

SYNTHESIS OF VANILLIN FROM LIGNIN

ABSTRACT

The research involves the production of principal flavour chemical Vanillin from lignin using photocatalytic oxidation. Vanilla, a commercial crop, takes approximately 3 years to produce its first substantial fruits, subsequently, a small amount of green vanilla is produced every six months. To sustain the venture to its frustration, food manufactures therefore need alternative and self-sustainable sources of vanilla flavour. Synthesis of vanillin from lignin is a biological waste recycling process that utilises lignin; a major by-product of the paper and pulp industries. In this project, prior to production of the lignin, which is the main source of vanillin, spruce sawdust was obtained and prepared from wood pulp in the laboratory through Kraft extraction process. The lignin obtained was then analysed using spectroscopic analysis to ascertain that it is similar to the commercial lignin. The lignin was thereafter oxidised using nitrobenzene and the product analysed using FT-IR against its standard prepared from pure vanillin. Conclusions and recommendations were thereafter provided.

Key words: Vanillin, FT-IR and Lignin

INTRODUCTION

Vanilla is a flavouring obtained from the vanilla orchid. It is one of the widely used expensive spice after saffron (Hocking et al, 1997). This is because growing vanilla is labour intensive. Despite being expensive, vanilla still stands as a highly appreciated flavour. Vanilla is widely used for both commercial and domestic purposes including, aroma and food flavouring, baking,

25 complementary flavouring in chocolate; caramel; custard or coffee, perfumes, and aromatherapy.
26 The major word vanilla is the *Vanilla planifolia* species, commonly known as the Bourbon or
27 Madagascar vanilla, which originates from Madagascar and neighbouring islands in the
28 southwestern region of the Indian Ocean and Indonesia. Combined sources of the vanilla produce
29 about two-thirds of the world vanilla (Rose 2017).

30 Due to scarcity and the high cost of the vanilla extracted from natural sources along with its
31 popularity, there is increasing interest in the synthesis of the predominant component vanillin
32 from alternative greener sources. Vanillin is one of the most popular flavours, but less than 1%
33 of it comes from a mature vanilla orchid. Big food brands that vowed to only use natural flavours
34 in products marked are experiencing shortages due to an emerging shortage of vanilla.

35 Food and beverage flavour industries are looking forward to supplying alternative sources to
36 curb shortage of vanilla flavour and to sustain the venture. In addition, vanillin obtained through
37 synthesis is not considered a sustainable method of obtaining alternative flavouring. This
38 therefore call for a need of synthesis of vanillin from renewable sources. Application of this
39 method is considered greener and more sustainable.

40 **MATERIALS AND METHODS**

41 **Preparation of Samples of Pulp for The Experiment**

42 Kraft cooking process was performed. The specified conditions for the process were; 10 grams
43 of fine wood ash was weighed and white liquor prepared under the conditions of active alkali
44 charge of 25% Sodium hydroxide and Sulphidity of 30 % Sodium Sulphide by weight in the
45 ration of 3:1, that is, the white liquor. A white liquor (NaOH and NaS_2) to wood Ratio of 6:1 at
46 cooking temperatures of 140 for 2 hours. (Shakeri, 2013).

47 **Lignin Extraction and Preparation of Sample**

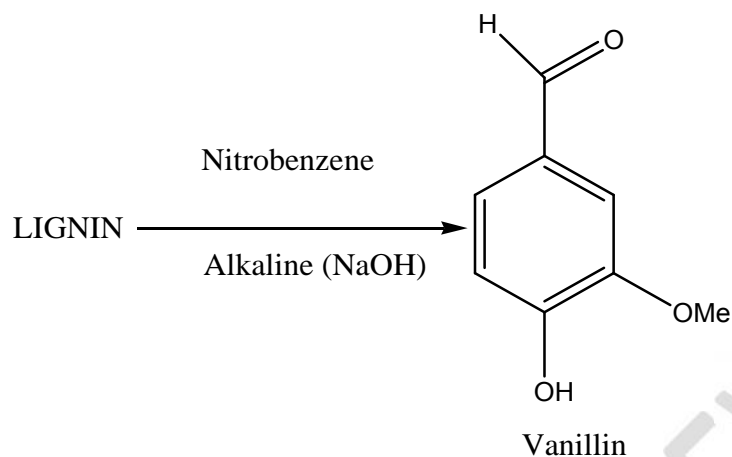
48 The black liquor was characterised by the pH value of about 13. In order to extract the lignin
49 component from the black liquor, dilute sulphuric acid (4 M, 22% by weight) was added to the
50 black liquor and agitated using a magnetic stirrer until the pH value reduced to 2. The pH value
51 of 2 was necessary to obtain an increased yield of extracted lignin (Mussato 2007). At this point,
52 the black liquor turned from black to brown resulting into a precipitate. The resulting precipitate
53 was then agitated for 1 hour. The Lignin mixture containing the lignin was filtered and washed
54 with 100 ml warm water to wash the excess sulphuric acid. The obtained product was dried at
55 100 °C for 30 minutes in a vacuum oven and then finely pulverized using a motor and pestle.
56 Without additional purification procedure, the pulverised product was tightly sealed and kept at
57 ambient temperature prior to use. A portion of the dried product was then subjected to FT-IR
58 analysis.

