

## SYNTHESIS OF VANILLIN FROM LIGNIN

### ABSTRACT

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the major flavour constituent of vanilla[1]. It has a wide range of applications in food industry and in perfumery. Vanillin is also very useful in the synthesis of several pharmaceutical chemicals. Lignin is a phenolic polymer which is found in plant cell walls with a structure depending strongly on the source of lignin and the process condition, which should be adjusted for different samples. In this work, lignin was extracted from kraft cooking liquor of wood ash. The amount of extracted lignin was 25.5%, based on oven dry weight of wood ash. The lignin obtained was then reacted with alkaline nitrobenzene and refluxed at 170 °C for 3 hours to obtain vanillin. The FT-IR spectrum of vanillin was similar to standard. The yield obtained from oxidation with nitrobenzene was 3.9%.

**Key words:** Vanillin, FT-IR and Lignin

### INTRODUCTION

Vanillin is a flavouring obtained from the vanilla orchid. It is one of the widely used expensive spice after saffron [2]. Despite being expensive, vanillin still stands as a highly appreciated flavour. Vanillin is widely used for both commercial and domestic purposes including, aroma and food flavouring, baking, complementary flavouring in chocolate; caramel; custard or coffee, perfumes, and aromatherapy. The major word vanillin is the *Vanilla planifolia* species, commonly known as the Bourbon or Madagascar vanilla, which originates from Madagascar and neighbouring islands in the southwestern region of the Indian Ocean and Indonesia. Combined sources of the vanilla produce about two-thirds of the world vanillin (Rose 2017).

24 Due to scarcity and the high cost of vanillin extracted from natural sources along with its  
25 popularity, there is increasing interest in the synthesis of the predominant component vanillin  
26 from alternative greener sources. Vanillin is one of the most popular flavours, but less than 1%  
27 of it comes from a mature vanilla orchid. Big food brands that vowed to only use natural flavours  
28 in products marked are experiencing shortages due to an emerging shortage of vanilla orchid.  
29 Food and beverage flavour industries are looking forward to supplying alternative sources to  
30 curb shortage of vanillin flavour and to sustain the venture. In addition, vanillin obtained through  
31 synthesis is not considered a sustainable method of obtaining alternative flavouring. This  
32 therefore call for a need to synthesize vanillin from renewable sources. Application of this  
33 method is considered greener and more sustainable.

## 34 MATERIALS AND METHODS

### 35 Preparation of Samples of Pulp for The Experiment

36 Kraft cooking process was performed. The specified conditions for the process were; 10 grams  
37 of fine wood ash weighed and white liquor prepared under the conditions of active alkali charge  
38 of 25% Sodium hydroxide and Sulphidity of 30 % Sodium Sulphide by weight in the ration of  
39 3:1, that is, the white liquor. A white liquor (NaOH and NaS<sub>2</sub>) to wood Ratio of 6:1 at cooking  
40 temperatures of 140 for 2 hours [4].

### 41 Lignin Extraction

42 The black liquor was characterised by the pH value of about 13. In order to extract the lignin  
43 component from the black liquor, dilute sulphuric acid (4 M, 22% by weight) was added to the  
44 black liquor and agitated using a magnetic stirrer until the pH value reduced to 2. The pH value  
45 of 2 was necessary to obtain an increased yield of extracted lignin [5]. At this point, the black  
46 liquor turned from black to brown resulting into a precipitate. The resulting precipitate was then

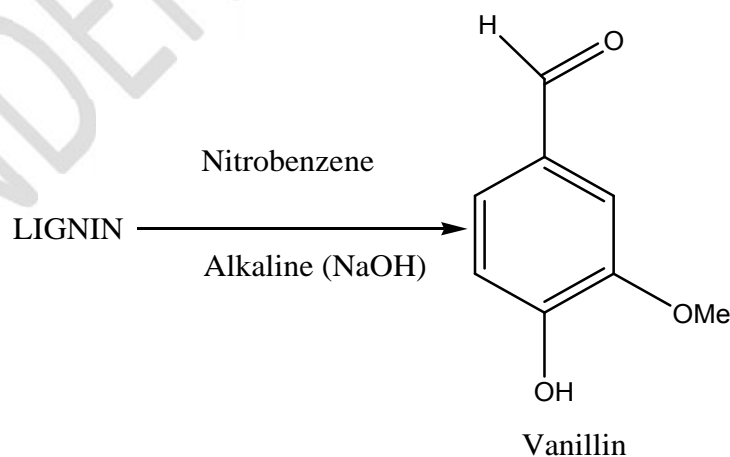
47 agitated for 1 hour. The Lignin mixture containing the lignin was filtered and washed with 100  
48 ml warm water to wash the excess sulphuric acid. The obtained product was dried at 100 for  
49 30 minutes in a vacuum oven and then finely pulverized using a motor and pestle. Without  
50 additional purification procedure, the pulverised product was tightly sealed and kept at ambient  
51 temperature prior to use. A portion of the dried product was then subjected to FT-IR analysis.

