# Synthesis and Characterisation of Sulfonated Polydivinylbenzene as Solid Acid Catalyst for the Production of Furfural

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Solid acid catalyst known as sulfonated polydivinylbenzene (PDVB-SO$_3$H) was synthesised in order to replace homogenous mineral acid in furfural production. In this study, swelling mesoporous polydivinylbenzene (PDVB) underwent the sulfonation process in dichloromethane (CH$_2$Cl$_2$) using pure chlorosulfonic acid (HSO$_3$Cl) with different concentrations (0.5% (wt/wt), 1.0% (wt/wt), 1.5% (wt/wt), 2.0% (wt/wt), and 2.5% (wt/wt). The sulfonation process was conducted in an ice bath (0 °C to 5 °C) under inert conditions using N$_2$ gas and was continuously stirred for 8 hours. Each PDVB-SO$_3$H was characterised by the acid-base titration and BET method. The catalytic activity of each PDVB-SO$_3$H was then examined on the yield of furfural by varying the reaction time (20 min to 40 min), temperature (160 °C to 180 °C), and catalyst loading (0.05 g to 0.2 g) using microwave extraction. The highest furfural yield was 83.3% obtained at 170 °C for 30 min using 0.1 g of the 2.0% (wt/wt) PDVB-SO$_3$H catalyst. The BET results showed that the surface area of 2.0% (wt/wt) PDVB-SO$_3$H was 224.67 m$^2$/g after sulfonation. Meanwhile, the acid-base titration indicated that the total acid content of 2.0% (wt/wt) PDVB-SO$_3$H was 4.04 mmol/g. The excellent performance of 2.0% (wt/wt) PDVB-SO$_3$H was attributed to the high concentration of the sulfonic group as well as its mesoporous structure.

**Keywords**: Solid acid catalyst; PDVB-SO$_3$H; chlorosulfonic acid; furfural

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Converting agricultural waste into fuels and chemicals is becoming significantly important due to the shortage of petroleum-based feedstock. Hence, a new renewable resource is needed to keep up with the high demand for both fuels and chemicals. For years, the conversion of lignocellulose biomass into fine chemicals relied on mineral acid as a homogenous catalyst. The most common mineral acids used were hydrochloric acid (HCl), sulfuric acid (H$_2$SO$_4$), and nitric acid (HNO$_3$). Mineral acid is chosen because it is cheaper and can be easily obtained. However, due to its homogeneity, the major drawbacks that commonly occur in using mineral acid include difficulties in separation from major reaction, corrosion, and it is also harmful toward both environment and humans [1]. Thus, scientists have found a new alternative to replace mineral acid in lignocellulosic conversion. Due to certain preferable advantages, solid acid has been actively created as a replacement for mineral acid. In fine chemical conversion from lignocellulose waste, solid acid is desirable in comparison to mineral acid due to its sustainability, reusability, separation in reaction medium, selectivity, and corrosion reduction [2]. Typically, solid acids are zeolite [3, 4, 5, 6], ion exchange resin [7, 8, 9, 10, 11], sulfated metal oxide [12,13, 14], and sulfonated carbon [15,16, 17].

In the catalysis industries, zeolite is the most widely used catalyst due to its selectivity, higher surface area, controllable acid strength, and framework versatility. However, since zeolite exists as micropores, bulky molecule access to most of the catalytic sites is restricted [18]. In recent years, polydivinylbenzene (PDVB) has been extensively studied as a polymeric-supported base for solid acid catalyst. PDVB exists in a crystalline mesoporous structure, large surface, and hydrophobic nature. The sulfonation of PDVB using either sulphuric acid (H$_2$SO$_4$) or chlorosulfonic acid (HSO$_3$Cl) results in solid Bronsted acid catalyst in which PDVB will bear the sulfonic group (-SO$_3$H) [19]. Due to the mesoporous network of PDVB, more –SO$_3$H can take up the space; thus producing a polymer base solid acid catalyst that is rich with catalytic active site [2]. Furfural production from lignocellulosic biomass using heterogenous catalyst is a newly evolved technology that has rarely been studied. Due to the major and countless harmful drawbacks of homogenous catalyst, more calls have been made to extensively explore furfural conversion using heterogenous catalyst.

Empty fruit bunches (EFB) are one of the highest agricultural wastes generated from oil palm plantations and it can easily be obtained due to its abundances [20]. EFB is categorised as lignocellulose biomass as it consists of the main plant cells, namely cellulose, hemicellulose, and lignin. One of the components, which are hemicellulose, can be converted into biochemical

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products such as furfural. In fact, most lignocellulose biomass that is rich in hemicellulose can be used as feedstock for furfural production such as oil palm frond [21], camellia olefera shell [22], corn stover [23], corncob [24], corn stalk [25], rice husk [26], and mango epicarp [27]. However, catalytic conversion of furfural using EFB was rarely reported in the past literature. Besides most of the hydrolysis process of furfural involved the use of mineral acid as catalyst. Hence, it is necessary to develop a heterogenous environmental friendly catalyst in order to overcome these disadvantages.

Thus, this study had synthesised five series of sulfonated PDVB with different concentrations of -$SO_3H$. The catalytic activity of each synthesised PDVB-$SO_3H$ was tested on the production of furfural using EFB as the feedstock. The reaction conditions were varied by three factors, which were temperature (160 °C - 180 °C), reaction time (20 min - 40 min), and catalyst loading (0.05 g - 0.2 g). The prepared catalysts were characterised using acid-base titration, CHNS elemental analyser, SEM-EDX, ATR-FTIR, XRD, TGA, and BET to investigate the physicochemical properties.

## EXPERIMENTAL

### Chemicals and Materials

All reagents were analytical grade and used without further purification. 50% divinylbenzene (DVB) was purchased from Alfa Aesar, azobisisobutyronitrile (AIBN) and gamma-butyrolactone (GBL) were purchased from R&M (UK), tetrahydrofuran (THF) and dichloromethane ($CH_2Cl_2$) were obtained from Systerm (Malaysia), while chlorosulfonic acid ($HSO_3Cl$) and standard furfural were obtained from Merck (Germany) and Sigma Aldrich (USA), respectively. Meanwhile, the EFB sample was collected from Seri Ulu Langat Palm Oil Mill Sdn. Bhd., Dengkil, Selangor. It was washed thoroughly to remove any dirt and dried in an oven at 100 °C for 24 hours. The dried EFB was then ground into the desired size of 1-2 mm.

