

Synthesis and Characterization of Polystyrene Sulfonic Acid from Expanded Polystyrene Foam as a Catalyst in the Synthesis of Triacetin

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Abstract: In Indonesia, the composition of waste has gradually changed over time. To reduce expanded polystyrene (EPS) foam waste, we converted it into a heterogeneous acid catalyst, namely Polystyrene Sulfonic Acid (PSSA). The catalyst was then used in an esterification reaction to generate triacetin. In this research, the synthesis of PSSA was performed using a sulfonation reaction with silver sulfate (Ag_2SO_4) as the catalyst. Based on FTIR analysis, the sulfonation reaction was successful. The use of 0.5% and 1% catalysts led to a significant increase in the degree of sulfonation of PSSA, while there was a relatively constant increase when using 1.5–2.5% catalysts. The highest degree of sulfonation (78.63%) was achieved when the reaction was performed using 2% Ag_2SO_4 catalyst for 25 min. The PSSA with the highest degree of sulfonation was characterized using X-Ray Diffraction (XRD), SEM-EDX, and BET-BJH. This PSSA had a semi-crystalline structure with a crystallinity of 73.83%, a particle size of 1.75 nm, mesoporous pores with a radius of 16.984 Å, and a sulfur content of 15% (% mass).

Keywords: EPS foam; sulfonation; catalyst; silver sulfate; characterization

■ INTRODUCTION

The composition of solid waste, notably the volume of expanded polystyrene (EPS) foam, has evolved and increased in line with industrial technology development and population growth. Cordova and Nurhati [1] reported that an approximate inflow of waste from nine river estuaries into the Indonesian Sea from June 2015 to July 2016 of approximately 23 ± 7.10 tons and 59% plastic waste, with EPS foam as the dominant type of waste. The disposal of EPS has therefore become an acute problem with an associated high environmental impact. As a result, there is increasing concern regarding the recycling of EPS waste, for which different options are developed. The tertiary recycling offers an alternative way of handling polymer waste, where waste is degraded/depolymerized into different materials such as styrene, toluene, and ethylbenzene to produce new polymers or other substances. In this context, the optimum catalyst and reactor design can enable catalytic degradation to occur at

a lower temperature and increase the selectivity of products. The catalytic degradation of polystyrene has mainly been studied using solid catalysts such as zeolite, silica-alumina, fresh FCC catalyst, and MCM-41, which are expensive [2-3]. Another approach to reduce the waste involves the conversion of EPS foam waste into an acid catalyst namely Polystyrene Sulfonic Acid (PSSA).

The PSSA has primarily been applied in industry in reversible osmosis membranes, ion exchangers, ultrafiltration, and plasticizers for conductive composites [4]. The PSSA is considered to have similar acidic properties to the $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyst, which can be used to manufacture triacetin via the esterification process [5-6]. There are various methods to prepare the PSSA catalyst. Martins et al. reacted polystyrene with acetyl sulfate as the sulfonating agent in CH_2Cl_2 at 40 °C for 30 min to produce PSSA with a sulfonation degree (SD) of 18–22% [4]. Bozkurt conducted sulfonation of polystyrene using sulfuric acid as the sulfonating agent in cyclohexane in the presence of P_2O_5 catalyst at 40 °C

to achieve the SD of 90–95% [7]. In the absence of catalyst, PSSA production would involve longer reaction time and resulted in lower degree of sulfonation. According to Carroll [8], employing the Ag_2SO_4 catalyst can improve the sulfonation yield by up to 100% in only 5–15 min. Therefore, this research was aimed to investigate the effect of the Ag_2SO_4 catalyst, the variation of the reaction time, the mass ratio of sulfuric acid as the sulfonating agent, and the mass ratio of ethyl acetate as the solvent on the degree of sulfonation of PSSA and the characterization of triacetin.

■ EXPERIMENTAL SECTION

Materials

The following instruments were used in this research: BET Surface Area and Pore Size Analyser (Quantachrome Nova 4200e), Fourier-Transform Infrared Spectrometer (Thermoscientific Nicolet iS-10), Scanning Electron Microscope (Hitachi SU-3500), and X-Ray Diffraction (Rigaku Smartlab).

