Effect of Size and Catalyst on the Production of Cellulose Acetate from *Acacia mangium* Pulp

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Abstract
The production of cellulose acetate primarily relies on the acetylation process itself, where certain manipulation on the exercise may reduce time consumption for the reaction rate, where among the condition referred to is the size of particles and amount of catalyst usage. As for this study, Acacia mangium pulp is reduced to four mesh sizes (35, 60, 100, and 200) while two different amount of catalyst (0.05 and 0.10 ml) with one controlled sample with no catalyst was used. After undergoing 48 hours of without-heat acetylation processes, the result shows that the smaller particle of 200 mesh size has a higher degree of substitution (DS) with a difference of approximately 82%, 68%, and 33% of percentage difference to the increasing mesh sizes. The higher amount of catalyst also provides vast differences in the DS, as the value increases about 20% or more with every increment of 0.05 mL catalyst used, showing increases and decreases in the intensity of the carbonyl and alcohol group, respectively, in the FTIR spectroscopy.

Keywords: Cellulose acetate, Degree of substitution, Catalyst, Mesh Size
1. Introduction
Bio-based materials produced from renewable resources or living organisms has garnered high demands due to its resourcefulness and sustainability. Developments in products such as fuels and coatings have been widely produced from lignocellulosic biomass or rejected crops to obtain eco-friendly bio-based materials, where most products were expanded from extracted oils or polysaccharides and could be obtained abundantly worldwide. Examples of bio-based materials include cellulosic ethanol from potato starch (Jeon et al., 2008) and sugarcane bagasse (Dawson and Boopathy, 2008), soy-based biodiesels (Tomei and Upham, 2009), and carboxymethyl cellulose (CMC) coatings from sugar beet pulp cellulose (Togrul and Arslan, 2004).

Raw materials derived from lignocellulosic however pose a potentially higher preparation and pretreatment cost as it contains higher unwanted substance in the composition. Certain modification in the preparation such as differentiation in particle size and usage of catalyst may alleviate the cost in processing due to better form. Diverse methods of pretreatments has been instigated with the scope of decreasing the particle size of the raw materials, as smaller particles offer an increase on the specific surface area available for reaction. Reviews have mentioned the advantage of particle size reduction in the biogas production sector, where rates in biomethanation have been increased successfully through the decrease of the material’s overall magnitude (Krishaniaet al., 2013). The increase of catalyst meanwhile gives the upper hand in terms of activation energy, where catalyst allows the lowering of energy for a reaction to occur, thus creating an alternative pathway that increases the rate of reaction and productivity such as for oxidation polymerization in conjugated poly-heterocycle (Qiao et al., 2000).

As for this project, the aim is to produce CA from Acacia mangium pulp, concentrating on the effect of different sizes of the particles and amount of catalyst used, on the production. The size of pulp particle and catalyst used were manipulated to obtain the effect of the exploited variables towards the rate of reaction for the production of CA, where four different mesh sizes will be used; 35, 60, 100, and 200, and three different amount of catalyst used which is 0.05 and 0.10 mL, including an additional control sample without the use of catalyst, to obtain the optimum and cost effective condition for production. Several other methods that may increase the rate of reaction, which includes the cellulose extraction methods, pretreatments used (Biswas et al., 2006), reaction time (Filho et al., 2007), and usage of additives (Cerqueira et al., 2007), among others.

2. Experimental
2.1 Materials
Acacia mangium pulp was obtained from Sabah Forest Industries Sdn. Bhd. (SFI), Malaysia. Acetic anhydride, sulphuric acid and acetic acid were obtained from Sigma Aldrich. FTIR spectra were obtained using Perkin Elmer Spectrum 100 FTIR Spectrometer.

2.2 Pre-treatment of Wood Pulp
The pre-treatment main purpose is to increase the accessibility of the reagent, acetic anhydride, to all the hydroxyl groups of cellulose. It includes two stages of the pre-treatment of the samples; the first is the mechanical disintegration, followed by the activation of pulp. For the mechanical pre-treatment, pulp samples underwent a series of mechanical comminution to obtain two different size of particles for the following acetylation process, which includes mesh sizes of 35, 60, 100, and 200, later followed by acidic
pre-treatment known as cellulose activation, where every gram of pulp are soaked in a 10 ml glacial solution of acetic acid to associate with the microstructure.