### Characterization Methods

### Polydivinylbenzene (PDVB) Preparation

0.05 g of azobisisobutyronitrile (AIBN) was added into the mixture containing 20 mL of tetrahydrofuran (THF), 2 mL of deionized water, and 2 g of divinyl-benzene (DVB). The mixture was continuously stirred for 3 hours. It was then transferred into a hydrothermal reactor and hydrothermally treated in an oven at 100 °C for 48 hours [2].

### Sulfonation of Polydivinylbenzene (PDVB-$SO_3H$)

The sulfonation of PDVB was conducted according to Liu et al. [2] with a slight modification. The obtained PDVB was left to evaporate at room temperature for

30 min before it was crushed and ground into powder. To completely remove excess solvent, the ground PDVB was transferred into a three-neck round bottom flask and outgassed at 100 °C for 3 hours. Next, 1.5 g of outgassed PDVB was transferred into a two-neck round bottom flask and 100 mL of dichloromethane ($CH_2Cl_2$) was added. Subsequently, 5 mL of chloro-sulfonic acid ($HSO_3Cl$) was added dropwise into the mixture and it was continuously stirred in an ice bath (0-5 °C) for 8 hours under nitrogen ($N_2$) atmosphere. The sulfonated divinylbenzene (PDVB-$SO_3H$) was obtained by washing and filtering with distilled water. To ensure that the excess $CH_2Cl_2$ was removed from the final product, the pH of filtrate was measured to be around 6-7. The PDVB-$SO_3H$ was then dried in an oven at 80 °C for 24 hours. For the comparison of productivity and yield of furfural, this procedure was repeated using different amounts of chlorosulfonic acid ($HSO_3Cl$) addition during the sulfonation processes, which were 10 mL (1.0% wt/wt), 15 mL (1.5% wt/wt), 20 mL (2.0% wt/wt), and 25 mL (2.5% wt/wt).

### Characterisation of Catalyst

### Total Acid Content

The total acid content of each PDVB-$SO_3H$ was determined using acid-based titration. It began by adding 40 mL of 0.01 mol/L of sodium hydroxide into a 50 mL round bottom flask containing 0.05 g PDVB-$SO_3H$. The mixture was continuously stirred for 24 hours before it was filtered and titrated with 0.01 mol/L of hydrochloric acid (HCl).

### CHNS Elemental Analyser

The presence of sulfur in each PDVB-$SO_3H$ sample was further confirmed using the CHNS elemental analyser (Perkin Elmer, 2400). 2.5 mg of PDVB-$SO_3H$ sample was placed in a clean vial. The sample must be homogenous, well-dried, and in powder form because the presence of dust or contamination could lead to abnormality in the final result.

### Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

The presence of sulfur element in each PDVB-$SO_3H$ sample was investigated using the Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX) (Hitachi TM3030Plus). PDVB-$SO_3H$ powder was placed on the sample stub and further observed under a low vacuum model with a magnification of ×500 and an accelerating voltage of 15.00kV without sputter coating.

### Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR)

The functional groups of sulfonic acid in each PDVB-$SO_3H$ sample were detected using the Attenuated Total Reflectance-Fourier Transform Infrared (ATR-

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FTIR). The spectra were obtained via the Perkin Elmer Spectrum One instrument with a wavelength of 650 $cm^{-1}$ to 4000 $cm^{-1}$.

### X-Ray Diffraction Analysis (XRD)

The crystallinity of sulfonated samples was determined using the X-Ray Diffraction Analysis (PANalytical X'Pert-Pro MPD PW3040/60 XRD). Dried powder samples were placed on an XRD sample holder. The surface of the samples was smoothened using a spatula and placed in the XRD slot. The reading was taken using (Cu $K_\alpha = 0.154$ nm) at a radiation angle from 5° to 80°.

### Thermogavimetric Analysis (TGA)

The thermal stability of PDVB and PDVB-SO₃H were analysed using the thermogravimetric analysis. As a typical run, 10 mg of powdered sample was weighed and placed into a crucible. The measurement was recorded at a heating rate of 10 °C/min under $N_2$ condition and a temperature ranging between 30 °C to 800 °C. The analysis was conducted using thermal analyser (NETZSCH TG 209F3).

### Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halendar (BJH)

The surface area of PDVB-SO₃H was evaluated using the $N_2$ physisorption isotherm via the Micromeritis ASAP 2060 system. 0.1 g of PDVB-SO₃H sample was weighted and transferred into a sample tube. The sample was outgassed at 150 °C for 8 hours prior the analysis. Both surface area and pore size distribution of PDVB-SO₃H were determined using BET and BJH, respectively.

### Catalytic Activity

### Furfural Extraction from Empty Fruit Bunches (EFB)

The production of furfural was performed in a microwave reactor (ETHOS, EASY, Milestone, Italy).

The extraction was done by investigating 3 parameters that affect the furfural production, namely temperature (160 °C – 180 °C), reaction time (20 min - 40 min), and PDVB-SO₃H loading (0.05 g – 0.2 g). In typical reaction, 0.2 g of EFB and PDVB-SO₃H (0.05 g - 0.2 g) were added into a vial containing a mixture solvent (biphasic) of 5 mL deionized water and 15 mL gamma-butyrolactone (GBL). The mixture was vorticed until it was homogenized. These steps were repeated with each PDVB-SO₃H concentration.

### Furfural Quantification

The liquid sample of furfural was analysed using the High-Performance Liquid Chromatography (HPLC) (Agilent 1100/1200) equipped with a Diode Array detector ($\lambda$= (254 nm) and C18 column. Furfural samples of 20 µL injection volumes were analysed with mobile phase comprising acetonitrile and deionized water (55:45) at a flow rate of 1 mL/min and the column temperature was maintained at 30 °C. The yield of furfural was calculated using the following equation.

$$\text{Furfural yield} = \frac{\text{Mass of furfural (g)}}{\text{Mass of sample (g)}} \; x \; 100$$

### RESULTS AND DISCUSSION

### Characterization Of Catalyst

### Total Acid Content

One of the important characteristics of solid acid catalyst is acid strength, which is related to its catalytic activities. First part of total acid content allowed NaOH solution to react with sulfonated sample which produce sodium polydivinylbenzene sulfonate (PDVB-SO⁻Na⁺). The reaction is known as alkaline hydrolysis [28]. As for the second part, excess hydrolysed NaOH was titrated with HCl. This acid base titration determines the HCl amount needed to neutralise unreacted NaOH. The amount of HCl added was used to obtained total acid content. Table 1 presents the acid content of PDVB and sulfonated samples.

