Original Research Article

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 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

Vanillinis 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).

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

MATERIALS AND METHODS

Preparation of Samples of Pulp for The Experiment

Kraft cooking process was performed. The specified conditions for the process were;10 grams of fine wood ash weighed and white liquor prepared under the conditions ofactive alkali charge of 25% Sodium hydroxide and Sulphidity of 30 % Sodium Sulphide by weight in the ration of 3:1, that is, the white liquor. A white liquor (NaOH and NaS_2) to wood Ratio of 6:1 at cooking temperatures of 140 for 2 hours [4].

Lignin Extraction

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

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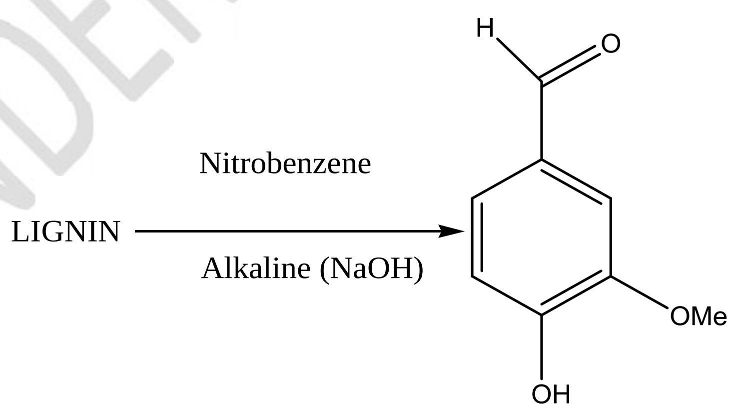
agitated for 1 hour. The Lignin mixture containing the lignin was filtered and washed with 100 ml warm water to wash the excess sulphuric acid. The obtained product was dried at 100 for 30 minutes in a vacuum oven and then finely pulverized using a motor and pestle. Without additional purification procedure,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

Preparation of Vanillin

To the 0.2 grams of the oven dried lignin, 7 mlof2 M NaOH was added. 0.5 ml nitrobenzene was measured and added to the mixture in a 500 ml round bottom flask and refluxed at 170 for 3 hours. The combined organic phase was then evaporated in a fume chamber. The sample was then transferred to a 50 ml volumetric flask and filled with methanol/water in the ratio 1:1. The solution was then filtered through a membrane filter of 0.45-micron pore size. The lignin oxidation product was then analysed using FT-IR and contrasted with the standards.

RESULTS AND DISCUSSIONS

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



Vanillin

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

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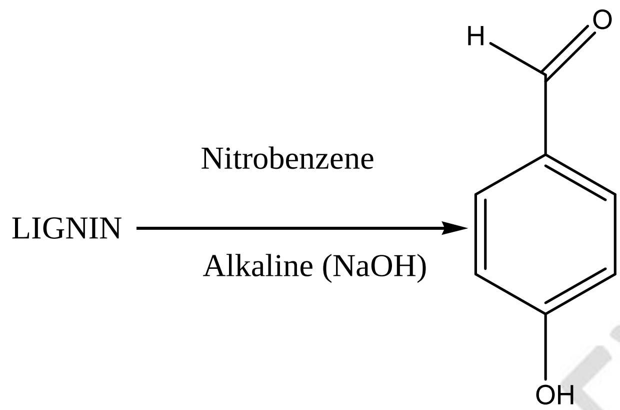
Lignin from grasses contains p-hydroxyphenyl propane unit (R1=R2=H). Grassy plants, therefore, contain relatively small amounts of lignin approximately 15 % of the biomass. Oxidation of this lignin leads to the formation of a more complex aldehyde and hence it is not used for the case of oxidative production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



P- Hydroxybenzaldehyde

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

Figure 3 below shows a picture of the formulated vanillin

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Figure 3: formulated vanillin

FT-IR characterization of obtained lignin

The purpose of FT-IR was to determine the functional groups present in the lignin. The analytes were in powder/solid form. The obtained results were in frequency range of 4000 and 400 cm^{-1}. Usually, the percentage of lignin in softwood is 30 % and 20% hardwood. In order to enhance the industrial application of lignin the precise structure as well as the functional groups has to be known in order to develop new application. The most important chemical functional groups present in the extractedlignin includedmethoxyl, hydroxyl, carboxyl and carbonyl. The results obtained from the FT-IR analysis of Kraft lignin were as follows;

