

BIODIESEL PRODUCTION OVER CARBON SULFONATED CATALYSTS

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May 2023

ABSTRACT

Biodiesel with improved sustainability can be produced by alcoholysis of low-grade fats, with high free fatty acid content, using heterogeneous acid catalysts. Carbon materials with sulphonic surface groups are reported to be active in such esterification reactions. Sugars and sugar alcohols are natural compounds and, therefore, renewable raw materials which can be used as raw materials for char production. Their acid-catalyzed hydro-carbonization results in the formation of carbon materials with acidic functional groups on the surface, which makes them suitable to be used as heterogeneous catalysts in esterification reactions. This work is dedicated to propose an economic and efficient methodology for acidic heterogeneous catalyst synthesis focused in biodiesel production via esterification. The major idea is to produce catalysts based on reduction of expensive reagents and valorizing glycerin, a biodiesel by-product. Catalysts were prepared by low-temperature slow carbonization of glycerol, xylitol sucrose, and glucose in the presence of different amounts of H₂SO₄ (mass ratios from 1 to 4). The carbonaceous materials were extensively characterized and tested in the methanolysis reaction of oleic acid. In terms of characterization, ATR-FTIR, Raman, TGA, XRD and SEM-EDS analysis were carried with all the catalysts. Data analyzed shows that all the carbon materials were amorphous with features of polyaromatic sheets with hydroxyl (-OH), carboxylic acid (-COOH), and sulphonic (-SO₃H) functional groups. It occurred under the conditions evaluated at 5% wt. of catalyst, methanol/oleic acid = 12 molar ratio, methanol reflux temperature. The sucrose-derived catalyst prepared with the highest H₂SO₄ content showed the best performance, followed by glycerol, allowing full conversion of oleic acid after 90 min.

Keywords: *Biodiesel; carbon sulfonated catalyst; acid heterogeneous catalysis; methyl oleate; esterification; glycerin valorization*

1 INTRODUCTION

In April 2020, oil prices hit a historic low due to the COVID-19 pandemic, highlighting the oil industry's longstanding economic instability. The use of fossil fuels has also raised concerns regarding greenhouse gas emissions (GHG). Biodiesel, a renewable alternative fuel derived from vegetable oils, is being encouraged as a

transition from fossil fuels. It offers advantages such as biodegradability, lower toxicity, reduced greenhouse gas emissions, and compatibility with existing diesel engines (Fonseca et al., 2022). Biodiesel production typically involves alkali or acid catalysts, each with its own advantages and drawbacks. Researchers are exploring the use of carbon-based

heterogeneous acid catalysts derived from biomass and sugar precursors, known as sulfonated carbons, to improve the efficiency of the biodiesel synthesis process (Toda et al., 2005). Crude glycerin, a by-product of biodiesel production, shows promise as a precursor for these catalysts, contributing to both its valorization and the concept of a circular economy in the energy sector. This paper investigates the synthesis sulfonated carbons with crude glycerol among similar precursors, namely sucrose, glucose, and xylitol and their application as catalysts for biodiesel production.

2 BIODIESEL

Biofuels, including biodiesel, have gained increased interest in recent years as a potential substitute for fossil fuels due to their lower air pollution and carbon emissions. Over the years, biofuels' contribution to total energy consumption has gradually increased. In 2016, biofuels accounted for 0.62% of total energy consumption, and by 2021, it reached 0.70% (EIA, 2021). Despite the slight increase, there is a need to accelerate the adoption of biofuels given ongoing political instability and supply shortages. In the European Union (EU), although it ranks third in biofuel production, it consumes more than it produces. Conventional ethanol and biodiesel dominate biofuel consumption, accounting for 55.9% and 37.2% respectively, while advanced ethanol and biodiesel, along with bioject kerosene, make up smaller shares (EIA, 2022). Further emphasis on different types of biofuel technologies is necessary to understand their role in the global economy.

