

## Furfural Synthesis from Maize Cob Using Co-Solvents

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### Abstract

Biofuels and chemicals can be produced from the lignocellulosic biomass would be promising platform in the upcoming decades. The maize cob is selected as lignocellulosic biomass to synthesis chemicals. The maize cob treated with meagre concentration of dilute sulfuric acid ( $H_2SO_4$ ) dehydrated with Tetrahydrofuran (THF) co-solvent and water in the ratio of 1:1 results with furfural formation. The maize cob sample acid catalysed dehydration process at 1, 2.5, 5 and 10% dilute  $H_2SO_4$  is substantial for sugar compounds production, these compounds can be further fermented to produce liquid fuels *viz.*, bioethanol, biobutanol in an efficient manner. The maize cob treated with 0.25, 0.5 and 0.75% of dilute  $H_2SO_4$  dehydrated with THF co-solvent and water (1:1) results with furfural formation and highest concentration was found in 0.5% acid catalyzed. The furfurals obtained can be downstream processed to recover and can be used as fuel precursor.

### 1. Introduction

Lignocellulosic biomass is considered as the renewable source for biofuel and chemical synthesis in environment friendly manner. In India, maize (*Zea mays* L.) is the third most important food crops after rice and wheat and has the highest production among the cereals. The production and productivity of maize in India was 28 million Mt and 2.4 Mt  $ha^{-1}$  during 2019-20 (USDA, 2019). Approximately, 180 kg of maize cobs are obtained from each ton of maize shelled. Fuel precursors are any biomass sugar monomer or sugar dehydration product of lignocellulosic biomass that can be biologically, chemically, or catalytically converted into fuels and chemicals. Furfural hydroxy methyl (HMF), furfural and levulinic acid (LA) can be used as fuel precursors (Yuriy *et al.*, 2007). Continued efforts to improve the synthesis of furans from sugar streams and their catalytic upgrading into fuel products have paved the way for biofuel platform. The present study deals with the production of these fuel precursors at different process conditions and the analysis of the pre-treated maize cob sample to find the concentration of these fuel precursors.

### 2. Materials and Methods

The maize cob was dried and size reduction was sequentially carried out in shredder, pin mill, and grinder. The size reduced biomass was sieved using ASTM 70 sieve as per ASTM E11-

13 procedure to obtain the maize cob particles less than 212  $\mu m$ . The characteristic of maize cob is much momentous for fuel precursors synthesis. The moisture content (ASTM E-871), volatile content (ASTM E-872), ash content (ASTM D-482), fixed carbon, elemental composition (ASTM D-3176), biochemical analysis *viz.*, cellulose, hemicellulose and lignin (ASTM D-3176) of maize cob were measured. The maize cob (5 wt %) were pre-treated at consecutive batch reactions with 0.25, 0.50, 0.75, 1, 2.5, 5 and 10% of dilute  $H_2SO_4$  were dehydrated with Tetrahydrofuran (THF) co-solvent and water in the ratio of 1:1 in hot air oven at 170 °C for 45 minutes (Chai *et al.*, 2013). THF is a promising green solvent which is relatively non-toxic, miscible with water over a wide range of reaction conditions (Nikolla *et al.*, 2011). The processed biomass was then centrifuged and the residues were characterised to assess the possible generation of energy. The supernatant after the centrifugation process were vacuum distilled to recover THF co-solvent as it is low boiling liquid. The post liquid is analysed in GCMS for the presence of fuel precursor.

### 3. Results and Discussion

The characterization of maize cob powder less than 212  $\mu m$  results with 6.7% moisture, 73.4% volatile, 2.5% ash, 17.4% fixed carbon, 45.4% carbon, 8.3% hydrogen, 45.8% oxygen, 0.4% nitrogen, 35% cellulose, 28% hemicellulose and 17% lignin content. The characterization of maize cob coincides

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with results of Anthony *et al.* (2017). The maize cob (5 wt %) were treated at consecutive batch reactions with 0.25, 0.5, 0.75% 1, 2.5, 5, 10 wt % of dilute H<sub>2</sub>SO<sub>4</sub> were dehydrated with THF co-solvent and water in the ratio of 1:1 in hot air oven at 170 °C for 45 minutes. The treated sample was then centrifuged and the residues were tested for the presence of cellulose, hemicellulose and lignin content to check the possibility of biofuel production. The supernatant after the centrifugation process were separated and vacuum distilled to recover the THF and the solution was analyzed in GC-MS to find the presence of fuel precursor.

