Furfural Synthesis from *Mikania mircantha* using Sulfonated Carbon Catalyst Derived from Candlenut Shell

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Abstract

Candlenut shell is an agricultural solid waste which can be utilized for low cost active carbon. The aim of this work was to examine candlenut shell as a carbon source for catalyst support, its modification with sulfuric acid, as well as its application in furfural synthesis. *Mikania mircantha* was used as a feedstock. Candlenut shell was carbonized at 350ºC for 4 h in a furnace. The carbon obtained was modified with sulfuric acid solution, followed by drying. The activated carbon formed was characterized by SEM-EDX, FTIR, and acid density test/H⁺ activity. Sulfonated carbon was utilized as solid catalyst in the hydrolysis reaction for furfural production. The reaction was conducted in a batch reactor at 100-120ºC, catalyst load of 30-40%, and reaction time of 0-140 min. The highest furfural yield achieved was 8.7% at 110ºC, reaction time of 120 minutes, and catalyst loading of 40% by weight. The results confirmed that candlenut shell based activated carbon is applicable as a solid catalyst in furfural synthesis.

Keywords: Candlenut shell, carbonization, sulfonation, hydrolysis, furfural yield

I. INTRODUCTION

Several lignocellulosic biomass can be used as feedstock to produce furfural such as rice husk, bagasse, corn cob, and wheat bran [1]. Lignocellulosic biomass contain 42-45% cellulose, 22-28% lignin, and 23-36% hemicellulose [2]. As the second largest content after cellulose, hemicellulose is the main material in synthesizing furfural. The most common type of hemicellulose is xylan, which is the polymer of pentose sugar (xylose) found in dicotyledonous plants such as *Mikania micrantha* (MM) [3].

MM is one of the most rampant weed species in the world because of its rapid growth, covering other plants around it, leading to sunlight deficiency and death of other plants [4]. The main chemical composition of MM are pentosan, holocellulose, and lignin, about 56.04 ± 0.86%, 14.05 ± 0.18%, and 23.54 ± 0.89% respectively [3]. Using MM as a furfural precursor is very potential because of the highest pentosan content of all biomass. As one of the furan derivatives, furfural can be produced from the hemicellulose fraction of lignocellulose, is considered a promising biochemical-based commodity because of its use in the production of several products such as fuel additives, antacids, paints, fertilizers, and various other products that are usually produced from non-renewable resources [5].

Production of furfural from lignocellulosic biomass through hydrolysis of biomass rich in pentosan and followed by dehydration of pentose using acid catalyst, is shown in the following equation [6]:

$$(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5 \qquad (1)$$

pentosans   pentoses

$$nC_5H_{10}O_5 \rightarrow nC_5H_4O_2 + 3nH_2O \qquad (2)$$

pentoses   furfural
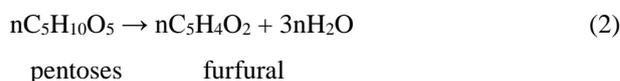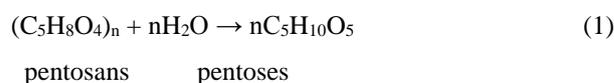
The catalyst commonly used is homogeneous acid in the form of inorganic acid such as sulfuric acid, phosphoric acid, and hydrochloric acid. However, the use of inorganic acid catalyst can cause corrosion in the reactor, difficulty in separating reaction products, and is not environmentally friendly [7]. On the other hand, the use of organic acid catalysts has been carried out, but the furfural yield obtained is still low [8,9]. Therefore, the use of carbon-based solid acid catalyst deserves consideration [10].