59 **Preparation of Vanillin with Nitrobenzene**

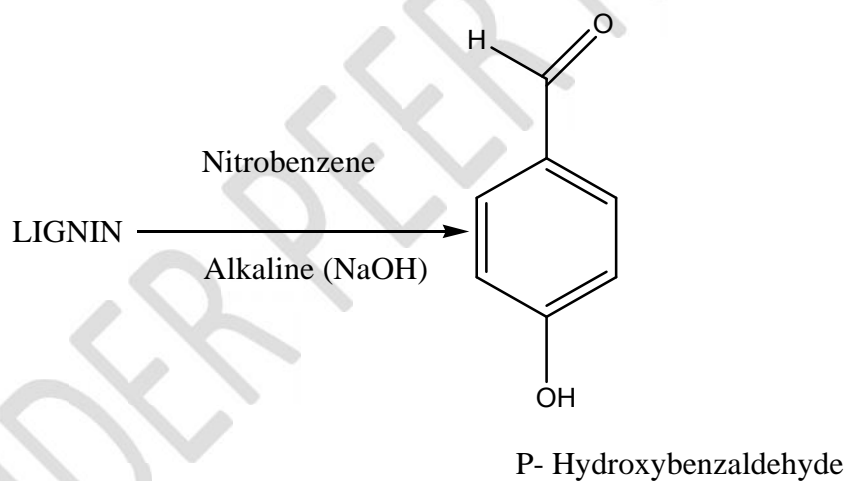
60 To the 0.2 grams of the oven dried lignin, 7 ml 2 M NaOH was added. 0.5 ml nitrobenzene was
61 measured and added to the mixture in a 500 ml round bottom flask. And refluxed at 170 °C for 3
62 hours. The combined organic phase was then evaporated in a fume chamber. The sample was
63 then transferred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

66 **RESULTS AND DISCUSSIONS**

67 Alkaline nitrobenzene oxidation of lignin resulted into the formation of vanillin.



68
 69 Figure 1: Proposed chemical equation for reaction of lignin and nitrobenzene to produce vanillin.
 70 Lignin from grasses contains p-hydroxyphenyl propane unit (R1=R2=H). Grassy plants,
 71 therefore, contain relatively small amounts of lignin approximately 15 % of the biomass.
 72 Oxidation of this lignin leads to the formation of a more complex aldehyde and hence it is not
 73 used for the case of oxidative production of vanillin.



74
 75 Figure 2: Proposed chemical equation for reaction of lignin and nitrobenzene to produce p-
 76 hydroxybenzaldehyde.
 77 Figure 3 below shows a picture of the formulated vanillin