2.1 Biodiesel Quality Standards

Standardization is crucial in the biodiesel sector to establish a common basis for comparison between samples. International organizations like ISO and ASTM have developed technical standards that are widely used in the industry. The two most important biodiesel standards are EN 14214 in Europe and ASTM D6751 in the USA, both published in 2002 (EU, 2003). These standards specify the

requirements and test methods for biodiesel. However, there may still be variations in biodiesel quality due to different manufacturing methods and raw material sources. Challenges and technical issues in using biodiesel include efficiency issues, poor raw material quality, and contamination. Studies have identified problems such as deterioration of rubber gaskets, corrosion of aluminum, flash point effects, and carbon deposits due to incomplete combustion (Altazari et al., 2022). To address these issues, pre-treatment of raw materials and purification processes for biodiesel are necessary to ensure compliance with standards and mitigate potential engine problems.

2.2 Biodiesel Production

Various technologies have been explored for biodiesel production using different raw materials such as vegetable oils and animal fats. However, simpler techniques like direct usage/blending, micro-emulsion, thermal cracking, esterification, and transesterification remain popular (Demirbas et al., 2016); (Ruhul et al., 2015); (Ma and Hanna, 1999). The choice of technology pathway depends on the raw material used, which can include vegetable oils (soybean, rapeseed, palm, sunflower, jatropha) and residues such as waste cooking oil (WCO), animal fat (AF), and fish viscera. These raw materials contain fatty acids (FAs) in the form of triglycerides (TAGs), which undergo reactions to produce biodiesel. Fatty acids have distinct physical and chemical properties, including polarity, which allows for their use as biodiesel. Europe commonly uses rapeseed and sunflower oils for biodiesel production, while there is increasing interest in using WCO and AF due to social, economic, and environmental factors. Pre-treatment processes involving mechanical cleansing and chemical treatment are necessary for raw materials like WCO and AF to remove impurities and reduce free fatty acid (FFA) content (Knothe et al., 2005). Methanol and ethanol are the preferred alcohols used in biodiesel production, with methanol being more commonly used due to its cost-effectiveness and favorable conditions. Ethanol, although

renewable, can lead to difficulties in separating biodiesel and its by-products. Combining both alcohols is seen as a potential solution to address the challenges associated with each alcohol type (Chakraborty et al., 2014).

2.2.1 Production Pathways

2.2.1.1 Transesterification

Transesterification is considered one of the most viable processes for obtaining biodiesel, according to European and American norms. In transesterification, a chemical reaction occurs between triglycerides (fat) and alcohol (methanol or ethanol) in the presence of a catalyst. This reaction results in the production of glycerin and fatty esters. The process involves the conversion of triglycerides into diglycerides, then into monoglycerides, and ultimately into glycerin and fatty esters (Koberg and Gedanken, 2013). Excess alcohol is used due to the reversibility of the reaction. The kinetics of the transesterification reaction is described by a sigmoidal function, indicating an S-curve, which represents the variation in the control of the reaction rate. The reaction initially faces diffusional control due to limitations in mass transfer, but as biodiesel is produced, the reaction proceeds at a higher speed and enters a kinetic control phase. Finally, the production rate slows down as the reaction reaches completion (Ma and Hanna, 1999).

2.2.1.2 Esterification

In esterification reactions, typically using methanol, an alcohol reacts with a fatty acid (FA) molecule to produce an ester and water. Fischer esterification, first proposed by Fischer & Speier in 1895, is an example of nucleophilic addition-elimination. A strong acid like sulfuric is used, and the reaction is carried out gradually under reflux. Due to the reversibility of the reaction, it is often conducted with a significant excess of alcohol. Removing water from the reaction mixture can also help shift the equilibrium forward. In Fischer esterification, the electrophilic carbonyl group is initially activated by protonation, followed by nucleophilic addition, proton transfer, and ultimately the elimination of

water. The oxygen in the ester is confirmed to come from the alcohol. Overall, the quantity of catalyst and the amount of oleic acid in the oil are factors that influence the speed of the esterification reaction, and the optimal amount of catalyst depends on the concentration of oleic acid.

