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Biochemicals synthesis from dead leaves of *Acacia auriculiformis* over zinc chloride and sodium hydroxide

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Abstract: This study was undertaken to investigate the biochemicals and biofuel feedstocks in the waste leaves of Acacia auriculiformis. A 50g mass of pulverized dead leaves of the tree were hydrolytically extracted using $ZnCl_2$ and NaOH catalysts at 100ºC for 30 minutes. The extracts were filtered with sheet cloth and 4g of each sample was analyzed with GC-MS. The highest fatty acid yield was 235.74 g over $ZnCl_2$ and 222.82 g over NaOH. The highest yields of other prominent chemicals found were 28.17g furan methanol over $ZnCl_2$, 14.18g spathulenol over NaOH, 55.55g Phytol over $ZnCl_2$, 15.94g caryophyllene over NaOH, 15.2g hydroxylamine octyl over $ZnCl_2$, 12.33g stigmasterol over NaOH and 16.85g Methyl α-D-galactopyranoside over NaOH. The biochemicals extracted from the leaves of Acacia auriculiformis are important chemical feedstocks for the pharmaceutical, cosmetics, agro-allied, and food industries.

Keywords: biochemicals, dead leaves, feedstock, synthesis, *Acacia auriculiformis*

Introduction

Petroleum refining industries are the largest industries worldwide but the potential hazards associated with them have caused a lot of concern to communities living in proximity to them. The products from petroleum are all harmful to our environment. Alternatively, these products can be produced from biomass which is sustainable and degradable hence, harmless to the environment. Their production, especially from waste biomass like dead leaves, is a cheaper source of feedstocks for which petroleum products are used. Fatty acids can be produced by hydrolysis of cellulose, furfural and its derivatives from hemicellulose and flavonoids, terpenes, and a lot of others from lignin of biomass which can be converted to biofuels, pharmaceuticals, agro-allied products etc. (Ibrahim et al., 2015: Ibrahim et al., 2017). The production of biochemicals for polymer, agro-allied products, and biofuel feedstocks from biomass can contribute to the reduction of dependence on petroleum sources (Gomes, et al., 2015). This will reduce the monopoly of marketing oil transactions by the current petroleum-producing countries. Ibrahim et al., 2015 claimed that furfural as a biomass product is a renewable building block for the synthesis of plastics and industrial and household chemicals. Also, 5-Hydroxymethylfurfural (HMF) is described as a key renewable platform compound for the production of fuels and chemical intermediates that can be produced cheaply obtained from fructose dehydration over phosphate (v) acid (Gomes et al., 2015). Lignocellulose, of biomass, comprises important polymers (cellulose, hemicellulose and lignin), and is of high importance, since their monomers fructose and glucose from cellulose, pentoses mainly from hemicellulose and phenolic compounds from lignin can be used as a carbon source for fuels and chemicals (Andreia et al., 2011). Furfural has numerous applications including as a solvent, gasoline additive, jet fuel blendstock, lubricant, organic fertilizer, fungicide, nematicide, resin, decorating agent, intermediate in the synthesis of pharmaceuticals, biochemicals, biopolymers, flavour enhancers for food and drink (Eseyin and Steele, 2015). A lot of important compounds can be synthesized from 5-hydroxymethyl furfural which includes propionoxymethyl furfural, 2,5-diformylfurfuryl ether, 2,5-bis(hydroxymethyl) furan, 2,5-bis-(hydroxymethyl) tetrahydrofuran, 2,5-furandicaborxylic acid and polyurethane (Lewkowski, 2001). In this study, the dead leaves of Acacia *auriculiformis* (acacia earleaf) were hydrolytically extracted over zinc chloride and sodium hydroxide catalysts. The products were analyzed with GC-MS to determine the biofuel and biochemicals benefits for industrial applications.

Materials and Methods

Materials

The materials used in this study include pulverized dead leaves of *Acacia auriculiformis*, 200µm sieve, ceramic mortar and pestle, 500ml measuring cylinder, spatula, aluminum foil paper, 1000ml conical flask, 1000ml beaker, sheet cloth, top-loading balance, GallenKamp hot plate magnetic stirrer, thermometer, distilled water and GC-MS machine.