## 52 Preparation of Vanillin

53 To the 0.2 grams of the oven dried lignin, 7 ml of 2 M NaOH was added. 0.5 ml nitrobenzene  
54 was measured and added to the mixture in a 500 ml round bottom flask and refluxed at 170 for  
55 3 hours. The combined organic phase was then evaporated in a fume chamber. The sample was  
56 then transferred to a 50 ml volumetric flask and filled with methanol/water in the ratio 1:1. The  
57 solution was then filtered through a membrane filter of 0.45-micron pore size. The lignin  
58 oxidation product was then analysed using FT-IR and contrasted with the standards.

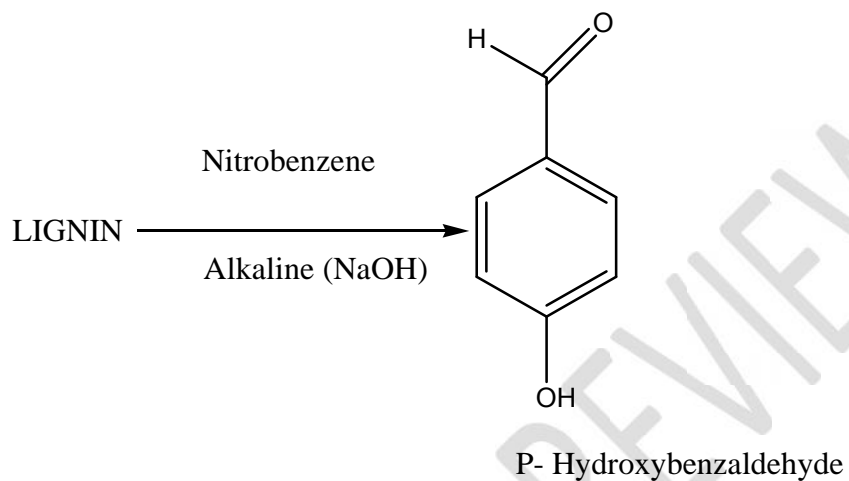
## 59 RESULTS AND DISCUSSIONS

60 In this research the amount of extracted lignin was 25.5% based on oven dry weight of wood ash.  
61 The synthesised vanillin was 3.9% of the obtained lignin. Alkaline nitrobenzene oxidation of  
62 lignin resulted into the formation of vanillin.



63  
64 Figure 1: Proposed chemical equation for reaction of lignin and nitrobenzene to produce vanillin.

65 Lignin from grasses contains p-hydroxyphenyl propane unit (R1=R2=H). Grassy plants,  
66 therefore, contain relatively small amounts of lignin approximately 15 % of the biomass.  
67 Oxidation of this lignin leads to the formation of a more complex aldehyde and hence it is not  
68 used for the case of oxidative production of vanillin.



69  
70 Figure 2: Proposed chemical equation for reaction of lignin and nitrobenzene to produce p-  
71 hydroxybenzaldehyde.

72 Figure 3 below shows a picture of the formulated vanillin

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Figure 3: formulated vanillin

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#### 77 **FT-IR characterization of obtained lignin**