2.3 Catalysis in Biodiesel Production

Catalysts play a crucial role in biodiesel production, particularly in the methanolysis process. They lower the activation energy and increase the reaction rate without being consumed or created during the process. Catalysts can be classified as homogeneous or heterogeneous and their behavior depends on their physical and chemical properties. The amount of acidic or basic strength present in the catalyst determines the reaction mechanism. The Brønsted-Lowry and Lewis theories are used to evaluate and categorize catalysts as acidic or basic, each with its own assumptions and definitions (Ruhul et al., 2015); (Ramos et al., 2019). Ongoing research aims to develop catalysts that improve yields and address challenges related to product separation and purification in the biodiesel industry.

2.3.1 Homogeneous Catalysis

In reactions with homogeneous reactions, the catalyst is in the same phase as the reactional media, that being solid, liquid, or gaseous. By definition, the catalyst and reagents combine to create a single phase, which they do in a single phase media. One of the greatest advantages of homogeneous catalysts is the resistance reduction of mass transfer, yielding a more efficient reaction with also higher biodiesel yield in less amount of time, Ahvad and Marchetti (2016) suggest.

2.3.2 Heterogeneous Catalysis

Heterogeneous catalysis involves the presence of a catalyst and reagents in separate phases, such as solid-liquid, solid-gaseous, or liquid-gaseous interfaces. Active sites on the catalyst surface are necessary for molecules to adsorb and initiate reactions. Diffusion and mass

transfer issues can arise in the complex environment with three phases (Leung, Wu and Leung, 2010). Heterogeneous catalysts can be acidic, alkaline, or bifunctional, consisting of Brønsted-Lowry or Lewis active sites. Despite lower activity and longer reaction times compared to homogeneous catalysts, heterogeneous catalysts are advantageous as they can be easily separated and recycled, minimizing post-reaction procedures and preventing side reactions. They are less corrosive and toxic, and can yield purer glycerin in transesterification reactions (Helwani et al., 2009). However, due to their complexity and longer reaction times, homogeneous catalysts are not predominantly used in industrial settings. Ongoing research aims to transition industrial production to the use of heterogeneous catalysts, particularly nanocatalysts with large surface areas and suitable catalytic properties, to overcome their limitations and facilitate the valorization of crude glycerin (Ahvad and Marchetti, 2016).

2.4 Carbons Sulfonated Catalysts

Sulfonated carbons are solid acidic catalysts that have SO₃H-functionalized carbon materials with Brønsted acidity similar to concentrated H₂SO₄. These catalysts are prepared by carbonizing precursor materials such as sugars, which undergo carbonization and sulfonation processes. Sulfonated carbons possess three main acidic groups - carboxylic acid, phenolic acid, and sulfonic acid - on their surface, making them unique compared to other acid catalysts (Fonseca et al., 2022). They can incorporate hydrophilic molecules and provide easy access to the sulfonic group, enhancing catalytic activity even with a small surface area. Sulfonated carbon-based materials have shown higher catalytic activity for esterification reactions compared to conventional solid Brønsted-acid catalysts. Sugars derived catalysts and glycerol-based catalysts have demonstrated excellent catalytic activity and operational stability, making them promising replacements for H₂SO₄ in biodiesel production (Su & Guo, 2014). Research continues to

explore low-cost and easily accessible precursors for sulfonated catalyst production, with glycerol being a potential candidate due to its abundance as a biodiesel by-product.

3 EXPERIMENTAL PROCEDURES AND METHODOLOGY

3.1 Catalyst Preparation

For the catalyst preparation, the following precursors were used: sucrose, glycerine, glucose, and xylitol. These precursors were combined with sulfuric acid (H₂SO₄) at different proportions. To prepare the catalyst, as carbonization took place, at a relatively constant temperature, sulfonation also took place.

3.2 Esterification Reaction

The reactional parameters and conditions were defined and standardized throughout the whole experiments. It was defined a pre-conditioning step for the raw material of 50g for 30 minutes at 70°C and a reactional temperature at 67 °C – methanol total reflux condition – under vigorous mixing, around 1000 rpm. The methanol: oleic acid molar ratio is 12:1. The catalyst amount in % wt. was 5 for all samples and the reactional time was 3 hours. Also, a preconditioning step, contact step, at 65 °C for 30 minutes between methanol and the catalyst was used to promote the formation of methoxide ionic species.