Methods

The fallen dead leaves of *Acacia auriculiformis* were collected within the premises of the National Research Institute for Chemical Technology, Zaria-Nigeria. They were dried, pulverized with ceramic mortar and pestle, and sieved with a 200µm sieve. A mass of 0.5g of $ZnCl_2$ was dissolved in 500ml distilled water in a 1000 ml conical Flask and placed on GalleKamp hot plate magnetic stirrer. A 50g of the pulverized leaves were added to the mixture and heated to 100^{o}C. The temperature was maintained at 100^{o}C for 30 minutes after which the content was removed and filtered into a 1000 ml beaker with a sheet cloth. The procedure was repeated over 0.75 g and 1.5 g of $ZnCl_2$ and also 0.5, 0.75 and 1.5 g of NaOH. The filtrates were weighed and 4.0 g of each of the extracts (filtrates) were collected into separate sample bottles and sent to Afe Babalola University, Ado Ekiti for GC-MS analysis as in Ibrahim et al., (2021).

Results and Discussion

The hydrolysis of *Acacia auriculiformis* over $ZnCl_2$ and NaOH had quite some important biochemicals which include fatty acids, 3-methyl butanol, furan methanol, eugenol, phytol, caryophyllene, stigmasterol, spathulenol, methyl α-D-galactopyranoside, and hydroxylamine octyl as presented in Figures 1, 2 and 3. Over zinc chloride, the masses of fatty acids extracted by 0.5, 0.75 and 1.5g of the catalyst were 194.08, 235.74 and 218.14g respectively, while over sodium hydroxide catalyst with the same amount as $ZnCl_2$ loading were 218.58, 207.85 and 222.82g respectively as presented in Figure 1. The fatty acids obtained from this process are far greater than oil extracted from seed oils for biodiesel production (Ibrahim and Bugaje, 2018).

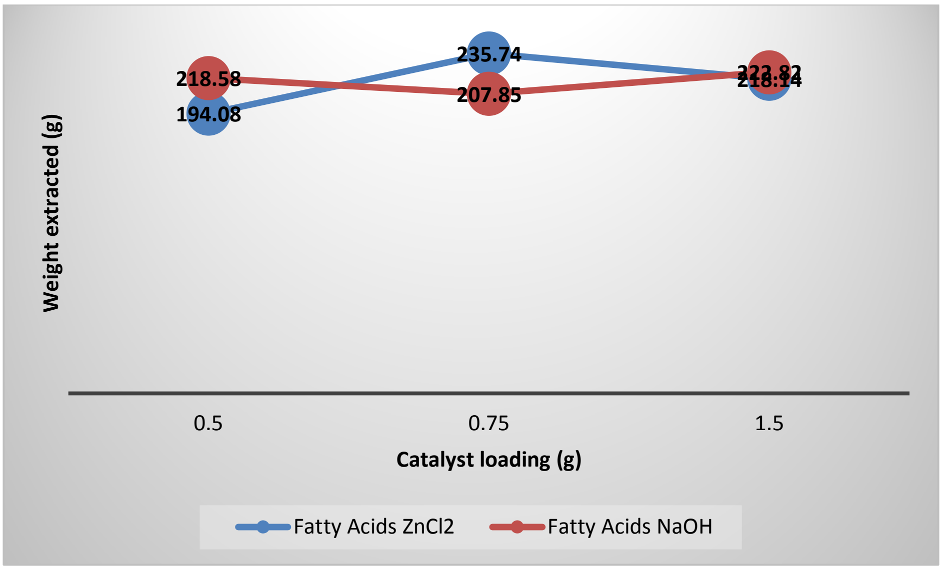

Figure 1: Quantity of fatty acids extracted over $ZnCl_2$ and NaOH from dead leaves of *Acacia* auriculiformis