Procedure

Preparation of polystyrene sulfonic acid (PSSA) catalyst

The EPS foam was cut into 2×2 cm pieces. In the first stage, a piece of EPS foam (5 g) was diluted in 100 mL of ethyl acetate (EPS foam to ethyl acetate ratio 1:20). The sulfonating agent of 98% sulfuric acid (166 mL) was poured into a three-neck flask (EPS foam to sulfuric acid ratio 1:33). The Ag_2SO_4 catalyst (mass ratio to EPS foam of 0.5–2.5%) was slowly introduced to the flask and the mixture was stirred with a magnetic stirrer. The EPS foam solution was then added dropwise to the previously made acid solution. The reaction was carried out over a fixed period (5–30 min) and at a steady temperature varying from 60 to 70 °C. After the reaction was completed, the formed solid was washed with deionized water. In the second stage, the best condition of the highest SD from the first stage (time, and % mass of Ag_2SO_4) was altered to mass ratios of EPS foam:sulfuric acid (1:23; 1:28; 1:33; 1:38 and 1:43) and EPS foam:ethyl acetate (1:10; 1:15; 1:20; 1:25 and 1:30). The SD of the obtained PSSA was determined using the following procedure, and the highest SD was analyzed using FTIR, X-Ray Diffraction (XRD), SEM-EDS, and BET-BJH.

Determination of the sulfonation degree (SD)

The EPS foam (0.1 g) was soaked in 0.1 M NaCl solution (10 mL) for 2 d. The mixture was filtered, and the obtained filtrate was titrated with 0.02 M of NaOH solution using phenolphthalein as the indicator. The degree of sulfonation was determined using Eq. (1).

$$SD = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}} \times MR_{\text{Monomer PSSA}}}{\text{Sample Weight}} \quad (1)$$

where V_{NaOH} = volume of NaOH (mL) and M_{NaOH} = concentration of NaOH (M).

Synthesis of triacetin

Initially, 25 g of glycerol were heated in a three-neck flask using a hotplate until it reached a reaction temperature of 100 °C. Acetic acid to glycerol with a molar ratio of 10:1 was then mixed and 1–5% of PSSA with the highest SD obtained from the previous synthesis (25 min, Ag_2SO_4 2%, EPS foam to sulfuric acid 1:38, and EPS foam to ethyl acetate 1:10) was added to glycerol. The solution mixture was maintained at its reaction temperature and stirred with a magnetic stirrer at speed of 650 rpm for 150 min. Stirring ended once the reaction time was reached, at which point the temperature on the hotplate was lowered. The reaction mixture was separated from the polystyrene sulfonic acid (PSSA) catalyst using Whatman filter paper and put into a separating funnel. The results of the esterification reaction were calculated for the conversion value of glycerol, selectivity of triacetin, concentration of triacetin, and the triacetin functional group.

Analysis of the esterification product

Analysis of the esterification product was conducted using Gas Chromatography-Mass Spectrometry (GC-MS) at the Laboratory of Organic Chemistry, Universitas Gadjah Mada, Yogyakarta. The instrument used was GCMS-QP2010S SHIMADZU with a 5 MS Rtx column, 30 m long, 0.25 mm ID, 0.25 μm film, helium carrier gas, and EI 70 Ev ionization. The results of this analysis were then used to calculate the selectivity of the triacetin compound based on Eq. (2) [9].

$$\text{Selectivity of Triacetin (\%)} = \frac{\text{Amount of glycerol converted to a product (Triacetin)}}{\text{Total amount of converted glycerol}} \times 100\% \quad (2)$$

