



## SYNTHESIS OF BIODIESEL FROM *Gmelina arborea* DEAD LEAVES WITH CALCIUM OXIDE CATALYST

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### ABSTRACT

The depletion of fossil fuel, increase in the world population and environmental hazard associated with fossil fuel have rechanneled the world's interest toward finding a new alternative source of energy that is renewable and sustainable. Forest resources such as biomass wastes can serve as an alternative source of energy due to their availability, renewability, sustainability, biodegradability and environmentally friendly. Reuse of solid wastes by converting them to something useful will better the live of the communities they are generated. In this investigation, *Gmelina arborea* dead leaves were collected, pulverized, sieved and hydrolyzed with Calcium oxide catalyst and distilled water. The product was filtered, dried with magnesium sulphate and then analyzed with GC-MS. The results of the analysis contained 77.64 g (54.59 %) biodiesel, 25.75 g (18.14 %) furfural and its derivatives, 15.18 g (10.69 %) free fatty acids, 11.49 g (8.03 %) benzene derivatives and 11.996 g (8.45 %) others. The results indicated that biorefining of *Gmelina arborea* leaves would provide important chemicals raw materials capable of replacing some from petroleum products for our industries. Instead of burning these dead leaves that can cause pollution to the environment, they are rather be refined to produce biofuel and oleochemicals for industrial applications than to be wasted. However, biodiesel produced from these needs purification to obtain high grade fuel for use in compression ignition engines.

**Keywords:** biodiesel, dead leaves, *Gmelina arborea*, waste reuse

### INTRODUCTION

The rapid increase in the world population has created the growing needs for energy and most of the energies are supplied through petrochemicals sources. In addition to high consumption, environmental challenges, increasing price and scarcity of fossil fuel have activated interest towards alternatives sources of energy such as biomass. Biomass is a renewable and cheap resource with abundant amount all over the globe for energy and chemical feedstocks (Yang et al., 2010) Biomass can be converted into biofuels, chemical feedstocks for products known to be sourced from fossil-based chemicals (Zhao et al., 2015). For Example, 5-hydroxymethylfurfural (5-HMF) is an important platform compound which can be synthesized from renewable biomass used as intermediates of many reactions and it has potentiality of resolving the crisis of resources and energy (Yang et al., 2010).

Dead leaves from trees we collect always as wastes are potential fuels and chemical feedstocks for chemical industries. 34.8 % of the extract by acid hydrolysis of *Acacia auriculiformis* dead leaves by Ibrahim et al., (2015) were fatty acids which can be converted to biodiesel using simple esterification. Besides the fatty acids, 35.3 % were furfural and its derivatives. The product of hydrolysis of waste *Gmelina arborea* leaves carried out by Ibrahim et al., (2017) contained 43.3 % furfural derivatives. Furfural and its derivatives have wide applications in many

industries such as plastics, pharmaceuticals and agrochemicals, (Eseyin et al., 2015). Furfural is used as a solvent for refining lubricating oils, as a fungicide and weed killer and in the production of tetrahydrofuran, an important industrial solvent (Elbert. 2019). Eseyin et al., (2015), described furfural as the sleeping beauty of all the bio-renewable chemicals, bioplastics and polymers. Waste leaves are therefore very important feedstock for industrial raw materials that are derived from petroleum products.

The present work is aimed at investigating the chemical constituents of *Gmelina arborea* leaves using bulk calcium oxide catalyst to determine its suitability for industrial application. This was carried out by hydrolyzing pulverized *Gmelina arborea* waste leaves collected from the premises of Umaru Musa Yar'Adua University, Katsina for 30 minutes at 100°C. The chemical components of the resulting extract were analyzed using (GC-MS).

### MATERIALS AND METHODS

#### Materials and Equipment

Pulverized leaves of *Gmelina arborea*, bulk calcium oxide (CaO) Catalyst supported on alumina, magnesium sulphate (MgSO<sub>4</sub>), distilled water, conical flask, beaker, heating mantle, magnetic stirrer, cotton wool, measuring cylinder, pH meter, mortar and pestle, GC-MS machine.