The treated biomass samples at the ratio of 1:1 (THF and water) with the use of 1, 2.5, 5, 10 wt % dilute H<sub>2</sub>SO<sub>4</sub> were analyzed in GC-MS and the result obtained were furnished in the following figures and tables. The sample was analyzed for a period nearly 40 min in GC-MS and the compounds present in the supernatant were noted at different retention time. The peaks in the graph represent that at that particular retention time the major compounds of the treated biomass samples were analyzed.

From the tables 1 to 4 and figures 1 to 4, it is found that the major compounds formed were hexadecanoic acid, pentadecanoic acid, Butylated Hydroxytoluene and methyl esters.

Table 1: Major compounds formed in 1:1 solvent ratio with maize cob and 1% dilute H<sub>2</sub>SO<sub>4</sub>

| Retention time | Compounds   |
|----------------|---|
| 12.06          | Butylated Hydroxytoluene<br>Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl<br>Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-, methylcarbamate                         |
| 20.79          | Hexadecanoic acid, methyl ester<br>Pentadecanoic acid, 14-methyl-, methyl ester<br>Hexadecanoic acid, 15-methyl-, methyl ester                                  |
| 24.57          | Methyl stearate<br>Heptadecanoic acid, 16-methyl-, methyl ester<br>Hexadecanoic acid, 15-methyl-, methyl ester  |
| 11.94          | 1,4-Benzenedicarboxylic acid, dimethyl ester<br>Benzene-1,4-dicarboxylic acid, monohydra-<br>zide, methyl ester<br>1,3-Benzenedicarboxylic acid, dimethyl ester |
| 3.14           | Butyrolactone<br>Butanoic acid, 4-hydroxy-<br>Tetrahydropyran   |

Table 2: Major compounds formed in 1:1 solvent ratio with maize cob and 2.5% dilute H<sub>2</sub>SO<sub>4</sub>

| Retention time | Compounds   |
|----------------|---|
| 21.50          | n-Hexadecanoic acid<br>l-(+)-Ascorbic acid 2,6-dihexadecanoate<br>Pentadecanoic acid                |
| 8.92           | 2-Methoxy-4-vinylphenol<br>Ethanone, 1-(2-hydroxy-5-methylphenyl)<br>4-Hydroxy-3-methylacetophenone |
| 24.88          | cis-13-Octadecenoic acid<br>cis-Vaccenic acid<br>Z-(13,14-Epoxy)tetradec-11-en-1-ol acetate         |

Table 3: Major compounds formed in 1:1 solvent ratio with maize cob and 5% dilute H<sub>2</sub>SO<sub>4</sub>

| Retention time | Compounds   |
|----------------|---|
| 12.08          | Butylated Hydroxytoluene<br>Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-,<br>methylcarbamate<br>Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl- |
| 20.80          | Hexadecanoic acid, methyl ester<br>Pentadecanoic acid, 14-methyl-, methyl ester<br>Hexadecanoic acid, 15-methyl-, methyl ester              |
| 20.80          | Butyrolactone<br>Butanoic acid, 4-hydroxy<br>Tetrahydropyran  |
| 24.58          | Methyl stearate<br>Heptadecanoic acid, 16-methyl-, methyl ester<br>Heptadecanoic acid, 10-methyl-, methyl ester                             |

Table 4: Major compounds formed in 1:1 solvent ratio with maize cob and 10% dilute H<sub>2</sub>SO<sub>4</sub>

| Retention time | Compounds   |
|----------------|---|
| 12.08          | n-Hexadecanoic acid<br>l-(+)-Ascorbic acid 2,6-dihexadecanoate<br>Pentadecanoic acid  |
| 20.80          | Butylated Hydroxytoluene<br>Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-<br>Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-,<br>methylcarbamate |
| 20.80          | 2-Methoxy-4-vinylphenol<br>Ethanone, 1-(2-hydroxy-5-methylphenyl)-<br>4-Hydroxy-2-methylacetophenone  |