For carbon solid acids catalyst formation, carbon material generally comes from biomass. For this purpose, candlenut shells can be considered as a source of activated carbon. As a catalyst support, activated carbon has many pores, large surface area, able to withstand high temperature and pressure, easy to recycle, and cheap. The carbon used must be in the form of polyaromatic hydrocarbon. Such structure occurs when the biomass carbonation is carried out at a temperature of about 400°C [11]. The carbon formed is sulfonated with sulfuric acid to produce sulfonated carbon. The sulfonate groups have H⁺ which acts like acid and attaches to aromatic structures [12]. Using solid acid catalyst has several advantages such as easier separation from the reaction product through filtration, reusable, does not corrode the equipment, and more environmentally friendly. In addition, carbon solid acids have high $-SO_3H$ density, high surface activity, and better thermal stability which is a very potential catalyst to convert pentose into furfural [10].

Research into the utilization of carbon active as catalyst support in biomass hydrolysis has received much attention in recent years, but research has so far been concentrated on carbon derived from bamboo [10], Jatropha Curcas [13], palm kernel shells [14], bagasse [15], corn stover [16], pine chips [17]. So far, the utilization of candlenut shells as carbon source for catalyst support in furfural formation has never been conducted. Therefore, the research objective was to evaluate candlenut shells as carbon precursor in solid acid catalyst formation and its application in the furfural synthesis.

II. MATERIALS AND METHODS

II.1. MATERIALS

Candlenut shells and MM were collected from Medan Selayang, Indonesia. Chemical used were sulfuric acid, Rochelle salt, barium chloride, sodium hydroxide, acetic acid, chloroform, aniline supplied by CVA Medan.

II.II. CATALYST PREPARATION

The candlenut shell was washed under running water to remove dirt on the surface. Then the shell were heated in an oven at 110°C for 2 hours, followed by carbonization in a furnace at 350°C for 4 hours [7]. The carbon obtained was crushed and sieved with a 50 mesh sieve. Five grams of carbon was placed in a beaker glass and 50 ml of 96% H_2SO_4 was added and stirred at 250 rpm for 15 minutes. Carbon containing H_2SO_4 was placed in a ceramic container and heated for 6 hours at 120°C to produce the catalyst. Then the catalyst was cooled and washed with deionized water at 90°C until no sulfate was detected using $BaCl_2$. The catalyst was dried at 110°C for 24 hours. Catalyst was analyzed for its morphology and composition, functional groups, and acid density by SEM-EDX, FTIR, and titration respectively.

II.III. MM POWDER PREPARATION

The mixture of leaves and stems of MM was washed to remove all dissolved impurities. MM was cut into small pieces of 1 cm using a knife, dried in an oven for 2-3 hours at 105°C, crushed in a ball mill, sieved to a size of 70 mesh [8], and stored in a tightly closed plastic container.

II.IV. FURFURAL SYNTHESIS

Synthesis furfural was done according to Taslim et al. and Li et al. [8,10] with modification. As much as 25 g dry powder MM, 25 g sodium chloride were introduced into a stainless steel batch reactor and then mixed with 7.5 g carbon solid acid catalyst and 700 ml of water. The reactor was equipped with a condenser to condense furfural vapor. The reaction was carried out at 100-120°C for 0-140 min. The liquid product of crude furfural was collected and filled into a separator funnel. The crude furfural was extracted by adding 50 ml chloroform and allowed to form two layers. The upper layer was rich in water, and the lower layer was rich in furfural and chloroform. The furfural was separated from chloroform by distillation at 70°C. For comparison purpose, the same procedure was repeated but using 250 ml of 20% sufuric acid. The furfural formed was identified by FTIR and GC-MS.

III. RESULTS AND DISCUSSION

III.1. PRELIMINARY ANALYSIS OF MM

Based on early analysis in this work, the mixture of leaves and stems of MM had an average water content 84.5%, and average pentosan content of 53.6%. The pentosan content is very close to that in other literature at ± 56.04% [3].

