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Effects of Catalysts on Production of Furfural and Its Derivatives from Fallen *Gmelina arborea* Leaves

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ABSTRACT

Furfural and its derivatives have been found to have the potential to replace petroleum products in the production of industrial chemicals that use petroleum products. Hence, fallen leaves of *Gmelina arborea* were pulverized and treated with NaOH, $ZnCl_2$, ZnO, MgO and $CaCl_2$ for production of furfural and its derivatives. About 50 g of the pulverized leaves were treated with 500 ml 3% solution of the abovementioned catalysts at 100^oC for 30 minutes. The quantity of extracts obtained were 35.03, 32.50, 11.18, 6.92 and 16.69 g respectively. The only noticeable furfural derivatives found in the extracts were furanmethanol and hydroxymethyl furfural with exception of that catalyzed by zinc oxide that has 5-methylfurfuralbesides the above mentioned two The quantities of furanmethanol and hydroxymethyl furfural obtained were; 4.63 and 9.91, 5.36 and 4.88, 1.62 and 1.60, 0.62 and 0.38 and 2.13 and 4.12g respectively. 5-methylfurfuralobtained from that catalyzed by zinc chloride weighed 2.57 g. Therefore, NaOH and $ZnCl_2$ are suitable for extraction of furanmethanol and hydroxymethyl furfural from *Gmelina arborea* leaves.

Keywords: Effects, fallen leaves, furfural derivatives, *Gmelina arborea*, production

INTRODUCTION

Attention is shifting to production of biochemicals from plant biomass sources as they are found suitable for replacing petrochemicals. The renewable approach for the production of biochemicals and biofuels are considered as green chemistry and engineering processes. This

process is environmentally benign and has no toxic effect to the workers [1]. Plants contain cellulose, hemicellulose and lignin as the major chemical components [2]. Cellulose is built on hexoses, hence its decomposition results in glucose, fructose and other simple sugars. Likewise, hemicellulose is a polymer of hexoses and pentoses; its decomposition yields hexoses and pentoses. It is revealed by Ibrahim et al., [2], that, hydrolysis of pentoses yield furfural and its derivatives. This furfural and its derivatives are highly biodegradable [3]. Hydrolytic extraction of plant parts breaks the cellulose, hemicellulose and lignin into useful chemicals that are found in petroleum products for various industrial applications [2]. The use of biomass to synthesize biochemicals and biofuels has become very important due to the renewability, sustainability and biodegradability of their sources [4].

There are a lot of chemicals that can be produced from biomass which are good replacement for petroleum-based chemicals as feed stocks. Furanmethanol has been found useful in the production of furan resins, polymers, solvents, flavour, fragrance, pesticides, pharmaceuticals and other chemicals [5]. Hydroxymethyl furfural is a very important intermediate block for the production of very useful compounds such as dimethyl furan (DMF), 2,5-furan dicarboxylic acid, levulinic acid, 2,5-diformylfuran (DMF), dihydroxymethyl furan (DHMF) and 5-hydroxy-4-keto-2-pentenoic acid [6].

Due to large numbers of derivatives of hydroxymethyl furfural it is regarded as a sleeping giant [7].As a fuel, ethyl levulinate, a derivative of hydroxymethylfurfural obtained from biomass is found useful in blending with biodiesel [1, 8] and additive to fossil fuel. 2,5-Dimethylfuran is another furfural derivative with high boiling point, energy density and Research Octane Number (RON). Itwasfound to be abetter liquid biofuel than the popular bioethanol [5,9,10]. Methyl furfural is also used as fuel [4]. Furan methanol has been used as rocket fuel [5] and also used for production of food flavour [4]. In food flavouring and fragrance industry, ethyl levulinate is used for the production of food flavour and fragrance [1]

In view of the importance of furfural and its derivatives which are found cheaply and abundant in biomass, this study investigated the production of furfural and its derivatives from fallen (dead) leaves of *Gmelina arborea* over six different catalysts. This was carried out by extracting the pulverized leaves with the following catalysts: sodium hydroxide, zinc chloride, zinc oxide, magnesium oxide and calcium chloride.

