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Synthesis and Characterization of Sulfonated Polydivinylbenzene Catalyst for Esterification of Glycerol

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The abundance of glycerol as a by-product of biodiesel production has led to an oversupply in the global market and a consequent decline in its price. Given the potential of glycerol as a valuable resource, it is essential to convert it into value-added derivatives through various processes. This research involves preparing sulfonated polydivinylbenzene (PDVB-SO_3H) catalysts by synthesizing PDVB, followed by sulfonation with sulfuric acid (H_2SO_4) at different concentrations (0.5%wt/wt, 1.0%wt/wt, 1.5%wt/wt, 2.0%wt/wt, and 2.5%wt/wt). The characterization of PDVB-SO_3H was carried out using acid-base titration, CHNS elemental analysis, ATR-FTIR, XRD, TGA, BET, and BJH to assess structural and functional properties. The results showed that the optimum H_2SO_4 concentration was 2.0%wt/wt, balancing catalytic activity and structural integrity. Acid-base titration revealed an increase in total acid content with higher H_2SO_4 concentrations. CHNS analysis indicated that sulfur content increased with increasing acid addition (up to 8.06%), whereas ATR-FTIR confirmed the presence of sulfonic functional groups with characteristic peaks at 1712 cm^{-1}. XRD analysis indicated crystallinity with distinct peaks at 38.50°, 44.97°, 65.10°, and 78.88°. TGA demonstrated high thermal stability, with significant weight loss beginning at 250 °C, and BET analysis revealed an increase in surface area with higher acid concentrations, from 268.12 m^2/g to 364.38 m^2/g at 2.0%wt/wt sulfonation. The esterification results highlighted that 0.5%wt/wt and 1.0%wt/wt acid concentrations achieved the highest selectivity for diacetin and triacetin, with 100% glycerol conversion. These findings demonstrate the efficiency of PDVB-SO_3H in converting glycerol to valuable acetins, enhancing the sustainability of the biodiesel industry.

Keywords: Glycerol; esterification; acetins; sulfonated polydivinylbenzene; sulfonation; biodiesel

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The circular economy strives to minimize waste generation in today's interconnected world by emphasizing extensive reuse and recycling. Recently, there has been interest in glycerol, a significant by-product of biodiesel production, as a viable and sustainable feedstock for various applications. Figure 1 shows data from 2022 to 2034 during which global biofuel production experienced rapid growth [1]. This leads to an increase in crude glycerol production, which explains the recent popularity of the biodiesel industry. The price difference between crude and refined glycerol is approximately 5–10 times higher, with refined glycerol costing between $0.8 and $1.2 per kilogram [2]. Therefore, industry and researchers must develop innovative uses for crude glycerol to create new markets in the near future.

The process of converting glycerol into acetin, or acetylated glycerol, is gaining increasing attention because the process produces a valuable and sustainable product with potential global market applications. Acetylation is an environmentally friendly approach to utilize glycerol for acetin production. Glycerol is commonly generated as a by-product during biodiesel production. Ion-exchange resins and sulfuric acid (H_2SO_4) are two frequently used catalysts for the esterification of glycerol into acetin. Although H_2SO_4 facilitates the conversion process, achieving high selectivity can be challenging and may lead to undesirable by-products. Ion-exchange resins act as heterogeneous catalysts, offering enhanced selectivity along with good conversion efficiency. The selection of catalysts for the glycerol-to-acetin process depends on various factors, including reaction conditions and the intended equilibrium between conversion efficiency and by-product minimization. The esterification of glycerol—a valuable by-product of biodiesel production in biorefineries—with acetic acid produces a mixture of mono-, di-, and triacetins, particularly diacetin and triacetin. These compounds are high-energy-density fuel additives that support the economic viability and environmental sustainability of the biorefinery concept by providing diverse applications in industry as fine chemicals and fuel components [2].

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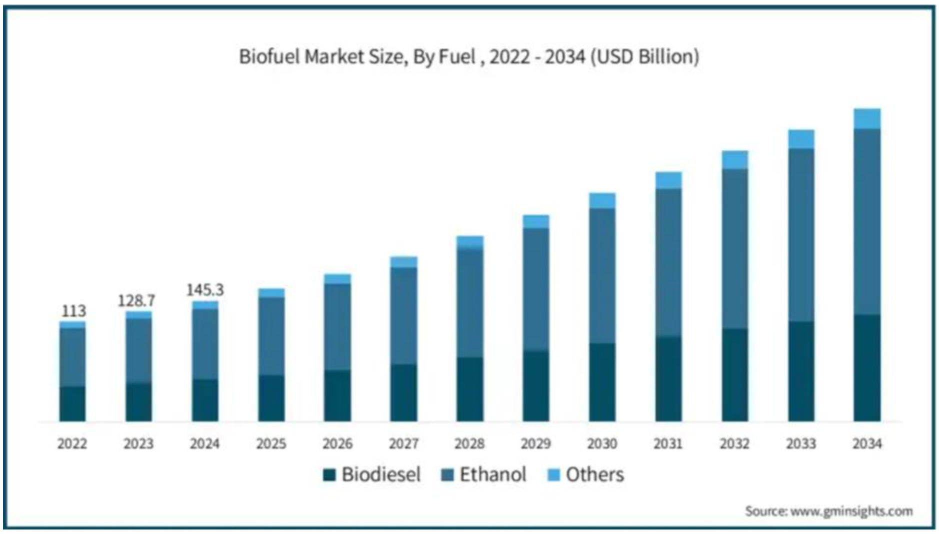

Figure 1. Global biofuel production. *Source:* [1].

This study highlights the potential of converting glycerol into value-added chemicals that support global sustainability goals. This conversion also reduces waste and its negative environmental impacts. The disposal of glycerol can be costly and environmentally damaging. By converting glycerol into acetin, the biodiesel industry can reduce its impact on the environment and the need for expensive waste treatment and disposal techniques. This approach aligns with the industry's goals of promoting sustainability and minimizing environmental impact. It is also important for biodiesel producers to diversify their product range. Acetin, sometimes referred to as acetic acid, is a versatile substance used in the chemical, dietary supplement, and medicinal industries. The introduction of a valuable chemical product into these markets presents a potential opportunity for biodiesel producers to improve their profitability and adapt to changing market conditions.

In line with the global emphasis on waste reduction and sustainability, catalysts are used in the synthesis of acetin from glycerol. Table 1 compares the glycerol esterification performance of various heterogeneous solid acid catalysts reported in recent studies. These catalysts exhibit significant differences in their selectivity profiles and overall glycerol conversion. For example, titanium dioxide/tin (IV) oxide (TiO_2/SnO_2) composites [3] and activated natural zeolite [4] both achieved full or near-complete glycerol conversion (≥95%) with high selectivity toward monoacetin and diacetin but low triacetin yields. Mesoporous silica SBA-15 [5] and graphene oxide [6] demonstrated improved triacetin selectivity, with graphene oxide achieving 25.6%, although at the expense of diacetin formation. Yttrium oxide/palm kernel shell (Y_2O_3/PKS)-T700 [7] favored diacetin production (60.2%) with moderate triacetin selectivity (29.6%), whereas mesoporous sulfonated carbon (OMSC) [8] exhibited the highest triacetin selectivity (66.5%) among the catalysts compared, alongside high glycerol conversion (97%). These variations highlight how catalyst composition, surface properties, and acid site characteristics strongly influence the distribution of acetin products, emphasizing the need for tailored catalyst design to achieve desired product selectivity.

Table 1. Previous studies of different catalysts for glycerol esterification.