■ RESULTS AND DISCUSSION

Preparation of Polystyrene Sulfonic Acid (PSSA) Catalyst

Effect of amount of silver sulfate catalyst on the SD of PSSA

The degree of sulfonation indicates the effectiveness of the sulfonation reaction [10-11] and represents the number of hydrogen atoms that have been substituted by sulfonate groups ($-\text{SO}_3\text{H}$) [12]. In this study, the sulfonation reaction was conducted in the presence of silver sulfate (Ag_2SO_4) catalyst, where the following mass ratios of catalyst to the mass of EPS foam were applied: 0.5–2.5%. Fig. 1 shows the degree of sulfonation of PSSA as a function of the amount of catalyst and reaction time. When 0.5% and 1% catalysts were used, a significant increase in the degree of sulfonation was observed with the greater amount of catalyst used, thus indicating that the amount of catalyst is proportional to the reaction rate. The increase in reaction rate is directly proportional to the number of colliding molecules. This situation results in the number of $-\text{SO}_3\text{H}$ atoms being successfully substituted and the increase of the SD [13]. However, the degree of sulfonation of PSSA was relatively constant when 1.5–2.5% catalysts were employed. This was most likely due to the number of available active sites on the catalyst approaching the capacity of catalysts.

Effect of reaction time on the SD of PSSA

The degree of sulfonation depended on several variables, such as reaction time [10]. Fig. 1 shows the effect of reaction time on the degree of sulfonation of

PSSA. In general, it can be observed that the degree of sulfonation increased as the reaction time increased before decreasing over the period of time. The highest degree of sulfonation in the presence of 0.5–2.5% catalysts was obtained at 25 min with values of 66.67–67.3%. There was a decrease in the degree of sulfonation at 30 min to 66.67–66.98%.

Effect of EPS foam-sulfuric acid ratio on the SD of PSSA

Fig. 2 shows that SD increased in line with the increasing ratio of EPS foam to sulfuric acid. The highest degree of sulfonation was obtained with the H_2SO_4 :EPS foam mass ratio of 1:38. It then began to decline at the ratio of 1:43 in all conditions of the solvent ratio. We presume that this decrease was due to the reaction conditions during sulfonation.

The sulfonation reaction is complex and is in equilibrium with the desulfonation (or hydrolysis of $-\text{SO}_3\text{H}$ groups) reaction. The reaction conditions were arranged in such a way that the equilibrium would shift towards sulfonation. The $-\text{SO}_3\text{H}$ group can be removed from the sulfonated compounds using dilute acid solutions or water. Hydrolysis represents the release of the $-\text{SO}_3\text{H}$ group with the participation of protons in this reaction. In the presence of sulfuric or hydrochloric acid, hydrolysis can occur simultaneously with sulfonation due to the high concentration of protons. In most cases, the sulfonation reaction occurs at high concentrations of sulfuric acid. However, partial desulfonation may occur in the presence of concentrated sulfuric acid [14].