Figure 3: formulated vanillin

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81 **FT-IR Lignin**

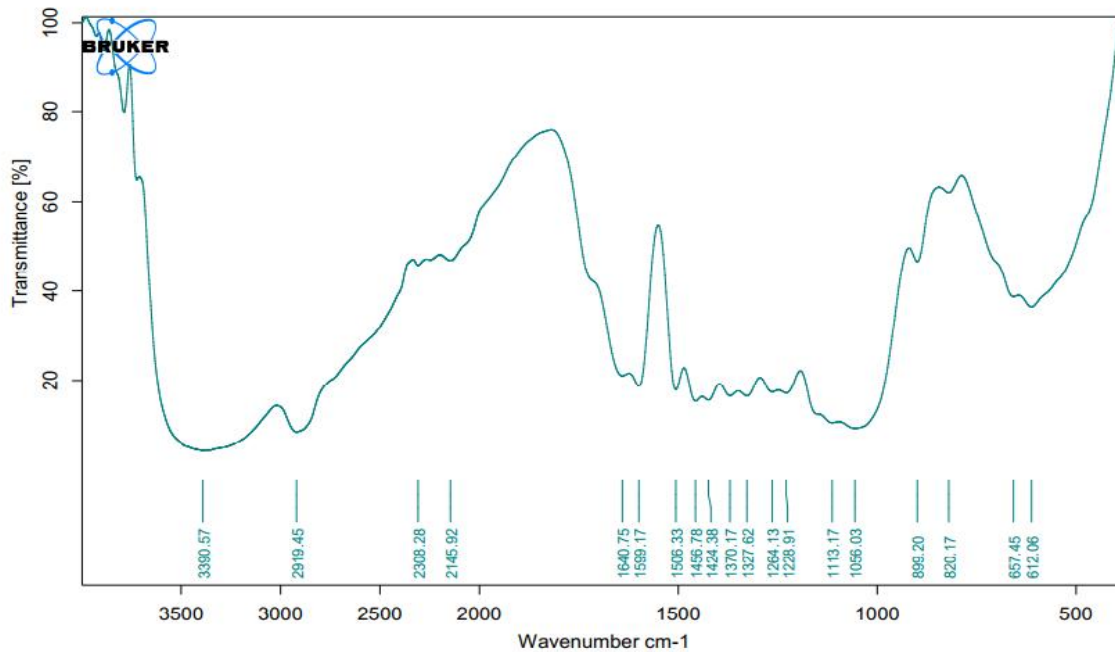
82 The purpose of FT-IR was to determine the functional groups present in the lignin. The analytes
83 were in powder/solid form. The obtained results were in frequency range of 4000 and 400 cm^{-1} .

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

86 known in order to develop new application. The most important chemical functional groups
87 present in lignin include methoxyl, hydroxyl, carboxyl and carbonyl in various proportions

88 depending on the process used to extract the lignin. The results obtained from the FT-IR analysis

89 of Kraft lignin were as follows;

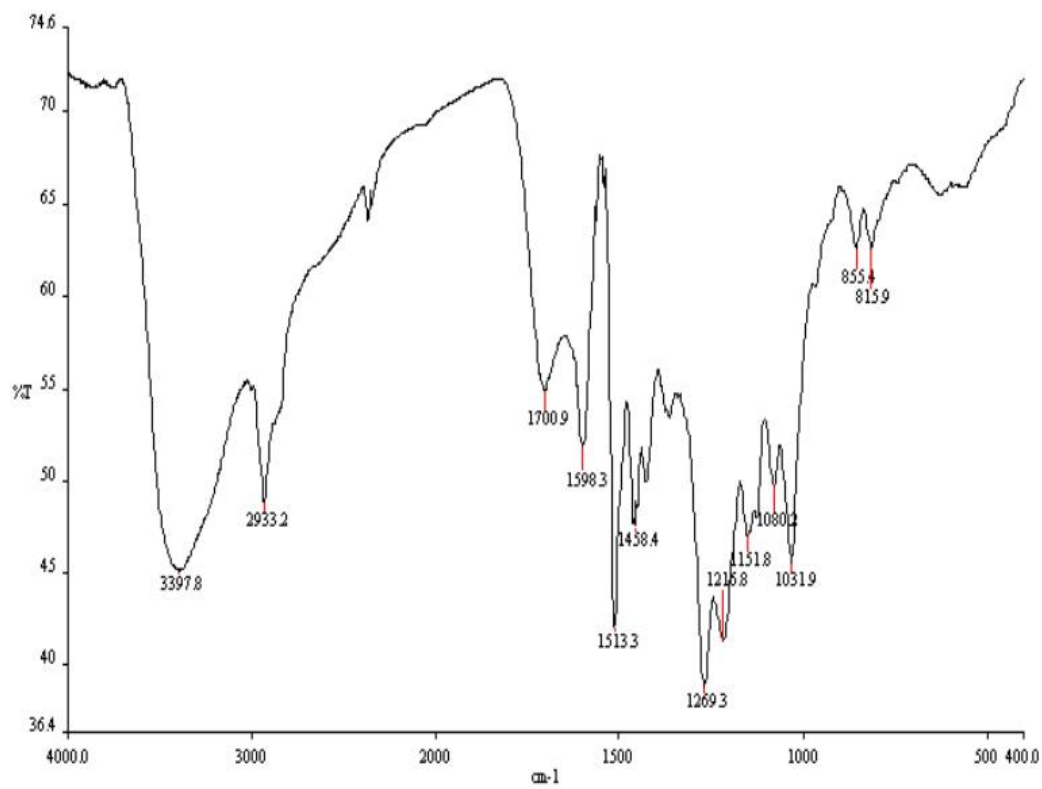


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92 *Figure 4: FT-IR Results for the Kraft Lignin.*