The mass of furan methanol extracted over 0.5, 0.75 and 1.5g $ZnCl_2$ were 0, 19.9 and 28.17g respectively as shown in Figure 2. This is an indication that furan methanol yield increases with an increase in catalyst loading. No furan methanol was extracted over 0.5g $ZnCl_2$ rather it was 21.1g 3-methyl butanol that was extracted. Furan methanol is a very good solvent for fats, waxes, resins, dyes, vegetable oil, paints, inks and many others as well as biofuel. In plastic industries, furan methanol is used in the production of furan resin, a polymer used in the production of corrosion-resistant cement, thermoset polymer matrix composites, adhesives, coatings and cast-moulded items (Ibrahim et al. 2015). As a rocket fuel, it is mixed with white or red fuming nitric acid in rockets which ignites herpergollically (Wikipedia, accessed, 2021). Due to its high-octane number, it is also used as an additive or blend with gasoline to boost the octane rating. Eseyin and Steele, 2015).

Over 0.5, 0.75 and 1.5g of $ZnCl_2$, 0, 10.2 and 10.2 g of spathulenol were extracted respectively as presented in Figure 2. Its yield does not depend much on catalyst loading. Spathulenol is useful for cytotoxicity, Antioxidant, anti-inflammatory, antiproliferative and antimycobacterial as reported by do Nascimento et al., (2017) and can also be used as an insecticide (Chen, et al., 2017). Within this range of $ZnCl_2$ catalysis, 18.2, 13.82 and 55.55g of phytol was extracted as presented in Figure 2. Phytol or 3, 7, 11, 15-tetramethyl 2-hexaden-1-ol is used in the food industry as an additive as well as medicine for antischistosomal therapy (Ezeanu and Ezeanu, 2014). It is also used in hypolipidemic, antidepressant, anxiolytic, shampoos, household cleaners, detergents, cosmetic and toilet soaps because of its fragrance (Costa et al., 2014).

As depicted in Figure 3, the yield of Caryophyllene oxide increases with an increase in catalyst loading from 0 to 7.5 and 9.65g over 0.5, 0.75 and 1.5g catalyst loadings. Caryophyllene oxide is an oxygenated terpenoid, used as a preservative in food, drugs and cosmetics and antifungal against dermatophytes. Over the same catalyst ($ZnCl_2$), 0, 9.2 and 15.2g of hydroxylamine octyl were produced. This indicates that octyl hydroxylamine yield increases with an increase in catalyst loading. Hydroxylamine octyl is used in the production of acrylic polymers (Jiang-Feng et al., 2002). And over the same catalyst 10.1, 10.1 and 15.2g methyl, α-D-

Galactopyranoside were produced. This indicates that methyl, α-D-Galactopyranoside requires higher catalyst loading. Methyl α-D galactopyranoside is found useful in the computational studies of protonated β-d-galactose and its hydrated complex (Viana et al., 2011).