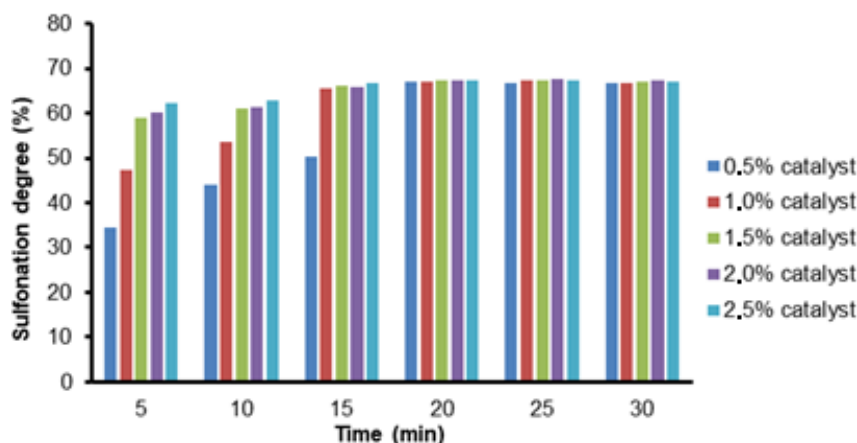


Fig 1. Effect of the amount of catalyst and reaction time on the SD of PSSA

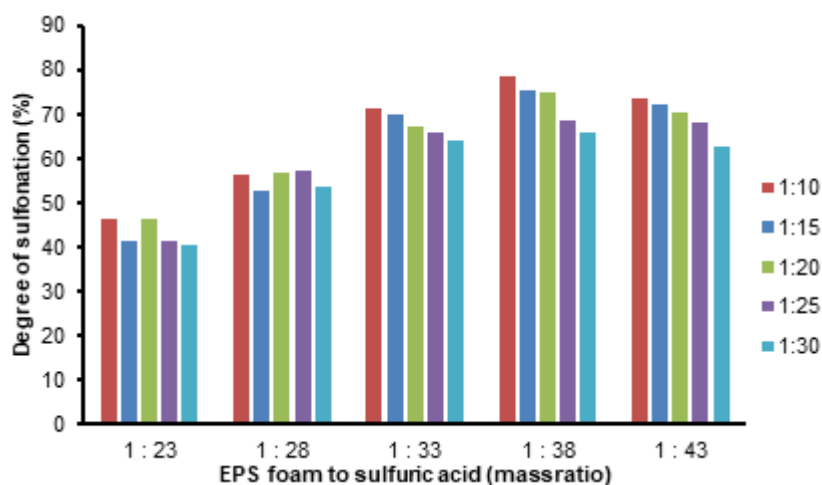


Fig 2. Effect of EPS foam-sulfuric acid and EPS foam-ethyl acetate on the SD of PSSA

Effect of EPS foam-ethyl acetate ratio on the SD of PSSA

Fig. 2 shows that the increase of the ethyl acetate-EPS foam ratio led to the decrease of the degree of sulfonation in the overall H_2SO_4 ratio. It is assumed that the more ethyl acetate is used, the lower the overall concentration of sulfuric acid in the reactor, which affects the equilibrium.

Characterization of PSSA

Based on the results of the previous section, the PSSA catalyst with the highest SD was obtained in a sulfonation reaction between EPS foam and sulfuric acid (1:38) in ethyl acetate (1:10) in the presence of 2% of Ag_2SO_4 catalyst at 60–70 °C for 25 min. The PSSA catalyst was then characterized using FTIR spectrometer, XRD, SEM-EDX, and BET-BJH.

The PSSA was analyzed using FTIR spectrometer at wavenumbers 4000–450 cm^{-1} . Based on the IR spectrum of EPS foam (in Fig. 3(a)), the absorption bands at 585 and 696 cm^{-1} represented the phenyl ring and C–H bond at the phenyl ring, respectively. Absorption at 906 cm^{-1} showed the stretching vibration of the aromatic C–H bond. The peaks at 2919 and 2849 cm^{-1} showed the asymmetric and symmetrical stretching of CH_2 . Absorption at 1599, 1491, and 1449 cm^{-1} came from the vibration of the C=C bonds [15-16]. All the absorption peaks referred to the structure of the polystyrene.

In Fig. 3(b), the IR spectrum of the PSSA showed vibration at 1034 cm^{-1} due to the presence of the C–H

bonds of the aromatic ring. Absorption at 1644 cm^{-1} represented the vibration of the S=O double bond group. The characteristic peak of the C–S bond of aromatic sulfonate appeared at 1165 cm^{-1} [13-14]. Then, the absorption peak at 3365 cm^{-1} showed the hydroxyl (–OH) bond [17,19]. These results demonstrate the existence of the sulfonate group – SO_3H in the structure of the polystyrene (EPS foam), indicating that the polystyrene has been sulfonated.

In this study, SEM analysis was conducted to determine the morphology of EPS foam and PSSA (Fig. 4). Based on Fig. 4(a), the EPS foam has a large ribbon-like shape, which is common in polymer morphology [20].