93 In the range of 3400 – 3100 cm⁻¹ are assigned to stretching vibrations of alcoholic, phenolic and
 94 OH group involved in hydrogen bonds. At 2919.45 cm⁻¹ of medium was assigned to the
 95 vibration of the methoxy group (-OCH₃). The range at 1599, 1506, 1424 were the aromatic ring
 96 vibrations / aromatic methyl group vibrations. The range 1113 was assigned to the vibrations of
 97 the C-H bond and C-O bond vibrations in the syringyl rings.

98 The range at 1056, 819 and the 820 could have been due to the presence of the guacyl group, C-
 99 H out-of-plane deformation, (-CH₂=CH₂) and C-H deformation and ring vibration. The weak
 100 intensity at 612 could have been due to the C-S stretching. The lignin revealed a very close
 101 resemblance to the lignin extracted from the Pinus eldrice (Shakeri et al, 2013).

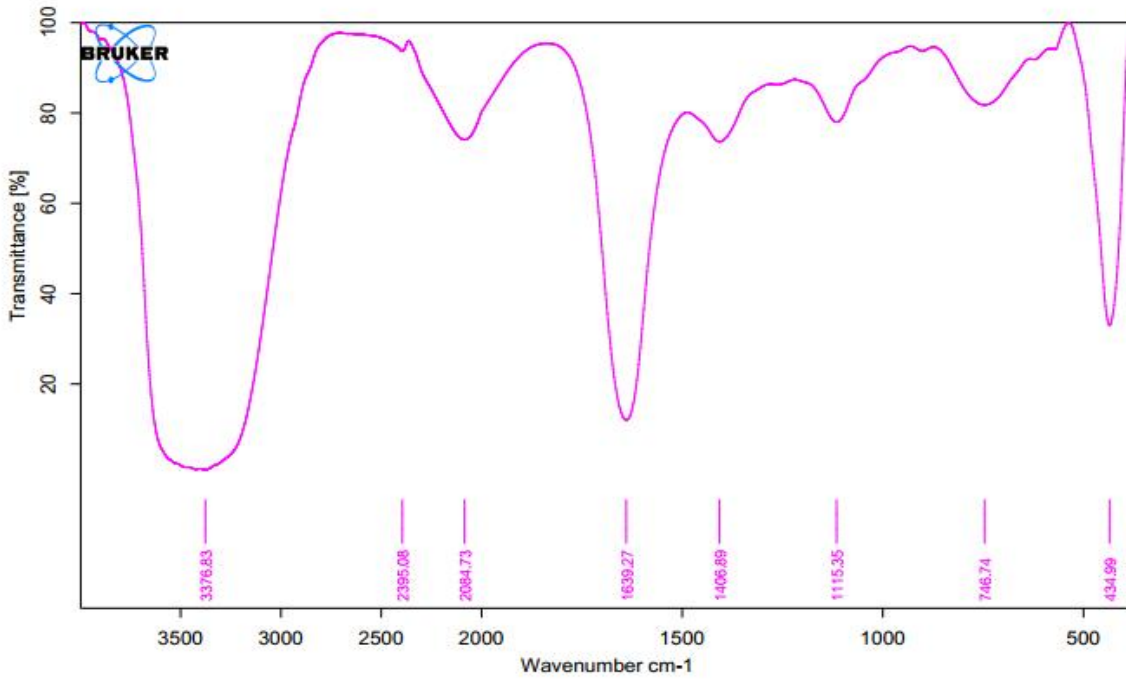


 103 *Figure 5: FT-IR Pinus eldarica Kraft lignin Lignin (Shakeri et al, 2013)*

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UNDER REVIEW

