NEW TECHNOLOGIES FOR THE VALORISATION OF LIGNIN AND PRODUCTION OF VANILLIN OR VANILLIC ACID

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ABSTRACT

Researchers at the **University Institute of Electrochemistry** at the University of Alicante have developed devices and methods for the **recovery of lignin** using photocatalysts and continuous electrocatalysts, respectively. The aim is to obtain **high added-value chemical compounds** such as vanillin or vanillic acid from lignin, which is present in plant biomass, in a more sustainable and economical way than nowadays.

The group is looking for companies in the emerging **biorefinery** sector with an interest in the valorisation of lignin or the use of bio-derived compounds such as vanillin or vanillic acid in the formulation of **pharmaceuticals, cosmetics and fragrances**.

INTRODUCTION

Currently, around 95% of organic compounds for industrial use **originate from petroleum**. Therefore, discovering alternative and renewable sources of these petrochemical compounds is crucial to ensure a sustainable economy.

Lignocellulosic biomass contained in agricultural and forestry residues has established itself as a potential source of petrochemicals for two main reasons:

1) its abundance, as it is considered to be the largest source of carbon that does not compete with food reserves.

2) its chemical composition, consisting of a carbohydrate fraction that is densely packed with a biopolymer, which constitutes the **lignin** fraction.

Biorefineries are now able to process the carbohydrates into biofuels, while the lignin is discarded and used as a lubricant or low-grade fuel.

However, **lignin**, given its composition rich in aromatic units, might become a source of aromatic compounds with high added value, provided that efficient strategies for its valorisation are available.

For years, there have been a wide variety of methodologies to recover lignin, i.e. by fragmenting it and releasing the aromatic units that compose it, but they are **energy-intensive**, which increases the cost and environmental impact, and also depends on **aggressive treatments** that irreversibly alter the nature of the aromatic compounds.

In this sense, the use of **photocatalytic systems** to carry out lignin fragmentation has recently been proposed. These systems allow a more selective fragmentation to be carried out, working under ambient conditions and using only **solar energy** to activate the process.

However, to date, only **batch reactors** have been described where the photocatalysts are dispersed in a reaction medium containing the lignin. These batch reactors have **disadvantages** for scale-up, mainly because:

a) The reactor must be completely stopped after each reaction to extract the contents of the system and isolate the reaction products.

b) Additional processes need to be implemented to recover the catalyst after each reaction.

On the other hand, the use of **electrochemical systems** has also been proposed to carry out the electro-oxidative fragmentation of lignin, with the advantage of simply using electricity as a reagent, which simplifies the purification of the products. Electrodes based on nickel metal have shown the best performance, but this means that the operating currents have to be kept at modest values to avoid degradation of the products, slowing down the valorisation process and limiting the fragmentation efficiency.

In response to these limitations, two inventions have been proposed. The first one presents a novel continuous-flow **photocatalytic reactor**, which eliminates the problem of photocatalyst recovery by immobilising the photocatalyst in the reactor, and offers the possibility of selectively obtaining **vanillin from lignin**. The second demonstrates a highly efficient **electrochemical reactor** that operates at high currents, comparable to those of conventional electrolysers for water electrolysis, selectively producing **vanillic acid** from lignin.

TECHNICAL DESCRIPTION

The present technologies solve the problems described above by providing a continuous **lignin fragmentation** process without the need to stop the system and with high selectivity. In addition, both technologies stand out for their low cost, as they do not rely on energy-intensive processes or expensive catalysts and work under ambient conditions, as well as for their potential for scale-up, given the simplicity of the technology.

Briefly, the flow photocatalytic method for selective lignin fragmentation comprises:

1) Immobilising a photocatalyst on a support, and introducing the support with the immobilised photocatalyst (bed) into a radiation-transparent column.

2) Continuously circulate a lignin solution through the column loaded with the bed, under illumination, to cause the fragmentation of the lignin, obtaining vanillin.

On the other hand, the lignin electro-oxidation method comprises coating anodes with metal electrocatalysts of a specific composition to selectively fragment the lignin and preferably produce vanillic acid.

ADVANTAGES AND INNOVATIVE ASPECTS

MAIN ADVANTAGES OF THE TECHNOLOGY

- **Lignin is not degraded** and therefore the intrinsic structures that can be useful to industry are not lost, unlike traditional valorisation methods, but is **selectively fragmented** to release high **value-added aromatic compounds** such as vanillin and vanillic acid.
- The materials used as photocatalyst or electrocatalyst are **low cost**.
- **Additional catalyst recovery steps are eliminated**.
- The use of a photocatalytic method or electrocatalysts for the production of vanillin or vanillic acid makes the **production of these compounds cheaper** compared to the extraction of natural vanillin or its production from biotechnological processes.

INNOVATIVE ASPECTS

- The photocatalytic valorisation of lignin **occurs continuously**, i.e. the photocatalyst is neither dissolved nor dispersed in the liquid in which the lignin is found, which also allows the process to be scaled up.
- These photocatalytic systems work under ambient conditions and use only **solar energy** to activate the process, i.e. no oil.
- The electrochemical system allows the lignin to be electro-oxidised and vanillic acid to be generated as the main product at **high industry-relevant working currents**.

CURRENT STATE OF DEVELOPMENT

The technology is at an important stage of development, with a **prototype** currently in the validation phase.

MARKET APPLICATIONS

Its most direct application is in the emerging **biorefinery** sector where the aim is to valorise lignocellulosic biomass. Currently, although strategies are available to recover the carbohydrate fraction contained in lignocellulosic biomass, the lignin fraction is ruled out due to the lack of a technology that allows it to be depolymerised in a controlled and economically competitive manner.

Vanillin and vanillic acid are among the most attractive products of lignin fragmentation due to their field of application. Thus, both compounds are an essential component in the formulation of **pharmaceuticals, cosmetics and fragrances**.

COLLABORATION SOUGHT

We are looking for companies interested in acquiring this technology for **commercial exploitation** through patent licensing agreements or for the development of the technology and its adaptation to the specific needs of their activity.

INTELLECTUAL PROPERTY RIGHTS

These technologies are protected by **two patent applications**:

- *Patent title: "Método fotocatalítico de flujo para la fragmentación de lignina" and "Método para la fragmentación electro-oxidativa de lignina con catalizadores de níquel y cobalto"*
- *Application number: P202431062 y P202431063.*
- *Application date: 17/12/2024*

MARKET APPLICATION (2)

Pharmacology, Cosmetics and Ophthalmology
Chemical Technology