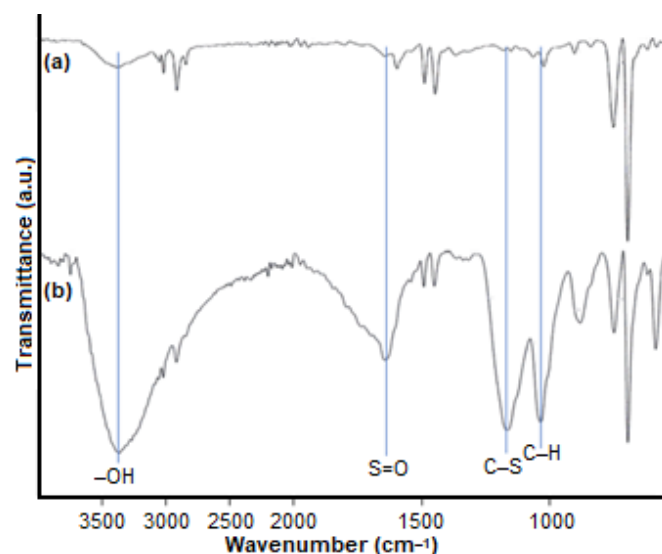


Fig 3. FTIR spectra of (a) EPS foam, (b) PSSA

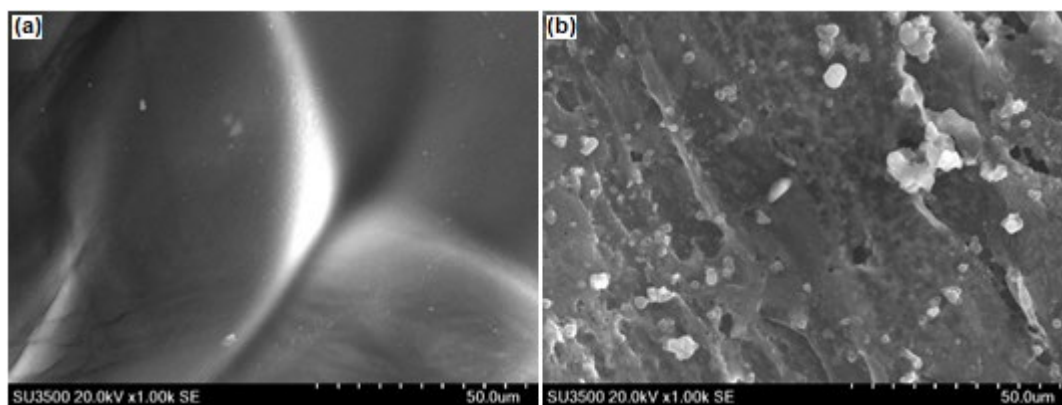


Fig 4. SEM images of (a) EPS foam, (b) PSSA with a magnification of 1,000 times

On the other hand, the PSSA has a smaller and more porous ribbon-like shape (Fig. 4(b)). These morphological changes occurred due to the sulfonation reaction of the EPS foam with the concentrated sulfuric acid [20-21]. There were two steps to the sulfonation reaction. The first involved the generation of sulfur trioxide from concentrated sulfuric acid. The second step comprised the reaction between sulfur trioxide and the aromatic rings in polystyrene, which led to the substitution of hydrogen atoms with the sulfonic acid group to produce polystyrene sulfonic acid [22]. This treatment may result in the ribbon shape becoming more porous.

In this study, the Energy-Dispersive X-ray (EDX) test was also carried out to determine the elemental composition of EPS foam and PSSA (Table 1). The results showed that EPS foam contained carbon (94.86%) and oxygen (5.14%). After the sulfonation process, sulfur (15.88%) and oxygen (11.69%) were observed due to the addition of $-SO_3H$ group to the EPS foam [14]. Other elements were present in only very small amounts, including aluminum (Al), iron (Fe), nickel (Ni), and copper (Cu), presumably due to contamination during the experiment, such as the iron sieve used to filter the PSSA.