**Table 1**. Acid content of PDVB and sulfonated PDVB.

| Samples | Acid Content [a] (mmol/g) |
|---|---|
| PDVB | 0 |
| 0.5% (wt/wt) PDVB-SO₃H | 3.4 |
| 1.0% (wt/wt) PDVB-SO₃H | 3.6 |
| 1.5% (wt/wt) PDVB-SO₃H | 3.8 |
| 2.0% (wt/wt) PDVB-SO₃H | 4.04 |
| 2.5% (wt/wt) PDVB-SO₃H | 4.65 |

[a] Measured by acid-base titration

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**Table 2.** Sulfur content in PDVB and sulfonated PDVB.

| Samples | Sulfur Content [b] (%) |
|---|---|
| PDVB | 0 |
| 0.5% (wt/wt) PDVB-SO$_3$H | 9.46 |
| 1.0% (wt/wt) PDVB-SO$_3$H | 10.05 |
| 1.5% (wt/wt) PDVB-SO$_3$H | 10.86 |
| 2.0% (wt/wt) PDVB-SO$_3$H | 12.65 |
| 2.5% (wt/wt) PDVB-SO$_3$H | 11.36 |

[b] Measured by elemental analysis

The results showed that the acid-base titration for 0.5% (wt/wt) PDVB-SO$_3$H, 1.0% (wt/wt) PDVB-SO$_3$H, 1.5% (wt/wt) PDVB-SO$_3$H, 2.0% (wt/wt) PDVB-SO$_3$H, and 2.5% (wt/wt) PDVB-SO$_3$H were 3.4 mmol/g, 3.6 mmol/g, 3.8 mmol/g, 4.04 mmol/g, and 4.65 mmol/g, respectively. It can be seen that the total acid content increased as the amount of chlorosulfonic acid added increased. This increment indicates that more sulfonic groups were attached to the polymer material [29]. However sample was further confirmed using elemental analyser.

**Elemental Analysis**

Table 2 presents the sulfur content in PDVB and sulfonated PDVB. The results indicate that the sulfonation of 0.5% (wt/wt) PDVB-SO$_3$H, 1.0% (wt/wt) PDVB-SO$_3$H, 1.5% (wt/wt) PDVB-SO$_3$H, 2.0% (wt/wt) PDVB-SO$_3$H, and 2.5% (wt/wt) PDVB-SO$_3$H were 9.46%, 10.05%, 10.86%, 12.56%, and 11.36%, respectively. It can be seen that the sulfur content in 2.5% PDVB-SO$_3$H significantly decreased while the sudden decrease of sulfur in 2.5% PDVB-SO$_3$H could plausibly be due to the chlorosulfonation of the sample instead of sulfonation.

**Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM -EDX)**

SEM –EDX was performed to further confirm the nature of sulfur content in each PDVB-SO$_3$H sample. Table 3 shows that the EDX analysis of 0.5% PDVB-SO$_3$H, 1.0% PDVB-SO$_3$H, 1.5% PDVB-SO$_3$H, 2.0% PDVB-SO$_3$H, and 2.5% PDVB-SO$_3$H gave the results of 12.54%, 13.23%, 14.12%, 15.54%, and 13.83%, respectively. In this analysis, the drop in sulfur content in 2.5% PDVB-SO$_3$H confirms the elemental analysis results that chlorosulfonation might occur during synthesis and some chlorine was introduced into 2.5% PDVB-SO$_3$H replacing the OH group.

**Attenuated Total Reflectance-Fourier Transform Infrared Analysis (ATR-FTIR)**

The existence of a functional group of sulfonic acid in each sulfonated sample was confirmed by the ATR-FTIR spectra. Figure 1 shows that the ATR-FTIR spectra of PDVB for 0.5% (wt/wt) PDVB-SO$_3$H, 1.0% (wt/wt) PDVB-SO$_3$H, 1.5% (wt/wt) PDVB-SO$_3$H, 2.0% (wt/wt) PDVB-SO$_3$H, and 2.5% (wt/wt) PDVB-SO$_3$H. The 3395 cm$^{-1}$ and 2919 cm$^{-1}$ bands in PDVB and sulfonated samples were due to –C=H stretching. Meanwhile, the peak presented at 1672 cm$^{-1}$ corresponded to the C=C stretching of PDVB [30]. All sulfonated samples exhibited a new peak at 1148 cm$^{-1}$ and 1447 cm$^{-1}$, which corresponded to the S=O symmetric and asymmetric stretching bands [21, 31]. Whereas, the peak observed at 694 cm$^{-1}$ in sulfonated samples was attributed to S-O stretching. These ATR-FTIR results thus confirm the successful sulfonation of PDVB.

**Table 3.** Sulfur content in PDVB and sulfonated PDVB from EDX.

| Samples | Sulfur Content [c] (wt%) |
|---|---|
| PDVB | 0 |
| 0.5% (wt/wt) PDVB-SO$_3$H | 12.54 |
| 1.0% (wt/wt) PDVB-SO$_3$H | 13.23 |
| 1.5% (wt/wt) PDVB-SO$_3$H | 14.12 |
| 2.0% (wt/wt) PDVB-SO$_3$H | 15.54 |
| 2.5% (wt/wt) PDVB-SO$_3$H | 13.83 |