### Sample preparation

Dead leaves of *Gmelina arborea*, were collected within Umaru Musa Yar'adua University, Campus, Katsina State. The leaves were washed, dried and pulverized using ceramic mortar and pestle. The pulverized dead leaves were sieved to 250 $\mu$ m and stored in air tight container.

### Extraction of the leaves

0.75 g of bulk calcium oxide catalyst was poured into 500 ml distilled water. 50 g of pulverized *Gmelina* leaves was added to the catalyst and water mixture, placed on a hot plate magnetic stirrer. It was heated to 100°C for 30 minutes. The product was filtered first with cotton wool and then with Whatmann filter paper to obtain clear solution. The filtrate was further treated with 0.02 % of magnesium sulphate to remove water and then filter with Whatmann filter paper. The final filtrate was weighed to determine the product yield.

The sample of filtrate was taken to GCMS for analysis to determine its chemical constituents. GC-MS Analysis was done using a Varian 3800 gas chromatograph equipped with an Agilent MS capillary column (30 m  $\times$  0.25 mm i.d.) connected to a Varian 4000 mass spectrometer operating in the EI mode (70 eV; m/z 1 – 1000; source temperature 230°C and a quadrupole temperature 150°C). The column temperature was initially maintained at 200°C for 2 min, increased to 300°C at 4°C/min, and maintained for 20 min at 300°C. The carrier gas was Nitrogen at a flow rate of 1.0 mL/min. The inlet temperature was maintained at 300°C with a split ratio of 50:1. A sample

volume of 1 $\mu$ L in chloroform was injected using a split mode, with the split ratio of 50:1. The mass spectrometer was set to scan in the range of m/z 1-1000 with electron impact (EI) mode of ionization. The Analysis of the sample now coded as A was carried out. Runtime were 70, 50 and 70 minutes respectively. Using computer searches on a NIST Ver.2.1 MS data library and comparing the spectrum obtained through GC – MS compounds present in the samples were identified. The samples and replicate was continuously injected as one batch in random order to discriminate technical from biological variations. Additionally, the prepared pooled samples were used as quality controls (QCs), which were injected at regular intervals throughout the analytical run to provide a set of data from which the repeatability can be assessed.

### RESULTS AND DISCUSSION

The extract product contained 49 compounds group under benzene compounds, furfural and its derivatives, sugars, nitrogen compounds, hydrocarbons, alkyl bromide, alkyl borane, fatty acids and alkyl esters (biodiesel) as revealed by GC-MS presented in Table 1. There are many furfural compounds but their compositions are very low as compared to that of biodiesel. The results indicate that, Calcium oxide catalyst was able to convert some compounds either directly or reacted with other relevant ones to produce alkyl esters as presented in Table 1 and Figure 1. The significant product here is alkyl esters due to its high content.

**Table 1: Chemical compositions revealed by GC-MS analysis**

Compound Detected	MF	Weight %
Phenol	C <sub>6</sub> H <sub>6</sub> O	0.932
1,2-Benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.735
Benzeneacetaldehyde	C <sub>8</sub> H <sub>8</sub> O	0.950
Phenol, 4-ethenyl-, acetate	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	2.256
n-propylbenzene	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	1.032
2-Methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	0.201
4-Methoxy-benzaldehyde	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	0.923
2H-Pyran-2,6(3H)-dione	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	0.968
2,3-dihydro-3,5-dihydroxy-6-methyl-4H-Pyran-4-one	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	1.343
6-methyl-5-Hepten-2-one	C <sub>8</sub> H <sub>14</sub> O	0.155
2-furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	2.411
Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	2.219
2-(2-propenyl)-Furan	C <sub>7</sub> H <sub>8</sub> O	1.059
5-methyl-2-Furancarboxaldehyde	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.950
5-Hydroxymethylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	2.603
4,5-Dimethylfurfural	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	1.945