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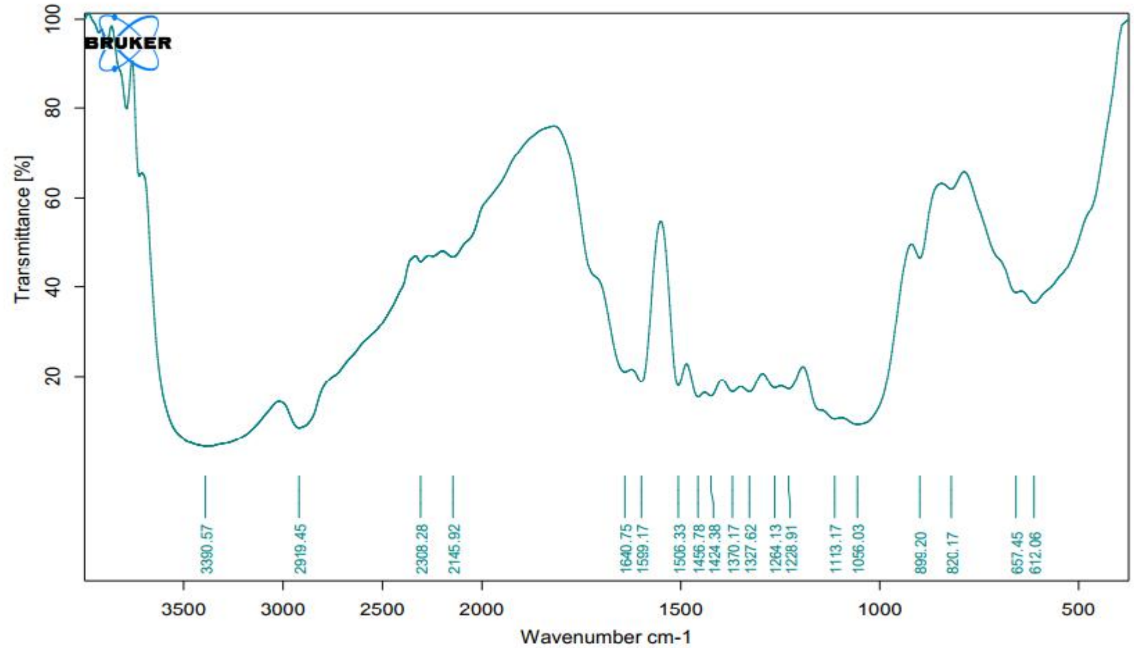

Figure 4: FT-IR Results for the Kraft Lignin.

The lignin revealed a very close resemblance to the lignin extracted from the Pinus eldrica [4] as in figure 5

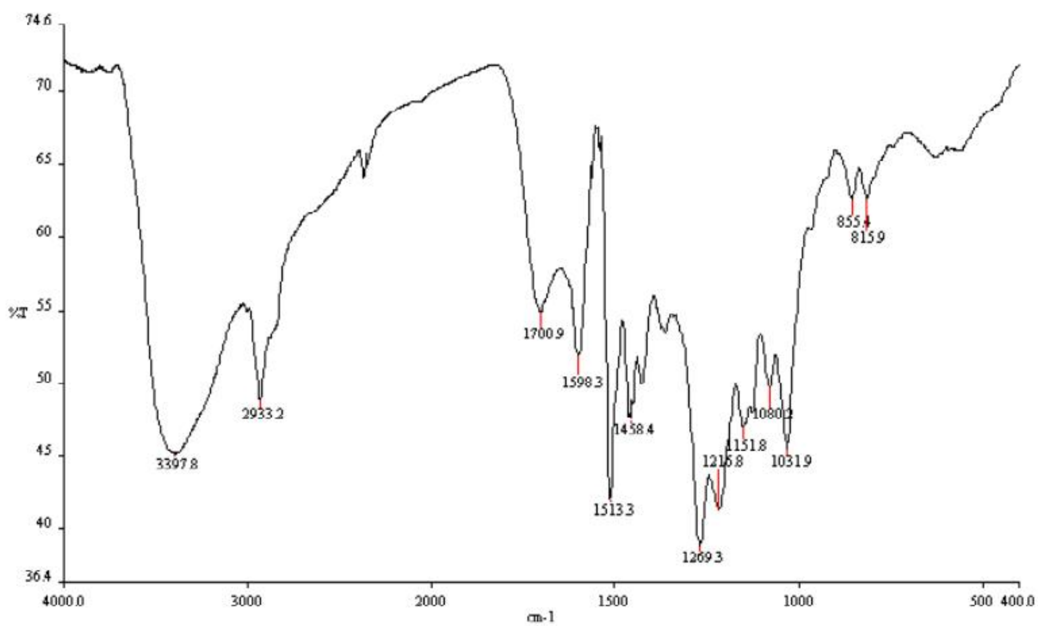

Figure 5: FT-IR spectra of Pinus eldarica Kraft Lignin [4]

