

Preparation of vanillin from lignin and lignified material

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SUMMARY

Experiments on alkaline Cupric Sulphate oxidation of Deodar (*Cedrus deodara*) Alkali lignins and saw dust are described for the preparation of Vanillin. Two sets of preliminary experiments were carried out separately to optimize experimental condition for high vanillin yield from Alkali lignin and saw dust. Estimation of Vanillin was done by a mixture of chromatographic and spectrophotometric techniques. Attempts were made to isolate Vanillin from the oxidation products mixture by carrying out large scale laboratory experiments. But only small quantity of Vanillin could be isolated in crystalline form.

Vanillin is the common name for 4-hydroxy-3-methoxybenzaldehyde. It was formerly called protocatechualdehyde-3 methoxy ether and vanillaldehyde. It is found widely in plant kingdom e.g. in vanilla beans, gum benzoin, Perubalsam and clove oil in trace amounts. It is mainly (85%) used as a flavouring agent in ice cream, candies, cookies, pudding, cake, soft drink etc and the rest (15%) is used in deodorants, perfumes and pharmaceuticals.

Today vanillin is principally manufactured from lignins, a by-product of pulp and paper industry, by hydrolysis and oxidation. Usually hydrolysis or alkaline oxidation is carried out under pressure at high temperature (150-200°C) for a period of 2-6 hours using lignins or lignins containing materials. Probably, V. Grafe in 1903 reported producing vanillin from lignins but systematic investigations started in 1927. Vanillin manufacture from lignin or lignins containing materials was delayed until 1936 for two very logic reasons viz.

1. Considerable technical handling difficulties and
2. A feasible scheme was lacking for utilizing lignin residue left over from vanillin manufacture without which vanillin manufacture is uneconomical.

Technical difficulties were later over come as revealed by the literature. And handling of 90% organic

matter left over from vanillin manufacture is used as binder for feed stuff pellets, ceramic and linoleum mastics and chelating material for industrial cleaners and dye. It is also used in cement making and soil amendments.

Tomlinson and Hibbert (1) obtained 2.6 g of vanillin per liter of waste sulphite liquor by alkaline hydrolysis. They reported that the yield per unit of lignin increased with an increase in sulphur content of the waste sulphite liquor.

In 1936 Salvo chemical corporation in co-operation with Marathon Paper Mills Wis. began manufacturing vanillin by alkaline hydrolysis of lignosulphonate basing its process on the patents of Howard *et al* (2,3,4). A year later Howard Smith chemical Ltd. Ont. began commercial production of vanillin from lignosulphonate by alkaline hydrolysis.

The use of cupric oxide as oxidant for lignin oxidation was first reported by Pearl (5). He reported 12-22% vanillin yield from Hemlock lignin on oxidation with Fehling solution. Later Pearl *et al* (6-10) did extensive work using precipitated cupric oxide. Fehling solution and alkaline copper sulphate to oxidize lignin and lignosulphonates of different origin.

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Freudenberg (11-12) found that the yield of vanillin increased substantially on oxidation with air or nitrobenzene as compared to alkaline hydrolysis. Vanillin yield was further increased by him on oxidation using catalysts such as cobalt and cupric hydroxides.

Chawla *et al* (13) have also reported vanillin preparation from deodar saw dust by cupric oxide oxidation. He has also reviewed the yields of vanillin, as reported in mostly patented literature, from lignin, lignosulphonates and saw dust in the same article.

EXPERIMENTAL

RAW MATERIAL : Deodar (*cedrus deodara*), alkali lignin is supposed to contain only *guaiacyl propane* building units which are responsible for vanillin production.

Alkali lignin was prepared by cooking chips in autoclave using 20% sodium hydroxide as Na_2O . Cooking temperature maintained was 170°C for 4 hours, while bath ratio was kept at 1:4. After cooking weak black liquor was acidified with dilute hydrochloric acid to precipitate lignin. Precipitate lignin was washed several times with water till free from chloride ions. Finally it was filtered off, dried and kept for further investigation.

Saw dust (—40+60 mesh) used was first extracted with alcohol-benzene (1:2) to remove extractives which otherwise might interfere in vanillin isolation.

OXIDATION PROCEDURE : The oxidation of alkali lignin or saw dust was carried out by placing reactants into a stainless steel bomb of 100 ml capacity immersed in water in an electrically heated and regulated autoclave. The mixture was heated to the desired temperature in one hour and kept at that temperature for varying intervals of reaction time. At the completion of reaction time the bomb was taken out from the autoclave after releasing the pressure of the autoclave. The contents of the bomb were removed and filtered. The cuprous oxide sludge and or saw dust was washed with water and the washing was mixed with filtrate. The filtrate was acidified with glacial acetic acid and extracted with solvent ether several times. The ether extract was concentrated first on steam bath and then under reduced pressure. The concentrated syrup was then dried in a vacuum desiccator and weighed. Experimental conditions are recorded in Table 1 and 2 separately for alkali lignin and saw dust.