References	Catalysts	Selectivity (%)			Glycerol Conversion (%)
		Monoacetin	Diacetin	Triacetin	
[3]	TiO_2/SnO_2 composite	43.0	49.0	8.0	100.0
[4]	Activated natural zeolite	43.0	48.6	8.3	95.0
[5]	SBA-15	19.0	59.0	22.0	95.0
[6]	Graphene oxide	70.2	4.2	25.6	92.1
[7]	Y_2O_3/PKS-T700	11.1	60.2	29.6	99.8
[8]	OMSC	4.9	27.8	66.5	97.0

Solid acid catalysts are essential in chemical synthesis as a class of heterogeneous catalysts that are readily recyclable and environmentally friendly [9]. Compared to mineral acids, solid acid catalysts are more cost-effective and environmentally benign, leading to their increasing use in various chemical processes. A solid acid catalyst that is both highly acidic and hydrophobic has attracted significant interest [10]. The esterification of glycerol to acetin can be effectively accomplished without the use of mineral acids when a solid acid catalyst, such as sulfonated carbon, is used. Due to its remarkable stability, which ensures a long catalyst lifespan, sulfonated carbon is well-suited for continuous biodiesel production processes. Furthermore, this catalyst's high selectivity facilitates the conversion of glycerol into acetin while reducing undesirable by-products. Sulfonated carbon is a reliable catalyst for biodiesel synthesis from glycerol because of its catalytic activity, which is attributed to its well-defined acidic sites, enabling an effective and targeted esterification process.

The application of solid acid catalysts highlights the benefits of integrating green chemistry principles into industrial processes while reducing the environmental impact of mineral acid-catalyzed esterification reactions. Utilizing solid acid catalysts to convert glycerol into acetin significantly influences the chemical industry and advances sustainable chemistry. Recently, polydivinylbenzene (PDVB) has garnered significant research attention for its role as a polymer-supported base for solid acid catalysts, owing to its large surface area, crystalline mesoporous structure, and inherent hydrophobic properties [11]. These unique qualities make PDVB a useful polymer-supported base for solid acid catalysts. Its large surface area enhances catalytic activity, while its hydrophobic nature ensures stability and efficacy across diverse chemical environments. Additionally, its crystalline mesoporous structure promotes efficient reaction pathways. All these characteristics position PDVB as a promising option for solid acid catalysis, especially for reactions such as esterification. The esterification of glycerol to acetin using solid acid catalysts aligns with global efforts to develop more environmentally friendly and efficient chemical processes in an increasingly eco-conscious world.

In this study, sulfonated PDVB (PDVB-SO_3H) was employed as a heterogeneous solid acid catalyst for the esterification of glycerol into acetin. The catalyst was characterized to analyze its total acid content, sulfur presence, functional groups, crystallinity, thermal stability, and surface area. The concentration of H_2SO_4 used was varied to study its effect on the PDVB catalyst in glycerol esterification. Monoacetin and diacetin are undesirable by-products that result from the challenge of achieving high selectivity in glycerol esterification, which aims to produce triacetin [12]. These by-products reduce the overall yield of triacetin and complicate waste management and purification processes. Sustainability depends on effectively converting surplus glycerol into useful products such as triacetin. To address the challenges related to the formation of glycerol by-products and improve the sustainability of the biodiesel industry, it is essential to identify and optimize the parameters for catalyst-driven esterification. Therefore, the sulfonation method using H_2SO_4 was employed to study the effect of its concentration on the PDVB catalyst for glycerol esterification.

EXPERIMENTAL

Chemicals and Materials

The chemicals required for this research are 50% divinylbenzene (DVB), azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and H_2SO_4.

Polydivinylbenzene Preparation

A mixture containing 20 mL of THF, 2 mL of deionized water, and 2.2 mL of DVB was mixed with 0.06 mL of AIBN in a small beaker. The beaker was covered with parafilm, and the mixture was continuously stirred for 3 h. Subsequently, the mixture was transferred into a hydrothermal reactor and hydrothermally treated in an oven for 48 h at 100 °C [11].

Sulfonation of Polydivinylbenzene

The resultant PDVB was allowed to evaporate at room temperature for 30 min before being crushed and ground into powder. The ground PDVB was transferred into a 100 mL beaker and heated directly on a heating mantle for outgassing at 100 °C for 3 h to completely remove excess solvent. Next, a 100 mL beaker was filled with 1.5 g of outgassed PDVB and 10 mL of CH_2Cl_2. The mixture was added with 5 mL of H_2SO_4 dropwise while it was constantly heated in a water bath at 70 °C for 3 h. PDVB-SO_3H was obtained by washing and filtering with distilled water. The pH of the filtrate was measured to be approximately 6–7, confirming that excess CH_2Cl_2 was eliminated from the finished product. Next, PDVB-SO_3H was dried in an oven at 80 °C. This process was repeated using various amounts of H_2SO_4 (10, 15, 20, and 25 mL) during sulfonation to compare the productivity and yield of acetin.

Esterification of Glycerol and Acetic Acid

Glycerol and acetic acid were esterified in the presence of the prepared catalyst using a three-neck round-bottom flask apparatus equipped with a heating mantle, a stirrer, and a thermometer. In the flask, 36 mL of acetic acid and 5 mL of glycerol were combined with the first sample of PDVB-SO_3H catalyst. The mixture was continuously stirred for 3 h. Subsequently, the product containing PDVB-SO_3H was filtered to remove solid particles. Finally, the mixture of monoacetin, diacetin, triacetin, glycerol, and unreacted acetic acid was subjected to rotary evaporation to remove the solvent.

Product Analysis

The liquid product obtained from the esterification of glycerol with acetic acid was analyzed using a gas chromatograph. Using a gas chromatography-mass spectrometry system (GC-MS, Agilent 6890), the products comprising glycerol, monoacetin, diacetin, and triacetin were identified. These products were also quantified through the external calibration method. The percentages of glycerol conversion (X_G), monoacylglycerol selectivity (S_{MAG}), diacylglycerol selectivity (S_{DAG}), and triacylglycerol selectivity (S_{TAG}) were determined based on glycerol, as shown in Equations 1–4 [13].

$$\% X_G = \frac{\text{Moles of glycerol converted}}{\text{Moles of glycerol fed}} \times 100\% \qquad (1)$$

$$\% S_{MAG} = \frac{\text{Moles of MAG formed}}{\text{Moles of glycerol converted}} \times 100\% \qquad (2)$$

$$\% S_{DAG} = \frac{\text{Moles of DAG formed}}{\text{Moles of glycerol reacted}} \times 100\% \qquad (3)$$

$$\% S_{TAG} = \frac{\text{Moles of TAG formed}}{\text{Moles of glycerol reacted}} \times 100\% \qquad (4)$$

Catalyst Characterization

The total acid content of the catalyst samples was determined by performing acid-base titration to quantify the acidity of the active sites. A CHNS elemental analyzer was used to investigate the presence and percentage of sulfur in each catalyst, confirming successful sulfonation. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to identify the functional groups, particularly the presence of sulfonic acid groups. X-ray diffraction analysis (XRD) was employed to determine the crystallinity and structural changes after sulfonation. Thermogravimetric analysis (TGA) was conducted to assess the thermal stability of both PDVB and PDVB-SO_3H. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to measure the surface area and pore size distribution, providing insights into the textural properties of the catalysts.

Acid-Base Titration

In characterizing the PDVB-SO_3H catalyst, acid-base titrations were conducted to determine the concentration of acidic functional groups present in the material. Using a burette, 40 mL of sodium hydroxide (NaOH) with a known concentration of 0.01 mol/L was added dropwise to a round-bottom flask containing 0.05 g of PDVB-SO_3H. This process allows the base to neutralize the acidic sites in the catalyst. The mixture was then stirred continuously for 24 h to ensure thorough interaction. Subsequently, the reaction mixture was filtered, and the remaining NaOH was titrated with 0.01 mol/L of hydrochloric acid (HCl). This titration provides quantitative information about the acidic sites in PDVB-SO_3H, aiding in the characterization of its catalytic properties. The results of the titration offer valuable insights into the acid-base behavior of the catalyst, which is crucial for understanding its reactivity and potential applications.