2.3 Acetylation
This process is the main procedure to produce cellulose acetate as it includes the launching of the acetic anhydride reagent to the pulp, in which enables the acetyl group substitution. The acetylation method is a type of esterification process, which basically substitutes the hydroxyl groups of the cellulose unit to acetyl groups. Acetylation was performed on the treated *Acacia mangium* pulps following methods from Rodrigues Filho *et al.* (2008) with some modification. About 2 g of pulp samples, each from different mesh sizes were mixed with a 60 ml mixture of acetic acid and acetic anhydride 3:2 ratio, with two different amount of catalyst, 0.05 g and 0.10 g respectively, and one controlled sample with no catalyst. Samples were left in room temperature until the predetermined 48 hours reaction time was up. Distilled water was added to the reaction medium to stop the acetylation process and filtered. The produced cellulose acetate was oven dried for 90 minutes at 103±2°C.

2.4 Hydrolysis
Hydrolysis is the reaction of water that reacts with a chemical compound that involves in splitting of bonds. It involves the reversal of the acetylation process where the sometimes unavoidable over-substitution of hydroxyl group by the acetyl group gives a high degree of substitution, can be repaired. Hydrolysis will help reduce the degree of substitution from three acetyl groups per cellulose to the preferable range of 1.8-2.4. The reaction involves the use of water as the main reactant (10%) and acids (1%) as catalyst.

2.5 Determination of the degree of substitution
Degree of substitution is the average value of the substituted hydroxyl group in the glucosidic units by the acetyl group. It is one of the most important processes to characterized cellulose acetate. It is determined through a saponification process, where a mixture of 75 ml ethanol and 5 ml nitric acid was mixed into 4 g of pulp samples and stirred for 10-15 minutes. The samples were then boiled for 5 minutes and filtered using warm ethanol. Samples were then oven dried at 70°C for 12 hours. About 0.7 g of the oven-dried samples was mixed with 100 ml sulphuric acid and 25 ml of sodium hydroxide 0.5 N and then heated for 15-30 minutes. The solution was then titrated using hydrochloric acid 0.5 N, with phenolphthalein as indicator.

Equation (1) was used in order to determine the percentage of acetyl groups.

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DS = 0.162 \frac{A}{(1-0.058 A)} \text{ .................(1)}
\]

Where;

- \(A = \frac{(BC – DE)}{F}\)
- \(B = \text{Volume of sodium hydroxide solution added}\)
- \(C = \text{Normality of sodium hydroxide}\)
- \(D = \text{Volume of hydrochloric acid required for titration}\)
- \(E = \text{Normality of hydrochloric acid}\)
- \(F = \text{Weight of cellulose acetate used}\)
2.6 Fourier Transform Infrared (FTIR) Spectroscopy
The identification of the end product was carried out in a Perkin Elmer Spectrum 100 FTIR through the determination of the infrared spectra. Scans were collected for each spectrum with a size step of 4 cm\(^{-1}\) from the range of 650 to 4500 cm\(^{-1}\), where the materials were prepared in the powder form to perform the analysis of the sample.

3. Results and Discussion
The properties of the cellulose acetates synthesized under the same reaction condition but with different mesh sizes (35, 60, 100, and 200) and amount of catalyst (0-0.10 mL/g) are shown in Figure 1 and 2, to 3 and 4, respectively. Based on the different sizes of particles used during acetylation, it appears that the smaller particle size used, 200 mesh size, has a higher rate of reaction in hydroxyl group substitution than the subsequent bigger mesh sizes. After a 48 hours allocated reaction time and decreasing the sizes of particles without any use of catalyst, the degree of substitution (DS) increases with the lowest being 0.55 and highest 1.28. It shows that smaller sized particles have a higher surface area in which is very important for the chemical kinetics, where reaction only occurs with particles colliding.

Based on Laidler (1969) on the theories of chemical reaction rates, the rate of reaction is directly proportional to the particle collisions, where the reactant and substrate has a higher interaction, which yields reaction, as can be seen from the increase on the weight percentage gained (WPG) and rate of efficiency (RE) in Figure 1. The increase in exposure between the reagent and substrate shows increase in reaction where the smallest size particle samples produces a higher degree of substitution comparison with roughly 10%, 23%, and 47% of percentage difference.