**Table 1: Chemical Composition revealed by GC-MS (Continued)**

Compound Detected	MF	Weight %
2-Furanmethanol, acetate	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	1.461
trans-2-(2-pentenyl)-furan	C <sub>9</sub> H <sub>12</sub> O	1.589
Furaneol	C <sub>6</sub> H <sub>8</sub> O <sub>3</sub>	0.996
5-dodecyldihydro-2(3H)-furanone,	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	2.904
2methoxy-3-(2-methylpropyl)-Pyrazine	C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> O	0.292
2,6,2',6'-Tetramethylazobenzene	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	0.703
N-butyl-2-Furancarboxamide	C <sub>9</sub> H <sub>13</sub> NO <sub>2</sub>	1.909
1,6-anhydro-β-D-Glucopyranose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	0.585
Borane, tris(1-methylethyl)-	C <sub>9</sub> H <sub>21</sub> B	0.082
2-Bromo dodecane	C <sub>12</sub> H <sub>25</sub> Br	0.429
Tetradecane	C <sub>14</sub> H <sub>30</sub>	0.146
Tetracosane	C <sub>24</sub> H <sub>50</sub>	0.100
Squalene	C <sub>30</sub> H <sub>50</sub>	1.270
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	C <sub>26</sub> H <sub>54</sub>	0.192
Hexatriacontane	C <sub>36</sub> H <sub>74</sub>	0.183
2-butyl-1-Octanol,	C <sub>12</sub> H <sub>26</sub> O	0.055
1,3-Butadiene-1-carboxylic acid	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	0.877
1,2-Benzenedicarboxylic acid	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	1.041
n-Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	1.534
9-Octadecenoic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	3.562
9,12-Octadecadienoic acid-	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	2.311
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	0.082
Dodecanoic acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	0.018
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	1.151
Eicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	0.110
Methyl 9-octadecenoate	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	14.357
Methyl stearate	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	4.338
1,2-Benzenedicarboxylic acid, diisooctyl ester	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	0.338
Methyl ester 8,11-octadecadienoate,	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	8.247
Methyl Docosanoate	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	8.722
Methyl tetracosanoate	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	9.462
Methyl eicosanoate	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	9.225
α-Tocopheryl acetate	C <sub>31</sub> H <sub>52</sub> O <sub>3</sub>	0.046

Biodiesel has the highest composition followed by furfural and its derivatives as presented in Figure 1. The extract, contained 77.84 g biodiesel, 25.75 g furfural and its derivatives, 15.18 g free fatty acids, 11.45 g benzene compounds and the remain other compounds were 11.99 g. The mass of the product depends on the mass of the pulverized leaves and mass of distilled water used. If we base our yield on quantity of leaves used as water is cheap material, the biodiesel yield from this process is 155.68 %. If the others components of the product can be successfully separated out i.e. if the biodiesel produced can be isolated completely, this process would be the best and cheapest biodiesel process.