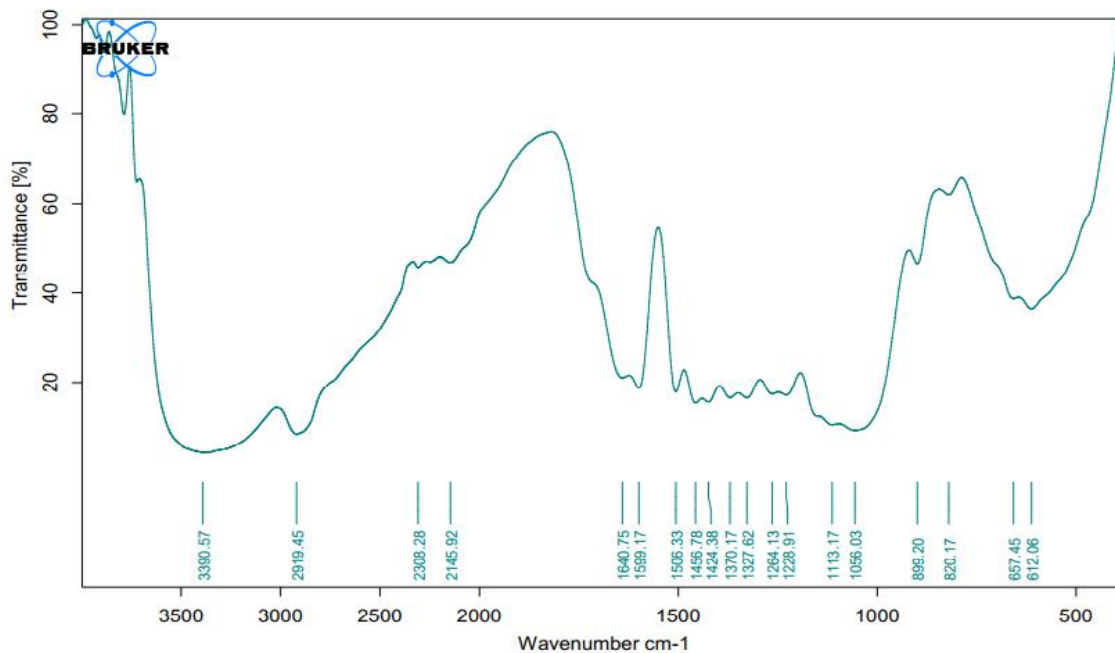
78 The purpose of FT-IR was to determine the functional groups present in the lignin. The analytes  
79 were in powder/solid form. The obtained results were in frequency range of 4000 and 400  $\text{cm}^{-1}$ .

80 Usually, the percentage of lignin in softwood is 30 % and 20% hardwood. In order to enhance  
81 the industrial application of lignin the precise structure as well as the functional groups has to be

82 known in order to develop new application. The most important chemical functional groups  
83 present in **the extracted** lignin included methoxyl, hydroxyl, carboxyl and carbonyl. The results

84 obtained from the FT-IR analysis of Kraft lignin were as follows;

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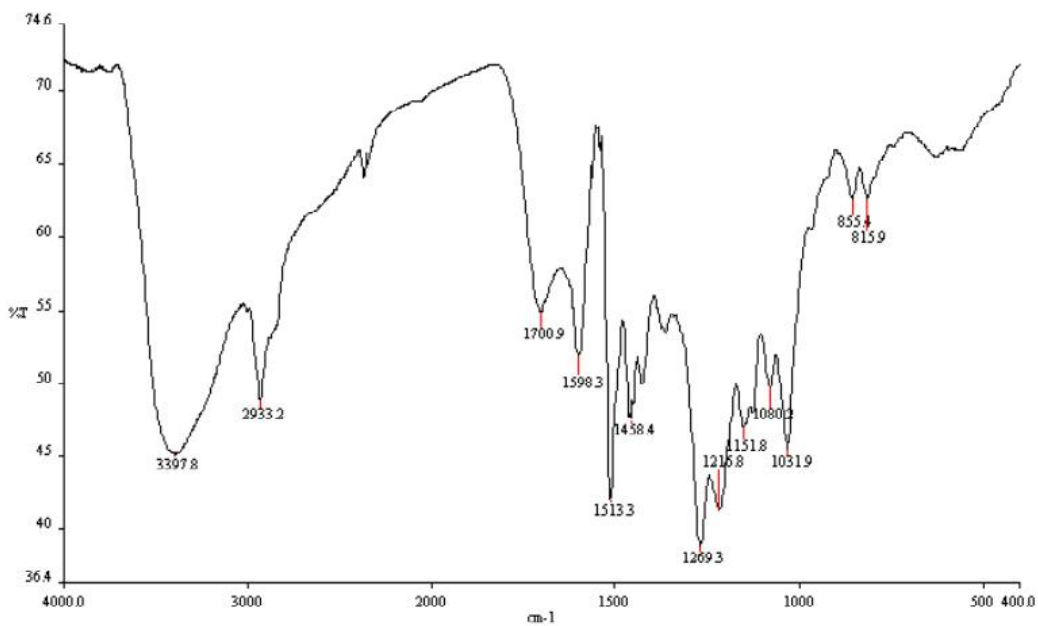


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87 **Figure 4: FT-IR Results for the Kraft Lignin.**

88 **The lignin revealed a very close resemblance to the lignin extracted from the Pinus eldarica [4] as**

