The influence of the amount of catalyst on the degree of sulfonation in the sulfonation process on waste-based Styrofoam (polystyrene) into Poly-(Styrene Sulfonic Acid)

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Abstract. This study aims to determine the influence of the amount of Ag₂SO₄ silver sulfate catalyst and amount of time on the degree of sulfonation in waste-based Styrofoam (polystyrene) into Poly-Styrene Sulfonic Acid (PSSA). The method used is sulfonation with sulfuric acid H₂SO₄ as a sulfonating agent. Based on the research, the sulfonation reaction was successfully carried out, which was shown by the functional group in the FTIR test and the highest degree of sulfonation achieved was 67.6%, which come from variation amount of 2% Ag₂SO₄ catalyst and 25 minutes of reaction time.

1. Introduction
The composition of solid waste, especially Styrofoam, will increase along with the advancement of industrial technology and the increasing number of people with practical modern culture. Cordova and Nurhati [1] explain from the observation result of the estimation in flowing waste from nine river estuaries into the sea of Indonesia in June 2015 - July 2016, obtained around 23 ± 7.10 tons and 59% of the waste, plastic, which is dominated by Styrofoam. One of the way to reduce the increasing of waste based Styrofoam is using a process of utilization or conversion on it. Waste based Styrofoam transformed into an acid catalyst which is called poly- (styrene sulfonic acid) then will be mentioned as PSSA.

PSSA has been used especially in the industrial sector, which can be use as ion-exchange agents, reversible osmosis membranes, ultrafiltration, and plasticizers for conductive composites [2]. Due to the acidic characteristics of PSSA, it is thought to have similar properties with amberlite catalyst which can be used in the esterification process. The preparation of the PSSA catalyst has been done by the following researchers, Martins [2] polystyrene reacted with acetyl sulfate sulfonating agent with CH₂Cl₂ solvent at a temperature of 40ºC for 30 minutes and obtained a sulfonation degree of 18-22%. Bozkurt [3] polystyrene reacted with cyclohexane with P₂O₅ catalyst at a temperature of 40ºC and obtained a degree of sulfonation of 90-95%. The production of PSSA without a catalyst tends to take longer time and obtain lower degree of sulfonation. According to Carroll [4], the use of the Ag₂SO₄ catalyst will increase the conditions to obtain a yield of 100% with a reaction time from 5-15 minutes. Therefore the purpose to do further research on the use of Ag₂SO₄ catalyst and variation of time on degree of sulfonation in making PSSA.

2. Materials and methods
2.1. Materials
The materials used in this experiment are Styrofoam (polystyrene) which functions as a carrier obtained from grocery store, ethyl acetate as a solvent for Styrofoam, sulfuric acid (H₂SO₄) as a sulfonating agent, and silver sulfate (Ag₂SO₄) which each purchased from Merck.

2.2. Preparation of styrofoam
The Styrofoam was cut into 2x2 cm in size and weighed to a certain weight. Styrofoam that has been cut and weighed as much as 5 grams, then dissolved it with 100 ml of an inert solvent which is ethyl acetate.

2.3. Preparation of sulfonating agent
Sulfonating agent, 98% sulfuric acid as much as 166 ml was put into the three-neck flat bottom flask. Then the Ag$_2$SO$_4$ catalyst is slowly put into a flask with a certain weight against Styrofoam and stirred with a magnetic stirrer.

2.4. Synthesis of PSSA
The Styrofoam solution is slowly dripped into the acid solution that has been previously prepared. The reaction is carried out at a constant temperature ranged from 60-70ºC for a certain time. After the reaction, the solid that has been formed is then washed.

2.5. Determination of sulfonation degree
PSSA (0.1 g) was soaked in 0.1 M NaCl solution (10 mL) for two days. The mixture was filtered and the filtrate obtained was titrated with 0.02 M NaOH using the PP indicator. The degree of sulfonation is determined using equation (1).

$$\text{DS} = \frac{\text{VNaOH} \times \text{MNaOH} \times \text{Monomer polystyrene}}{\text{Sample Weight}} \times 100\%$$

Where \(\text{VNaOH}\) = Volume of NaOH (ml)
\(\text{MNaOH}\) = concentration of NaOH (M)

3. Results
3.1. Analysis of functional groups
PSSA was analyzed using FTIR at wavenumbers 4000-450 cm$^{-1}$. Figure 1 shows the analysis of the Styrofoam functional groups and the PSSA catalyst produced from the sulfonation between Styrofoam and H$_2$SO$_4$ with 1.5% Ag$_2$SO$_4$ catalyst and 20 minutes of reaction. In Figure 1 (a) shows the spectrum of Styrofoam, there is an absorption of 585,74, 74 cm$^{-1}$ which shows the phenyl ring, the absorption 696,29 cm$^{-1}$ which shows the CH bond on the phenyl ring, the absorption 906 cm$^{-1}$ which shows the CH bond stretching aromatic, 2,919,26 and 2,849 cm$^{-1}$ which showed asymmetric and symmetrical stretching of CH2, then the absorption 1,599,71, 1,491,71 and 1,449,64 cm$^{-1}$ showed the vibration of the CC bond [5]. All of the absorptions refer to the structure of the polystyrene.

