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Chemical modification of lignocellulosic materials by irradiation with Nd-YAG pulsed laser

V.R. Botaro[a,*], C.G. dos Santos[a], G. Arantes Júnior[a], A.R. da Costa[b]

[a]*Departamento de Química, Instituto de Ciências Exatas e Biológicas (ICEB), Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, CEP 35400-000, Ouro Preto, MG, Brazil*

[b]*Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, CEP 35400-000, Ouro Preto, MG, Brazil*

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Abstract

Most reports about modification of lignocellulosics are mainly based on chemical modifications such as specific reactions on hydroxyl groups of cellulose. In this work, we describe the irradiation of Whatman 5 filter paper, microcrystalline cellulose and organosolv lignin with Nd-YAG laser pulses at 1064 nm. The chemical and structural properties of the degraded products were investigated by using FTIR and UV spectroscopies, conductimetrical and SEC analyses. While irradiation affects molar mass and polydispersity of lignin, no detrimental effects caused by Nd-YAG laser treatments were observed for cellulose samples. These results demonstrate that Nd-YAG laser can be used as a practical and selective degradation tool, opening a new field for obtaining surface modified natural fibers. © 2001 Published by Elsevier Science B.V.

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1. Introduction

A great variety of fibers has been employed in new composite materials and a very special class of these materials includes those obtained by using natural fibers as reinforcing elements in synthetic polymer matrices. For any kind of composite, though, one of the major problems have always been the lack of compatibility between the reinforcing agent and the polymeric matrix.

For cellulose fibers, one option to increase this compatibility is to modify their surface characteristics in order to make them structurally more similar to traditional synthetic polymers. Most reports found in the literature relate to grafting reactions onto cellulose hydroxyl groups [1]. In this context, reagents such as anhydrides and isocyanates have been broadly used [2]. Modifications involving corona discharge or plasma sources have also been reported [3].

The use of laser irradiation in such modification processes, however, is less common [4,5]. Energy densities up to 10 J m^{-2} can be achieved depending on equipment characteristics. A very fast and efficient local heating is one of the main possibilities of a laser

* Corresponding author. Tel.: +55-31-3559-1717; fax: +55-31-3559-1707.
E-mail address: botaro@iceb.ufop.br (V.R. Botaro).

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operating in a pulsed mode [6]. The incidence of laser pulses onto the surface for long periods may cause evaporation of the treated material and even the ejection of small molecules to the vapor phase. Otherwise, in the context of conservation or artworks and documents, laser cleaning of ancient papers is another increasingly research branch due to all aspects related to cultural heritage conservation. Conventional dry and wet cleaning have proved inadequate in several cases such as brittle papers and sensitive inscripts. This work aims at investigating the effects of Nd-YAG laser to some lignocellulosic samples and how this treatment affects some parameters such as lignin polydispersity.

2. Experimental

All experiments were carried out with a Q-switched Neodymium-YAG laser under conditions listed in Table 1. An experimental set-up is shown schematically in Fig. 1.

For all essays, the voltage was fixed in 1400 V and relative humidity inside the laboratory was maintained around 60%. All samples were irradiated for 90 s inside a chamber so that all emerging gases could be recovered for further analysis.

Table 1
Data of the laser apparatus

Type	Nd-YAG laser
Wavelength	1064 nm
Energy pulse (100%)	500 mJ
Length type	Cylindrical or spherical
Focusing length	$F = 50$ mm
Fluence	1.8–4.0 kJ cm^{-2}
Repetition rate	10 Hz
Pulse duration	4 ns
Spot diameter	4–6 mm

2.1. Samples

The lignin used in our studies was an organosolv acetone/water lignin of sugar cane supplied by DEDINI. The cellulose was an industrial microcrystalline Avicell and Whatman 5 filter paper. Sugar cane bagasse was previously washed in water (60°C) for 24 h and dried before being mechanically sieved. The fraction used was recovered from the sieve of 60 mesh.