CHNS Elemental Analyzer

The percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen in the samples were determined using a CHNS elemental analyzer (PerkinElmer, 2400). In this study, the instrument was used to detect the presence of sulfur in each catalyst. A clean vial was filled with 2.5 mg of the PDVB-SO_3H sample. The sample was uniform, well-dried, and in powder form to avoid contamination or dust, which could cause anomalies in the results. The instrument's detection capabilities were fine-tuned to distinguish and quantify each element accurately. Quality control measures, including running blank analyses and calibrating the instrument with known standards, were implemented to ensure the precision and reliability of the CHNS elemental analysis. The results were reported as the percentage of each element in the PDVB-SO_3H sample, with a specific focus on the detection of the sulfur content in the catalysts.

Attenuated Total Reflectance-Fourier Infrared Transform Spectroscopy

This analysis examined the chemical structure of polymer materials and the presence or absence of specific functional groups. Attenuated total reflectance-Fourier transform infrared spectroscopy was employed to identify the sulfonic acid functional groups in each PDVB-SO_3H sample. To prepare the samples, the material was homogenized and formed into either pellets or thin films, depending on the analysis requirement. Pellets were prepared by mixing the ground sample with a binder, whereas thin films were prepared by applying the sample onto a suitable substrate. Care was taken to ensure uniformity and the absence of air bubbles. After any solvents or binders were thoroughly dried or cured, the prepared sample was placed onto the ATR crystal of the FTIR instrument. Parameters, including a wavelength range of 650–4000 cm^{-1}, were set, and spectra were acquired by measuring the infrared absorption of the sample. The resulting spectra were analyzed to identify characteristic peaks indicative of specific functional groups, such as H_2SO_4 in PDVB-SO_3H.

X-Ray Diffraction Analysis

A non-destructive method for obtaining comprehensive details about a material's chemical composition, physical characteristics, and crystallographic structure, known as XRD, was conducted using a diffractometer (PANalytical X'Pert-Pro MPD PW3040/60 XRD). Samples of dried powder were placed on an XRD sample holder. After smoothing the surface using a spatula, the samples were positioned in the XRD chamber. Cu-Kα radiation with a wavelength of

0.154 nm was used for the measurements, and the diffraction angle ranged from 5° to 80°.

Thermogravimetric Analysis

One effective method for measuring the thermal stability of materials, including polymers, is TGA. The thermal stability of PDVB and PDVB-SO_3H was investigated using TGA. In a standard run, a crucible was filled with 10 mg of powdered sample. Under a nitrogen (N_2) environment, the measurement was conducted at a heating rate of 10 °C/min, with the temperature ranging from 30 °C to 800 °C. A thermal analyzer (NETZSCH TG 209F3) was used for the analysis.

Brunauer-Emmett-Teller and Barrett-Joyner-Halenda Methods

The surface area of PDVB-SO_3H was determined using the N_2 physisorption isotherm measured with the Micromeritics ASAP 2060 system. A 0.1 g sample of PDVB-SO_3H was weighed and placed into a sample tube. Prior to analysis, the sample was outgassed for 8 h at 150 °C. The BET and BJH methods were employed to calculate the surface area and pore size distribution of PDVB-SO_3H, respectively. The acquired data were subjected to the BET analysis to determine the specific surface area of the sample. Following the BET analysis, the desorption branch of the N_2 isotherm was analyzed using the BJH method to calculate the pore size distribution.

RESULTS AND DISCUSSION

Catalyst Characterization

Determination of Total Acid Content

The total acid content of solid acid catalysts was accurately determined using acid-base titration to evaluate their catalytic activity. During alkaline hydrolysis with NaOH solution, which reacts with the acidic sites of the catalyst, sodium polydivinylbenzene sulfonate (PDVB-SO-Na^+) is created. The excess unreacted NaOH is then titrated with a standard HCl solution, allowing for precise determination of the total acid content. This multi-step process provides a comprehensive measurement of the acidity of the catalyst, a crucial factor influencing its performance [14].

Table 2, which presents the acid content of PDVB and PDVB-SO_3H samples, shows a progressive increase in total acid content as the concentration of PDVB-SO_3H rises. In particular, the acid contents were 2.12, 2.68, 2.78, 2.84, and 3.16 mmol/g for PDVB-SO_3H concentrations of 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% (wt/wt), respectively. This trend suggests a proportional attachment of sulfonic groups to the polymer material, reflecting a direct correlation between the amount of H_2SO_4 added and the resulting acid content. Further confirmation was provided by elemental analysis, which verified the existence and number of sulfonic groups, supporting the accuracy of the observed variations in acid content.

Higher concentrations of PDVB-SO_3H correspond to an increased acid content, indicating the incorporation of more sulfonic groups into the polymer matrix, which serve as active sites for various chemical reactions [14]. This direct correlation emphasizes the significance of precise control over sulfonation and highlights the role of sulfonic group attachment in improving catalytic performance. The primary objective of synthesizing PDVB-SO_3H as a solid acid catalyst is successfully demonstrated through the progressive increase in total acid content as the concentration of PDVB-SO_3H increases. The data show that sulfonation, which involves the introduction of H_2SO_4 to the polymer, successfully attaches sulfonic groups to the PDVB matrix. This attachment is crucial because these sulfonic groups act as active sites for catalytic reactions, specifically glycerol esterification. The observed trend of increasing acid content with higher PDVB-SO_3H concentrations, ranging from 2.12 mmol/g at 0.5% to 3.17 mmol/g at 2.5%, indicates successful synthesis and provides a quantitative basis for optimizing the sulfonation process to achieve the desired catalytic properties.

Table 2. Acid content in PDVB and PDVB-SO_3H.

Sample	**Acid Content (mmol/g)**
PDVB	0
0.5%(wt/wt) PDVB-SO_3H	2.12 ± 0.04
1.0%(wt/wt) PDVB-SO_3H	2.69 ± 0.01
1.5%(wt/wt) PDVB-SO_3H	2.78 ± 0.01
2.0%(wt/wt) PDVB-SO_3H	2.85 ± 0.01
2.5%(wt/wt) PDVB-SO_3H	3.17 ± 0.01

Table 3. Sulfur content in PDVB and PDVB-SO_3H.

Sample	**Sulfur content (%)**
PDVB	0
0.5%(wt/wt) PDVB-SO_3H	5.39
1.0%(wt/wt) PDVB-SO_3H	5.81
1.5%(wt/wt) PDVB-SO_3H	7.67
2.0%(wt/wt) PDVB-SO_3H	7.68
2.5%(wt/wt) PDVB-SO_3H	8.06

Determination of Total Sulfur Content

One important process for improving the characteristics of PDVB is sulfonation. The introduction of sulfonic groups, which incorporate sulfur into the polymer matrix, significantly affects the material's ion exchange capacity and catalytic activity. Table 3 presents the sulfur content of both PDVB and PDVB-SO_3H samples, providing valuable insights into the efficiency of the sulfonation process.

The successful incorporation of sulfonic groups into the polymer matrix is evidenced by the progressive increase in sulfur content with higher concentrations of PDVB-SO_3H. The data in Table 2 reveal a clear trend, showing sulfur contents of 5.39%, 5.81%, 7.67%, 7.68%, and 8.06% for 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% (wt/wt) PDVB-SO_3H, respectively. This correlation indicates that sulfonation is efficient and scalable, resulting in a higher density of sulfonic groups, which are crucial for the catalytic activity required in esterification reactions [9].

The CHNS elemental analysis results shown in Table 3 quantitatively measure the sulfur content in PDVB-SO_3H, which directly correlates with the number of sulfonic acid groups (–SO_3H) attached to the polymer matrix. These groups are crucial for the material's ion exchange capacity and catalytic activity [15]. The data indicate an efficient sulfonation process, as higher PDVB-SO_3H concentrations result in increased sulfur content, enhancing the catalyst's properties for applications such as glycerol esterification. However, the slight increase in sulfur content from 7.68% to 8.06% between 2.0% and 2.5% (wt/wt) PDVB-SO_3H suggests diminishing returns at higher sulfonation levels. This finding indicates a saturation point or decreased reaction efficiency due to factors like steric hindrance or limited accessibility of reactive sites. This trend highlights the need for optimization to maximize the incorporation of sulfonic groups without wasting reagents or creating inefficiencies, emphasizing the importance of fine-tuning parameters such as sulfonating agent concentration, reaction time, and temperature to develop highly effective PDVB-based solid catalysts.