Figure 1 (b) shows the spectrum of the PSSA which appearance that the polystyrene used has been sulfonated well. Infrared absorption at 1,034,95 cm$^{-1}$ is a vibration due to the presence of C-H bonds on the benzene ring which is influenced by symmetrical vibrations of the sulfonate groups (S = O = S stretch). The absorption at 1,644,87 cm$^{-1}$ is the trading vibration of the S = O double bond group, and the absorption due to the CS bond is shown at 1,165,92 cm-1, which is a significant characteristic peak for connecting benzene and sulfonate [6,7]. Then, the absorption peak at 3,365,80 cm$^{-1}$ showed a hydroxyl (-OH) bond[6,8]. These circumstances indicate the presence of the sulfonate group -SO$_3$H in the polystyrene (Styrofoam) structure.
Fig 1. FTIR Spectra of (a) Styrofoam (b) PSSA

3.2. The influence of the amount of catalyst on sulfonation degree

The degree of sulfonation shows the success rate of the sulfonation reaction [9]. The degree of sulfonation shows the number of hydrogen atoms (H) that have been replaced with sulfonate groups (-SO$_3$H) [10]. The sulfonation reaction in this study used a catalyst, silver sulfate (Ag$_2$SO$_4$). The amount of catalyst was varied from 0.5%; 1%; 1.5%; 2%; and 2.5% by the weight of Styrofoam used. Figure 2 shows a comparison between the degree of sulfonation, amount of catalyst, and reaction time. When using 0.5-1% catalyst it can be seen that there is a significant increase in the degree of sulfonation with the amount of catalysts used. This shows that the amount of catalyst is proportional to the magnitude of the reaction speed. If the catalyst percentage is increased, the reaction speed will increase. The number of colliding molecules will increase if the reaction is accelerated [11]. This situation causes the degree of sulfonation to increase with increasing the amount of catalyst. With the use of a catalyst from 1.5 to 2.5%, it appears that the increase in the degree of sulfonation is not significant enough and starts to be constant. This is because the number of active sites available on the catalyst is close to the maximum required.
3.3. Effect of reaction time on sulfonation degree

The value of the degree of sulfonation is influenced by several variables, one of it was time [9]. Figure 3 shows the value of the degree of sulfonation for several time periods using the Ag₂SO₄ catalyst. It can be seen that the degree of sulfonation increasing with time, then decreasing over a period of time. When the use amount of catalyst 1-2.5% in the 25th minute is the peak with the value of the degree of sulfonation of 67.3% each; 67.3%; 67.6%; and 67.3%, there was a decreasing in the 30th minute, respectively to 66.6%; 66.9%; 67.3%; and 66.9%. The decrease is thought to be because the sulfonation reaction is a reversible reaction, and at the 25th minute a desulfonation reaction occurs. Desulfonation (hydrolysis of -SO₃H groups) is a term that describes the reverse process of sulfonation. Desulfonation itself has several causes, such as i) the -SO₃H group is not conjugated with the benzene ring; ii) a strong, partly positive charge on the sulfur atom increases the electron density at the meta position of the benzene ring and on the carbon atom of the C - S bond; iii) after proton release, the negative charge located on the -SO₃H group can make hydrolysis of the -SO₃H group more likely. Substituents that support sulfonation can also increase the hydrolysis of the -SO₃H groups, due to the increased electron density of the carbon atoms of the C-S bond. When the formation of sulfonic acid is easy, hydrolysis is also easy [12].
4. Conclusions

From the research on the influence of the amount of catalyst catalysts and reaction time on the degree of sulfonation in the sulfonation process in waste-based Styrofoam (Polystyrene) into Poly (Styrene Sulfonic Acid), the following conclusions can be drawn: the sulfonation reaction succeeded in synthesizing Styrofoam into PSSA as indicated by the presence of the $\text{SO}_3\text{H}$ functional group on FTIR test. The highest degree of sulfonation is 67.6% was obtained at variations of 2% Ag$_2$SO$_4$ catalyst amount and 25 minutes reaction time. The weight of the catalyst and reaction time have an important role in the degree of sulfonation, in general, the degree of sulfonation is directly proportional to the weight of the catalyst and reaction time, up to an optimum point where the degree of sulfonation starts to be constant and tends to decrease.

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