89 **in figure 5**

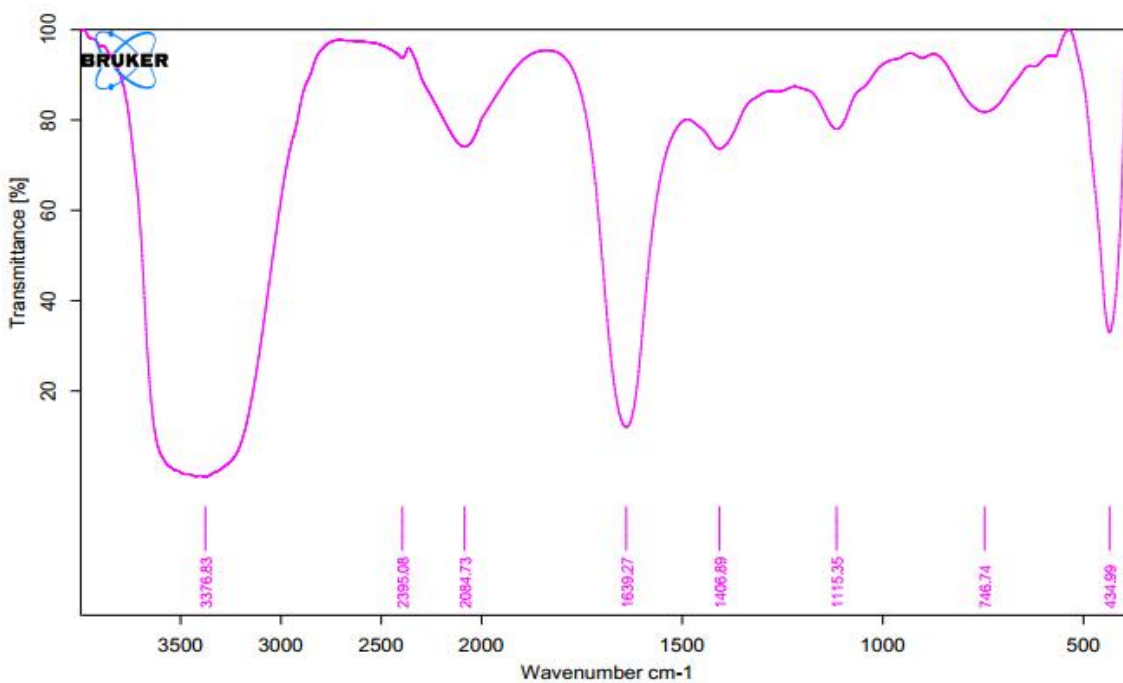


91 **Figure 5: FT-IR spectra of Pinus eldarica Kraft Lignin [4]**

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93 **FT-IR characterization of synthesised vanillin**

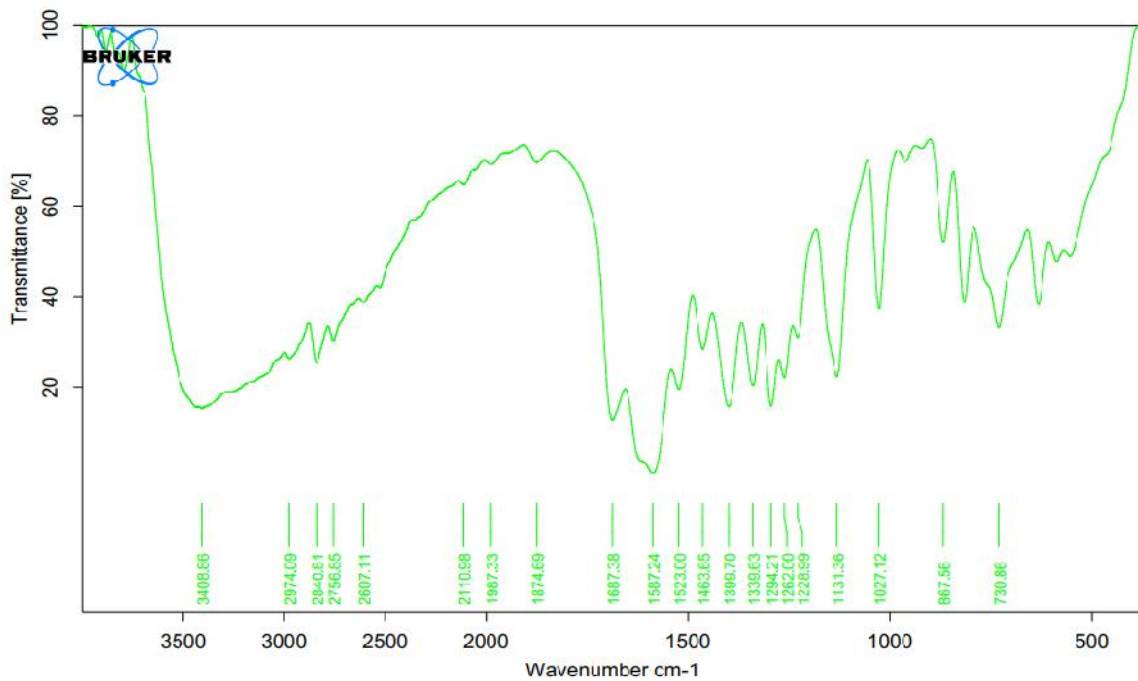
94 Figures 6 and 7 below shows the FT-IR spectra of the synthesized vanillin and the commercial  
95 standard vanillin respectively.