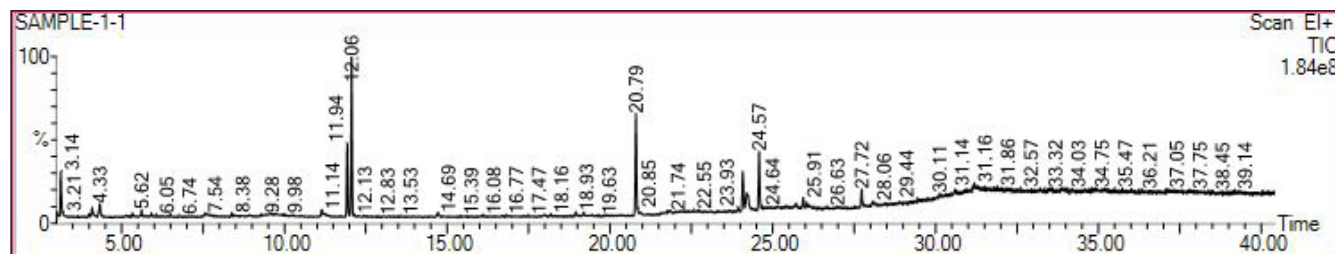


Figure 1: GC-MS Spectra of maize cob treated with 1% dilute H<sub>2</sub>SO<sub>4</sub> dehydrated with THF co-solvent and water 1:1 ratio

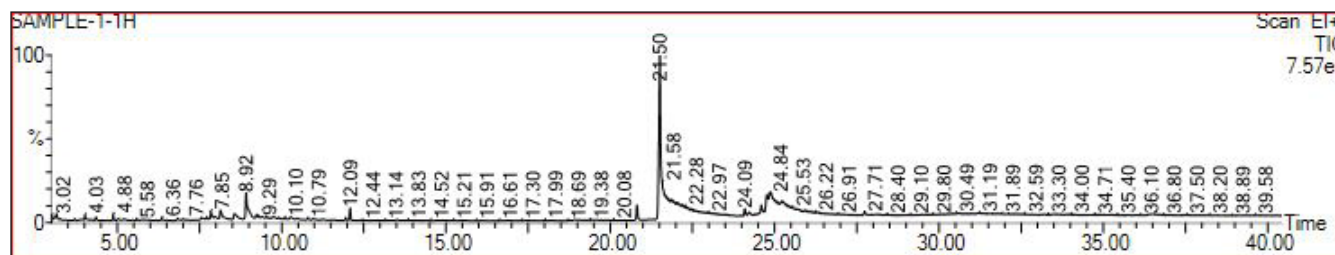


Figure 2: GC-MS Spectra of maize cob treated with 2.5% dilute H<sub>2</sub>SO<sub>4</sub> dehydrated with THF co-solvent and water 1:1 ratio

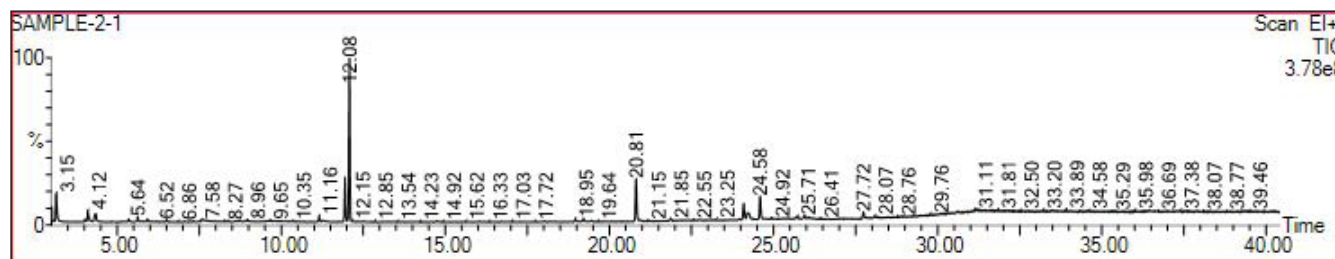


Figure 3: GC-MS Spectra of maize cob treated with 5% dilute H<sub>2</sub>SO<sub>4</sub> dehydrated with THF co-solvent and water 1:1 ratio