[c] Measured by energy dispersive x-ray

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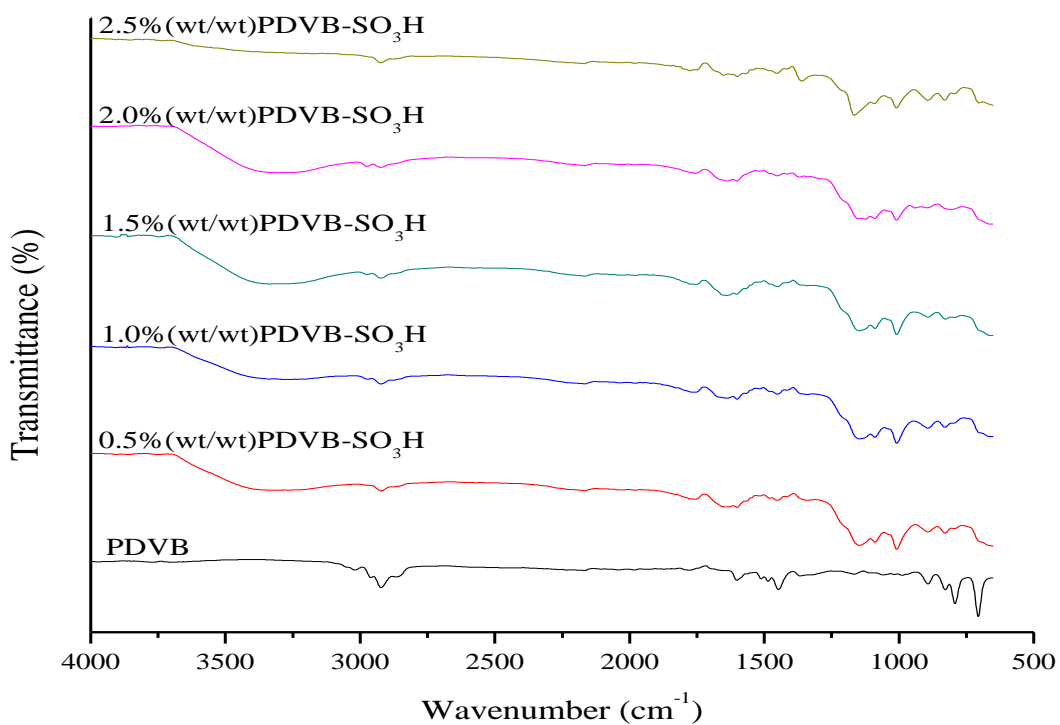                                                          the Production of Furfural
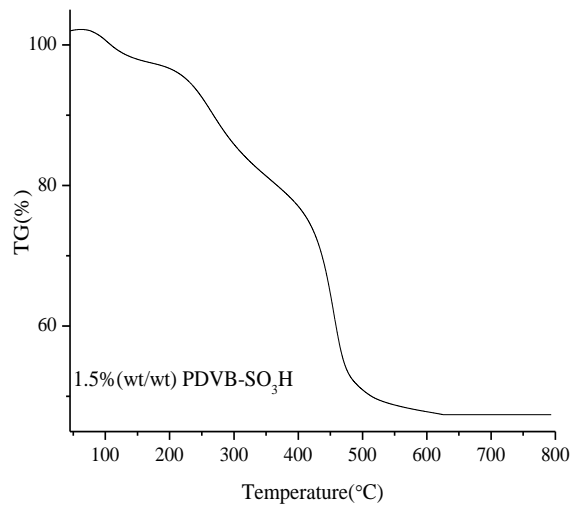
**Figure 1.** IR spectra for PDVB and sulfonated PDVB.
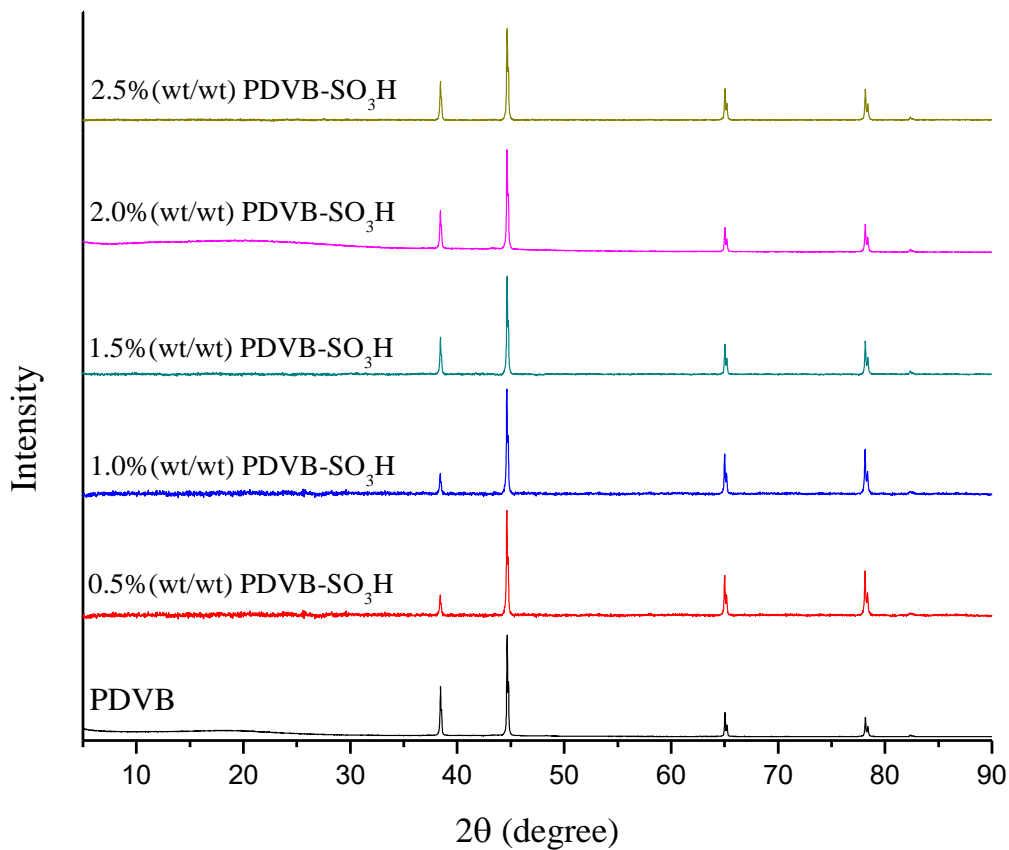