FT-IR characterization of synthesised vanillin

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

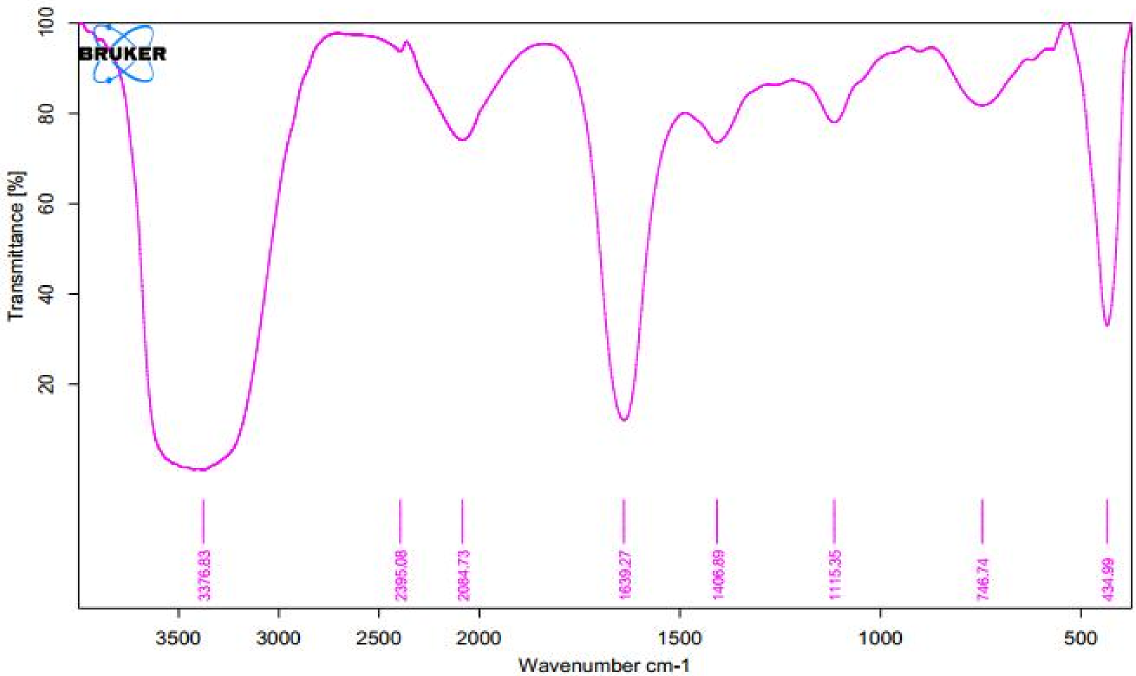

Figure 6: FT-IR spectra of synthesizedVanillin

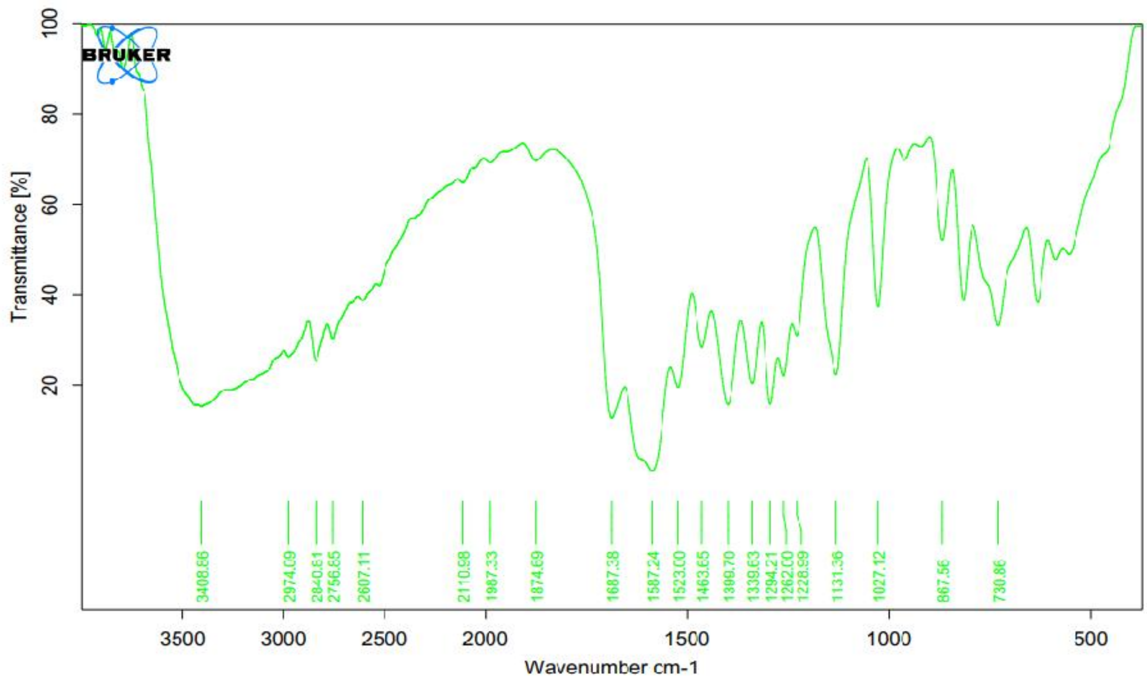

Figure 7: FT-IR Standard/ commercial vanillin

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

Conclusion

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

Acknowledgement

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