The characterization of crystal properties using the XRD instrument was intended to identify the bulk phase of catalyst and to determine the crystallinity. The higher the peak of a catalyst following XRD analysis, the more crystalline the compound [23-24]. Fig. 5 shows the crystal structure of the EPS foam before and after sulfonation. The XRD diffractogram of EPS foam (Fig. 6(a)) shows the

highest peak at 2θ of 19.32° . Meanwhile, the XRD diffractogram of PSSA (Fig. 6(b)) showed a sharper peak at 2θ of 19.8° . Therefore, it can be concluded that the sulfonation process of EPS foam in the presence of silver sulfate (Ag_2SO_4) catalyst can produce PSSA with a semi-crystalline structure.

Table 1. Composition of the elements of EPS foam and PSSA

No.	Component	Percentage (%w)	
		EPS foam	PSSA
1	C	94.86	67.67
2	O	5.14	11.69
3	Al	-	3.27
4	S	-	15.88
5	Fe	-	0.39
6	Ni	-	0.34
7	Cu	-	0.75

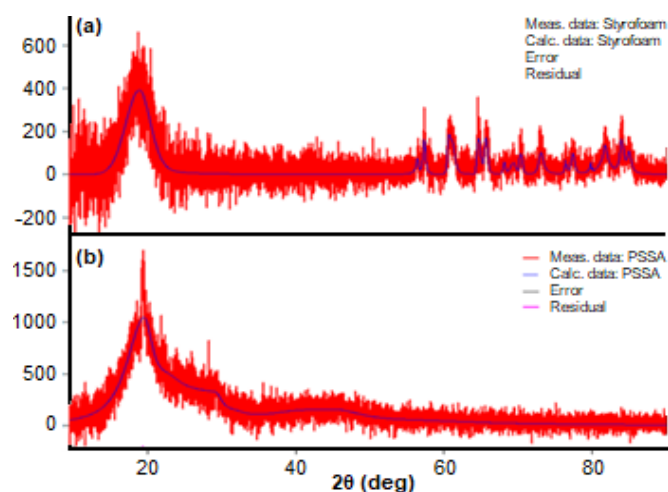


Fig 5. XRD diffractogram of (a) EPS foam, (b) PSSA

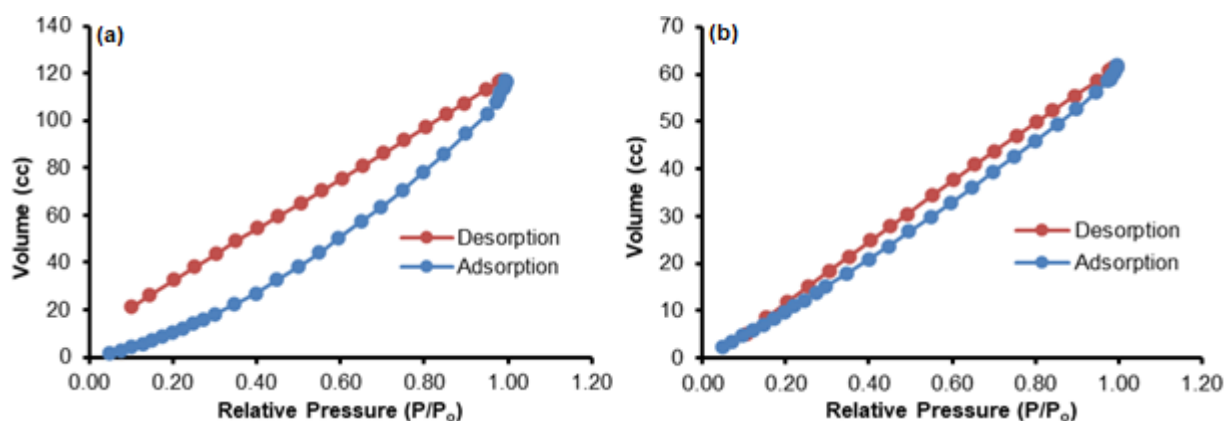


Fig 6. Adsorption-desorption isotherm curve of (a) EPS foam, (b) PSSA

Fig. 6 displays the nitrogen gas adsorption-desorption BET analysis of EPS foam and PSSA as depicted by the isothermal adsorption-desorption curve. The adsorption-desorption isotherm curve for EPS foam and PSSA is Type II, characterized by a sigmoidal-shaped curve and is generally found in materials with larger pores than micropores. A Type II curve includes a macropore-size or non-porous type of material [25-26].