ESTIMATION OF VANILLIN :

Vanillin was separated from other oxidation products by paper partition chromatography using benzene-water developer (14) Whatman No 1 filter paper, impregnated with 0.05 M Sodium tetraborate solution and dried in air, was used. The descending technique was applied for irrigation of the solvent. It took 6-hours for complete resolution of the products at 30°C . The developed chromatogram was viewed under an ultraviolet lamp. The presence of vanillin was indicated by violet fluorescent colour (also confirmed by the reference vanillin spots on left and right side of the chromatogram).

Vanillin containing band from the chromatogram was removed and cut into small pieces. Vanillin from these paper cuttings was taken out by eluting them with 50 ml of alkaline ethanol for 30 minutes. The absorbance of this solution was determined in an ultraviolet spectrophotometer at 352 nm wave length. The quantity of vanillin was directly calculated with the help of vanillin absorbance-concentration curve. Results of vanillin estimations are recorded in Table 1 & 2 (and also depicted in Figure 1 & 2) separately for alkali lignin and saw dust respectively.

TABLE—1 TOTAL ETHER EXTRACTS AND VANILLIN YIELD (ON LIGNIN BASIS) BY OXIDATION OF LIGNIN WITH ALKALINE CUPRIC SULPHATE

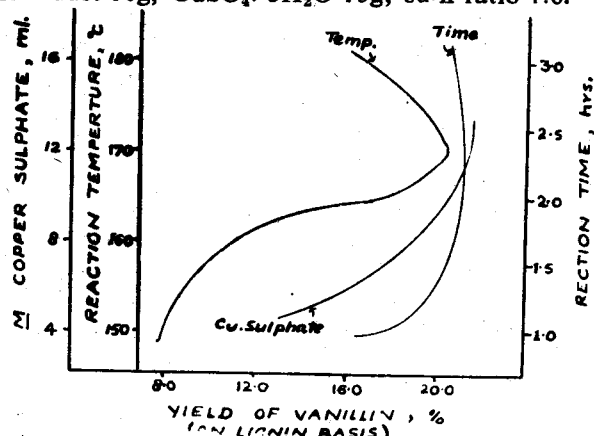
S.No.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (molar) ml	Time Hrs	Temperature $^\circ\text{C}$	Total yield %	Vanillin %
1.	5.0	1.5	170	18.4	14.6
2.	10.0	1.5	170	23.8	20.8
3.	12.5	1.5	170	24.2	21.4
4.	10.0	1.5	170	20.5	18.2
5.	10.0	1.6	170	23.8	20.8
6.	10.0	2.0	170	24.3	21.2
7.	10.0	3.0	170	24.0	20.8
8.	10.0	1.5	150	11.8	8.1
9.	10.0	1.5	160	14.1	11.6
10.	10.0	1.5	170	23.8	20.8
11.	10.0	1.5	180	21.1	16.8

Lignin 1g NaOH 1.5g, Sod. Pot. Tartrate 2g, Total Volume 80 ml.

TABLE -II VANILLIN YIELD (ON SAW DUST BASIS) BY OXIDATION OF SAW DUST WITH ALKALINE CUPRIC SULPHATE

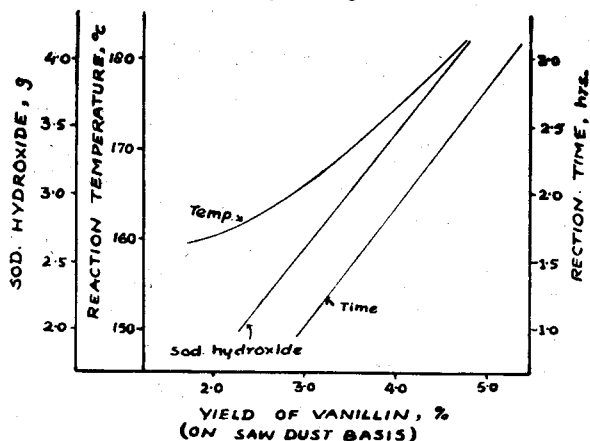
S.No.	NaOH (g)	Time (Hrs)	Temperature (°c)	Vanillin (%)
1.	2.0	1.5	170	2.3
2.	3.0	1.5	170	3.5
3.	4.0	1.5	170	4.6
4.	3.0	1.0	170	3.0
5.	3.0	1.5	170	3.8
6.	3.0	2.0	170	3.8
7.	3.0	3.0	170	5.3
8.	3.0	1.5	160	2.0
9.	3.0	1.5	170	3.5
10.	3.0	1.5	180	4.6

Saw dust 10g, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 15g, bath ratio 1:8.