3.3 Methodology

The experimental part of this work focused on carrying several characterization analysis. Namely, X-Ray Powder Diffraction (XRD), Attenuated Total Reflectance (ATR) - Fourier Transform Infra-Red (FTIR) Spectroscopy, Raman Spectroscopy, Thermogravimetry, and a Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). The FAME yield quantification was evaluated by using the infrared spectral range 1675 cm⁻¹ – 1775 cm⁻¹, (Soares Dias et al., 2019). The calculation methodology is done in terms of area ratio of a specific peak at 1742 cm⁻¹ limited between 1755

– 1735 cm⁻¹ and the whole area of the IR range, as indicated by Figure 1. Finally, the FAME conversion was calculated by the equation 1.

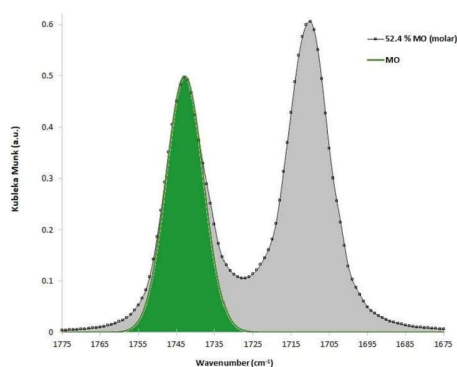


Figure 1 – Gaussian calibration curve for methyl oleate determination by FTIR.

$$\%FAME = 7e^{-5} \left(\frac{A_1}{A_t}\right)^2 + 0.0029 \left(\frac{A_1}{A_t}\right) \quad \text{Equation 1}$$

4 RESULTS AND DISCUSSIONS

The data collected for this work is presented in separated sections, specifically, focused on the raw materials, the catalysts (pre and post esterification), and methyl oleate characterizations.

4.1 Fresh Catalysts

The ATR-FTIR spectra analysis of catalysts obtained with low and high concentrations of H₂SO₄ reveals the presence of characteristic bands related to different functional groups. The activated carbons show reflectance bands corresponding to the asymmetric and symmetric stretching modes of sulfonic acid groups (-SO₃H) at different wavenumbers. The intensity and position of these bands can be influenced by factors such as hydrogen bonding and neighboring functional groups (Zhang et al., 2021). Other characteristic bands related to the carbonization of sugar-derived catalysts are also observed, including bands associated with aromatic rings and carboxylic groups. The reflectance intensity of the bands related to the -C=C bond suggests differences in the degree of graphitization

among the catalysts. For the catalysts with higher concentrations of H₂SO₄, the intensity of the bands attributed to the -SO₃H groups increases, indicating a higher amount of these groups. The presence of bands associated with carbon-sulfur (C-S) and carboxylic groups (-COOH) stretching modes is also observed. The analysis suggests that sulfonation with H₂SO₄ leads to the formation of both sulfonic acid and weak acid groups. The presence of bands related to -C=C stretching indicates the formation of bonds during the carbonization process.

The SEM micrographs reveal that the catalysts with a 1:4 ratio of sugar to sulfuric acid exhibit increased pore formation compared to the catalysts with a 1:1 ratio due to the corrosion and oxidation caused by concentrated sulfuric acid during sulfonation. The presence of interconnected pores is beneficial as it enhances contact between reagents and active sites during the catalytic process. However, the catalysts in all cases are less porous compared to what they would be if carbonization occurred at higher temperatures (Correa et al., 2023). The SEM also show no fibrous structure, likely because the precursors are hydrocarbons with a short chain. Some catalysts exhibit agglomeration of clusters with an angular nature. Glucose1 and xylitol1 samples have large crystallites surrounded by fine material, while sucrose1 and glycerol1 samples have smaller crystallites, indicating that the sulfuric acid attack was more aggressive on the grain size in these catalysts. The glycerol4 sample appears to be the most porous and significantly attacked by sulfuric acid.