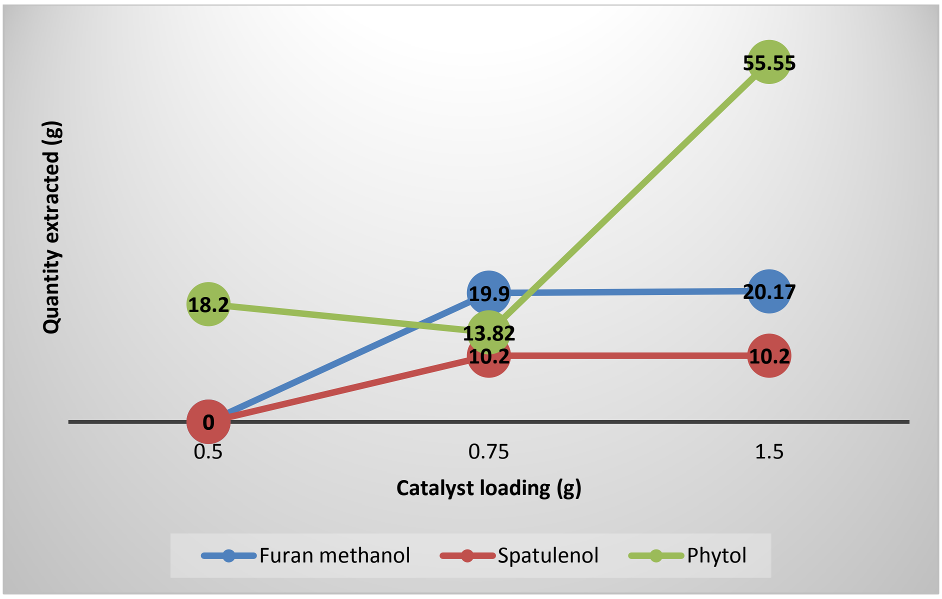

Figure 2: Quantity of Chemicals extracted over zinc chloride

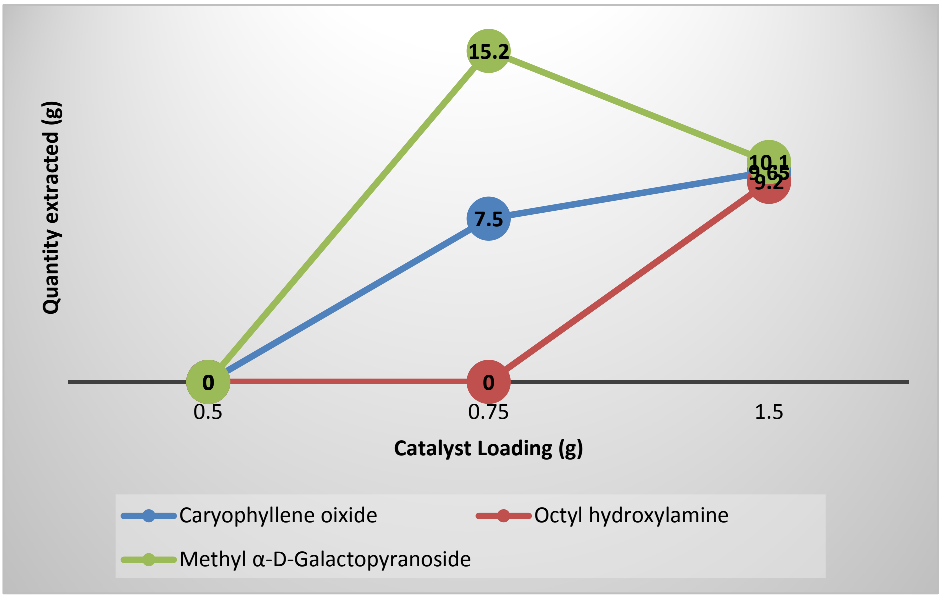

Figure 3: Quantity of chemicals extracted over zinc chloride

Over 0.5, 0.75 and 1.5 g of sodium hydroxide (NaOH), 12.57, 12.80 and 13.33g of furan methanol were produced from dead *Acacia auriculiformis* leaves as shown in Figure 4. The quantity of furan methanol is lower than that produced by Ibrahim et al. (2015) from waste *Acacia auriculiformis* leaves over sulphuric acid. The yield increases with catalyst loading. Furan methanol is found useful in addition to the above mentioned as a solvent for cellulose ethers and esters, ester gum, dyes, coumarone and natural resins; in the manufacture of phenolic resins & dark-coloured thermosetting resins; liquid propellant (NIH Accessed, 09/11/2021). Also, 12.85, 14.17 and 13.16g of spathulenol were produced. The weight of phytol obtained from the same process was 31.78, 27.99 and 26.80g respectively indicating a decrease in yield with the catalyst loading as depicted in Figure 4.

