



## Full Length Article

# Valorization of steam-exploded wheat straw through a biorefinery approach: Bioethanol and bio-oil co-production



E. Tomás-Pejó<sup>a,1,\*</sup>, J. Feroso<sup>b,1,\*</sup>, E. Herrador<sup>a</sup>, H. Hernando<sup>b</sup>, S. Jiménez-Sánchez<sup>b</sup>, M. Ballesteros<sup>a,c</sup>, C. González-Fernández<sup>a</sup>, D.P. Serrano<sup>b,d</sup>

<sup>a</sup>IMDEA Energy Institute, Biotechnological Processes Unit, 28935 Móstoles, Spain

<sup>b</sup>IMDEA Energy Institute, Thermochemical Processes Unit, 28935 Móstoles, Spain

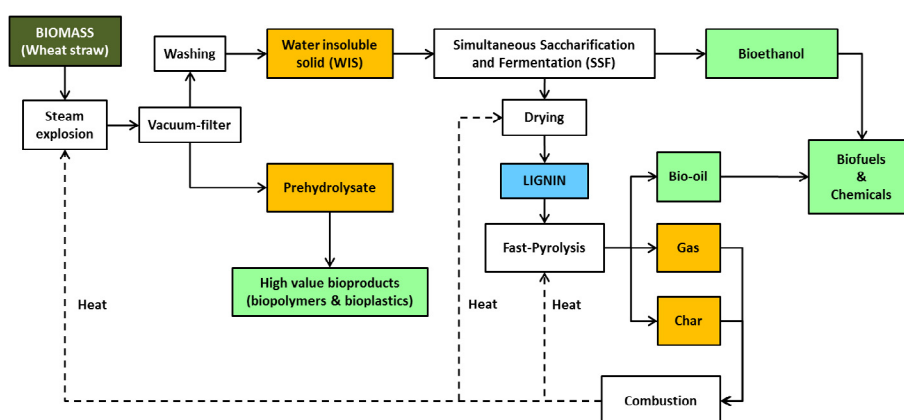
<sup>c</sup>CIEMAT, Biofuels Unit, 28040 Madrid, Spain

<sup>d</sup>Rey Juan Carlos University, Chemical and Environmental Engineering Group, ESCET, 28933 Móstoles, Spain

## HIGHLIGHTS

- A washing step makes the material more easily fermentable by thermotolerant yeasts.
- Combined fermentation and fast-pyrolysis maximizes mass and energy yield to biofuel.
- Co-production of bioethanol and bio-oil is an promising option for lignocellulose.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The potential of co-producing two different biofuels from a lignocellulosic substrate (wheat straw), according to a biorefinery concept, has been investigated. For such a purpose, simultaneous saccharification and fermentation (SSF) from the hemicellulosic and cellulosic fractions was performed for maximizing bioethanol production. The non-washed water-insoluble solid (WIS) fraction from the pretreated wheat straw totally inhibited the production of ethanol by *Kluyveromyces marxianus* independently of the inoculum size. In contrast, when using washed-WIS, higher ethanol productivities at 24 h of SSF were attained when increasing the inoculum size from 1 g/L to 3 g/L. The residual lignin from the bioethanol process was transformed by fast-pyrolysis into bio-oil that can be further converted into other biofuels or biochemicals.

Thermal fast-pyrolysis of the residual lignin fraction produced 31.9 wt% of bio-oil\* (water free basis) mostly composed by oxygenated aromatics coming from the lignin monomers (guaiacol-, syringol- and phenol-derived compounds). On the other hand, catalytic fast-pyrolysis of the residual lignin fraction over HZSM-5 zeolite was used as preferentially promoted decarbonylation and cracking of the primary vapours.

\* Corresponding authors.

E-mail addresses: [elia.tomas@imdea.org](mailto:elia.tomas@imdea.org) (E. Tomás-Pejó), [javier.feroso@imdea.org](mailto:javier.feroso@imdea.org) (J. Feroso).

<sup>1</sup> These authors contributed equally to this work.

Coupling both processes significantly enhanced the production of liquid products from lignocellulose, improving the efficiency in the use of the raw material. In this way, compared to a simple process of bioethanol production, this approach allowed to increase the mass and the chemical energy yields 1.9 and 1.7-fold, respectively.

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## 1. Introduction

In future scenario for 2040, the International Energy Agency foresees a continuous world dependence of fossil fuels as energy source, implying a 1/5 increase in CO<sub>2</sub> emissions [1]. This fact will provoke, if no preventive measures are taken on time, an increase in the global average temperature of 1.3 °C up to 4.0 °C by the end of XXI century. The Intergovernmental Panel on Climate Change (IPCC) considers that with the aim of limiting the temperature increase to 2 °C, no more than 1000 Gt of CO<sub>2</sub> can be release from 2014 forward. Therefore, urgent actions should be taken to direct energetic and productive systems towards safe and environmental friendly routes to produce biofuels. In this context, biorefineries have emerged in recent years as attractive alternatives for the co-production of energy and bioproducts with minimum waste generation [2].