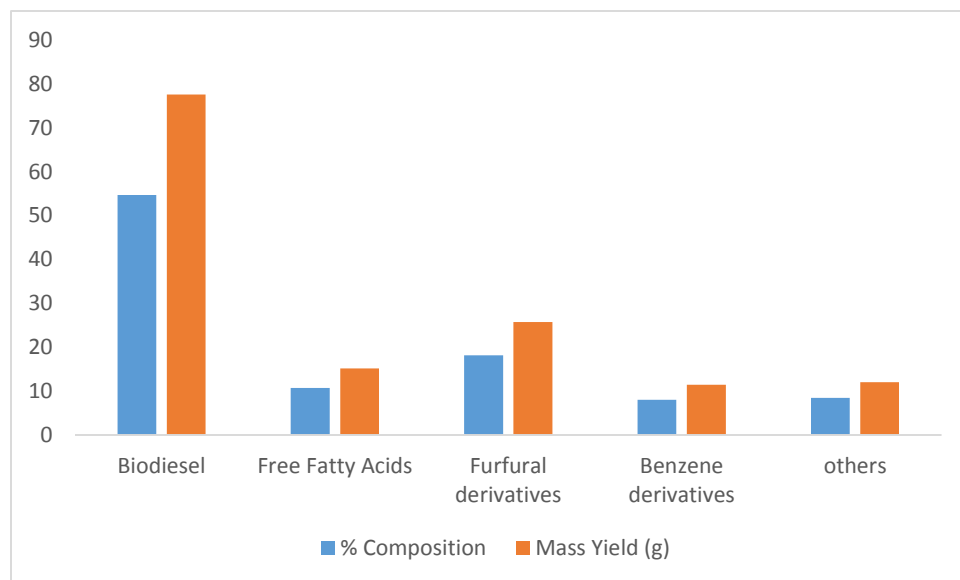


Fig. 1: Percentage compositions and mass quantity of components in the extract

## CONCLUSION

Biodiesel, fatty acid, benzene derivatives, furfural and its derivatives are produced from calcium oxide catalyzed hydrolysis of *Gmelina arborea* dead leaves. 77.84 g of biodiesel was produced from 50 g of *Gmelina arborea* dead leaves which yielded 155.68 % the highest selectivity ever in biodiesel process technology. This process technology converts wastes to fuel and industrial chemicals which is capable of generating energy, employment and empower rural dwellers, regenerates our forests and cleanse our environment.

## REFERENCES

Eseyin A.E. and Steele P.H. (2015). An overview of the applications of furfural and its derivatives Review Paper. *International Journal of Advanced Chemistry*, 3 (2) (2015) 42-47 doi: 10.14419/ijac. v3i2.5048: Retrieve from: [www.sciencepubco.com/index.php/IJAC](http://www.sciencepubco.com/index.php/IJAC)

Endalew A.K., Kiros Y. and Zanzi R. (2011). Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO). *ELSERVIER, Energy*. 2011; xxx:1-8.

Ebert J. (Accessed, 2019). Furfural: Future Feedstock for Fuels and Chemicals

Ibrahim H., Ayilara S., Nwanya K.O., Zanna A.S., Adegbola O.B. and Nwakuba D.C. (2017). Exploring *Gmelina arborea* Leaves for Biofuels and Petrochemical and Pharmaceutical Feedstocks. *Chemical Science International Journal* 18(2): 1-7; Article no .CSIJ.31407 Previously known as *American Chemical Science Journal* ISSN: 2249-0205

Ibrahim H., Nwanya K. O., Ayilara S., Adegbola O.B., Nwakuba D. C., Tyoor A. D., Ba'are A.M. and Shuaibu H. (2015). Potential of Earleaf Acacia (*Acacia auriculiformis*) Leaves for Industrial Raw Materials. *International Journal of Scientific Engineering and Applied Science (IJSEAS)* - Volume-1, Issue-4, July 2015 ISSN: 2395-3470 Retrieved from: [www.ijseas.com](http://www.ijseas.com)

Ibrahim H., Ahmed A.S., Bugaje I.M. and Mohameed-Dabo I.A. (2017). Transesterification of *Jatropha* Oil Devoid of Co-product, Glycerol. *American Chemical Science Journal* 15(4): 1-13, Article no. ACSJ.26425 ISSN: 2249-0205 SCIENCEDOMAIN international Retrieved from: [www.sciencedomain.org](http://www.sciencedomain.org)

Rosatella A.A., Simeonov S.P., Frade R.F.M. and Afons C.A.M. (2011). 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *The Royal Society of Chemistry, Green Chem.*, 13, 754-793

Yang L., Liu Y., Ruan R., Wang Y., Zeng W., Liu C. and Zhang J. (2010). Advances in Production of 5-Hydroxymethylfurfural from Starch. *The Second China Energy Scientist Forum Scientific research* 978-1-935068-37-2, pp 332-337 BioResources.com

Zhao S, Xu G., Chang J., Bai C.C.J., Fang S. and Lia Z. (2015). Direct Production of Ethyl Levulinate from Carbohydrates Catalyzed by H-ZSM-5 Supported Phosphotungstic Acid. *Bioresources* 10 (2) 2223-2234.