MATERIALS AND METHODS

The materials were used in this study includes; Fallen *Gmelina arborea* leaves, ceramic mortar and pestle, 250 µm mesh sieve, 1000 ml conical flask, 500 ml beaker, 250 ml conical flask, thermometer, GallenKamp hot plate magnetic stirrer, 500 ml measuring glass cylinder, top loading balance, cotton wool, Whatmann filter paper, glass funnel and GC-MS machine. The analytical reagents included; sodium hydroxide, zinc chloride, zinc oxide, calcium oxide and magnesium oxide.

Fallen *Gmelina arborea* leaves were collected from Langtang, Plateau State, Nigeria. They were cleaned, pulverized with ceramic mortar and pestle, sifted with 250 µm mesh sifter and kept airtight. About 15 g sodium hydroxide was dissolved in 500 ml distilled water (3% solution) prepared in 1000 ml conical flask. 50 g of the pulverized *Gmelina arborea* fallen leaves was added to the sodium hydroxide solution. The mixture was placed on GallenKamp hot plate magnetic stirrer and heated to 100^{o}C for 30 minutes. The extract was filtered, first with cotton wool in a glass funnel, and then, with Whatmann filter paper. The filtrate was weighed on a top loading balance. The same procedure was carried out with zinc chloride, zinc oxide, calcium chloride and magnesium oxide catalysts respectively. About 4 g of each sample were collected into sample bottles for GC-MS analysis. Analysis was done using a Varian 3800 gas chromatograph equipped with an Agilent fused silica capillary CP-Sil 5 CB column (30 m × 0.25 mm i.d) connected to a Varian 4000 mass spectrometer operating in the EI mode (70 eV; m/z 30– 600 amu; source temperature 230 °C and a quadruple temperature 150 °C) [11].

RESULTS AND DISCUSSION

All the extracts have 2-furanmethanol and 5-hydroxymethyl furfural (HMF) as the only noticeable furfural derivatives except zinc chloride catalyzed extract that had 5-methyl furfural (5-methyl-2-furan carboxaldehyde). The masses of the extracts and furfural derivatives found in the extracts were calculated from their percentage compositions and are presented in Table 1.

Table 1: Mass of extracts and furfural derivatives

Catalysts used	Mass of Extract	Mass of furan methanol	Mass of 5-MHF	5-methyl-2-furan carboxaldehyde
NaOH	35.03	4.63	9.91	-
$ZnCl_2$	32.50	5.36	4.88	-
ZnO	11.18	1.62	1.60	-
MgO	6.92	0.60	0.38	
$CaCl_2$	16.69	2.13	4.12	2.57

Figure 1 depicts the composition and the percentage of products catalyzed by sodium hydroxide on *Gmelina* leaves. It showed that 5-hydroxymethyl furfural has the highest quantity of 28.3% and furanmethanol 13.21%. Figure 2 exhibits the performance of zinc chloride with furan methanol 16.43 % and HMF 15.03%. Figure 3 depicts the performance of zinc oxide catalyst with Furanmethanol consisting 14.53% of the products and HMF 14.27%. Magnesium oxide exhibited very poor performance for extraction of furfural derivatives as 8.74% Furanmethanol produced were and 5.52% HMF as presented in Figure 4. Calcium oxide exhibited good performance for extraction HMF in which 24.68% was HMF but Furanmethanol composition was 12.94% as shown in Figure 5. Among the five catalysts studied in this work, for extraction of furan methanol, zinc chloride is best and sodium hydroxide is best for hydroxymethyl furfural extraction as shown Figures 1 and 2 respectively. In the absence of sodium hydroxide, calcium chloride can be employed for the extraction of HMF.