**Figure 2.** Diffractogram of PDVB and sulfonated PDVB.

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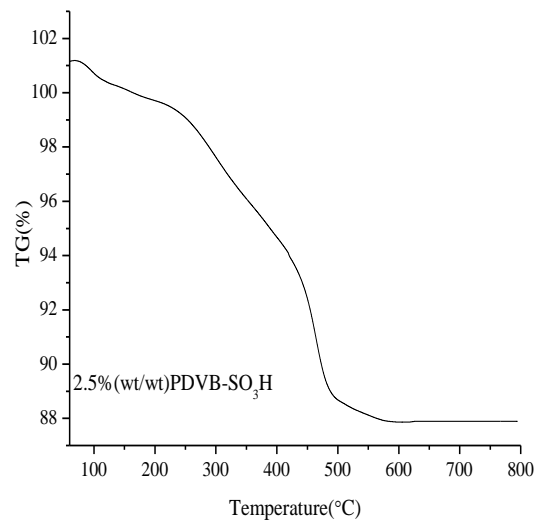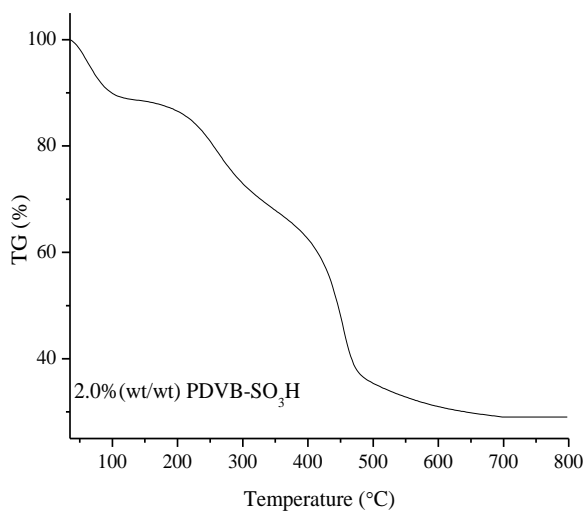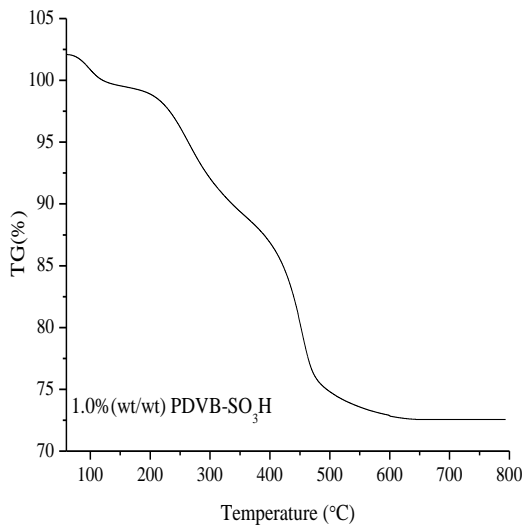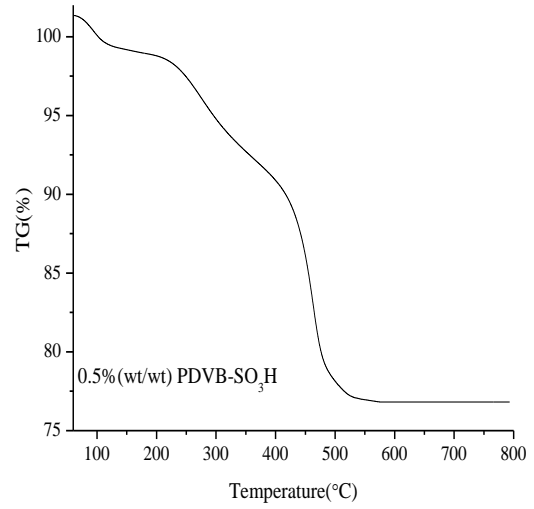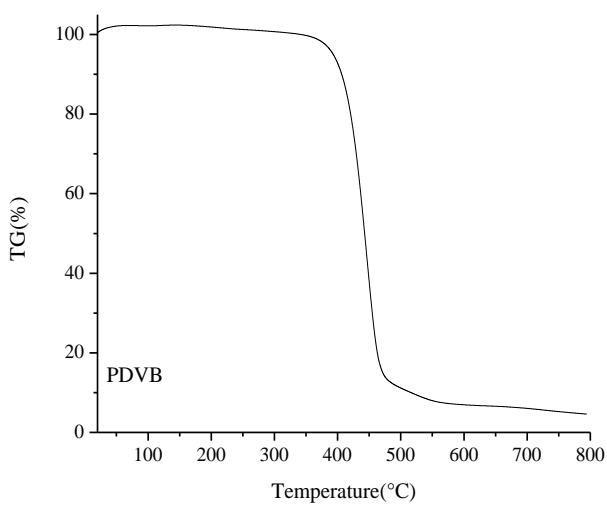


**Figure 3.** Thermogravimetric curve for PDVB and sulfonated PDVB.

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**X-Ray Diffraction Analysis (XRD)**

The crystalline phases formed in freshly prepared samples were analysed by X-ray diffraction. Figure 2 shows the diffractogram of PDVB and sulfonated PDVB. PDVB exhibited sharp peaks at $2\theta$ with the values of 38.36°, 44.85°, 65.22°, and 78.41°. All these peaks represent the crystalline character of carbon that exists in PDVB. Meanwhile, the diffractogram of sulfonated PDVB recorded a drop in intensity, which could be due to the sulfonation process. However, no new or distorted peaks were found in the sulfonated PDVB. This suggests that sulfonation does not affect the crystalline structure of PDVB.

**Thermogravimetric Analysis (TGA)**

The thermal stability of PDVB and sulfonated PDVB were comparatively analysed using thermogravimetric analysis. Figure 3 shows the decomposition range of PDVB and sulfonated PDVB. The TG curve of PDVB indicated that PDVB only had one step weight loss at 400 °C – 600 °C, which was assigned to the destruction of the polymer framework. It is believed that PDVB only has one phase of weight loss because it only consists of divinlybenzene isomer. Meanwhile, the TG curve for sulfonated samples showed two additional weight losses at 60 °C – 120 °C and 222 °C – 324 °C (0.5% (wt/wt) PDVB-SO$_3$H), 60 °C – 122 °C, 209 °C – 321 °C (1.0% (wt/wt) PDVB-SO$_3$H), 54 °C – 120 °C, 194 °C – 320 °C (1.5% (wt/wt) PDVB-SO$_3$H), 40 °C – 101 °C, 203 °C – 300 °C (2.0% (wt/wt) PDVB-SO$_3$H), and 61°C – 115 °C, 227 °C – 370 °C (2.5% (wt/wt) PDVB-SO$_3$H). The additional decomposition range was assigned to water desorption and functional group destruction [21, 32, 33]. It was due to the introduction of –SO$_3$H as a new functional group into the mesoporous polymer framework. Meanwhile, it

was observed that the destruction of the polymer framework of sulfonated samples occurred at 554 °C, which was slightly lower compared to PDVB which occurred at 600 °C. The slight decrease in thermal stability of the sulfonated sample was due to the introduction of –SO$_3$H [34].

**Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halendar (BJH) Analyses**

The surface area and pore size distribution of PDVB and sulfonated PDVB were investigated using the BET and BJH analyses. Table 4 summarises the textural properties of PDVB and sulfonated PDVB. It was observed that the surface area, pore volume, and pore diameter of PDVB were 661.0 m$^2$/g, 1.47 cm$^3$/g, and 13.05 nm, respectively, subsequently indicating the mesostructure of PDVB [2]. Meanwhile, the surface area, pore volume, and pore diameter for sulfonated samples gradually decreased as the concentration of HSO$_3$Cl increased. This was caused by the impregnation of –SO$_3$H group into PDVB, which occupied the surface areas and pores [35]. Meanwhile, Figure 4 shows the N$_2$ isotherm results for PDVB and sulfonated PDVB. It was observed that both PDVB and sulfonated PDVB recorded a sharp increase in relative pressure (P/P$_o$) at 0.85<P/P$_o$< 1.0. This corresponded to the type of iv isotherm that indicated the mesostructure of PDVB and sulfonated PDVB [1, 36]. Finally, Figure 5 shows the results for pore size distribution that was conducted using the BJH method. It was reported that the distribution region for PDVB was 4.09 nm - 22.03 nm while the distribution regions for sulfonated PDVB were 4.04 nm - 21.14 nm, 4.03 nm - 18.45 nm, 4.0 nm - 18.33 nm, 3.89 nm - 17.65 nm, and 3.66 nm - 17.03 nm, respectively. These results are within the range of 2 nm - 50 nm, which highly corresponds to the mesoporous structure [2].

**Table 4.** Textural properties of PDVB and sulfonated PDVB.

| Samples | $S_{BET}^d$ (m$^2$/g) | $V_p^e$ (cm$^3$/g) | $D_p^f$(nm) |
|---|---|---|---|
| PDVB | 661.0 | 1.47 | 13.05 |
| 0.5% PDVB-SO$_3$H | 385.50 | 0.76 | 12.0 |
| 1.0% PDVB-SO$_3$H | 302.75 | 0.69 | 11.75 |
| 1.5% PDVB-SO$_3$H | 272.28 | 0.62 | 11.65 |
| 2.0% PDVB-SO$_3$H | 224.67 | 0.58 | 10.97 |
| 2.5% PDVB-SO$_3$H | 196.0 | 0.23 | 8.30 |

[d] Surface area, [e] Pore volume, and [f] Pore diameter

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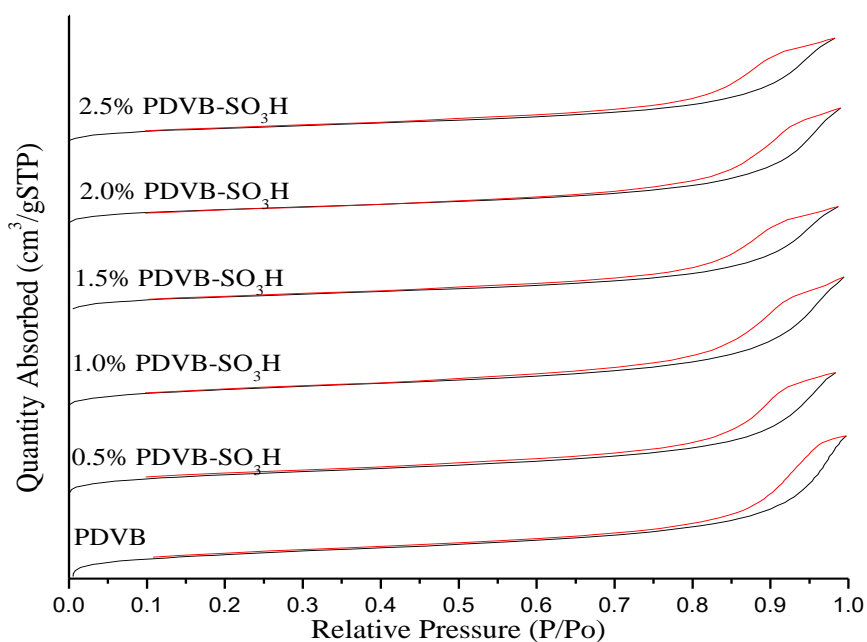


**Figure 4.** $N_2$ isotherm of PDVB and sulfonated PDVB.
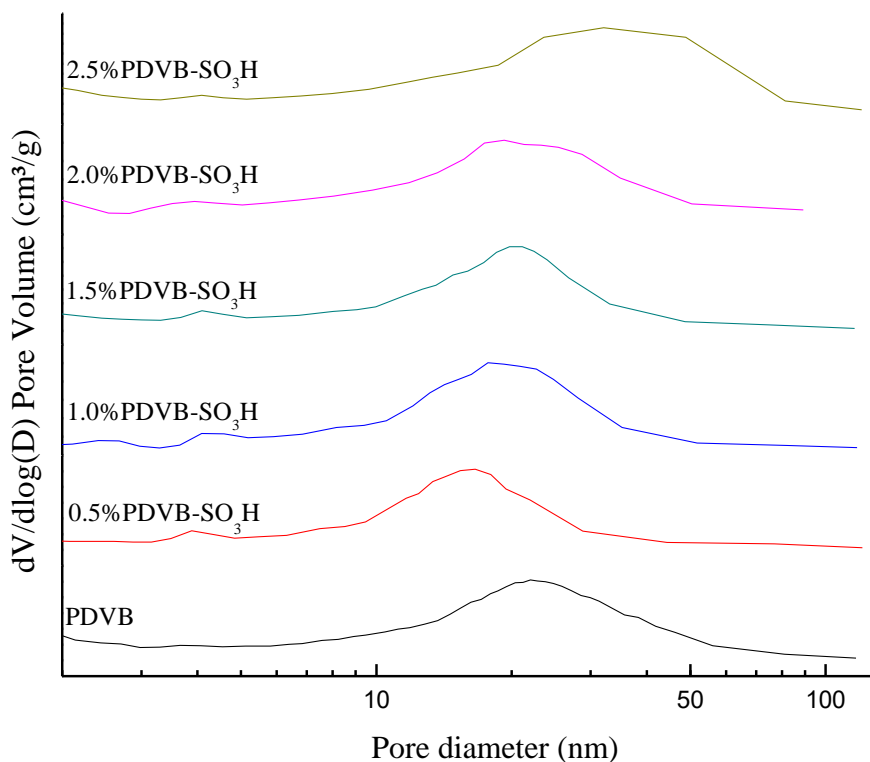


**Figure 5.** Pore size distribution of PDVB and sulfonated PDVB.

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## Furfural Production from Empty Fruit Bunches using the Prepared Catalyst