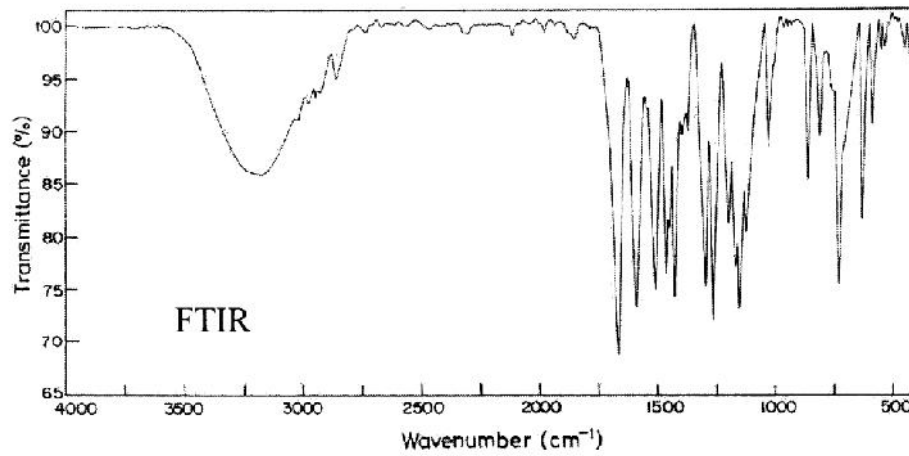
105 FT-IR Vanillin



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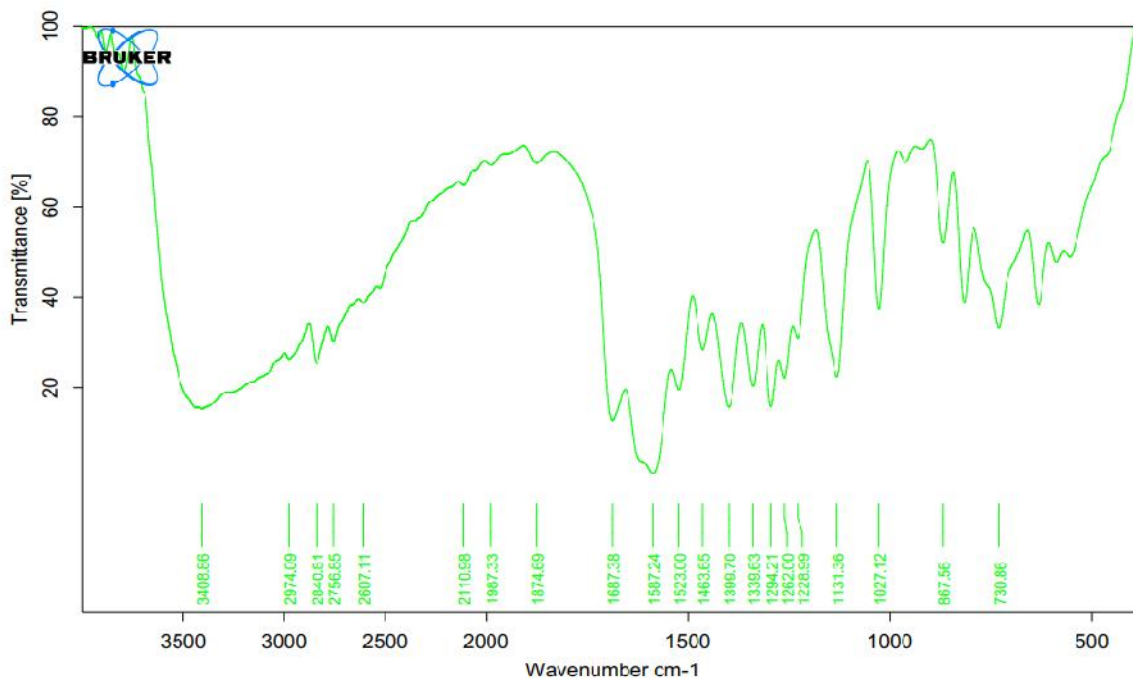
107 Figure 6: FT-IR Synthesized Vanillin

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110 Figure 7: Vibrational Spectra on an organic non-Linear Optical Crystal 3-methoxy-4-hydroxy benzaldehyde (Gunasekaran et
111 all, 2005)



112

113 *Figure 8: FT-IR Standard/ Pure Vanillin*

114 In this particular project, lignin was isolated from black liquor from wood saw dust. The lignin
 115 was thereafter oxidised in a controlled reflux heating system with nitrobenzene. The reaction
 116 system enabled for formation of vanillin from lignin as a result of oxidation of the coniferyl
 117 alcohol which has a similar resemblance to vanillin. The products were also formed in the
 118 process, however, for this project, identification of vanillin was important.

119 **Acknowledgement**

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