The ideal DS of functional cellulose acetate ranges from as low as 1.8 to 2.4 for production purposes, as every degree of acetyl content influences the characteristic of the material, which includes the viscosity and solubility properties. Products such as lacquers require a higher DS for production, where alcohol-soluble lacquer requires a substitution degree of about 1.94 – 2.06 DS, differing from the higher quality ester-soluble lacquer, which in turn requires a higher DS range of about 2.20 – 2.32. With that being said, the preferable value of DS rarely exceeds 2.8 as it signifies a higher hydroxyl group substitution out of the three free carbons in the glucose monomer itself, where uniformity in substitution is far from top priority for the chemical replacement, as penetrability and surface area is more accountable, hence the various mesh sizes used.

![Figure 1: Effect of different mesh size of particles used on the degree of substitution (DS)](image-url)
Different amount of catalyst used also shows a vast difference in the substitution of hydroxyl group, as catalyst contributes to lowering the activation energy needed for a reaction to occur. Based on Figure 4, a decrease in the required energy for activation will result in a higher collision rate, thus giving a higher reaction rate. The results further justify the theory of particle collision as the increase of catalyst directly increases the value of the degree of substitution of the 60 mesh sized particles for a reaction time of 48 hours, with the highest amount of catalyst shows the highest value within the optimum cellulose diacetate range, which is 2.41 with a more drastic decrease in DS from the absence of catalyst with more than 100% percentage difference, as further supported by the increasing WPG and RE result.

According to Boreskov (2003) on heterogeneous catalysis, a higher amount of catalyst used would contribute to a higher degree of substitution in a shorter time theoretically, which was unfortunately restricted to a maximum of 0.10 ml per gram, to prohibit the nature of the catalyst reagent itself, which is the sulphuric acid, from promoting hydrolysis which will consequently decrease the substitution degree, instead of promoting it as it was primarily used for.
Based on the FTIR result on the other hand, shows a notable difference between the infrared spectra intensity between different sizes and amount of catalyst both, increasing and decreasing the intensity among the same functional group. Figure 7 shows four (4) spectra from different sizes of CA samples. With constant appearance from five (5) types of functional group, which includes the alcohol/phenol, carboxyls, alkanes, aliphatic amines, and carbonates, the intensity of the transmittance differ from size to size. Noticeably, the alcohol group decreases as the particle sizes decreases, but with constant transmittance from one of the most significant peak, the carbonyl (1760 – 1665 cm\(^{-1}\)). However for the samples with different amount of catalyst used (Figure 8), the alcohol group (3550 – 3200 cm\(^{-1}\)) decreases as the particle sizes decreases, but increases in the carbonyl group which includes the alcohols, carboxylic acids, esters, and ethers, testifying the effect that the particle sizes have on the chemical modification of the cellulose.
Conclusion
The effect of size or particle and amount of catalyst used is shown to be greatly influential in the production of cellulose acetate. The conversion rate of the cellulose-to-cellulose acetate immensely depends on the rate of reaction, which in this study, was focused on the surface area and concentration of gradient. It can be concluded that decreasing the particle size within limit is proven to be a great help in increasing the degree of substitution of the cellulose conversion. This is because based on the results, there is a difference of nearly 50% of the degree of substitution between the smallest to the biggest particle size used after undergoing the same duration of reaction time, in which the area of exposed surface increases the interaction between the reagent and the substrate.

The best size following the reaction time condition, however, is chose based on the range of cellulose diacetate of 1.8 to 2.4, which is the 60 mesh size particles. Meanwhile for the amount of catalyst used for the acetylation of cellulose also show differences in the substitution degree, such as the former situation, where, by increasing the frequency of catalyst particle collision to the substrate through the addition of catalyst, it elevated the substitution up to a staggering difference of nearly a 2.0 degree of substitution. All in all, both particle size and amount of catalyst used can notably reduce the reaction time or yield a product with a higher degree of substitution in the production of cellulose acetate from *Acacia mangium* pulp, and are highly suggestible as one of the manipulative variables in production.

References