### Furfural Production under Different Temperature

To verify that furfural can be prepared from EFB, the reaction was conducted at different temperatures of 160 °C, 170 °C, and 180 °C at 30 min reaction time using the biphasic solvent of gamma-butyrolactone (GBL) and deionized water. GBL was chosen as the solvent due to its high selectivity in furfural production and the addition of water was necessary to reduce the solvent viscosity as it enhanced the capacity of reducing sugar intermediated for furfural production [21]. The fixed parameter for reaction time (30 min) and catalyst loading (0.1g) were decided according to past literature which obtained high yield for furfural yield [21,25,26]. Figure 6 shows the percentage yield of furfural with different temperatures, reaction time (30 min), and catalyst loading (0.1g). The results showed a parallel increase between the yield of furfural with temperature where furfural yield obtained using 0.5% (wt/wt) PDVB-SO$_3$H, 1.0% (wt/wt) PDVB-SO$_3$H, 1.5% (wt/wt) PDVB-SO$_3$H, 2.0% (wt/wt) PDVB-SO$_3$H, and 2.5% (wt/wt) PDVB-SO$_3$H recorded a similar pattern, in which it steadily increased from 160 °C to 170 °C before decreasing once it reached 180 °C. The highest furfural yield was 83.1% obtained from 2.0% (wt/wt) PDVB-SO$_3$H at 170 °C. As the temperature increased to 180 °C, it not only accelerated the production of furfural but also caused furfural degradation [19, 21].



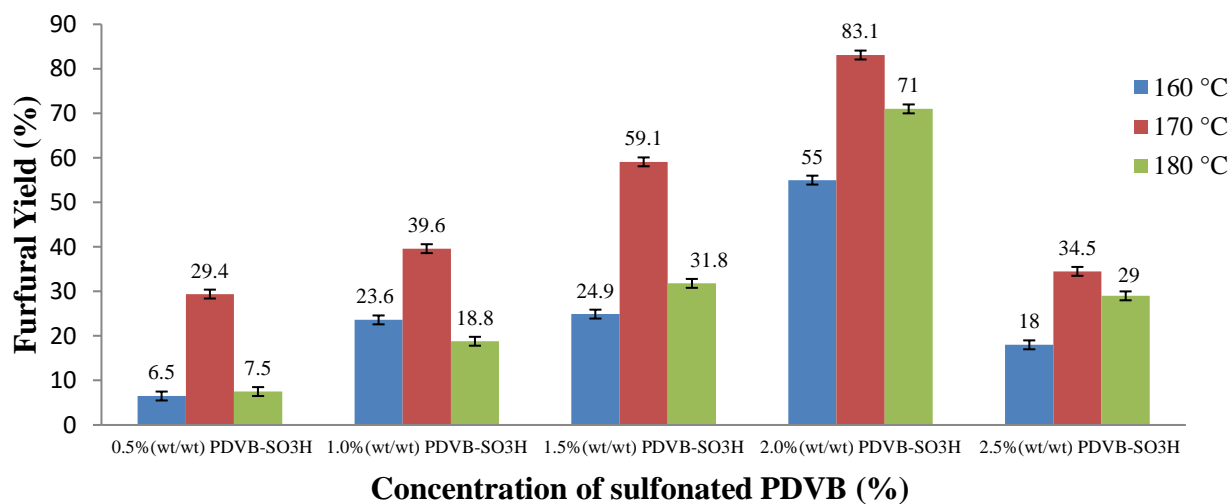**Figure 6.** Percentage yield of furfural with different temperatures, reaction time (30 min), and catalyst loading (0.1 g).
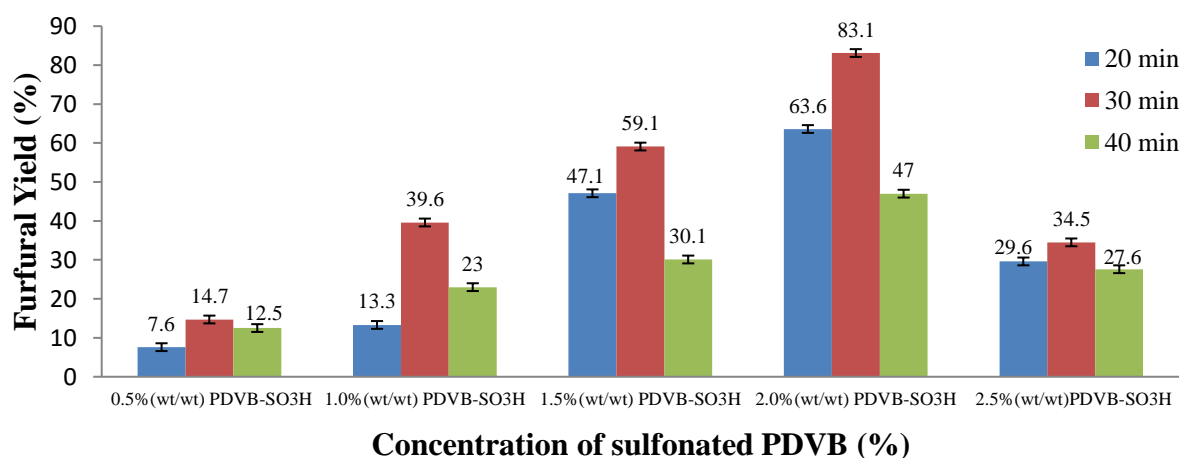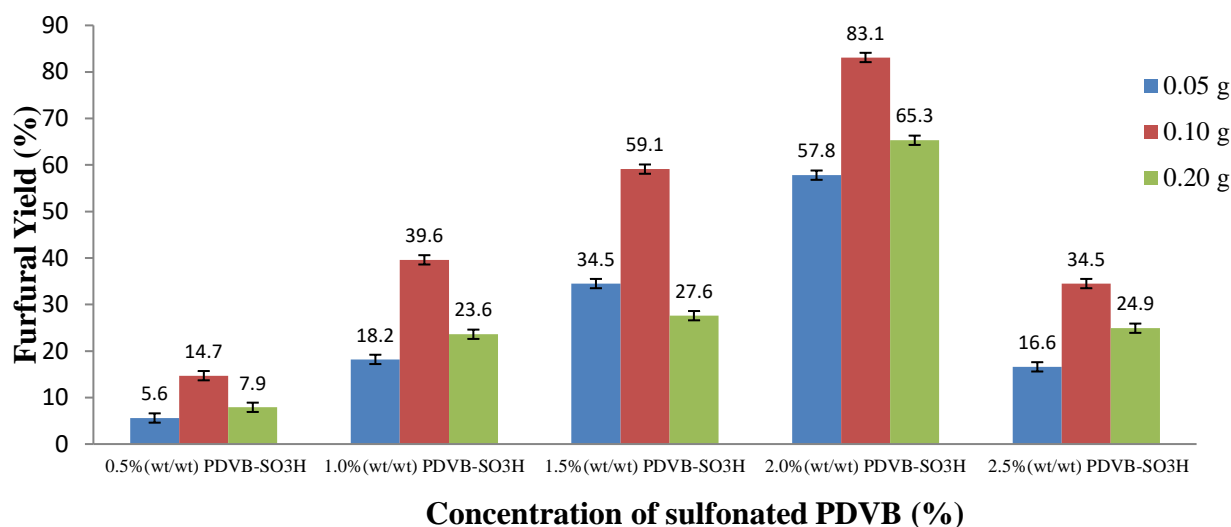