Elemental analysis using energy-dispersive X-ray spectroscopy (EDS) reveals that carbon is the main element in all catalysts, as expected from the carbonization process. Oxygen is the second most predominant element, likely due to the low carbonization temperature used, which correlates with the amount of fixed carbon and the number of oxygenated species. The sulfonation process promotes the formation of oxygenated groups

due to the oxidizing properties of concentrated sulfuric acid. The presence of sulfur indicates that the sulfur insertion process was efficient, with higher sulfur content in the catalysts with a 1:4 ratio. The higher sulfur content in glycerol4 is confirmed by FTIR analysis, which also shows a higher intensity of the SO₂ bands. The O/C ratio, as seen in table 1, varies with sulfuric acid concentration, with lower concentrations favoring higher O/C ratios. This suggests that higher sulfuric acid concentrations not only promote the formation of sulfonic groups but also enhance the carbonization process, leading to increased carbon composition (Correa et al., 2023).

Table 1 – Elemental analysis of catalysts obtained from EDS technique.

Samples	Elemental Composition (%)			Elemental ratio O/C
	C	O	S	
Sucrose1	66.7	33	0.8	0.49
Sucrose4	74.4	29.9	0.85	0.40
Glycerol1	63.5	23.4	1	0.37
Glycerol4	76.3	22.2	2.4	0.29
Glucose1	71.7	28.3	0.6	0.39
Glucose4	71.8	27.7	0.5	0.39
Xylitol1	73.3	26.3	1.1	0.36
Xylito4	75.7	23	1.7	0.30

The Raman spectra show characteristic bands of carbon material at 1350 cm⁻¹ (band D - Defect) and 1600 cm⁻¹ (band G - Graphite). The intensity of these bands was evaluated using deconvolution techniques, and low intensity values were observed despite the low carbonization temperature. Higher degrees of structural order in carbonized materials resulted in the disappearance of smaller bands and sharper bands D and G. The presence of smaller aromatic clusters indicated by the shift of the bands to higher values. The G band shift from 1580 cm⁻¹ to 1600 cm⁻¹ suggests the presence of nanocrystalline graphite, indicating a structure consisting of dispersed graphitic carbon within the amorphous carbon bulk. The intensity ratio of band D to band G (ID/IG ratio) increases with higher sulfuric acid

concentrations. This suggests that with increased sulfonation, there is limited decrease in smaller aromatic rings and substituting groups, and significant growth of poly-condensed aromatic rings occurs, leading to a higher ID/IG ratio (Spataru et al., 2021). Based on this ratio, it can be inferred that sucrose4 and glycerol4 have the lowest growth of poly-condensed aromatic rings and the highest degree of graphitization, while xylitol4 and sucrose1 have the lowest degree of graphitization and a more disordered carbon structure.

X-ray diffraction (XRD) analysis was conducted to examine the crystallographic structure of the catalysts. The notation used in labeling diffraction peaks followed the Miller indices system, where each set of indices represented specific crystallographic planes. These peaks provided information about the arrangement and orientation of atoms along these crystallographic planes. The catalysts prepared with lower sulfuric acid concentration (1:1 ratio) exhibited broad diffraction peaks at around 2θ = 14° to 25° and a weak peak at 2θ = 26° to 45°, assigned to the (002) and (101) planes, indicating the presence of small graphitic domains. The broadening of these peaks suggests a disordered carbon structure with a low content of crystalline graphite (Sapataru et al., 2021). In contrast, the catalysts prepared with higher sulfuric acid concentration (1:4 ratio) showed a shifted (002) peak at 23°, indicating the presence of graphite oxide (Singh and Vander Wal, 2022). Despite the presence of amorphous carbons, all catalysts displayed graphitizing behavior in their XRD spectra, indicating a high graphitic composition. The intensity and shape of the (002) peak provided insights into the degree of graphitization, with sharper and more intense peaks suggesting a higher degree of graphitization.