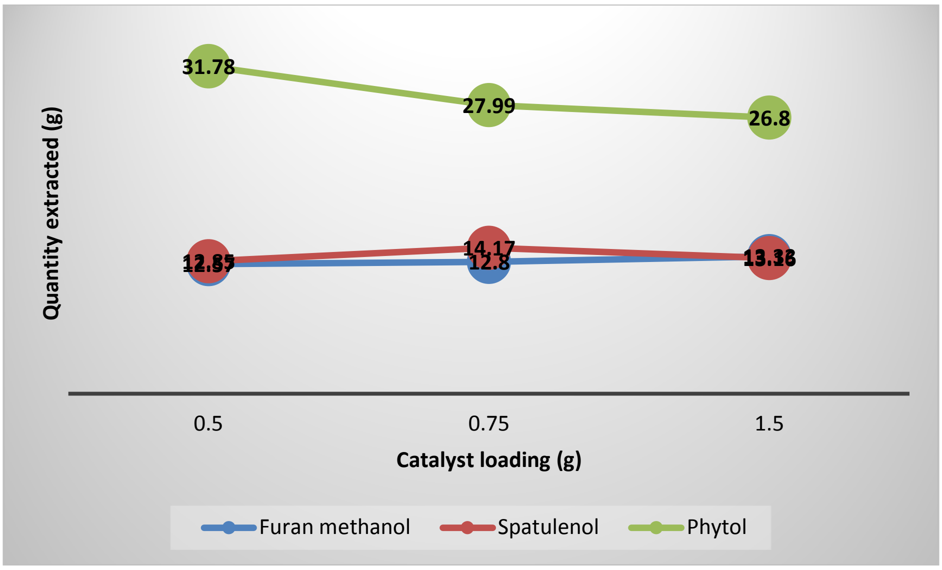

Figure 4: Biochemicals I extracted from *Acacia* auriculiformis over NaOH

The weight of caryophyllene oxide obtained over 0.5, 0.75 and 1.5g NaOH were 15.94, 14.11 and 12. 62g indicating a decrease in yield with catalyst loading. Stigmasterol yields from the same process were 12.33, 11.63 and 10. 25g respectively. It also follows phytol and caryophyllene oxide in terms of decreasing yield with catalyst loading. Stigmasterol is an important constituent for the synthesis of many hormones like progesterone, androgens, estrogens and corticoids (Kaur et al., 122 2011). The last biochemical produced from the hydrolysis of *Acacia auriculiformis* was methyl α-D-galactopyranoside with the following yields 14.79, 15.52 and 16.85g respectively. Unlike phytol, caryophyllene oxide and stigmasterol, its yield increases with the catalyst loading as shown in Figure 5. Methyl α-D-galactopyranoside is found useful in computational studies of protonated β-d-galactose and its hydrated complex and potent inhibitory activities toward the Debaryomyces hansenii UFV-1 as claimed by Chemical Book (2021). The biochemicals found in this study are presented in Figure 6. Apart from furan methanol, no other products here have been produced from a similar method for comparison. Figure 6 presents the chemical structures of the compounds extracted from the waste leaves of Acacia auriculiformis discussed above.