Determination of Functional Groups Present in the Catalyst

Figure 2 shows the ATR-FTIR spectra of PDVB-SO_3H at different concentrations: 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% (wt/wt). This analysis is essential for achieving the objectives of synthesizing PDVB-SO_3H as a solid acid catalyst for glycerol esterification and understanding the properties that contribute to its catalytic activity. The spectra reveal key functional groups that confirm the successful sulfonation of PDVB, particularly the presence of –SO_3H, which are essential for the catalyst's acidic properties and its role in promoting glycerol esterification [16].

The ATR-FTIR spectra reveal significant differences between PDVB and PDVB-SO_3H, confirming successful sulfonation [17]. The sulfonated samples exhibit distinct peaks at 1712, 2288, and 3750 cm^{-1}, which are absent in PDVB. The peak at 1712 cm^{-1} indicates the presence of carbonyl groups introduced or enhanced during sulfonation, while the peak at 2288 cm^{-1} suggests the introduction of nitrile or isocyanate groups. The peak at 3750 cm^{-1} corresponds to O-H stretching vibrations, indicating the presence of hydroxyl groups likely introduced during sulfonation. Both PDVB and PDVB-SO_3H show the aromatic C-H bending peak at 1462 cm^{-1}, confirming the structural integrity of the PDVB backbone. The presence of these new peaks in the sulfonated samples, along with the absence of corresponding peaks in PDVB, confirms the successful introduction of new functional groups into the PDVB matrix, thereby enhancing its functionality as a solid acid catalyst [17].

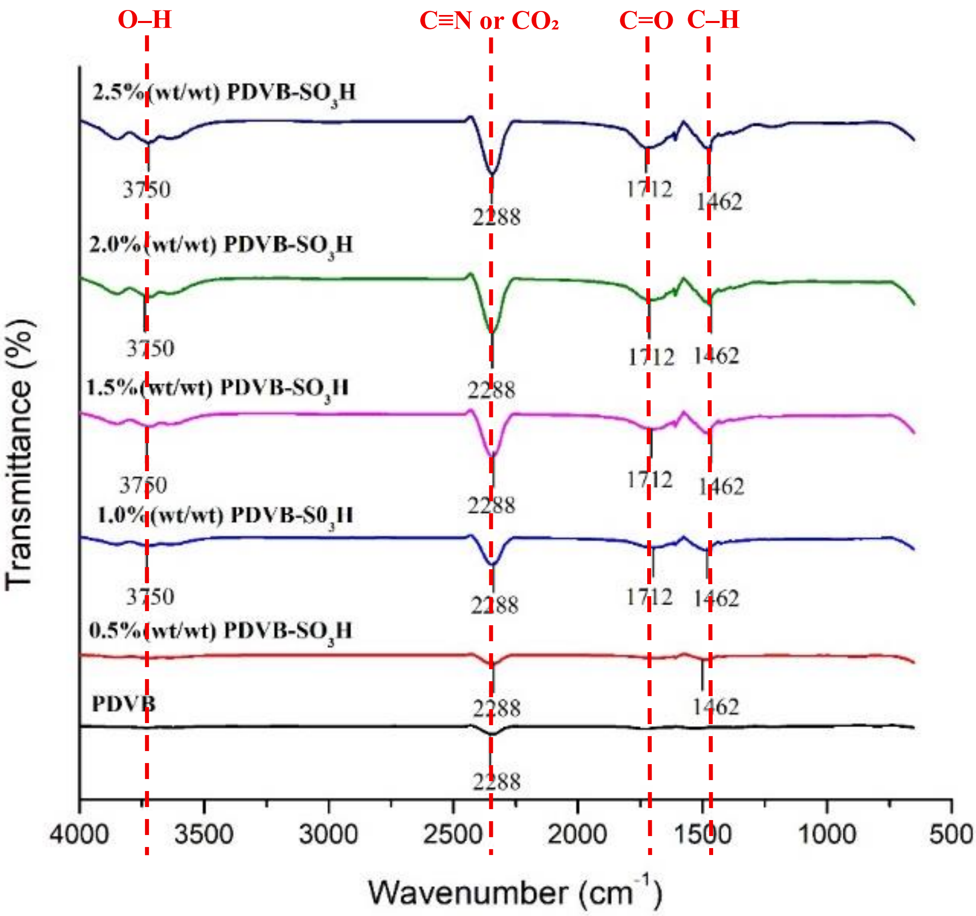

Figure 2. ATR-FTIR spectra for PDVB and PDVB-SO_3H.

The peaks related to sulfonic acid groups are particularly significant, as these are the active sites responsible for the catalyst's acidic properties. The intensity and presence of these peaks across different concentrations of PDVB-SO_3H suggest that higher sulfonation levels result in more active sites, enhancing catalytic performance in glycerol esterification [16]. The consistent presence of these functional groups across all samples demonstrates the robustness and effectiveness of sulfonation in producing a solid acid catalyst. This comprehensive ATR-FTIR characterization confirms the successful synthesis and sulfonation of PDVB, ensuring that the material possesses the desired properties for its intended application and highlighting the importance of this technique in developing high-performance catalytic materials.

Determination of Crystallinity of the Catalyst

An effective method for determining a material's crystalline structure is XRD analysis, which involves monitoring the diffraction of X-rays as they interact with the arrangement of atoms in a sample [18]. This technique is particularly useful for detecting structural changes in materials, such as those induced by chemical modifications. Polydivinylbenzene exhibits a notable structural modification due to sulfonation, as evidenced by its XRD pattern.

The XRD patterns of PDVB and PDVB-SO_3H are shown in Figure 3. Unmodified PDVB is amorphous, as evidenced by the absence of distinct peaks in its XRD pattern [12]. This amorphous nature is typical of PDVB due to the lack of long-range order and the random arrangement of polymer chains. On the other hand, the XRD pattern of PDVB-SO_3H shows distinct peaks at 2θ values, suggesting the existence of ordered regions within the polymer matrix. In the modified polymer structure, the specific peak positions detected at 2θ values of 38.50° (JCPDS reference no. 96-901-6612), 44.97° (JCPDS reference no. 96-901-1567), 65.10° (JCPDS reference no. 96-901-3088), and 78.88° (JCPDS reference no. 96-154-1405) correspond to diffraction angles associated with crystallographic planes. These sharp peaks suggest the sulfonation-induced formation of crystalline features.

