Appendix B2

Pemisahan vanilin daripada lignin yang diekstrak daripada likuor hitam tandan kelapa sawit kosong dan pembuatan minyak wangi vanillin

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ABSTRAK

Kajian peringkat awal ini dijalankan untuk memisahkan komponen vanilin yang telah diekstrak daripada likuor hitam tandan kelapa sawit kosong menggunakan asid hidroklorik 20 % (v/v). Proses pengoksidaan nitrobenzena digunakan untuk memecahkan komponen lignin. Proses ini dilakukan dengan menambahkan 2M NaOH dan larutan nitrobenzena ke dalam bom keluli pada suhu 165 °C selama 3 jam. Hasil utama pemecahan komponen lignin ialah vanilin. Seterusnya, proses penyulingan vakum dilakukan untuk memisahkan vanilin daripada komponen lain. Hasil sulingan tersebut terdiri daripada vanilin dan komponen lain. Kemudian, hasil sulingan dianalisa melalui kromatografi cecair berprestasi tinggi (HPLC), kromatografi gas (GC) dan kromatografi gas-spektrum berat (GC-MS). Analisis tersebut membuktikan komponen yang dipisahkan ialah vanilin. Sebanyak 8.034 % vanilin diperoleh daripada setiap 1000 mg lignin. Kemudian, hasil sulingan vanilin ini digunakan sebagai bahan utama pembuatan minyak wangi. Selain itu, etanol dan air digunakan sebagai pelarut sewaktu pencampuran pelarut untuk menghasilkan minyak wangi vanilin. Minyak wangi vanilin dianalisa melalui spektrometri infra merah (FTIR). Keputusan penganalisaan menunjukkan minyak wangi telah homogen.

Kata kunci : tandan kelapa sawit kosong, likuor hitam, lignin, vanilin, minyak wangi vanilin

Vanilla From Black Liquor

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VANILLA, which is a favorite flavor among the cooks and chefs, originally comes from vanilla orchid or scientifically known as vanilla planifolia. The vanilla flavor actually comes from the fruit of this orchid. Mexican scientists pioneered the extraction of this flavor back in 1858. Since then the extraction method had been improved tremendously in order to produce vanilla at the commercial scale. The Lignin Research Team (LRT) of the Industrial Chemistry section has identified a new source of vanillin from pulping waste or better known as black liquor. The material used to produce pulp in this project is the oil palm empty fruit bunch (EFB).

The process of producing cellulosic pulp from EFB and other wood and non-wood fibers requires delignification with sodium hydroxide under pressure [1]. This process frees cellulosic fiber from EFB and produces a large quantity of black liquor that is discharged into surface water without effective treatments [2]. This research project aims to overcome EFB disposal problem at palm oil processing mills as well as produce a variety of lignin-based products such as drilling mud thinner, adhesive for wood and chipboard and the latest addition to the list is vanilla.

The EFB raw material used in this study was supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, a local company specializing in recycling EFB. The fiber was washed with water prior to pulping. EFB fiber was pulped by soda pulping in a 20 L stainless steel rotary digester (Ibsutek ZAT92) unit with 25% NaOH (cooking liquor) for 3 h at a maximum cooking temperature of 170 ÚC at a pressure of 10 psi, with a cooking liquor to EFB ratio of 10:1 by weight. The soda lignin was precipitated from the black liquor by acidifying it to pH 2 and recovered by filtration through Buchner funnel before drying in a vacuum oven at 55 ÚC for 24 h [3].

Nitrobenzene oxidation was carried out by adding 50 mg dry soda lignin into a mixture of 7 mL of 2 M NaOH and 4 mL of nitrobenzene in a 15 mL steel autoclave. The autoclave was sealed tightly with a screw cap fitted with Teflon gasket and heated to 165 °C for 3 h in a preheated thermostat oil bath. After the heating period, the autoclave was cooled with ice water. The mixture was then transferred to a liquid-liquid extractor for continuous extraction with chloroform (5 x 20 mL) to remove any nitrobenzene reduction product and excess of nitrobenzene. The oxidation mixture was acidified by concentrated HCl to pH 3-4 and further extracted with chloroform (5 x 15 mL). The solvent from the second chloroform solution was removed by using a rotary evaporator at 40 °C under reduced pressure to obtain the nitrobenzene oxidation mixture. The mixture was then dissolved into dichloromethane and made it up to 10 mL. High performance liquid chromatography (HPLC) was used to analyze the nitrobenzene oxidation mixture [4].

HPLC results presented in Table 1 indicate that vanillin is a major component in the EFB soda lignin. With around 10 % of lignin successfully extracted from black liquor, we could estimate that around 3-4 % vanillin can be isolated from each liter of black liquor used in this process. After further separation of the nitrobenzene oxidation mixture using crystallization technique, we finally obtained yellowish powder with a smell similar to vanilla. Now we are trying to prove that the yellowish powder is actually vanilla using several methods such as FTIR, GCMS and ^{13}C-FTNMR. The purity and toxicity studies of this product also need to be carried out as it originally came from black liquor, which is the waste from pulping that is currently discharged into surface water without effective treatments. We hope that in the near future, the vanilla ice creams that people buy from the markets originally come from black liquor!

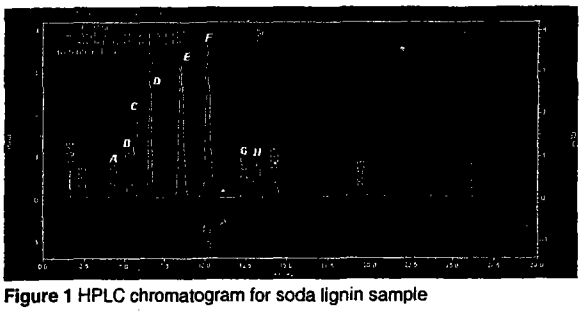

Figure 1 HPLC chromatogram for soda lignin sample

Table 1 Yield of degradation pruducts of the soda lignin by nitrobenzene oxidation

Oxidation peak	Oxidation product (%) w/w to the internal standard	RT	Yield (%)
A	*p*-Hydroxybenzoic acid (H_1)	4.3	0.64
B	Vanillic acid (V_1)	5.28	5.65
C	Syiringic acid (S_1)	5.6	4.92
D	*p*-Hydroxybenzaldehyde (H_2)	6.58	15.97
E	**Vanillin (V_2)**	**8.51**	**36.86**
F	*p*-Coumaric acid (B)	10.17	31.95
G	Syiringaldehyde (S_2)	12.42	3.69
H	Ferulic acid (C)	13.23	0.33

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