**Figure 7.** Percentage yield of furfural with different reaction times, temperature (170 min), and catalyst loading (0.1 g).

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**Figure 8.** Percentage yield of furfural with different catalyst loading, temperature (170 min), and reaction time (30 min).

### Furfural Production under Different Times:

The effect of time was also investigated on the furfural yield by varying the reaction time between 20 min, 30 min, to 40 min while the temperature was fixed at 170 °C. The results in Figure 7 show that the highest yield of furfural (83.1%) was obtained at 30 min reaction time using 2.0% (wt/wt) PDVB-SO₃H as the catalyst. It was further observed that the furfural yield decreased as the reaction time was extended to 40 min. This was due to the high availability of xylose sugar in the initial reaction and maximum conversion of reducing sugar was already achieved at 30 min reaction time, and as the time prolonged to 40 min under a high temperature of 170 °C, the rate of furfural degradation accelerated faster compared to its conversion [37,38, 39].

### Furfural Production with Different Catalyst Loading

The influence of catalyst dosage on furfural production was investigated by altering the amount of catalyst in each reaction between 0.05 g, 0.1 g, and 0.2 g while the other reaction conditions were fixed at where the highest yield was produced, which were 170 °C and 30 min reaction time (see Figure 8). Usually, a higher amount of catalyst dosage will result in higher yield of furfural; however, excessive amount of catalyst dosage will result in yield reduction as the higher acid content will induce degradation reactions such as fragmentation, resinification, and condensation of furfural [19, 37]. This theory was proven by the results shown in Figure 8 where an increase in the amount of catalyst from 0.5 g to 0.1 g also increased the yield of furfural for 0.5% (wt/wt) PDVB-SO₃H, 1.0% (wt/wt) PDVB-SO₃H, 1.5% (wt/wt) PDVB-SO₃H, 2.0% (wt/wt) PDVB-SO₃H, and 2.5% (wt/wt) PDVB-SO₃H from 5.6% to 14.5%, 18.2% to 39.6%, 34.5% to 59.0%, 57.8% to 83.1%, and 16.6% to 34.5%, respectively. However, as the dosage exceeded 0.2 g, the results showed a

decline in the yield of furfural. As a result, the highest furfural yield was obtained with the addition of 0.1 g of 2.0% (wt/wt) PDVB-SO₃H at a reaction condition of 170 °C and 30 min reaction time.

In every reaction condition shown in Figure 6, Figure 7, and Figure 8, it was observed that furfural yield seemed to be reduced using 2.5% (wt/wt) PDVB-SO₃H. When sulfonation occurs, the SO₃H group will typically impregnate PDVB and act as a bronsted acid group that provides PDVB with a catalytic active site. This active site is responsible to encourage catalytic performance in furfural conversion [21]. However, for sulfonation to occur using HSO₃Cl, the reaction needs to be in mild condition (1 molar equivalent of reagent, -5 °C to 25 °C, in an inert reagent) since HSO₃Cl is a powerful sulfonating agent [40]. Supposedly, when one of the conditions was missed, chlorosulfonation would occur instead. The excessive use of HSO₃Cl resulted in the replacement of Cl⁻ with OH⁻, which then produced sulfonyl chloride (SO₂Cl). SO₂Cl is a hindered molecule; hence, it will prevent the conversion of EFB into furfural. This resulted in low furfural yield with 2.5% (wt/wt) PDVB-SO₃H as the catalyst.

### CONCLUSION

In conclusion, this study has successfully synthesised and characterised solid acid catalyst using the mesoporous framework (PDVB-SO₃H). The catalyst has high total acid content due to the SO₃H group, abundant mesoporosity, and a large surface area as confirmed by the acid-base titration and BET analysis. The highest furfural yield was 83.1% obtained at 170 °C in 30 min reaction time using 0.1 g of 2.0% (wt/wt) PDVB-SO₃H as the catalyst in biphasic solvent. Additionally, 2.0% (wt/wt) PDVB-SO₃H containing a high catalytic active site with 4.04 mmol/g of acid

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content and a surface area of 224.67 m$^2$/g was filled with the SO$_3$H group. The findings also show that excessive amount of catalyst, higher temperature, and longer reaction time will accelerate furfural degradation.

## ACKNOWLEDGEMENTS

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