

Resumo

Estuda-se a produção de vanilina a partir de lenhina kraft de *Pinus pinaster*. A vanilina (4-hidroxi-3-metoxi-benzaldeído) é usada como flavorizante na indústria alimentar, aditivo em perfumes e desodorantes, precursor na indústria farmacêutica e aditivo na indústria de revestimento de zinco.

A vanilina era inicialmente obtida a partir das vagens de baunilha. Outras vias surgiram: oxidação da coniferina com CrO_3 e hidrólise ácida, isomerização do eugenol seguida de oxidação, transformação do guaiacol e oxidação de materiais lenhocelulósicos com nitrobenzeno.

A via mais importante de obtenção da vanilina é a oxidação da lenhina com oxigénio (ou ar). A indústria de celulose e pasta de papel é a principal fonte de lenhina: lenhina sulfito (ou lenhosulfonato do processo sulfito) e lenhina kraft (processo kraft).

Anualmente produzem-se 30 milhões de ton de lenhina sendo dois terços de lenhina kraft. Somente 6% de toda a lenhina produzida é recuperada e vendida. Há um mercado de 2 milhões de toneladas (sendo praticamente 20% de toda a lenhina sulfito produzida). A lenhina kraft gerada é queimada contribuindo para um bom equilíbrio energético do processo kraft. Contudo no caso de um aumento de produção limitada pela capacidade da caldeira é interessante obter produtos de alto valor acrescentado.

Construiu-se uma instalação para o estudo da oxidação da lenhina kraft de *Pinus spp.* com vista à produção de vanilina. Inclui um reactor que pode ser operado até 200°C e 12 bar. O sistema permite aquisição de dados de temperatura, pressão e caudal de oxigénio através de um computador IBM PS2/55. As amostras são recolhidas em um colector de fracções e são analisadas a concentração de vanilina por CG, a MWD da lenhina por HPLC e a alcalinidade.

A concentração de oxigénio dissolvido foi estimada por um modelo (modger) usando informações da literatura.

Foram usadas três fontes de lenhina: *Pinus spp.* (Westvaco), *Pinus pinaster* (Portucel) e lixívia negra (Portucel). A lixívia negra contém 14,4% de sólidos. Análise elementar e termogravimetria (TG) confirmaram a alta pureza da lenhina de *Pinus spp.* usada no estudo do processo.

A vanilina é produzida por oxidação da lenhina, mas não por hidrólise (120°C, 120 min). Atingiram-se rendimentos de 8% em relação a lenhina original. A temperatura aumenta geralmente entre 10 a 15°C durante a reacção. A pH inferiores a 12,5 a degradação da vanilina é mais rápida.

Uma boa condição para a oxidação da lenhina de *Pinus spp.* (Westvaco) situa-se em: 60 g. ℓ^{-1} de lenhina, 80 g. ℓ^{-1} de hidróxido de sódio, temperatura de 120°C (inicial), pressão parcial de oxigénio de 4,0 bar (inicial) e pressão total de 9 bar. O máximo rendimento é encontrado entre 45-70 min.

Um modelo cinético apoiado em mecanismos de reacções sugeridos na literatura é desenvolvido e simplificado com vista a obter a constante de velocidade de degradação da lenhina e a constante da velocidade de degradação da vanilina que é uma função do pH.

A concentração máxima de vanilina ($8 \text{ g. } \ell^{-1}$ para $60 \text{ g. } \ell^{-1}$ de lenhina) foi obtida pela oxidação com nitrobenzeno. A oxidação com oxigénio na presença de sais de cobre II não, melhorou a produção de vanilina.

A oxidação da lenhina de *Pinus pinaster* (Portucel) produziu $3,4 \text{ g. } \ell^{-1}$ para $82,5 \text{ g. } \ell^{-1}$ de lenhina e $4 \text{ g. } \ell^{-1}$ para $500 \text{ m } \ell$ de lixívia negra.

A actividade de células e enzima extraídas de *Acinetobacter anitratus* foi medida usando lenhina kraft da Portucel (precipitada ou presente na lixívia negra). Usou-se também álcool benzílico (um substrato modelo) e água oxigenada (co-substrato). A oxidação biológica conduziu à produção de veratraldeído. Foi estudada a sequência de tratamento químico mais biológico.

Ensaíram-se estudos de isolamento de vanilina do meio reaccional usando resina catiónica (Duolite C20 e Dowex 50W X8). Estudo de adsorção em reactor "batch" revelou um valor muito baixo de capacidade. Também foram realizadas experiências em leito fixo com alimentação em degrau (Duolite C20). Experiências com pulso (Dowex 50W X8) mostram eventualmente a exclusão da vanilina da lenhina.

Abstract

The production of vanillin to enhance the value of kraft lignin from *Pinus pinaster* was studied. Vanillin (4-hydroxy-3-methoxybenzaldehyde) is widely used as flavour. It is the most popular agent of this kind and can be found in ice-creams, candies, cookies, puddings, cakes, soft drinks. Others uses, like additive in perfumes and deodorants, pharmaceuticals precursor, and metal-plating industries (bath additive), as zinc electrodeposition, are also found.

Initially, vanillin was obtained from vanilla beans. With increase of its demand and consequently price, other routes of production have been studied. Oxidation by CrO_3 of coniferin and acid or enzymatic hydrolyze, isomerization of eugenol, followed by oxidation, transformation of guaiacol with Reimer-Tiemann, Gatterman, Fries, or modified Sandmeyer reaction are some examples of the several routes to obtain it. The oxidation of lignocellulosic materials by oxygen or other oxidants agents like nitrobenzene and CuO have been used too. The first route for lignin oxidation is the more important route to obtain vanillin.