III.II. SEM-EDX ANALYSIS

Fig 1 shows the surface morphology of candlenut shell powder using SEM. The powder has irregular shape, uneven, and non-porous surface. These phenomena is also reported by other researchers [7,18,19]. This situation indicates that the powder has small surface area.
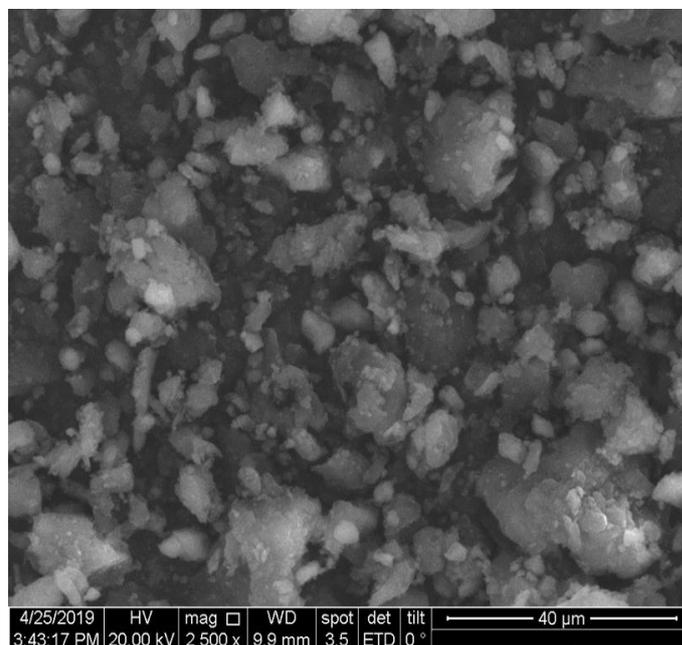
Fig 1. Candlenut shell powder

Carbon from candlenut shell powder after carbonization at 350°C for 4 hours was observed using SEM and the results is depicted in fig 2. During carbonization, carbon content increased while organic compounds in candlenut shell such as cellulose, hemicellulose, lignin and other extractive matters decomposed and produced gas products. Consequently, pores are formed and surface area increases. The pore formation plays an important role in sulfonate groups uptake during sulfonation, because sulfonate groups adhere to the pore surface.

Fig 2. Carbon derived from candlenut shell

Fig 3 presents carbon morphology after sulfonation at 120ºC for 6 h. Chemical treatment on candlenut shell changes its structure. The morphology of carbon was modified after sulfonation. Sulfonate groups were adsorbed and dispersed on carbon surface and it penetrated in the pore channels. Drying after sulfonation will vaporize volatile matters and strengthen sulfonate groups bounds on carbon surface.
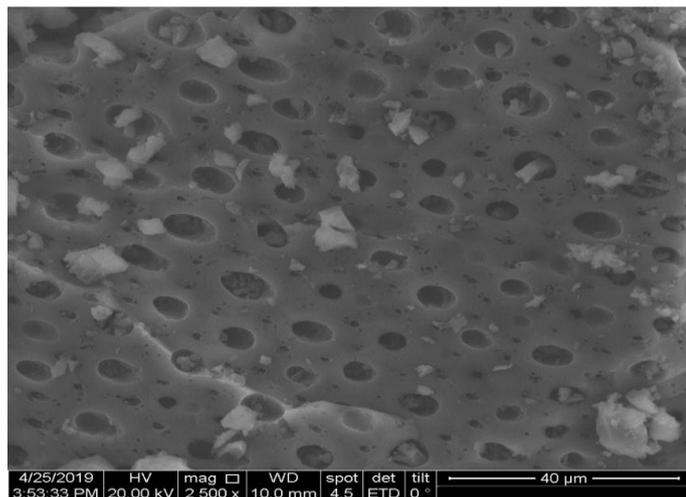
Fig 3. Sulfonated carbon

EDX analysis was conducted on candlenut shell, carbon and sulfonated carbon. The results are displayed in table 1. Initially, candlenut shell contained 43.86% C and 47.81% O. Carbon and oxygen elements dominated over other elements. During carbonization, carbon atoms will coalesce and form more stable bonds while other elements may break off the bond or evaporate [20]. As a result, carbon content increased while oxygen content decreased after carbonization. After sulfonation, sulfur content was tracked at 5.29%. This indicated that sulfonate groups had adsorbed on carbon surface.