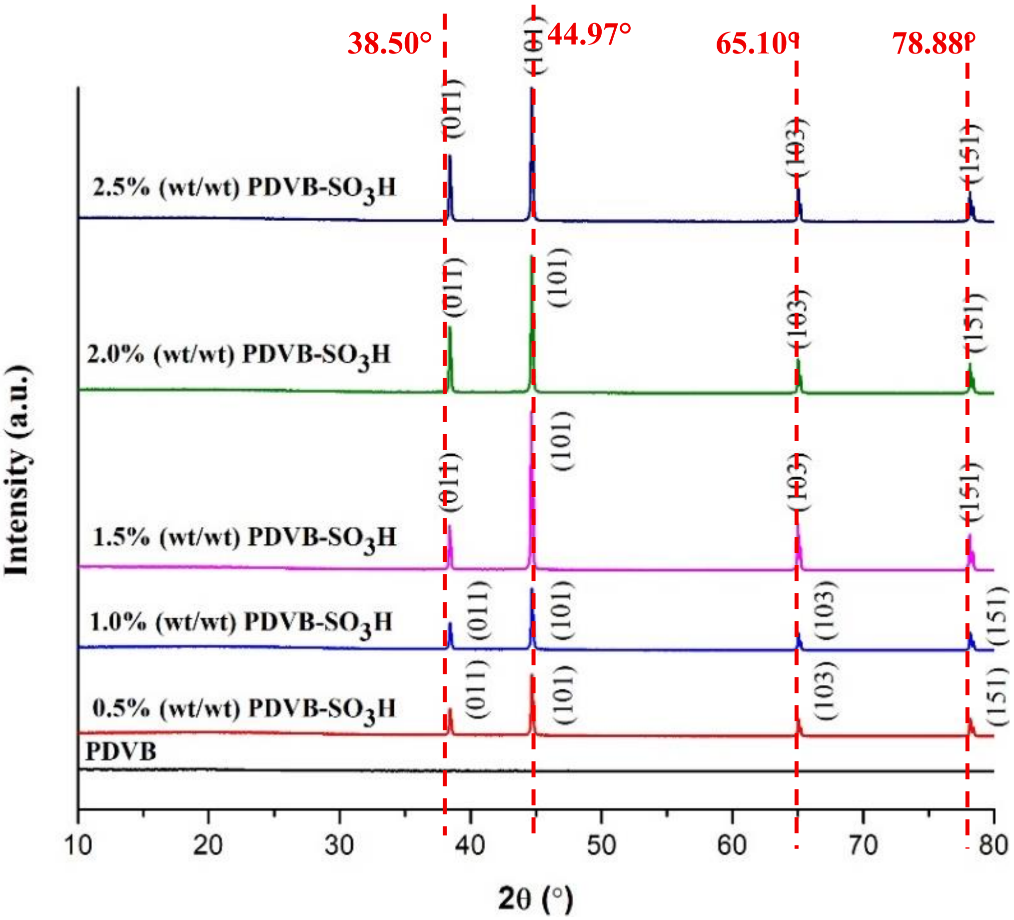

Figure 3. XRD diffractogram of PDVB and PDVB-SO$_3$H.

The presence of sulfonic acid groups results in structural alterations that lead to the appearance of sharp peaks in the XRD pattern of PDVB-SO$_3$H. Sulfonation can promote the formation of crystallites or crystalline domains within the polymer matrix, causing the polymer chains to arrange in an ordered manner [19]. These ordered regions give rise to the XRD pattern, indicating a transition from an amorphous to a partially crystalline structure. Besides introducing ionic sites, the sulfonic acid groups facilitate interactions that promote the organization of polymer chains into more ordered configurations [15].

The XRD analysis of PDVB-SO$_3$H provides crucial insights into the structural changes induced by sulfonation. The development of crystalline regions is indicated by the emergence of sharp peaks in the XRD pattern, which represents a notable departure from the amorphous nature of unmodified PDVB [18]. These XRD patterns confirm the synthesis of PDVB-SO$_3$H as a solid acid catalyst for glycerol esterification. As the degree of sulfonation increases from 0.5%(wt/wt) to 2.5%(wt/wt), corresponding changes in the diffraction patterns reflect the structural modifications caused by sulfonation. The crystalline nature of PDVB is preserved, which is beneficial for catalytic performance, as higher crystallinity is associated with well-defined active sites essential for the esterification process.

The structural properties revealed by XRD, including the retention of crystallinity and the introduction of sulfonic acid groups, are crucial for understanding the catalyst's effectiveness [19]. The shifts and changes in peak intensities with increasing sulfonation levels indicate a higher concentration of acidic sites, which enhances catalytic efficiency in glycerol esterification [15]. These findings demonstrate that the synthesized PDVB-SO$_3$H catalysts maintain their crystalline structure while incorporating active acidic sites, contributing to their effectiveness in catalytic applications.

Determination of Thermal Stability of the Catalyst

The TGA and differential scanning calorimetry (DSC) curves for pure PDVB and PDVB-SO$_3$H provide important insights into the synthesis and characterization of PDVB-SO$_3$H as a solid acid catalyst for glycerol esterification [17]. Figure 4 shows the TGA curve for pure PDVB, which exhibits an initial slight weight loss between 100 °C and 200 °C due to the loss of adsorbed water or volatile impurities. This is followed by a significant weight loss between 350 °C and 450 °C, indicating the thermal decomposition of PDVB. The corresponding DSC curve displays an endothermic peak around 350 °C, correlating with the onset of thermal decomposition, and an exothermic peak between 450 °C and 500 °C, likely due to the combustion of decomposed polymer fragments.

In comparison, Figure 5 shows the TGA curve for PDVB-SO_3H, which exhibits similar initial weight loss due to water or volatile impurities [20]. However, the major weight loss begins earlier, between 250 °C and 350 °C, indicating that sulfonation decreases the thermal stability of PDVB. This earlier weight loss can be attributed to the decomposition of sulfonic acid groups, while the continued decomposition from 350 °C to 600 °C suggests further breakdown of the polymer backbone. The DSC curve for PDVB-SO_3H displays an endothermic peak between 250 °C and 350 °C, corresponding to the decomposition of sulfonic acid groups, and exothermic peaks around 450 °C and 600 °C, indicating further decomposition and combustion processes.

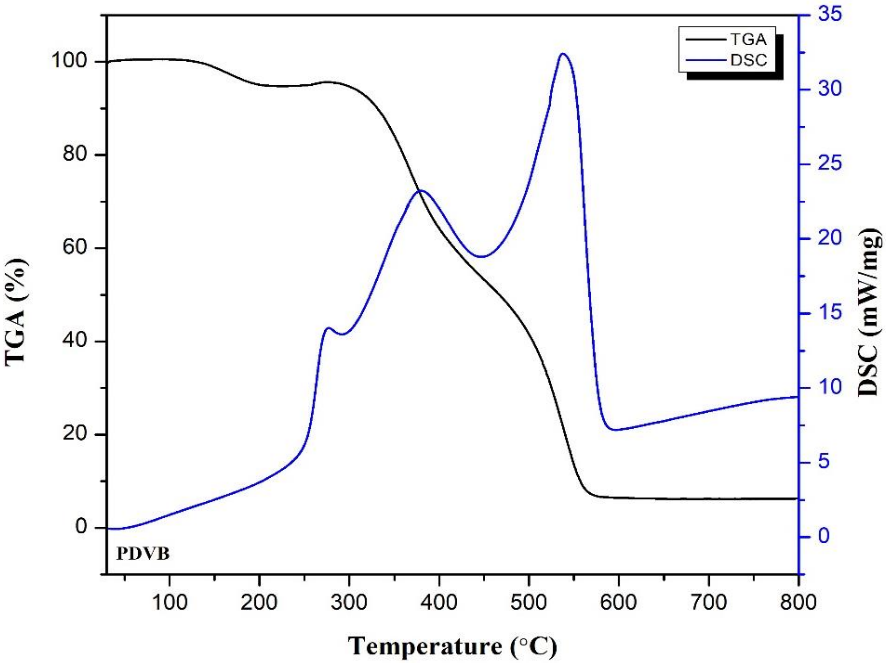

Figure 4. Thermogravimetric curve of pure PDVB.

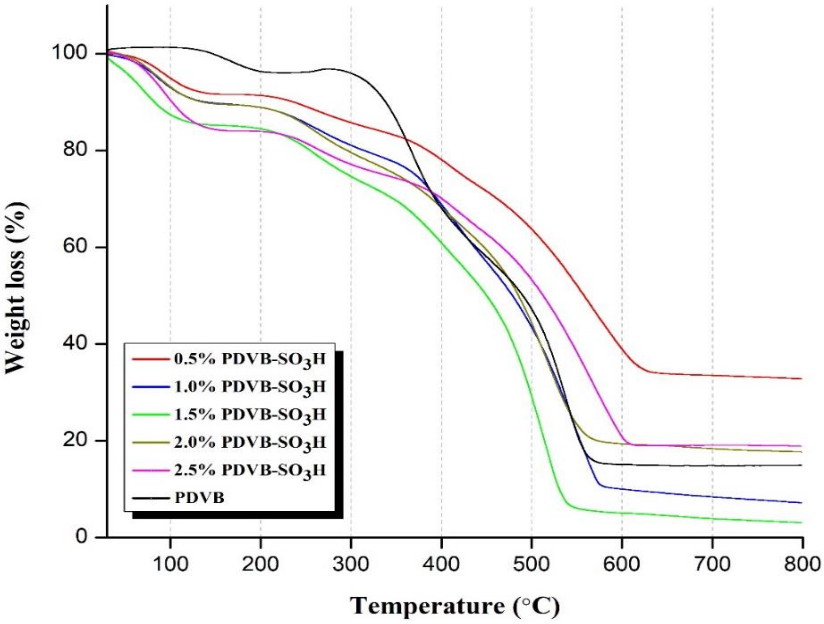

Figure 5. TGA graph of PDVB and PDVB-SO_3H.