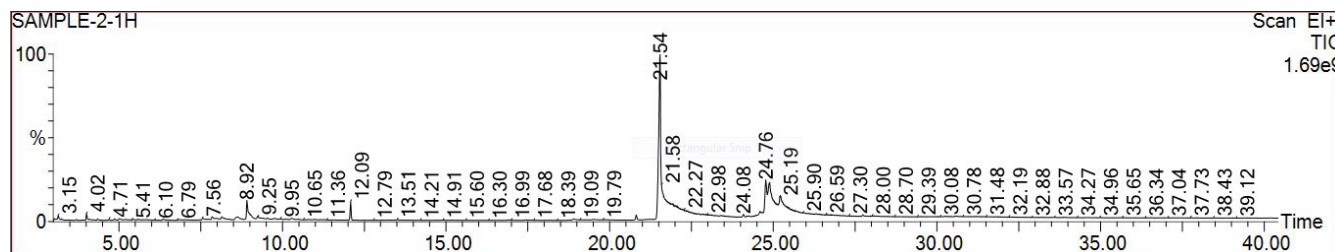


Figure 4: GC-MS Spectra of maize cob treated with 10% dilute H<sub>2</sub>SO<sub>4</sub> dehydrated with THF co-solvent and water 1:1 ratio

Apart from those major compounds formed, the C<sub>5</sub> and C<sub>6</sub> sugar compounds were also obtained (Table 5). The production of furfural after the acid catalysed dehydration process at 1, 2.5, 5 and 10% dilute H<sub>2</sub>SO<sub>4</sub> is not significant only sugar compounds was formed. This shows that only hydrolysis has taken place during the treatment process that lead the

Table 5: C<sub>5</sub> and C<sub>6</sub> sugar compounds formed after acid catalysed treatment

| Sample treated with THF co-solvent and water 1:1 ratio | 1% dilute H <sub>2</sub> SO <sub>4</sub>   | 2.5% dilute H <sub>2</sub> SO <sub>4</sub> | 5% dilute H <sub>2</sub> SO <sub>4</sub>  | 10% dilute H <sub>2</sub> SO <sub>4</sub>                            |
|--|--|--|---|--|
| Retention Time (min)                                   | -  | -  | 5-7   | 8-9  |
| Sugar Compounds  | Only phenols, esters and acids were formed | Only phenols, esters and acids were formed | L-Glucose<br>L-Arabinose<br>D-Fructose<br>d-Mannose<br>L-Lyxose<br>DL-Arabinose | L-Lyxose,<br>L-Glucose<br>d-Glucoheptose<br>D-Galactose<br>d-Mannose |

THF: Tetrahydrofuran; H<sub>2</sub>SO<sub>4</sub>: Sulfuric acid

way forward for ethanol production rather than the furfural production. This result is significant with the results of Werpy and Peterson (2014) as the maize cob with higher percentage of dilute acid treatment as a potential candidate for synthesis of sugars. This is because the higher concentration of acid catalyst was added that results insufficient to convert the biomass sample to furfural.

The maize cob samples treated with 1:1 solvent ratio and 0.25, 0.50 and 0.75% dilute  $H_2SO_4$  were analysed in GC-MS and the result obtained were furnished in the following figures 5, 6 and 7.

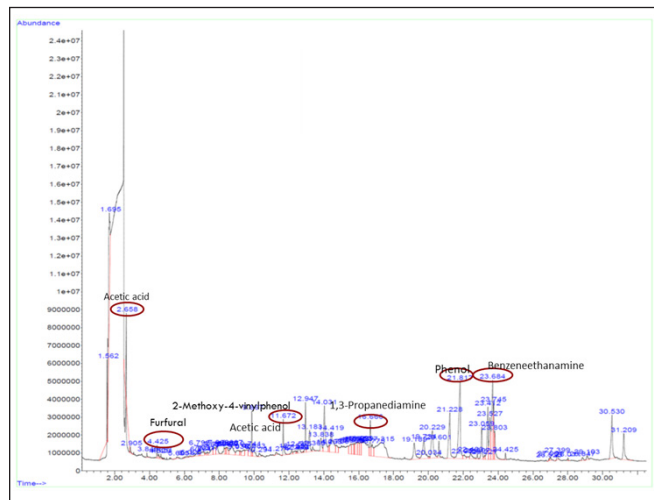


Figure 5: GC-MS Spectra of maize cob treated with 0.25% dilute  $H_2SO_4$  dehydrated with THF co-solvent and water 1:1 ratio