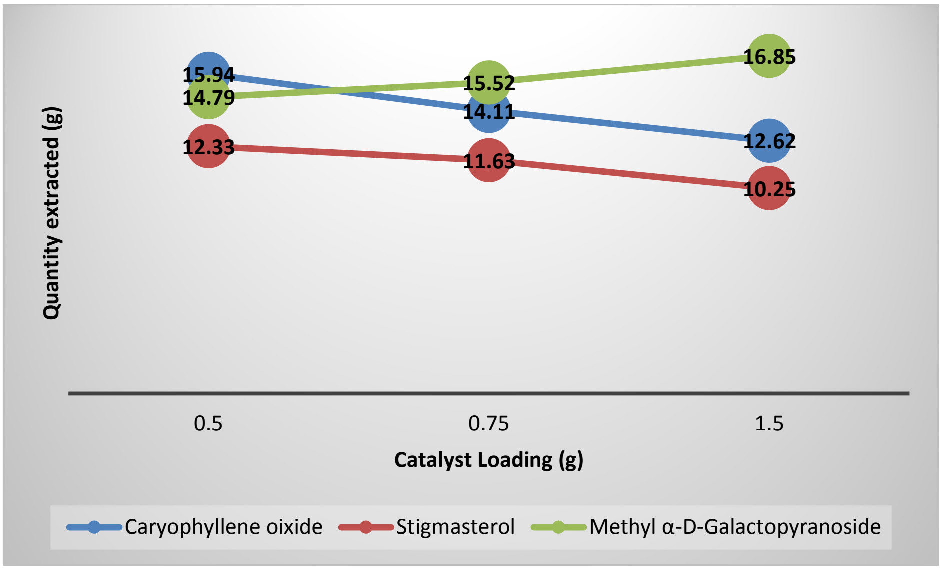

Figure 5: Biochemicals II extracted from *Acacia* auriculiformis over NaOH

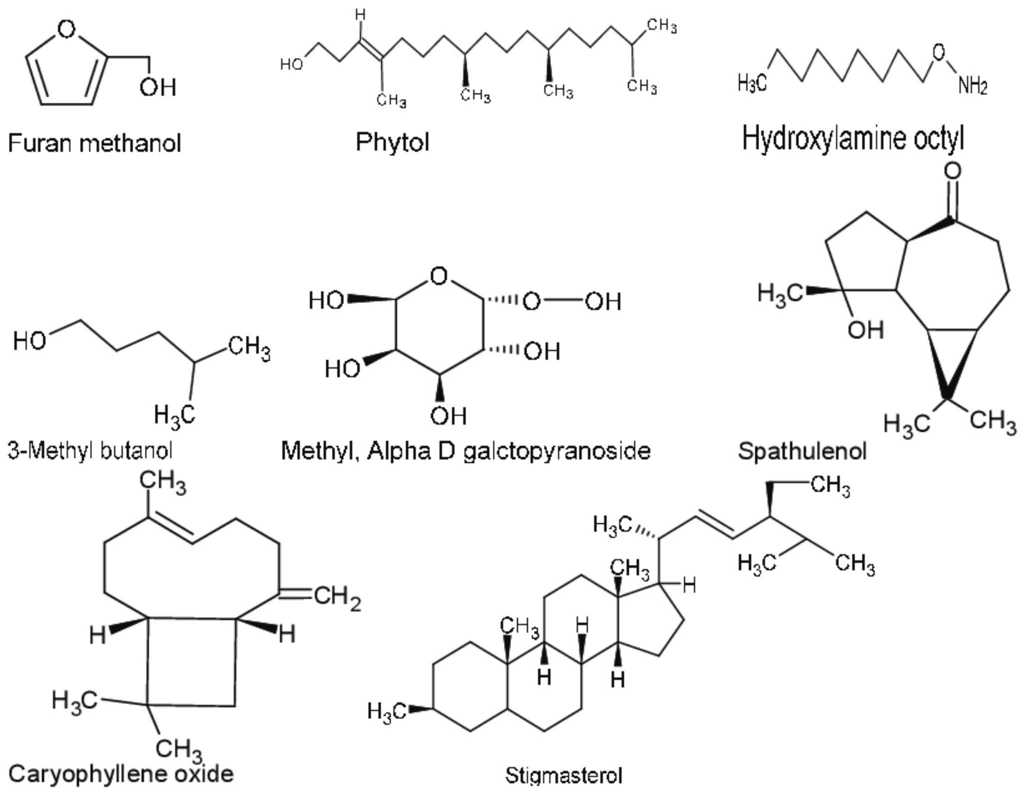

Figure 6: The Prominent biochemicals extracted from *Acacia auriculiformis* over $ZnCl_2$ and NaOH

Conclusion

The dead leaves of *Acacia auriculiformis* were pulverized and hydrolytically extracted over $ZnCl_2$ and NaOH. The prominent biochemicals extracted were Fatty acids, 3-methyl butanol, furfural, phytol, hydroxylamine octyl, caryophyllene oxide, spathulenol, furan methanol, methyl α-D galactopyranoside and stigmasterol. The highest weight of products extracted were 235.74, 28.17, 14.18, 55.55, 15.94, 15.2, 13.33 and 16.85g of fatty acids, furan methanol, spathulenol, phytol, caryophyllene oxide, hydroxylamine octyl, stigmasterol and methyl α-D-galactopyranoside respectively. These products can provide cheaper feedstocks to biodiesel, pharmaceutical, cosmetic, agro lied and food industries. The process not only generates feedstocks for chemical companies but also reduces solid waste from the waste stream.

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