Fig. 7 shows the differential curves of pore size distribution, where the relationship between pore size and pore volume is due to many pores. The two similar-shaped curves in Fig. 7 indicate a significant decrease in pore volume due to the presence of meso-sized pores, as shown

in the pore size distribution curve as an increase in the average pore radius of more than 17.004 Å (1.7004 nm) for EPS foam and 16,984 Å (1.6984 nm) for PSSA. By converting these value to the diameter measurements, EPS foam and PSSA have diameters of 3.4008 and 3.3698 nm, respectively. It can thus be concluded that EPS foam and PSSA have meso-sized pores (2–50 nm).

Based on Table 2, it can be concluded that all the parameters of the EPS foam samples, including surface area, pore volume, and pore radius, tend to decrease following the sulfonation reaction to produce PSSA. Therefore, it can be concluded that the sulfonation process affects the area and morphology of PSSA products.

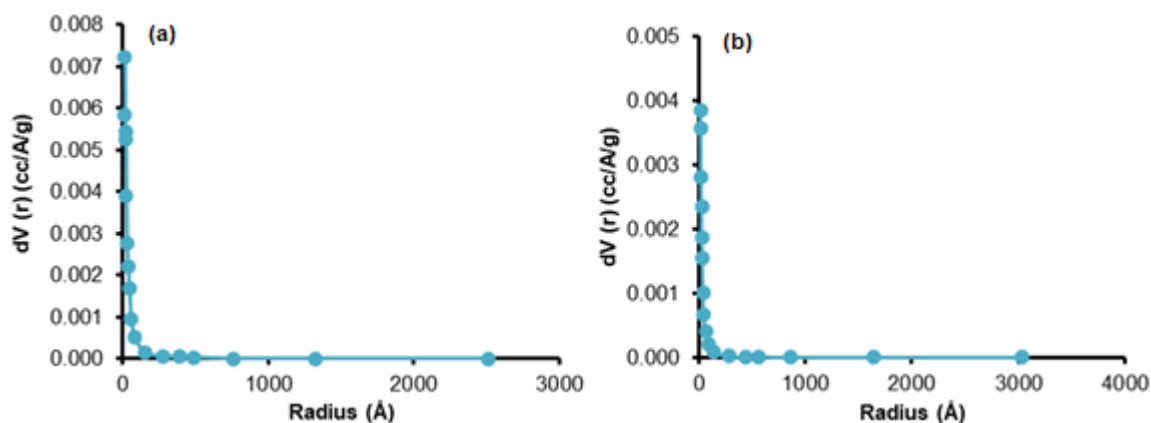


Fig 7. Catalyst pore size distribution of (a) EPS foam, (b) PSSA

Table 2. Physical properties data of EPS foam and PSSA pore

Component	Surface Area (BET) (m ² /g)	Pore Volume (BJH) (cm ³ /g)	Average Pore Radius (BJH) (Å)
EPS foam	567.668	0.191	17.004
PSSA	91.600	0.090	16.984

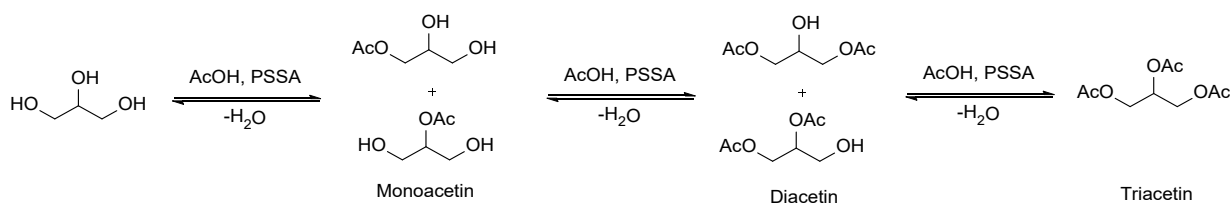


Fig 8. Esterification reaction of glycerol and acetic acid in the presence of PSSA catalyst