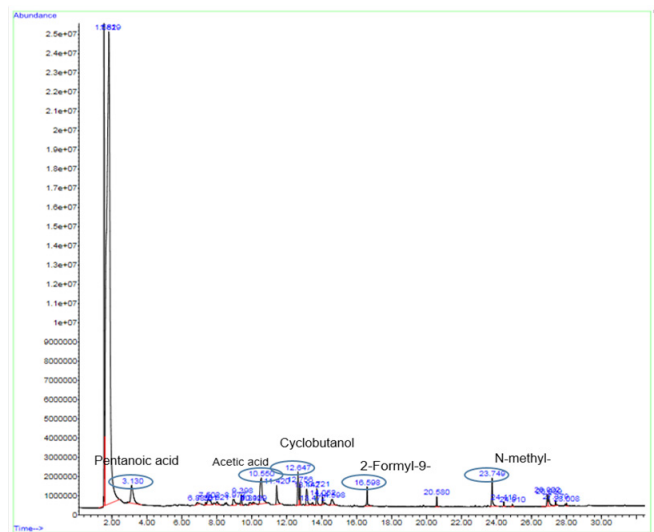


Figure 6: GC-MS Spectra of maize cob treated with 0.50% dilute  $H_2SO_4$  dehydrated with THF co-solvent and water 1:1 ratio

The maize cob treated with 0.25, 0.50 and 0.75% of dilute  $H_2SO_4$  dehydrated with THF co-solvent and water in the ratio of 1:1 results with furfural formation. This coordinated with the results of Zeitsch (2000). The higher yield of furfural is obtained when the maize cob treated with 0.50% of dilute

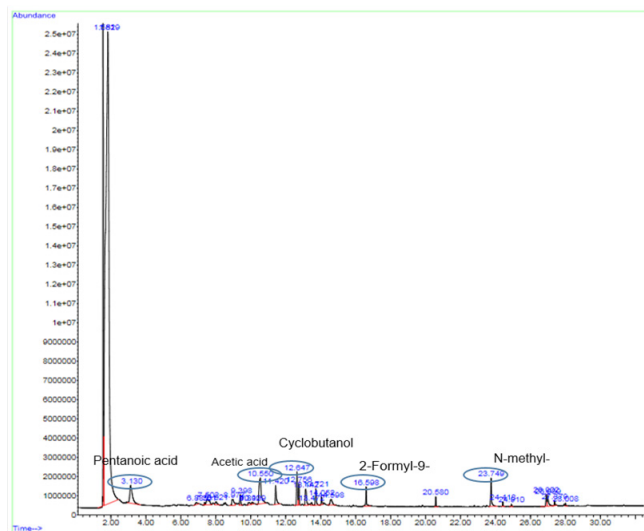


Figure 7: GC-MS Spectra of maize cob treated with 0.75% dilute  $H_2SO_4$  dehydrated with THF co-solvent and water 1:1 ratio

$H_2SO_4$  dehydrated with THF co-solvent and water in the ratio of 1:1. The dilute acid with THF and water dehydrate the sugars biomass to yield furfural and their derivatives. The furfurals can be further concentrated by downstream processing and converted into chemicals for further applications as fuel precursor (Huber *et al.*, 2016).

#### 4. Conclusion

Liquid fuels and fuel precursors production from lignocellulosic biomass is a renewable method. The maize cob is a promising sample to synthesis of fuels and chemicals. The corn cob treated with meagre concentration of dilute  $H_2SO_4$  dehydrated with THF co-solvent and water in the ratio of 1:1 results with furfural formation. The maize cob sample acid catalysed dehydration process at 1, 2.5, 5 and 10% dilute  $H_2SO_4$  is substantial for sugar compounds production, these compounds can be further fermented to produce liquid fuels viz., bioethanol, biobutanol in an efficient manner. The corn cob treated with 0.25, 0.5 and 0.75% of dilute  $H_2SO_4$  dehydrated with THF co-solvent and water (1:1) results with furfural formation and highest concentration was found in 0.50% acid catalyzed. The furfurals obtained can be downstream processed to recover and can be used as fuel precursor.

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