The prepared catalysts were subjected to thermogravimetry under airflow to further characterize their properties. The thermograms (mass loss curves) revealed three significant stages of mass loss. The weight loss between

150°C and 275°C can be attributed to the removal of water, as the catalysts tend to adsorb water from the environment. This mass loss indicates the decomposition of volatile components, including water, residual sugars, and other organic species present in the catalysts. Between 300°C and 450°C, the catalysts exhibited another significant mass loss associated with the decomposition of sulfonic (-SO₃H) and carboxylic (-COOH) groups. Additionally, decomposition of the carbon structure, characterized by C-O and C-C bonds, was observed between 450°C and 775°C. The catalysts demonstrated good thermal stability in the range of 25°C to 150°C before the decomposition of the -SO₃H groups, which is important for their application in the esterification of oleic acid conducted at 67°C. Comparing the catalysts prepared with 1:4 and 1:1 ratios, the glycerol with 1:4 ratio catalyst exhibited a higher residual mass. This can be attributed to the partial carbonization of that, resulting in the formation of carbonaceous residues such as char, carbon black, or amorphous carbon, which have relatively high thermal stability. This higher residual mass indicates that catalyst is the most thermally stable catalyst among all the others. Conversely, the catalyst samples prepared with sucrose 1:1 had a smaller residual mass compared to the other molar ratios.

4.2 Catalysts Post Reaction

The ATR-FTIR characterization of the catalysts after the reaction provided valuable information about the chemical changes and functional groups present in the catalysts. In the range of 1700-1750 cm⁻¹, there were carbonyl stretching groups (C=O), indicating the presence of esters formed during the esterification reaction. The acidic groups (SO₃H) were still prominent in the catalysts, as evidenced by the bands in the range of 1100 to 1300 cm⁻¹, which corresponded to the asymmetric and symmetric stretching modes of these groups. Bands in the range of 2900 to 3200 cm⁻¹ indicated the presence of O-H vibrations, suggesting the presence of residual hydroxyl groups and water, which could be a by-product of methyl oleate.

When comparing these spectra with those of the fresh catalysts, it can be observed that all the groups were still present but with lower reflectance. For example, the band at 1600 cm⁻¹, which represents -C=C bonds, was not as prominent in the catalysts after the reaction. This suggests that the chemical changes during the reaction resulted in a decrease in the intensity of certain functional groups.

The SEM technique was employed to analyze the morphology of the catalysts after the reaction. The sugar-derived catalysts with a 1:4 ratio exhibit less agglomeration compared to the catalyst with a 1:1 ratio. Leaching of sulfonic groups is reported as one of the main causes of reduced catalytic efficiency in sulfonated sugars (Correa et al., 2023). This means that the sulfonic acid groups and sulfur-containing species could have leached out of the catalysts into the reaction medium, resulting in the loss of sulfur from the catalysts. Elemental analysis of the catalysts after the reaction reveals that the glucose₄ catalyst experiences greater leaching of the sulfur element. Consequently, this may lead to a more significant reduction in its catalytic activity compared to the other catalysts. Glycerol₄ and sucrose₁ catalysts have not experienced significant sulfur loss, while xylitol₄ shows a greater amount of sulfonic groups after reuse, suggesting it may have better catalytic performance. Another possible reason for sulfur loss after the reaction is the decomposition of sulfur-containing compounds due to the acidic environment in which the reaction occurred. This decomposition could result in the release of sulfur in the form of sulfur dioxide (SO₂) or other gaseous sulfur compounds, leading to sulfur loss from the catalysts.

4.3 Oleic Acid

In the FTIR spectrum of oleic acid, various functional groups can be identified. The strong reflectance between 2600 and 3200 cm⁻¹ corresponds to the carboxylic acid groups (-COOH). The C-H stretching vibrations of the alkyl chains in oleic acid are observed in the range of 2800 to 2900 cm⁻¹. The carbonyl group (C=O) stretching vibration appears as a

prominent band around 1710 to 1745 cm^{-1} . The presence of a carbon-carbon double bond ($\text{C}=\text{C}$) in oleic acid is indicated by a characteristic band around 1400 to 1450 cm^{-1} . It is important to note that since this is a pure oleic acid sample (99%), the presence of impurities in the spectra is disregarded.