Zinc oxide catalyzed extraction produced 5-methyl furfural next to HMF in quantity. This chemical is very useful as flavour and fragrance, hence it is used in alcohol beverage for its flavour and in cosmetic industries for its fragrance[12]. Therefore, zinc oxide can be employed for the production of 5-methyl furfural from fallen *Gmelina arborea* leaves.

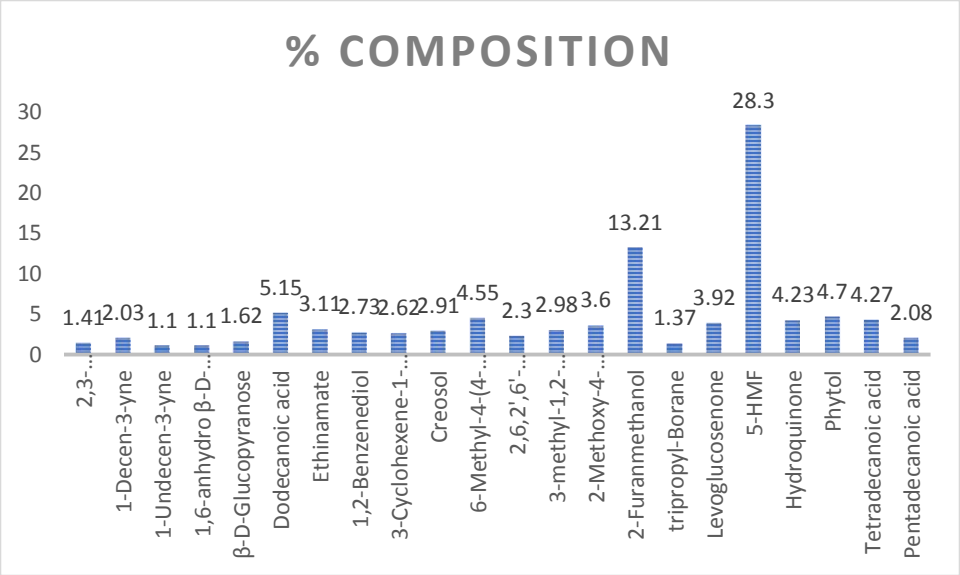

Figure 1: Quantity of products extracted with sodium hydroxide

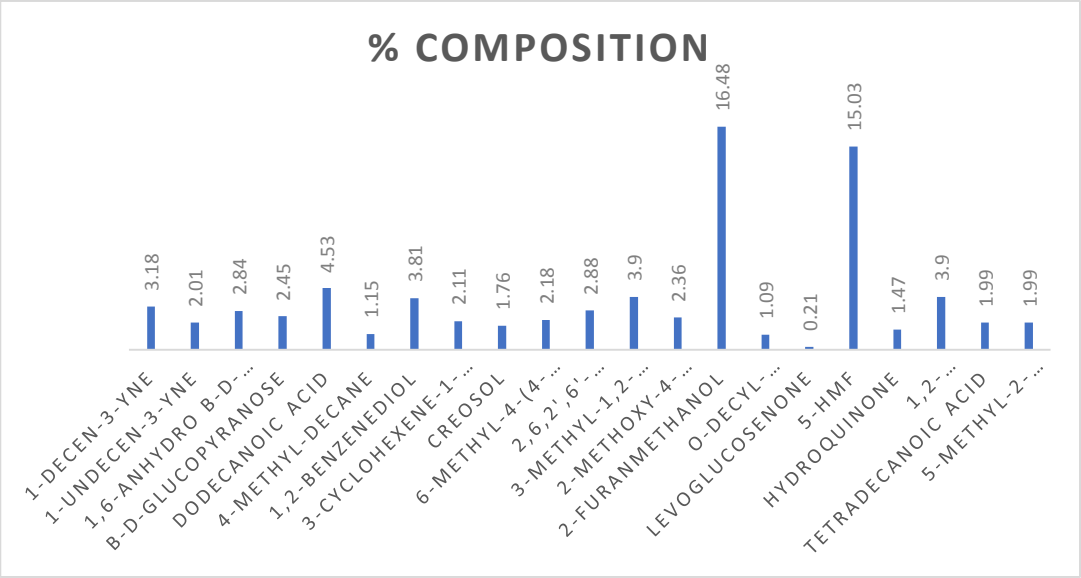

Figure 2: Quantity of products extracted with zinc chloride

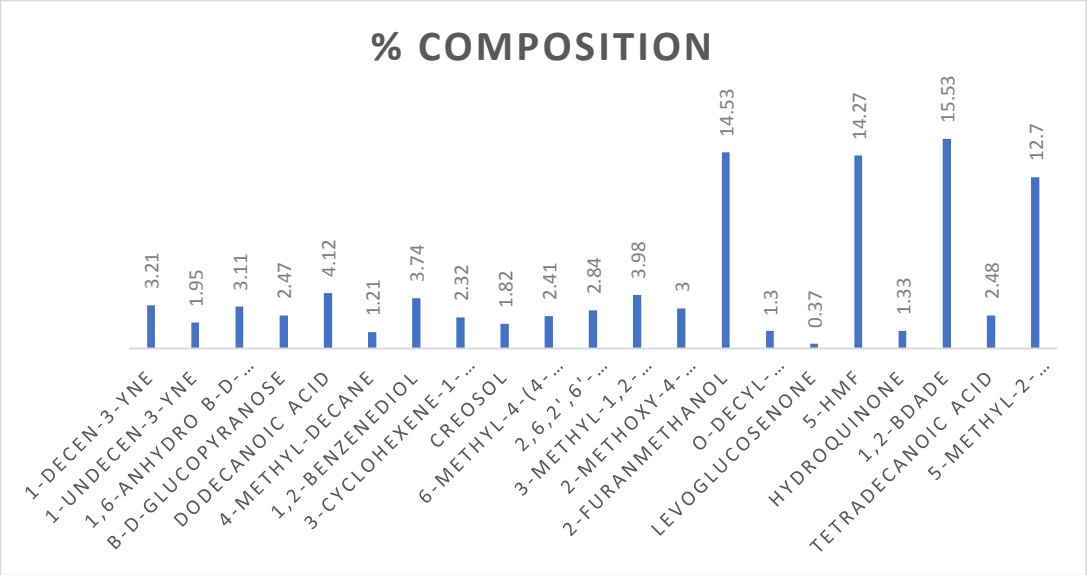