Table 4. Textural properties of PDVB and PDVB-SO_3H.

Samples	S_{BET} (m²/g)	V_P (cm³/g)	D_P (nm)
PDVB	268.12	0.34	10.21
0.5%(wt/wt) PDVB-SO_3H	353.31	0.51	10.49
1.0%(wt/wt) PDVB-SO_3H	263.24	0.50	14.43
1.5%(wt/wt) PDVB-SO_3H	103.99	0.18	10.95
2.0%(wt/wt) PDVB-SO_3H	364.28	0.64	13.83
2.5%(wt/wt) PDVB-SO_3H	127.90	0.22	11.70

These thermal analyses demonstrate that the synthesis of PDVB-SO_3H introduces new thermal decomposition stages and reduces overall thermal stability due to the presence of sulfonic acid groups [20]. This is crucial for the catalyst's performance in esterification reactions, as PDVB-SO_3H contains active acidic sites essential for catalysis. The retention of a crystalline structure after sulfonation, as indicated by XRD results, combined with detailed thermal stability data from TGA and DSC analyses, confirms that the synthesized PDVB-SO_3H catalysts are effective for catalytic applications. They maintain stability up to approximately 250 °C while providing the necessary acidic sites for glycerol esterification.

Determination of the Porosity Properties of the Catalyst

The surface area of PDVB and its sulfonated derivatives, as determined by BET analysis, provides crucial insights into the material's potential as a solid acid catalyst for glycerol esterification [17]. Table 4 presents the porosity results of PDVB and PDVB-SO_3H. The pristine PDVB exhibits a surface area of 268.12 m²/g. Upon sulfonation, notable changes in surface area were observed. The 0.5%(wt/wt) PDVB-SO_3H shows a significant increase to 353.31 m²/g, indicating that a low level of sulfonation enhances the surface area, potentially exposing more active sites for catalysis. This initial increase suggests that sulfonation introduces porosity or modifies the structure to increase the accessible surface area. However, as the degree of sulfonation increases to 1.0%(wt/wt) and 1.5%(wt/wt), the surface area decreases to 263.24 m²/g and 103.99 m²/g, respectively. This trend implies that higher levels of sulfonation may cause pore blockage or collapse of the polymer matrix, reducing the overall surface area available for catalytic activity [20].

Interestingly, at 2.0%(wt/wt) sulfonation, the surface area increases to 364.28 m²/g, which is the highest among the samples, suggesting that an optimal level of sulfonation can significantly enhance surface properties. This increase may result from a more uniform distribution of sulfonic acid groups, which prevents pore collapse and ensures a more accessible surface. However, a further increase to 2.5%(wt/wt) sulfonation results in a decreased surface area of 127.90 m²/g, likely due to excessive sulfonation causing structural collapse or pore blockage. These observations highlight the importance of optimizing sulfonation levels to maximize surface area and, consequently, catalytic efficiency for glycerol esterification [17].

The pore volume, measured by the BJH method, provides additional information about the porosity and potential catalytic activity of PDVB and PDVB-SO_3H. The pristine PDVB exhibits a pore volume of 0.34 cm³/g. The 0.5%(wt/wt) PDVB-SO_3H shows a higher pore volume of 0.51 cm³/g, indicating that low levels of sulfonation enhance the material's porosity, likely by creating more accessible pathways for reactants and products during esterification. As sulfonation increases to 1.0%(wt/wt), the pore volume remains relatively high at 0.50 cm³/g, suggesting that moderate sulfonation levels can improve porosity without causing structural damage. However, at 1.5%(wt/wt) sulfonation, the pore volume drastically decreases to 0.18 cm³/g, suggesting pore blockage or collapse. Interestingly, at 2.0%(wt/wt) sulfonation, the pore volume significantly increases to 0.64 cm³/g, which is the highest among all samples, indicating that an optimal sulfonation level can enhance both surface area and pore volume. At 2.5%(wt/wt) sulfonation, the pore volume decreases again to 0.22 cm³/g, reinforcing the idea that excessive sulfonation adversely affects porosity and catalytic efficiency. These findings highlight the importance of controlling sulfonation levels to optimize the porosity and catalytic properties of PDVB for glycerol esterification [17].

The pore diameter, as determined by BJH analysis, provides insights into the pore size distribution in PDVB and its sulfonated derivatives, which influences catalytic activity. The pristine PDVB exhibits a pore diameter of 10.21 nm. Upon sulfonation, the pore diameter slightly increases to 10.49 nm for the 0.5%(wt/wt) sulfonated sample, indicating minimal alteration in pore size distribution and retention of mesoporosity. At 1.0%(wt/wt) sulfonation, the pore diameter significantly increases to 14.43 nm, suggesting that moderate sulfonation creates larger pores or opens existing ones, enhancing mass transport during catalytic reactions. For the 1.5%(wt/wt) sulfonated sample, the pore diameter decreases to 10.95 nm, indicating partial pore collapse or blockage. At 2.0%(wt/wt) sulfonation, the pore diameter increases again to 13.83 nm, optimizing the pore structure to enhance accessibility and mass transport, which correlates with the highest surface area and pore volume observed. At 2.5%(wt/wt) sulfonation, the pore diameter decreases to 11.70 nm, supporting the idea that excessive sulfonation leads to pore blockage or collapse, negatively impacting catalytic properties. These findings emphasize the importance of balancing sulfonation levels to achieve an optimal pore size distribution for efficient catalytic activity in glycerol esterification [15].

Figure 6 shows the adsorption-desorption isotherms for PDVB and PDVB-SO_3H samples, revealing significant insights into the surface and pore characteristics of these materials, which are critical for their effectiveness as solid acid catalysts in glycerol esterification. The pristine PDVB exhibits a type IV isotherm with a hysteresis loop, indicating mesoporosity [20]. This suggests that the base material has a structure capable of accommodating reactants and products during the catalytic process. The initial adsorption at low relative pressures signifies the presence of micropores, whereas the hysteresis loop at higher pressures indicates mesopores, which are essential for enhanced diffusion and catalytic activity.

Upon sulfonation, the 0.5%(wt/wt) PDVB-SO_3H sample shows a noticeable increase in the amount adsorbed, indicating enhanced surface area and porosity. The more pronounced hysteresis loop suggests that sulfonation at this level creates additional mesopores or enlarges existing ones, improving the material's accessibility to reactants. This enhancement is crucial for catalytic applications, as it enhances the material's ability to interact with glycerol molecules. The observed increase in surface area and porosity is consistent with the BET and BJH data, reinforcing the idea that moderate sulfonation improves structural properties favorable for catalytic activity.

As the sulfonation level increases to 1.0%(wt/wt), 1.5%(wt/wt), and 2.0%(wt/wt), the isotherms exhibit variations in adsorption capacity and hysteresis behavior. The 1.0%(wt/wt) and 2.0%(wt/wt) sulfonated samples demonstrate higher adsorption capacities and significant hysteresis loops, indicating optimal pore structures for catalytic activity. However, at 2.5%(wt/wt) sulfonation, the isotherm reveals a reduction in adsorption capacity, suggesting that excessive sulfonation may lead to pore blockage or structural collapse, which hinders catalytic performance. These observations underline the importance of optimizing the sulfonation level to achieve the best balance of surface area, porosity, and structural integrity for effective glycerol esterification.