4.4 FAME Yield

In this study, an esterification test was conducted to determine the most effective catalyst. The yield of each reaction was evaluated, and the results showed that all catalysts had significant conversion. Sucrose4 exhibited the highest yield, while glucose1 had the lowest (table 2). The catalyst loading and reaction time were consistent for all reactions, but some catalysts reached their peak yield before the end time. FTIR analysis suggested that an earlier equilibrium shift might have occurred for certain catalysts, requiring more excess methanol. Catalysts with high sulfur content showed rapid deactivation compared to others. Additionally, sucrose4 demonstrated a high and stable conversion throughout the reaction time. Overall, all catalysts demonstrated high activity during the initial stage, indicating lower activation energy. However, calculating the rate of reaction was challenging due to varying rates over time. A more detailed analysis would be needed to determine the exact rate of reaction for certain catalysts.

Table 2 – FAME Yield obtained through FTIR analysis of the esterification of oleic acid.

Catalyst	% FAME
Sucrose4	92.1
Sucrose1	83.1
Glycerol4	72.4
Glycerol1	71.6
Xylitol4	71.5
Xylitol1	69.2
Glucose4	68.3
Glucose1	66.3

4.5 Esterification Reaction

The catalysts were tested for the esterification of oleic acid with methanol to produce biodiesel. The catalysts acted as acidic catalysts, facilitating the reaction between oleic acid and methanol. The sulfonic acid groups on the catalyst surface protonated the carboxylic acid group of oleic acid, increasing its reactivity towards methanol. This led to the formation of FAME and water as by-products. The FTIR spectra of methyl oleate obtained from the esterification reaction showed characteristic functional groups and absorbance peaks. The ester functional group ($\text{C}=\text{O}$) exhibited a strong absorption band around 1740 - 1730 cm^{-1} , indicating successful esterification. As conversion occurred, the absorbance in the range of 1799 - 1729 cm^{-1} decreased, while it increased in the range of 1740 - 1730 cm^{-1} , confirming the presence of esters. The FTIR spectra also revealed that catalysts with a higher concentration of sulfuric acid resulted in higher FAME yields and a more pronounced peak in the C-H bond region. Glycerol4 demonstrated the highest yield of carbon bonds among all the catalysts tested. The presence of a carbon-carbon double bond ($\text{C}=\text{C}$) in the methyl oleate resulted in an absorption band in the FTIR spectra around 1640-1620 cm^{-1} , indicating the stretching vibration of the $\text{C}=\text{C}$ bond. The influence of water in the reaction medium was also considered.

Water, which is often generated as a by-product during esterification reactions, can negatively impact the reaction equilibrium by favoring the reverse direction. It can react with FAME to form free fatty acids and methanol through hydrolysis. Water can also hinder the reactant's access to the catalyst and decrease reaction rates, thereby reducing FAME yield. Experimental esterification reactions were conducted with different water concentrations (10% and 20%) in the presence of the selected catalyst (sucrose4), which yielded the highest

FAME yield. The results showed that higher water concentrations led to lower FAME yields, and in the presence of 20% water, no conversion was observed. The presence of water can shift the reaction equilibrium towards the reactants rather than the desired product, FAME. Water can also participate in side reactions, reversing the esterification reaction and reducing FAME yield. Additionally, the presence of water can deactivate the catalyst or cause leaching of active species, decreasing catalytic efficiency and potentially affecting reaction rate and FAME yield. To enhance conversion and increase FAME yield, it is crucial to remove water from the reaction mixture. Controlling water content in the reaction is essential for optimizing esterification reactions.

5 FINAL CONSIDERATIONS

The data collected via XRD, FTIR and SEM-EDS indicate the most prominent catalysts developed were glycerol₄ and sucrose₄, both following an equal methodology, and holding very equivalent crystalline structures. Beyond that, these catalysts achieved equivalent conversion levels for FAME when compared to traditional catalysts.

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