(Lignin-1 g, sod. hydroxide-1.5 g, Total volume-80 ml.)

Fig. 1 : Vanillin yield by oxidation of lignin by alkaline copper sulphate



[Saw dust 10g, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 15g, bath ratio 1:8]

Fig. 2 : Vanillin yield by oxidation of sawdust by alkaline copper sulphate

VANILLIN ISOLATION

Various attempts were made to isolate vanillin from the oxidation products of deodar lignin or saw dust. Large scale laboratory oxidation experiments were carried out in rotary electrically heated and regulated digester to isolate vanillin in pure crystalline form from the oxidation products. Conditions of oxidation were as follows :

TABLE 3—LARGE SCALE OXIDATION CONDITION FOR LIGNIN AND SAW DUST

Parameters	Alkali lignin	Saw dust (Extracted)
Lignin Saw dust, g	100	300
Sodium Hydroxide, g	150	90
Copper Sulphate, g	250	450
Sod. Pot. Tartrate, g	200	—
Time at Max. Temp, hrs	1.5	1.5
Maximum Temp, °C	170	170
Total Volume, litre	4.0	4.0
Time to raise max. Temp, hrs	1.0	1.0

Isolation procedure of vanillin from the oxidation products is essentially the same in both the cases. Reaction mixture was taken out from the digester and filtered. The residue (saw dust and other reduction products) was washed with water and washing was mixed with the filtrate. Filtrate was acidified with dilute sulphuric acid to pH₃ and heated to 80°C. Hot acidified filtrate mixture was passed through sintered glass funnel to remove insoluble substances (impurities). Filtrate as well as the residue were extracted with benzene (three times). Both the benzene extracts were mixed and concentrated first by distillation followed by vacuum distillation. At the end water was added to the concentrated benzene extract for solvent exchange. The water extract was then heated to 85°C and filtered while hot. filtrate was treated with activated charcoal to remove colouring matters and other impurities. The content was again filtered while hot to remove charcoal and the filtrate thus obtained was concentrated under vacuum and then kept for crystallization in freezer for over night. It was noticed that very less quantity of vanillin was crystallized out as fine needles.

In another experiment vanillin water extract as obtained above was treated with sulphur dioxide gas in cold, to convert vanillin into its bisulphite form. The insoluble tarry mass was removed from the mixture by filtration. The clear solution was treated with sulphuric acid to precipitate vanillin. Crude vanillin thus obtained was separated from

the mixture by filtration. Finally crystallization was done by petroleum ether. Here also only a small amount of vanillin could be obtained in crystalline form.

Initially vanillin in crystalline form could not be obtained after repeated trials. We were getting strong fragrance of vanillin in the mixture or extract obtained from oxidation products but all trials of crystallization failed e.g., by methanol 50%, petroleum ether or hot water. The reason behind it was loss of vanillin during purification process.

RESULTS & DISCUSSIONS

It is seen (Table 1) that on increasing cupric sulphate, yield of vanillin is increasing. It is assumed that on further increase of cupric sulphate the yield may fall due to decrease in free alkali content taking part in the reaction. Alkali is also an important parameter in oxidation (Table 2) as on increasing alkali the yield is also increasing.

Vanillin yield is falling after attaining a maximum on increasing the time of oxidation (Table 1). It may be chiefly ascribed to the further oxidation of the vanillin already formed, and the subsequent conversion to compounds of greater affinity to water than the ether. In the case of saw dust (Table 2) increasing pattern of yield shows an incomplete oxidation at the optimum time used. Similarly vanillin yield decreased after attaining a maximum during the increase of the temperature of reaction (Table 1) which may again be due to further degradation of vanillin already formed. In the case of saw dust the increase in yield with the increase of temperature concludes that saw dust needs severe oxidation conditions than alkali lignin.

Quantitative isolation of vanillin in crystalline form could not be achieved due to loss of vanillin during the process of purification. It is noticed that activated charcoal absorbs vanillin and also there is great loss during solvent exchange for vanillin. Vanillin in very small amounts could be obtained when large scale laboratory experiments were carried out. Further experiments are needed to improve yield of vanillin.

Confirmation of vanillin crystal formed was done by I.R. Spectrophotometry and by checking mixed melting point.

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