Table 1. Composition of candlenut shell powder, carbon and sulfonated carbon

Element	Candlenut shell (%)	Carbon (%)	Sulfonated carbon (%)
C	43.86	66.29	63.86
O	47.81	28.92	27.90
Ca	6.73	4.79	2.32
Mg	1.60	-	-
S	-	-	5.92

III.III. EFFECT OF REACTION TIME ON FURFURAL YIELD AT VARIOUS TEMPERATURES

Figure 4 shows the effect of reaction time and temperature on the furfural yield at a concentration of 40% by weight of the sulfonated carbon catalyst. At a temperature of 100 °C the furfural yield begins to form at 30 minutes and reaches a peak at 120 minutes with a yield of 6.5% and decreases in the following minutes. In fig 4, it can be seen that the best furfural yield is at 110°C. At temperature of 120°C, furfural formation begins at 10 minutes. The increase in reaction time caused the yield to increase to a peak of 7.3% at 90 minutes, then the yield decreased as reaction time increased. For the reaction temperature of 110°C furfural was formed after 20 minutes, and the highest yield was 8.7%, which was obtained after 120 minutes, which then decreased with increasing time. At a temperature of 120°C, it was observed that the evaporation rate of water was higher than the temperatures of 100 and 110°C. As mentioned in equations 1 and 2, the hydrolysis of pentosan in acidic conditions requires water, while pentose dehydration releases water. If the rate of evaporation of water is too fast, the hydrolylis of pentosan will become imperfect, causing less pentose to be formed. As a consequence, the furfural yield is also low. As reported by Rao et al. [21] that an increase in temperature will also affect the increase in furfural yield, but with the increasing temperature it will cause degradation in furfural formation and produce byproducts.

From fig 4 it can be seen that with constant reaction temperature, increasing reaction time can causes better contact between reactants, therefor increasing the furfural yield. However, if the reaction time is too long and the temperature is too high, it will cause the furfural yield to decrease. This is because furfural cannot last long in acidic conditions at high temperatures and for a long time, side products will form. This was also reported by Li et al. [22] where the furfural formation increased until the 120th minute and the furfural yield became constant after the 120th minute. The same results were reported by Guche et al. [23], that furfural yield will increase with reaction time. After a certain time, an increase in time will lead to a reduction in furfural yield due to side reactions. As reported by Liu et al. [22], furfural degradation can form small molecules and cations, causing furfural to undergo a

condensation reaction with xylose to form insoluble polymers such as humin.
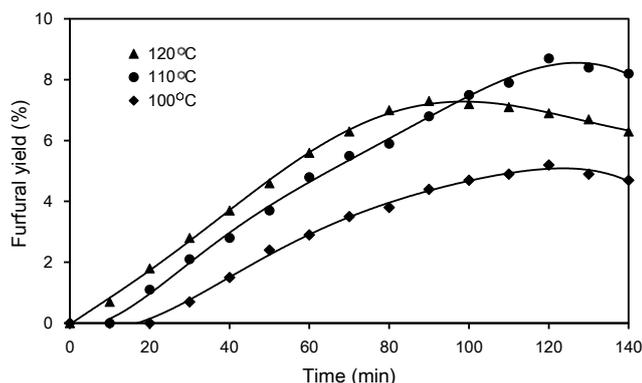
Fig 4. Effect of reaction time on furfural yield at various temperatures and 40% catalyst concentration.