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97 **Figure 6: FT-IR spectra of synthesized Vanillin**

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100

101 **Figure 7: FT-IR Standard/ commercial vanillin**

102 From the FTIR spectra in it is clear that there is a close semblance on the functional groups  
 103 present in both the synthesized and the commercial vanillin.

#### 104 **Conclusion**

105 From this study Lignin was isolated from black liquor of wood ash and the lignin was then  
 106 oxidised in a controlled reflux heating system with nitrobenzene. The reaction system involved a  
 107 step where vanillin was formed from lignin and because of the similarity of coniferyl OH groups  
 108 to the vanillin structure; this monomer was oxidized to vanillin. Other monomers were also  
 109 oxidized but recognition of the vanillin was important in this research. The yield of vanillin  
 110 obtained from this study was significant.

#### 111 **Acknowledgement**

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113 **References**

- 114 1. Borges Da Silva EA, Zabkova M, Araujo JD, Cateto CA, Barreiro MF, Belgacem MN,  
115 Rodrigues AE. 2009. An integrated process to produce vanillin and lignin-based  
116 polyurethanes from Kraft lignin, *Chemical Engineering Research and Design* 87:1276–  
117 1292.
- 118 2. Hocking, Martin B. (September 1997). Vanillin Synthetic Flavouring from Spent  
119 Sulphite Liquor (PDF). *Journal of Chemical Education*. 74(9): 1055-1059.
- 120 3. Rose C, Kennedy (2017). *The Flavour Rundown: Natural Vs Artificial Flavours*. Harvard  
121 University. Retrieved 2018 -08-01.
- 122 4. Shakeri A, M Sepideh, Ghasemian, 2013. Oxidative Production of Vanillin from  
123 Industrial Lignin Using Oxygen and Nitrobenzene: A Comparative Study. *International*  
124 *Journal of farming*. Pg 1166-1170.
- 125 5. Mussato SI, Fernandes M, Roberto IC. Lignin recovery from brewer's spent grain black  
126 liquor.
- 127 6. Araujo JDP, Grande Carlos A, Rodrigues Alirio E. 2010. Vanillin production from lignin  
128 oxidation in a batch reactor, *Chemical Engineering Research and Design* 88: 1024-1032.
- 129 7. Boeriu C G, Bravo D, Gosselink R J A & Van Dam JEG. 2004. Characterization of  
130 structure dependent functional properties of lignin with infrared spectroscopy. *Ind. Crops*  
131 *Prod.* 20:205-218.
- 132 8. S Gunasekeran, S. Ponusammy (2005). Vibrational spectra and normal Coordinate  
133 analysis on organic non-linear optica crystals 3- methoxy-4-Hydroxy benzaldehyde.  
134 *Indian Journal of Pure and Applied physics* Vol. 43, November 2005, pp. 838-843.
- 135 9. Shamsuri A, D. K Abdullah. (2013). A Preliminary Study of Oxidation of Lignin from  
136 Rubber Wood to Vanillin in ionic Liquid Medium. *Oxidation Communications* 34, No 3,  
137 767-775 (2012).

138 10. Baptista C, Robert A, Duarte Ap. 2006. Effects of pulping conditions on lignin structure  
139 and delignification degree in Pinus Pinaster Kraft pulps, Bioresource Technology 121:  
140 153-158.

141 11. C. Glidewell, J.N. Low, M, Melguizo and A. Quesda, 4-Amino-2, 6-  
142 Dimethoxypyrimidine: hydrogen-bonded sheets of R22 (8) and R66 (28) rings, reinforced  
143 by an aromatic Pi-Pi stacking.

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UNDER PEER REVIEW