Pulp and paper industries are the most important sources of quasi pure lignin, although it is known that original structure of lignin has been changed. There are mainly two types of lignin resulting from the sulfite process (lignosulfonate) and from the sulfate process (kraft lignin). The first process has been abandoned slowly, mainly because of higher pollution, and although new methods to obtain pulp and paper have been studied, the use of kraft process has grown.

About 30 million ton. of lignin are produced per year: almost two-third are kraft lignin and one-third are lignosulfonate. Only 6% of lignin produced is recovered and marketed. It was created an annual

market for about 2 million of ton (or 20% of lignosulfonate). Burning of kraft lignin has been environmentally acceptable and contributes to the nice energy balance of the pulp and paper process. Therefore, only if it is used to produce high added value (products or products with price higher than its fuel value), or in the case production capacity increase of the plant is limited by the boiler capacity.

An experimental set-up was built in order to study the oxidation of kraft lignin from *Pinus* spp. for the production of vanillin. It includes a reactor (glass cylindrical autoclave with stirrer) which was heated by circulating the silicone oil from thermostatic bath. Temperature, total pressure and, some times, oxygen flow were acquired by a IBM PS2/55 computer and samples were collected with fraction collector.

Vanillin concentration and other similar compounds was followed by gas chromatography (GC), after acidification and extraction with diethyl ether. The evolution of molecular weight distribution (MWD) of the samples of lignin was followed by high pressure liquid chromatography (HPLC). Alkalinity was followed by acid-base titration or pH measurement.

The oxygen concentration was estimated using a model (modger) created by using literature information. *Pinus* spp. lignin (Westvaco), *Pinus pinaster* lignin (Portucel) and black liquor with *Pinus pinaster* lignin (Portucel) were used in this study. Kraft black liquor with 14,4% of solids content (9,6% of organic and 4,8% of inorganic) were used in chemical and biological oxidation. Inorganic compounds were not eliminated by treatment with barium chloride. Humidities of *Pinus* spp. lignin and of *P. pinaster* lignin were equal (3,7%), but residues to 575°C were 2,8 and 28,2%, respectively. Elemental analysis (CHNS) and termogravimetry (TG) confirm the high purity of *Pinus* spp. (Westvaco) lignin. Therefore, it was chosen to study the process and the kinetics of oxidation with oxygen. Fourier transformed infra-red spectroscopy (FTIR) was not enough to measure vanillin concentration, when it was mixed with lignin. They showed similar absorption. Combustion energy of vanillin was very small as compared with coniferyl alcohol (lignin's precursor) and the lignins.

Vanillin was not found by hydrolysis (120°C by 120 min). Results with CG were confirmed by HPLC since MWD did not change. However, when oxygen was fed to the reactor (time zero), vanillin was produced with yield of 4 to 8%. MWD for sample with 40 min of oxidation showed an increase of compounds with molecular weight near vanillin. Vanillin was not detected after 90 min and the MWD did not change after this sample time.

Temperature increased generally 10-15°C as compared with initial temperature, before reaching the maximum vanillin concentration. The time to reach this maximum was lower as bigger was the temperature, oxygen partial pressure or total pressure. pH decreased with oxidation. Vanillin was consumed vary fast at pH lower than 12.5 therefore, high alkali concentration protects it. The increase of lignin concentration did not increase vanillin concentration in high concentration range (120 g. ℓ^{-1}).

A kinetic model was developed to allow understanding experimental results. The model considered the influence of pH in the vanillin degradation rate. The model fails in explaining the influence of lignin concentration in high concentration range and lower temperature (100-110°C). The maximum vanillin concentration (8 g. ℓ^{-1}) was determined by oxidation with nitrobenzene.

Oxidation of Pinus spp. lignin in presence of copper II salt did not increase the vanillin maximum production, but decreased the vanillin degradation. Oxidation with copper II salt did not produce high vanillin concentration.

Pinus pinaster (Portucel) produced $3.4 \text{ g} \cdot \ell^{-1}$ of vanillin by using 82,5 g of crude lignin and $4.0 \text{ g} \cdot \ell^{-1}$ by using $500 \text{ m} \ell$ of black liquor, which correspond the usual concentration of Pinus spp. (Westvaco).

The activity of Acinetobacter anitratus cells and ligninase enzyme extracted from bacteria was measure with kraft lignin from Pinus pinaster (precipitated or in black liquor). The activity of this intracellular enzyme was measured with model substrate (benzyl alcohol), showing a sigmoid Michaelis curve for constant H_2O_2 concentration. Enzymatic activity on treated black liquor leads to the production of low molecular weight compounds and to partial polymerization of lignin. Vanillin was not detected, but veratraldehyde was detected by thin layer chromatography.

Combined oxidation (in the sequence: chemical + enzymatic) was realized. Black liquor with additional NaOH ($40 \text{ g} \cdot \ell^{-1}$) was oxidized with oxygen ($120\text{-}138^\circ\text{C}$, oxygen partial pressure = 1.5 bar, total pressure = 2,5-4,5 bar). This reaction produced $1.2 \text{ g} \cdot \ell^{-1}$ ($0.9 \text{ g} \cdot \text{g}^{-1}$ of solids) of vanillin in 54 min of reaction. Two samples of chemical oxidation (43 min and 83 min) was incubated with enzyme (35°C , pH 6.2 with H_2O_2) for 0,6 and 20 hours. Vanillin produced by chemical reaction was not detected after enzymatic incubation.

Isolation of vanillin from reaction medium was studied by batch adsorption using cationic exchange resins (Duolite C20 and Dowex 50W X8). However the adsorption capacity is very low. Fixed bed experiments using step changes in concentration were carried out with Duolite C20 resins; pulse experiments (with Dowex 50W X8) showed eventually exclusion of vanillin from lignin.