Impact of PSSA as a Catalyst on the Synthesis of Triacetin through Esterification Reaction

At this stage, synthesis of triacetin was carried out by reacting acetic acid and glycerol through the esterification reaction, as shown in Fig. 8. The esterification reaction was carried out with fixed variables, at the stirring speed of 650 rpm at 100 °C for 2.5 h. The catalyst used in this reaction was PSSA, with the highest degree of sulfonation from the previous synthesis.

Fig. 9. shows the effect of varying the amount of catalyst from 1% to 5% in the esterification process, where the highest yield of triacetin (44.42%) was obtained by using 2% of catalyst. Fig. 9 shows that the catalyst loading of 1–2% leads to significant increase in the yields of 28.94–44.42% due to the greater availability of active sites, thus allowing more simultaneous protonation of acetic acid [27]. The yield then decreases with catalysts of 3% to 5%, which is probably due to the use of excess catalyst. In the excess amount of catalyst, the density of the solid catalyst in the solution become sufficiently large to reduce the contact area between the catalyst and the reactants. In addition, the high solids concentration in the solution produces a reactor dead zone [28] due to the accumulation of the PSSA catalyst. As a result, the limited mass transfer leads to fewer reactants diffuse into the active site of catalyst [29]. The shift in the reaction equation is due to the formation of water that deactivates the active site of the PSSA catalyst and changes the direction of the reaction. The spontaneous reaction occurred when the catalyst is added, resulting in the greater conversion of acid. Increasing the acid conversion leads to the corresponding rise in the water concentration. Water can deactivate a solid acid catalyst due to its high affinity for the acidic active sites of the catalyst. This is due to the influence of water produced as a by-product, where water tends to shift the reaction to the left. In addition,

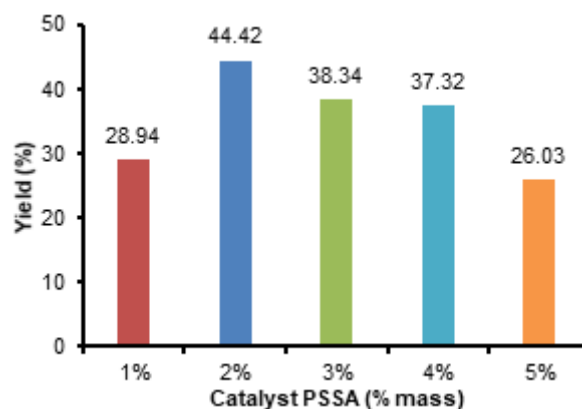


Fig 9. Impact of total polystyrene sulfonic acid as a catalyst on the esterification reaction of glycerol and acetic acid (molar ratio 1:10)

water has a very strong interaction among the components in the system, which greatly affects the rates of diffusion and reaction [28].

CONCLUSION

Synthesis of PSSA was carried out by optimizing several variables, namely time, the amount of catalyst, and EPS foam ratios to sulfuric acid and ethyl acetate. The PSSA with the highest degree of sulfonation (78.63%) was obtained when the reaction was conducted at 25 min, using 2% Ag₂SO₄ catalyst, and ratios of EPS foam to sulfuric acid and ethyl acetate of 1:38 and 1:10, respectively. Synthesis of PSSA using 0.5–1% Ag₂SO₄ catalyst gave significant increase in the degree of sulfonation with increasing of the reaction time. In contrast, the catalyst loading of 1.5–2.5% led to an insufficiently strong rise in the degree of sulfonation despite showing a constant increase. The PSSA with the highest degree of sulfonation had a semi-crystalline structure with a crystallinity of 73.83% and a particle size of 1.75 nm. The esterification reaction between glycerol and acetic acid in the presence of PSSA with the highest

degree of sulfonation (2%), produced triacetin in 44.42% yield.

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