2.2. Discs preparation

Discs of 1 mm thickness and 110 mm in diameter were pressed under 1000 kg during 15 min in order to have flat surfaces for the experiments. This procedure was critical for the reproducibility of the experiment,

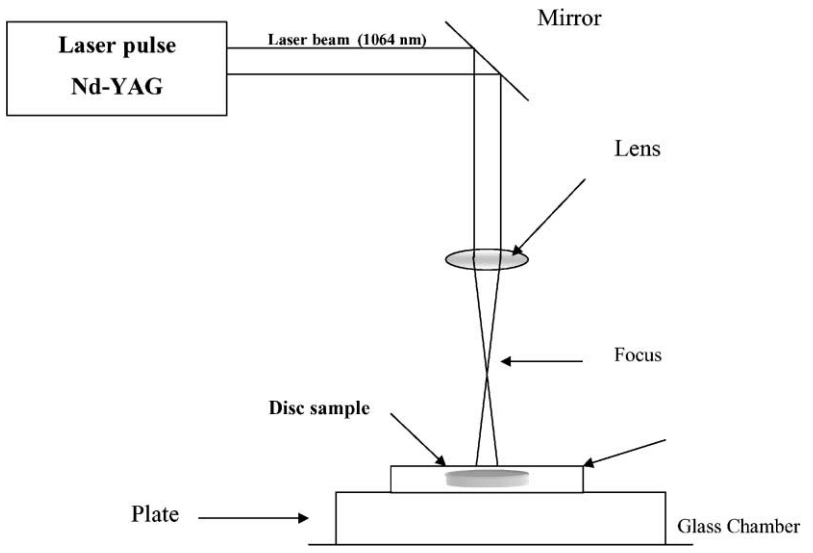

Fig. 1. Experimental set-up.

Table 2
Experimental data of SEC analysis

SEC parameters	Data
Solvent	THF (HPLC grade)
Flow	1.0 ml/min
Detection system	Ultraviolet at 254 nm
Columns	PS-gel in series: Shimadzu — 823 and 8025
Injection volume	15.0 μl
Concentration of the sample	5.0×10^{-3} g/ml

which was assured by a constant energy density upon the irradiated surfaces.

2.3. Conductimetry

Lignin (0.5 g) was added to a mixture of acetone/ethanol/water in proportions of 3:6:9 in volume, respectively. The mixture was titrated with a standard NaOH solution (0.500 mol l^{-1}), while variations in conductivity were monitored. The temperature was maintained at 20°C during the analyses.

2.4. SEC analyses

SEC traces of lignin were obtained from THF solutions. Polystyrene standards were used to build a calibration curve using the universal calibration method. Experimental conditions for SEC analyses are listed in Table 2.

2.5. UV analyses

UV spectra of aqueous solution of lignin fragments were run on a HP 3453 Spectrometer in the 200–400 nm range.

3. Results and discussion

3.1. Energy density dependence of vaporized materials

When Whatman 5 paper or microcrystalline Avicell were irradiated by Nd-YAG laser pulse, no visual modification was observed. On the other hand, when lignin was irradiated, a considerable amount of vaporized materials was released as a white cloud and changes in the aspect of lignin discs were apparent. This difference in behavior is related to the way lignin absorbs the incident photons. The energy supplied by the absorbed photon excites the electronic structure of the lignin. Its relaxation may subsequently proceed by emission of heat or light, by photolysis, by undergoing a chemical change within the lignin macromolecule or by transfer of energy to another atom or molecule. Gravimetrical analyses confirmed those possibilities and, in Fig. 2, one can see the ensuing weight loss for different energy densities applied.

It is important to observe the substantial weight loss of lignin samples as opposed to the cellulose discs with total absence of weight loss. An intermediate situation was obtained for discs prepared with fibers of sugar cane bagasse containing approximately 20% weight of lignin in its structure. It is known that incident laser light possess a great amount of energy and only the energy absorbed by the substances can cause chemical modifications. From our results, only lignin showed fast absorption of energy and considerable weight loss to the vapor phase. Ether linkages such as α-O-4 and β-O-4 might be responsible for those specific absorption of energy, causing the degradation of its structure.