III.IV. EFFECT OF REACTION TIME ON FURFURAL YIELD AT VARIOUS CATALYST CONCENTRATIONS

In this study, the concentrations of sulfonated carbon catalyst used were 30 and 40%, and 20% sulfuric acid catalyst was used as a comparison. Furfural yield is strongly influenced by the concentration of the catalyst used as shown in fig 5. Increasing the concentration of the sulfonated carbon catalyst from 30 to 40% can increase the yield of furfural. In general, increasing the catalyst concentration in the production of furfural can improve the contact area between the reactants and the catalyst molecule, causing the conversion of pentosan (hemicellulose) becomes higher. As reported by Luo et al. [24] the addition of catalyst can accelerate the breakdown of inter and intra bonds in the reaction. This can promote the selective breakdown of hemicellulose and facilitate furfural formation.
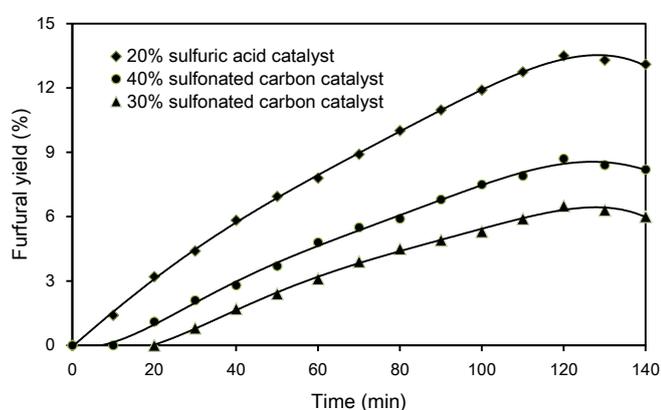
Fig 5. Effect of reaction time on furfural yield at various catalyst concentration and 110°C reaction temperature.

Fig 5 shows that the furfural yield using sulfonated carbon catalyst is lower than using sulfuric acid catalyst. This is related to the difference in acidity or H^+ activity of the two types of

catalysts used. The H^+ value of each catalyst used can be seen in table 2.

Table 2. H^+ activity or acidity of catalyst

Catalyst	Concentration (%)	H^+ activity or Acidity of catalyst (mmol/g)	Highest Yield (%)
Sulfonated carbon	30	4.88	6.5
Sulfonated carbon	40	4.88	8.7
Sufuric acid	20	200.04	13.5

At the same temperature, furfural formation with 20% sulfuric acid catalyst was faster than making furfural with sulfonated carbon catalyst, this is because the H^+ value of sulfuric acid is higher than the H^+ value of sulfonated carbon. Furfural formation with sulfuric acid catalyst began to form at the 10th minute, and continued to increase with time until the 120th minute with the highest yield of 13.5%. In addition, sulfonated carbon is a solid catalyst that generally causes mass transfer resistance, and also influences furfural formation. As a result, the furfural yield obtained is lower than the use of sulfuric acid catalyst.

III.V. FURFURAL ANALYSIS

III.V.I. FTIR Analysis

FTIR analysis to determine functional groups was needed to confirm that the resulting distillate was furfural. The results of FTIR analysis can be seen in Figure 6. Based on FTIR analysis, the aldehyde functional groups in furfural compounds were identified by the presence of C-H stretching vibrations (2900-2700) and C=O (1740-1620) at peak of 2870 cm^{-1} and 1681 cm^{-1} for both sulfonated carbon catalyst and sulfuric acid catalyst. Meanwhile, the presence of C-H aromatic function is absorbed in the area (3060-3010) with 3020 cm^{-1} peak. The C=C aromatic group (1620-1560 cm^{-1}) was shown at a vibration peak of 1567.8 cm^{-1}, and the C-O-C group is absorbed in the 1040-1070 cm^{-1} region with evidence at vibration peak of 1070 cm^{-1}. The vibration values obtained in this study are very close to those reported in the literature [8, 9].
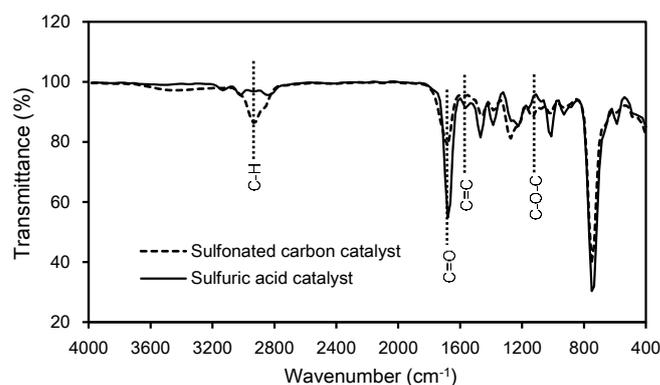
Fig 6. FTIR analysis using sulfonated carbon and sulfuric acid catalyst

