaction temperature studies at which the catalyst was used for reaction at a temperature lower and a temperature higher that the 230°C. The results of such study demonstrated that glycerol conversion is highly dependent on temperature, the higher the temperature, the higher/better the glycerol conversion; these results were also confirmed in other literature work. As discussed for the standard 230°C etherification reaction, selectivities did not show the tendency that conversion exhibited, this due to the fact that mainly selectivities are dependent on pore size and available pore volume as previously stated.
In general, the combination of both supercritical and impregnation treatments proved to not only enhance morphological/physical catalyst properties, but also the catalytic activity of the material as well. The results here presented potentially present a feasible and alternate way by which industrial value-added products can be obtained from glycerol. It is believed that the continuous studies and research on heterogeneous catalysts for polymerization purposes are the promising future of this billion-dollar industry.

5.2 Future Work

In this study, the effect of supercritical and impregnation treatments was studied while varying impregnation concentration, and reaction temperature/time. Despite the amount of work performed, there are several other suggested studies that, if performed, could help to better understand catalyst behavior and performance and that can potentially get the technology closer for it to be used at an industrial scale.

The conditions employed in this work for supercritical treatment were initially used given that they proved to be ideal in other experiments performed at SEAM Lab on clay. It is known that supercritical treatment is dependent on carbon dioxide’s solubility and that the conditions used in the treatment will influence/affect the catalyst, in this case zeolite Y sodium’s morphology. Because of this, future studies should focus on performing supercritical treatment at different temperature and pressure conditions in order to find the optimum treatment that maximized catalyst performance.

In the present work it was demonstrated that not only supercritical treatment, but also impregnation affects the catalyst performance. In the performed experiments the catalyst was exposed to sodium carbonate solutions at concentrations of 0.0012 and 0.005 M. Although the concentration of 0.0012 M proved to better enhance the catalyst performance, as the 0.005 M caused catalyst partial collapsation, it does not necessarily mean that the best results will be obtained at this concentration. Future studies should focus on exposing
the catalyst to different concentrations of sodium carbonate and determine the optimum concentration for impregnation treatment. The same applies to the type of solute. Although sodium carbonate was used, it is known that other types of compounds have proven to enhance catalytic activity. Changing the solute for other catalytic activity enhancers could provide more in-depth information as to whether sodium carbonate remains to be the optimum or not. Finally, calcination temperatures for catalyst can be changed as well for better temperature studies.

Catalyst basicity is known to play a major role when determining catalyst performance and studies to determine this property were not made in this work. On the other hand, the etherification reactions performed in this work were run with a 2 wt.% catalyst loading. No changes in this ratio was done nor studied. Future studies suggest that these variables should be taken into account as they might play a major role on the final reaction performance in an etherification reaction setup.

Other less focused, yet important future studies that should be performed are those of analyzing the etherification reaction samples in look for alternate reaction by-products. As the results in the performed work showed, the possibility of the pores being big enough could potentially be leading to the formation of higher order polyglycerols and other secondary products such as oxygenated compounds, acrolein, among others. Identification of these molecules in the GC spectra should provide a deeper insight as to what is being formed, at what rate/concentrations, and how to minimize the formation of these.

Finally, more in-depth kinetics and mass transfer studies can be performed in the future to better understand the reaction pathways and intrapore activities such as diffusion and adsorption/desorption processes.
REFERENCES