Figure 3: Quantity of products extracted withzinc oxide

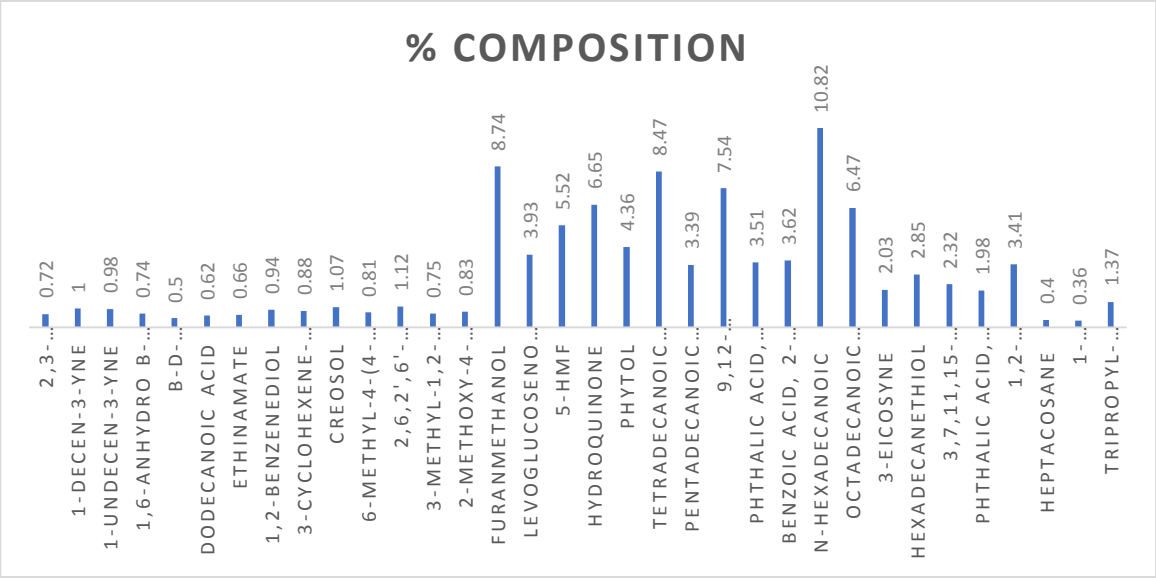

Figure 4: Quantity of products extracted with magnesium oxide

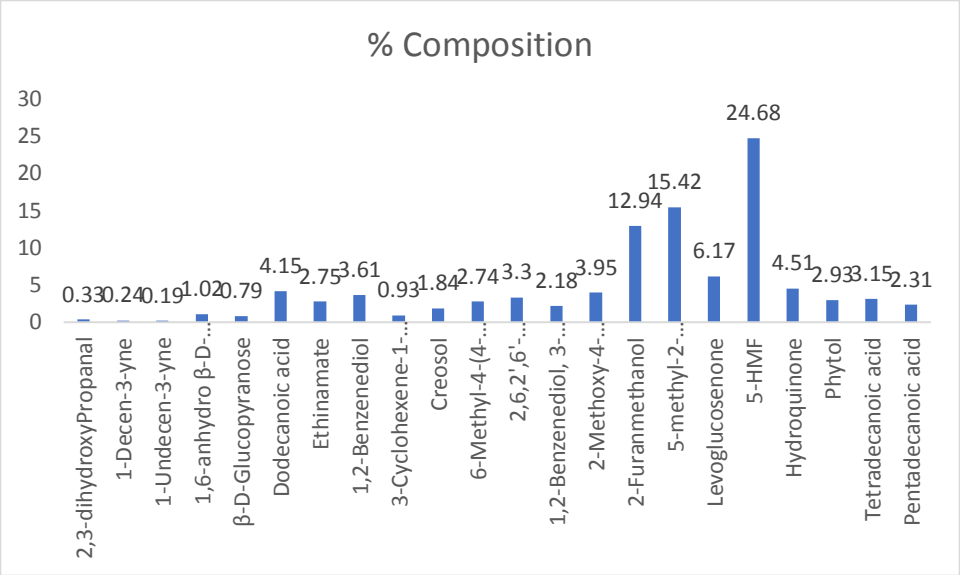

Figure 5: Quantity of products extracted with calcium chloride

CONCLUSION

Fallen *Gmelina* leaves were investigated for production of furfural and its derivatives with sodium hydroxide, zinc chloride, zinc oxide, magnesium oxide and calcium chloride catalysts. None of the productions had pure furfural. However, furan methanol and 5-hydroxymethyl furfural were produced from the five reactions carried out. The third furfural derivative 5-methyl furfural was produced by that catalyzed by zinc oxide in addition to furan methanol and 5-hydroxymethyl furfural. The percentage of furan methanol and HMF from the five reactions were; 13.21 and 28.3, 16.43 and 15.03, 14.53 and 14.27, 8.74 and 5.52 and 12.94 and 24.68 respectively. The percentage of 5-methyl furfural produced from that catalyzed by zinc oxide was 12.7. Therefore, dead *Gmelina* leaves can be used for production of furan methanol and 5-hydroxymethyl furfural. From this study, more will be produced with zinc chloride and sodium hydroxide.

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