By comparing the vibration values obtained with the standard furfural vibration values which are shown in table 3 [25], it can be confirmed that the compound produced from MM hydrolysis was furfural. To strengthen the results obtained, the analysis was also carried out with GC-MS.

Tabel 3. Standard furfural vibration

Vibration	Standard furfural (cm^{-1})
C-H aromatic streching	3060-3010
C-H aldehyde Streching	2900-2700
C=O aldehyde streching	1740-1620
C=C aromatic streching	1620-1560
C-O-C streching	1140-1070

III.V. II. GC-MS Analysis

GCMS analysis result of the furfural is shown in fig 7 and 8.
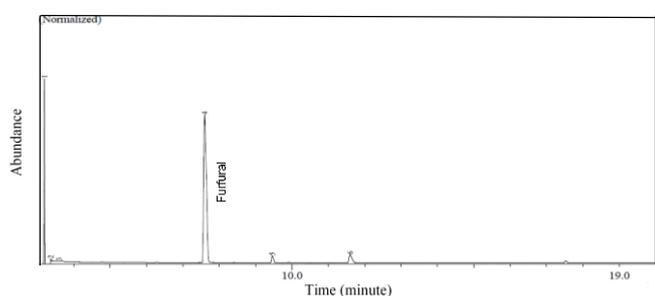
(a)
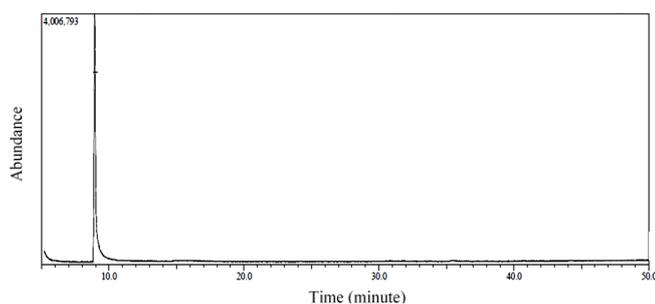
(b)

Fig 7. GC analysis of furfural catalyzed by (a) sulfonated carbon, (b) sulfuric acid

Based on fig 7, the results of GC analysis shows the quantity of furfural compound in MM hydrolysis result. This is shown at peak 4 (fig 7a) with a retention time of 7.58 minutes and a percent area of 60.35% for a sulfonated carbon catalyst, while for a sulfuric acid catalyst 20% is shown at peak 1 with a retention time of 8.975 minutes and a percent area of 100% (fig 7b)

Meanwhile, mass spectroscopy result is used to determine the molecular weight of a chemical compound and it is useful to determine the molecular structure based on the resulting fragmentation pattern. The mass spectroscopy result of GC-MS is shown in Figure 8.
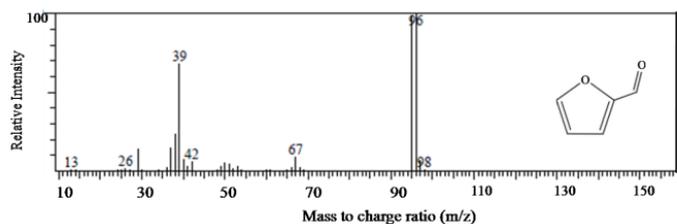
(a)
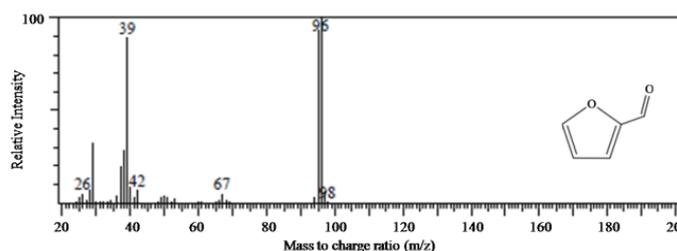
(b)