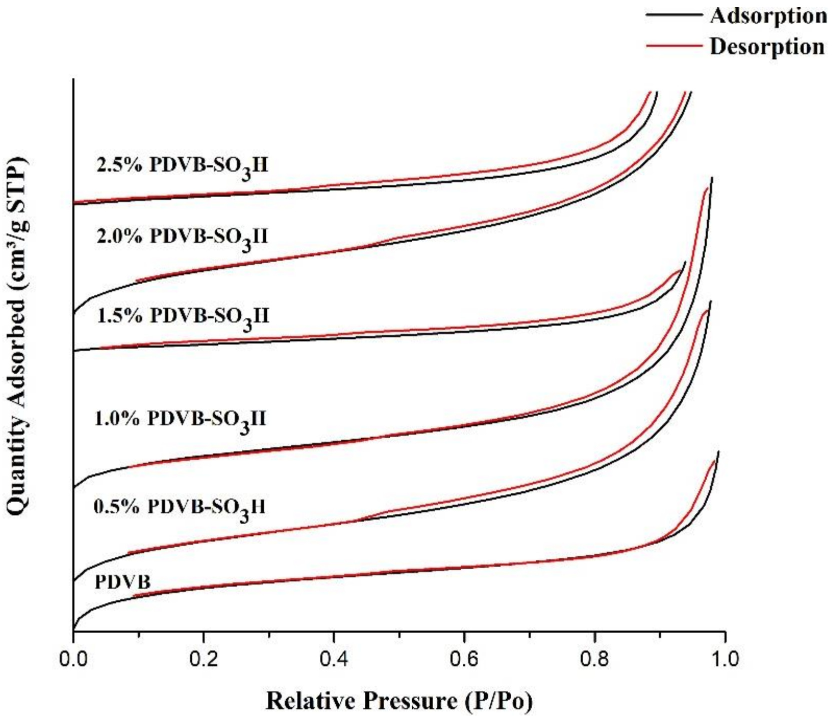

Figure 6. N_2 isotherm of PDVB and PDVB-SO_3H.

Analysis of Esterification Products

Functional Groups of Acetin

Acetin is a collective term for acetylated derivatives of glycerol, including monoacetin, diacetin, and triacetin, which can be obtained through esterification, as shown in Figure 7. Monoacetin has one acetyl group attached to one of the hydroxyl groups of glycerol. Diacetin has two acetyl groups attached to two of the hydroxyl groups, whereas triacetin, or triacetylglycerol, is the fully acetylated form with three acetyl groups. These compounds are esters produced by the esterification of glycerol with acetic acid and are commonly used as plasticizers, solvents, and in the food industry.

Figure 8 presents the FTIR spectra illustrating the transmittance profiles of PDVB sulfonated with varying concentrations of H_2SO_4 (0.5%, 1.0%, 1.5%, 2.0%, and 2.5% (wt/wt)) after glycerol esterification. Key absorption bands were observed at wavenumbers 2370, 1710, 1370, 1230, and 1040 cm^{-1}. The band around 1710 cm^{-1} is particularly significant, corresponding to the C=O stretching vibration of ester groups, which indicates successful glycerol esterification [10]. For the 0.5% ester sample, this band is present but relatively weak, suggesting lower catalytic efficiency at this concentration of H_2SO_4. The bands observed at 1370, 1230, and 1040 cm^{-1} represent different vibrational modes associated with sulfonic acid groups and the ester product, reflecting the interaction between the catalyst and glycerol [17].

Increasing the H_2SO_4 concentration to 1.0%(wt/wt) results in a more pronounced absorption band at 1710 cm^{-1}, indicating enhanced ester formation. This trend continues with the 1.5%(wt/wt) sample, where the band becomes even more intense, signifying improved catalytic activity. The increase in ester production at these concentrations suggests that greater sulfonation enhances the acidity and, consequently, the catalytic properties of the PDVB catalyst. The peaks at 1370, 1230, and 1040 cm^{-1} also become more defined, further supporting the improved interaction between the catalyst and the reactants, leading to more effective esterification [16].

At 2.0%(wt/wt) sulfonation, the absorption bands, including the one at 1710 cm^{-1}, reach their highest intensity, indicating that this H_2SO_4 concentration provides the optimal balance between catalytic activity and structural integrity for glycerol esterification. However, at 2.5%(wt/wt) sulfonation, there is a noticeable decrease in the intensity of the 1710 cm^{-1} band, suggesting a decline in catalytic efficiency. This reduction may be due to over-sulfonation, which could cause pore blockage or structural collapse of the catalyst, negatively impacting its effectiveness [17]. Thus, the FTIR analysis indicates that a 2.0%(wt/wt) H_2SO_4 concentration on PDVB provides the optimum conditions for glycerol esterification, balancing high catalytic activity with structural stability.

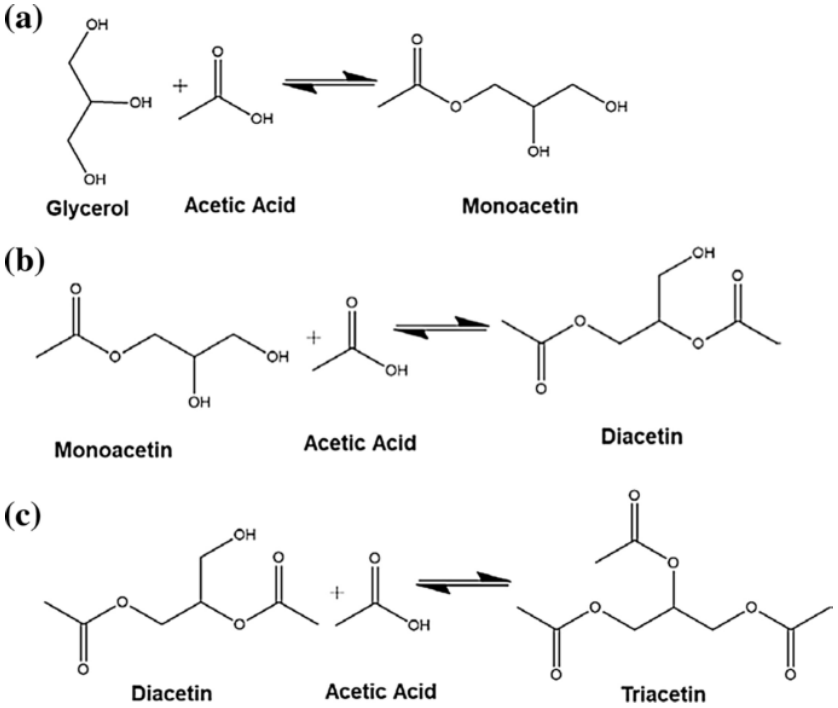

Figure 7. Esterification of glycerol to monoacetin, diacetin, and triacetin. *Source:* [21].