In order to achieve prices that can be competitive with those of conventional fuels, production cost of biofuels still needs to be reduced. One way to achieve this goal is the use of widely distributed low-cost raw materials. In this context, lignocellulosic sources, widely available as agricultural and forestry wastes, are considered a promising choice. Furthermore, owing to its particular structure, in addition to the well-known process of bioethanol production from carbohydrates, lignocellulosic biomass can be employed to obtain a wide spectrum of chemicals.

Among different lignocellulosic raw materials, wheat straw is very suitable for liquid biofuels production [3,4]. The production of 1 kg of wheat grain entails the generation of 1.1 kg of straw [5] and according to the Food and Agricultural Organization (FAO), 715 million tonnes of wheat straw were produced in 2013 worldwide [6]. Taking into account the wheat straw already used for animal feeding and soil maintenance, about 60% of the world production is still available for energy purposes [7].

Several studies have already been published proving the effectiveness of using wheat straw for producing bioethanol by means of separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF) processes [8,9]. Independently of the strategy used, the biomass pretreatment is a crucial step to increase the enzyme accesibility to cellulose and hemicellulose being the steam explosion one of the most widely employed [10]. Steam explosion is based on a hydrothermal reaction in which the biomass is subjected to pressurised steam for a period of time ranging from seconds to several minutes, and then suddenly depressurised. This technology combines mechanical and chemical effects due to the hydrolysis (autohydrolysis) of acetyl groups present in hemicellulose. Steam explosion process shows some advantageous features when compared to other pretreatment methods. These include the significantly lower environmental impact, higher energy efficiency, possibility of using high chip size, unnecessary addition of acid catalyst (except for softwoods), high sugar recovery and high hydrolysis yields in the following enzymatic hydrolysis [10]. However, the main drawbacks encountered during steam explosion are the partial hemicellulose and lignin degradation which leads to the formation of inhibitory compounds that affect negatively enzymes and microorganisms. Major inhibitors are furan derivatives, mainly 5-hydroxymethyl furfural (HMF) and furfural, weak acids and phenolic compounds. These soluble inhibitors

are present in the liquid fraction of the steam-explosion pretreated material together with most of the xylose and thus, their separation by filtration is an straightforward method to diminish their negative effect. In a lignocellulosic biorefinery, this liquid fraction has been proposed to be employed to obtain biopolymers or bioplastics by means of different microorganisms [11,12].

*Kluyveromyces marxianus* strains have lately appeared as promising fermenting microorganisms for bioethanol production [13,14]. *K. marxianus* is a thermotolerant yeast that can ferment sugars at temperatures close to the optimum for enzymes which implies higher hydrolysis yields and consequently, higher ethanol concentration in the SSF. Furthermore, the use of thermotolerant yeasts in SSF leads to other advantages such as the reduction of cooling costs and contamination risks, as well as the continuous ethanol removal [15]. Among all possible strategies for producing ethanol from wheat straw, SSF processes with *K. marxianus* have shown very promising results, reaching ethanol yields up to 0.40 g/g [16].

With the current emphasis of lignocellulosic bioethanol, increasing reserves of lignin are expected to be available in short-medium term as a by-product of this process [17]. Due to the polyaromatic structure of lignin, this by-product appears as an interesting alternative resource for aromatic chemicals and building-blocks such as phenols, but also as raw material for the production of advanced fuels and additives [18,19]. Nevertheless, hardly 2% of the produced lignin is commercially used nowadays for low-value products such as dispersing or binding agents while the rest is used as energy source for direct combustion [20].

In this sense, the conversion of lignin into biofuels/biochemicals via thermal and catalytic fast-pyrolysis is envisaged as a promising approach [18,21,22]. Lignin, however, is more difficult to be depolymerized and produces more residual char than cellulose and hemicellulose [21,23,24]. Several works have been dealt the valorization of lignin through fast-pyrolysis [18,23,25]. Some of them are related to simple thermal processes [26,27], while others refer to catalytic fast-pyrolysis [18,21–23,26,28–30]. In this way, different zeolites, such as HZSM-5 [18,21,22,28–30], have been shown very effective catalysts in the pyrolysis of lignocellulosic biomass, allowing the removal of oxygen from the thermal bio-oil through three deoxygenation pathways: decarbonylation (CO), decarboxylation (CO<sub>2</sub>) and dehydration (H<sub>2</sub>O).

There are a few examples in the literature related to the valorisation of the residual products after the bioethanol process. Lignin recovered after ethanol production from corn stover and rice straw was used for pyrolytic production of phenolic compounds [31]. On the other hand, residuals from starch-based ethanol production were used to produce bio-oil by catalytic liquefaction [32]. However, to our knowledge, this is the first time that lignin residue from steam-pretreated wheat straw is studied to co-produce an alternative liquid biofuel (i.e. bio-oil).

In the present work, *K. marxianus* CECT 10875 has been used to produce bioethanol from the water-insoluble solid (WIS) fraction of pretreated wheat straw. The effects of implementing a washing process to remove the inhibitors and increasing the inoculum sizes are studied for maximizing the bioethanol production. On the other hand, the residual lignin has been studied as raw material for thermal and catalytic (over HZSM-5 zeolite) fast-pyrolysis.

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