Fig 8. Mass spectroscopy analysis of furfural catalyzed by (a) sufonated carbon, (b) sulfuric acid

The results of mass spectroscopic analysis for furfural using both sulfonated carbon and sulfuric acid show ion fragmentation at mass/charge ratio (m/z) 26, 39, 42, 67, 96, and 98. The molecular ion peak at m/z = 96 is for furfural. This m/z values are suitable to the standard furfural m/z value. The standard furfural m/z values can be seen in table 4 [26].

Table 4. Standard furfural m/z values

Compound	m/z	Relative Intensity (%)	m/z	Relative Intensity (%)
	97	6	41	14
	96	100	40	5.9
	95	88.6	39	56.2
	68	1.5	38	14.3
	67	5.8	37	8.5
Furfural	66	1.0	36	56.2
	53	21.6	29	14.3
	51	2.5	28	3.9
	50	2.3	26	1.7
	49	1.3	25	1.0
	42	4.7	14	1.2

Ion fragmentations at m/z 26, 39, 42, 67, 96, and 98 show the breakdown of furfural into several fragments. Each m/z

represents one element. The fragmentation patterns and element names produced by the two catalysts used in this study are shown in table 5.

Table 5. Fragmentation patterns

Compound	m/z	Element
	96	$C_5H_4O_2^+$ (furfural)
	67	C_4H_3O (2-furyl)
Furfural	42	$(C_2H_2O)^+$ (ketene)
	39	$C_3H_3^+$ (cyclopropenyl)
	26	$C_2H_2^+$ (acetylene)

Initially the furfural cation ($C_5H_4O_2^+$, m/z = 96) will dissociate to form the following ions such as $C_4H_3O^+$ (m/z = 67), $C_3H_3^+$ (m/z = 39), $C_2H_2O^+$ (m/z = 42), and $C_2H_2^+$ (m/z = 26). The decomposition mechanism begins when the furfural ion $C_5H_4O_2^+$ (m/z = 96) splits into the first fragment, the $C_4H_3O^+$ ion (m/z = 67) due to the loss of CO group and the $C_3H_3^+$ ion (m/z = 39) which is formed due to the loss of $C_2H_2^+$. Then the $C_2H_2O^+$ cation (m/z = 42) appears as continuation of the dissociation of $C_4H_3O^+$ ion (m/z = 67). The minor ion $C_2H_2^+$ (m/z = 26) is formed due to the loss of $C_3H_3^+$ as a continuation of the fragment dissociation of the $C_4H_3O^+$ ion (m/z = 67) [27].

IV. CONCLUSIONS

The evaluation of sulfonated carbon catalyst derived from candlenut shell for furfural synthesis of MM has been successfully carried out. The highest furfural yield of 8.7% was achieved at 120 minutes, the reaction temperature was 110°C, and the amount of catalyst used was 40% by weight. FTIR analysis result shows the presence of C-H and C=O aldehyde functional groups were traced to wavenumber of 2870 and 1681 cm^{-1}. GCMS test results shows that furufural compound were detected at retention time of 7.58 minutes with 60.35% percent area for sulfonated carbon catalyst, and retention time of 8.975 minutes with 100% percent area of for 20% sulfuric acid catalyst. The m/z value obtained was 96 according to the furfural standard.

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