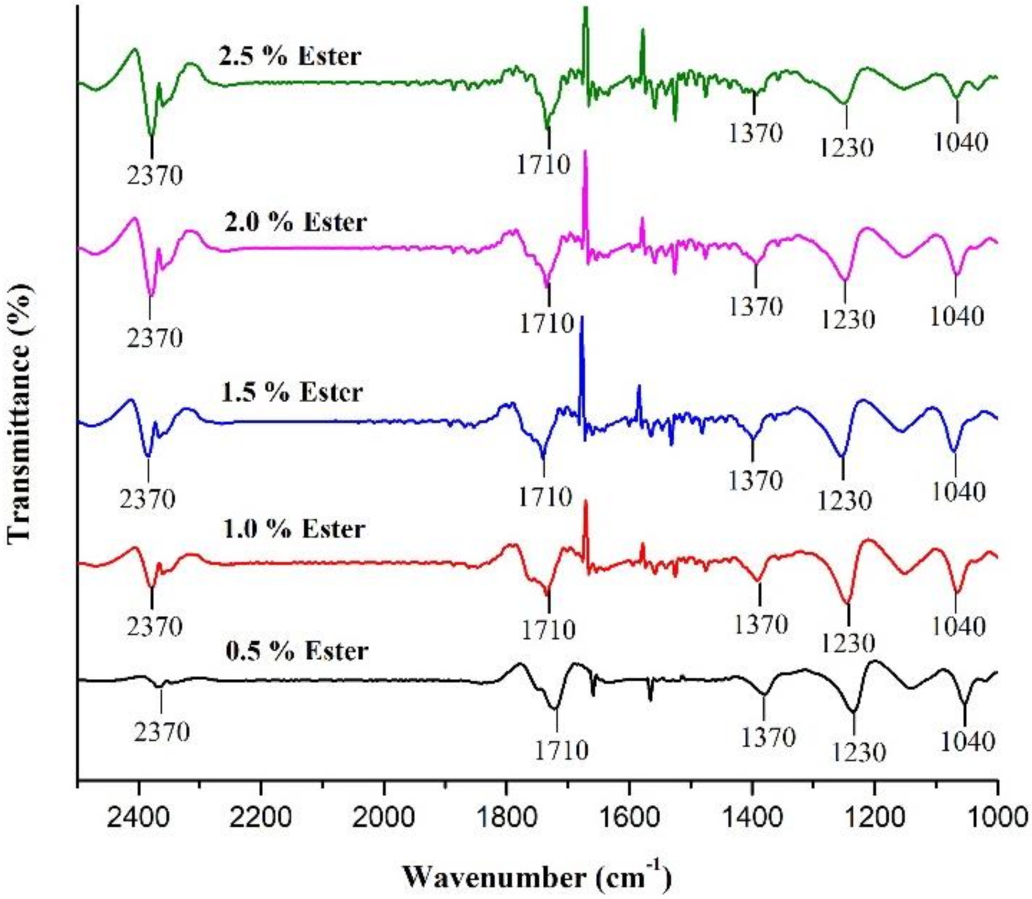

Figure 8. FTIR spectra for ester products.

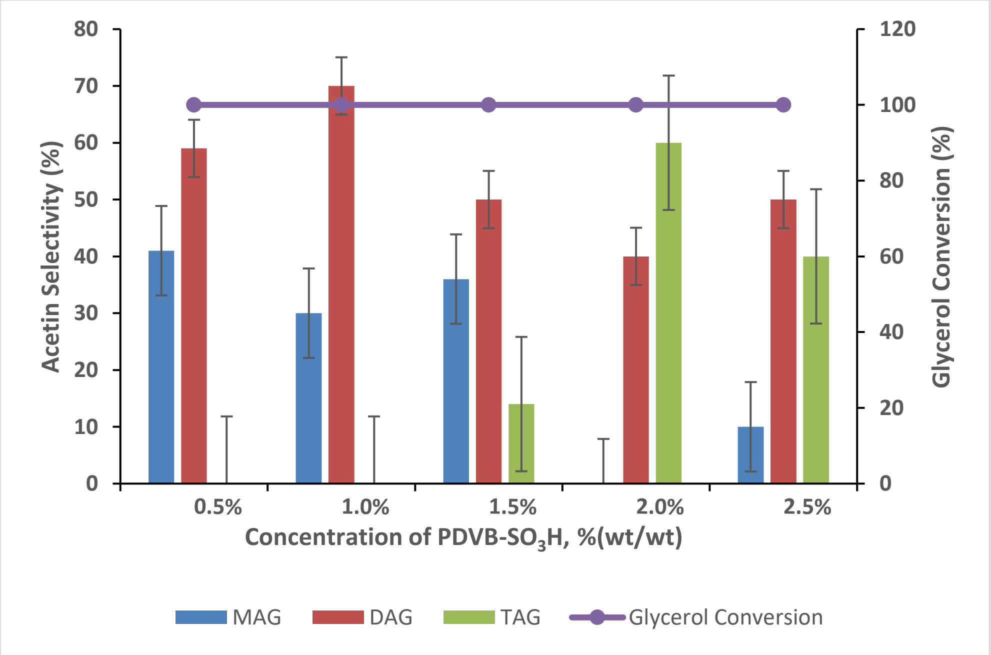

Figure 9. Glycerol conversion and acetin selectivity.

Glycerol Conversion and Acetin Selectivity

Figure 9 presents the results of glycerol conversion and selectivity toward monoacetin, diacetin, and triacetin products using different concentrations of H_2SO_4 on the PDVB catalyst. The initial mole of glycerol used in these reactions was 0.07 mole. For all catalyst concentrations tested (0.5%(wt/wt), 1.0%(wt/wt), 1.5%(wt/wt), 2.0%(wt/wt), and 2.5%(wt/wt)), the glycerol conversion achieved was 100%. This indicates that, under the given reaction conditions, complete conversion of glycerol was accomplished [22]. The high conversion rate can be attributed to the efficiency of the H_2SO_4 on the PDVB catalyst in promoting the esterification reaction, ensuring that all glycerol reacted under the experimental conditions [5].

Analyzing the selectivity data for each catalyst concentration provides insights into the product distribution [23]. For 0.5%(wt/wt) PDVB-SO_3H, the selectivity toward monoacetin, diacetin, and triacetin was 41% and 59%, respectively. This suggests that at this lower catalyst concentration, the reaction favors the formation of monoacetin and diacetin, with no detectable triacetin formation.

At 1.0%(wt/wt) catalyst concentration, the selectivity for triacetin remained at 0%, while diacetin selectivity increased significantly to 70%, and monoacetin selectivity slightly dropped to 30%. This indicates a shift toward more diacetin formation with increasing catalyst concentration. At 1.5% (wt/wt) catalyst concentration, the selectivity toward monoacetin, diacetin, and triacetin was 36%, 50%, and 14%, respectively. These results reveal that triacetin formation begins at the catalyst concentration of 1.5%(wt/wt). For 2.0%(wt/wt) catalyst concentration, triacetin selectivity increased to 60%, while diacetin selectivity decreased to 40%, and monoacetin was not detected. Finally, at 2.5%(wt/wt) catalyst concentration, triacetin selectivity decreased to 40%. This reduction can be attributed to excessive sulfonation at higher catalyst loadings, as indicated by the BET analysis, which showed a significant decrease in surface area and pore volume. The oversupply of acid sites may have led to diffusion limitations within the catalyst pores, restricting the accessibility of reactants to active sites. In addition, the high acidity could promote side reactions or partial hydrolysis of triacetin, thereby lowering its selectivity. The findings imply that careful tuning of catalyst concentration is essential for maximizing the desired esterification products, providing insights for optimizing industrial glycerol esterification processes.

CONCLUSION

This study successfully synthesized PDVB-SO_3H as a solid acid catalyst for the esterification of glycerol using various H_2SO_4 concentrations. The catalyst exhibited desirable characteristics, including substantial total acid content, confirmed presence of sulfur, and appropriate functional groups indicative of sulfonation. Additionally, the characterization of the crystallinity, thermal stability, and surface area of PDVB-SO_3H was comprehensively achieved through techniques such as acid-base titration. The FTIR analysis confirmed successful esterification at the optimal H_2SO_4 concentration, indicated by the strongest absorption band at 1710 cm^{-1}, corresponding to ester groups. These results suggest that PDVB-SO_3H can function effectively as a solid acid catalyst in glycerol esterification, providing a viable option for biodiesel production. Comprehensive analysis using ATR-FTIR and GC-MS determined that a 2.0%(wt/wt) H_2SO_4 concentration yielded the best catalytic activity with the highest selectivity toward triacetin. This study demonstrates the application of PDVB-SO_3H synthesized with H_2SO_4, which exhibits good catalytic activity for the esterification of glycerol to produce acetins. These acetins have significant potential as fuel additives, plasticizers, and versatile chemical intermediates in various industrial applications.

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