3.2. SEC analysis

The change in molecular weight of lignin before and after laser irradiation are noticeable (Table 3). Not only the average molecular weight decreased, but also the molecular weight distribution became narrower after the laser treatment (Fig. 3).

The low molecular weight fragment and also the partial degradation of high molecular weight fragments of lignin are the most important parameters to explain this decrease in molar mass of the irradiated lignin. The laser degradation process produces a decrease of M_w value and an increase of M_n value of irradiated sample promoted by a lignin structure degradation and vaporization of low molecular weight fragments. It is noteworthy that this is a fast and

Table 3
SEC data for organosolv lignin and irradiated sample

Lignin	M_n (average)	M_w (average)	Polydispersity
Organosolv	4600	13,402	2.9
Irradiated	5761	12,115	2.1

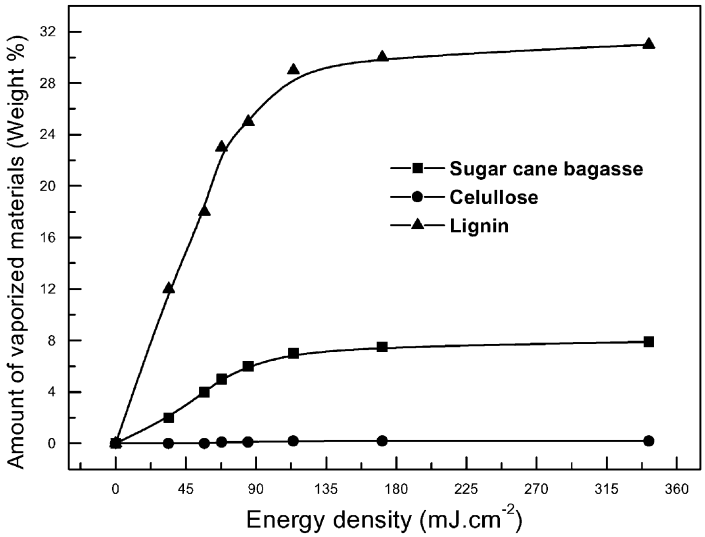

Fig. 2. Weight loss dependence of treated materials with energy density provided by laser pulses.

simple treatment that allows one to obtain very homogeneous lignin samples.

3.3. UV analysis

The presence of aromatic units was indicated in the UV spectra by an absorption band around 278 nm for the sample collected from the vapor evolving from discs during irradiation.

A strong absorption band at 278 nm is an indication of an increase of water-soluble fraction (Fig. 4). Degradation of lignin after laser treatment gives rises do smaller fragments, increasing the amount of water-soluble material.

Conductimetric data of the determination of phenolic hydroxyl groups show an increase of phenolic OH percentage after the irradiation. This behavior can be attributed to the breaking of α and β-O-4 ether bonds in the lignin macromolecule. This corroborates the data obtained by SEC analyses which showed a decrease in the molar mass of the lignin after irradiation (Fig. 5). Finally, the results are also in accordance with the data

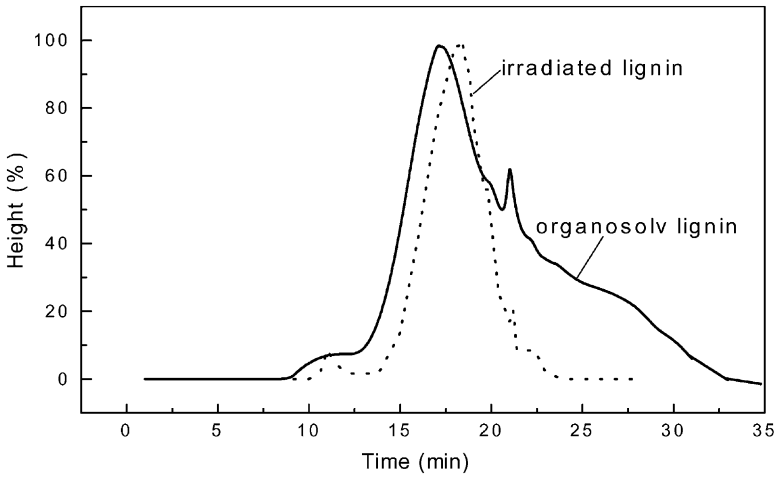

Fig. 3. SEC traces of organosolv lignin and irradiated sample.

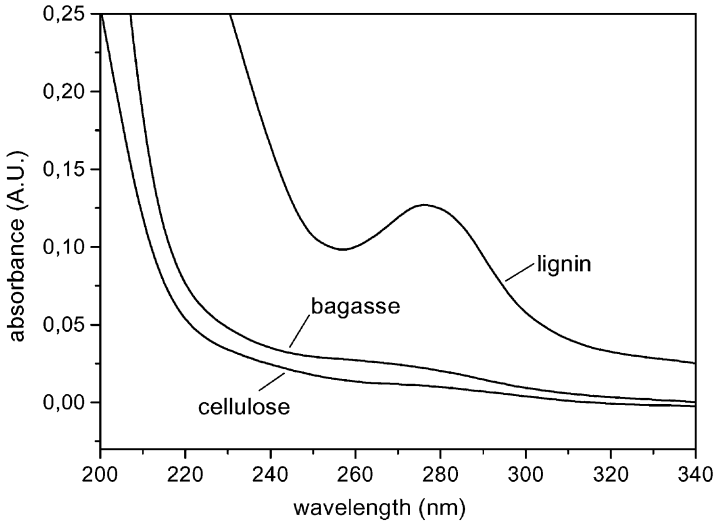

Fig. 4. UV analysis of vapor collected during lignin discs irradiation.

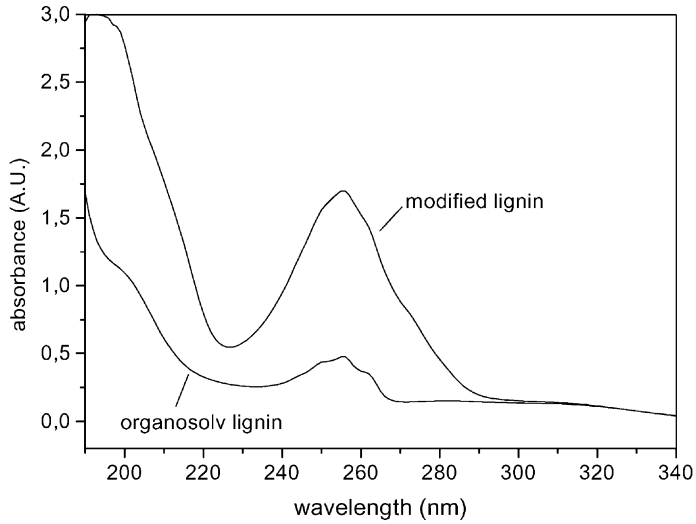

Fig. 5. UV analysis of water-soluble materials from organosolv lignin and irradiated sample.

Table 4
Conductimetric data for organosolv lignin and irradiated sample

Sample	Mass of lignin	Mass of phenolic OH (g)	Phenolic OH (%)
Organosolv lignin	0.330	0.033	10.0
Modified lignin	0.330	0.046	14.0

obtained by UV analyses regarding larger solubilization of the lignin in water after irradiation process, due to the presence of smaller fragments (Table 4).

4. Conclusions

Nd-YAG pulsed laser is an excellent tool for structural modification and treatments of lignocellulosic

materials. Lignin suffers great weight loss and structural changes due to irradiation process, while degradation effects on cellulose samples appear to be negligible. The polydispersity of lignin after the treatment is smaller than the untreated sample. This methodology is interesting because it points to a cleaner and simpler technology when compared to solvent extraction or preparative size exclusion chromatography.

Acknowledgements

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