Applied Catalysis B: Environmental 145 (2014) 43–55

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Microwave-assisted depolymerisation of organosolv lignin via mild hydrogen-free hydrogenolysis: Catalyst screening

Ana Toledano [a], Luis Serrano [a], Antonio Pineda [b], Antonio A. Romero [b], Rafael Luque [b,*], Jalel Labidi [a,**]

[a] *Environmental and Chemical Engineering Department, University of the Basque Country, Plaza Europa, 1, 20018 Donostia-San Sebastián, Spain*
[b] *Departamento de Quimica Organica, Universidad de Cordoba, Ctra Nnal IV-A, Km 396, E-14014 Córdoba, Spain*

ARTICLE INFO

Article history:
Received 7 August 2012
Received in revised form 9 October 2012
Accepted 14 October 2012
Available online 23 October 2012

Keywords:
Organosolv lignin
Hydrogenolysis
Lignin depolymerisation
Heterogeneous catalysis

ABSTRACT

Lignin depolymerisation to simple aromatics was investigated by using a mild microwave-assisted approach. The reaction was catalysed by different supported metal nanoparticles on mesoporous Al-SBA-15 including -nickel (2, 5 and 10 wt.%), palladium (2 wt.%), platinum (2 wt.%) and ruthenium (2 wt.%). Three main products were indentified in the proposed lignin valorisation protocol, namely a bio-oil, a bio-char and a fraction of residual lignin. These have been characterised by means of several techniques including GC–MS, MALDI-TOF, HPSEC and elemental analysis in order to evaluate the extension and mechanism of the selected depolymerisation approach. In this work, the objective has been the maximisation of bio-oil yield as well as its content in phenolic monomeric compounds. All tested catalysts exhibited improved results as compared to the blank depolymerisation (without catalyst), demonstrating a synergetic effect of metal nanoparticles in lignin hydrogenolysis. The most abundant phenolic products observed in most studied catalysts have been solvent derived products such as diethyl phthalate and butyl-octyl phthalate ester. Interestingly, phenolic compounds derived from lignin were also obtained including mesitol and syringaldehyde as well as desaspidinol and aspidinol, depending on the utilised solvent in the systems. The bio-oil obtained was primarily composed of monomers, dimers and trimers. Biochar yield was relatively high in most cases (>35% in some cases) due to existing oligomerisation reactions under the investigated conditions except for the case of the use of formic acid which gave no biochar in the process. Residual lignin content was often high and repolymerisation was observed in some cases. The catalyst containing 10 wt.% nickel was confirmed to achieve the highest lignin depolymerisation degree, with a maximum yield of 30% bio-oil after a short time of reaction (typically 30 min of microwave irradiation).

1. Introduction

Lignin is a natural phenolic macromolecule present in vegetal cell walls comprising of three main phenylpropane units, namely guaiacyl alcohol (G), syringyl alcohol (S) and *p*-coumaryl alcohol (H) [1]. Lignin has a highly complex structure which consists of a 3D randomised net linked to hemicelluloses (LCC), functioning as a biological barrier and as glue to retain linked hemicelluloses and celluloses. Tonnes of lignins are readily available from the pulp and paper industries and such quantities are expected to increase by the implementation of second generation bioethanol plants. Profiting from its unique structure in nature, lignin holds a significant potential to be valorised to produce phenolic platform chemicals. In view of these premises, lignin valorisation practises to produce high added value phenolic compounds have recently attracted a great deal of attention from the scientific community.

A wide range of chemical transformations can be envisaged to produce aromatic compounds from lignin. These have been generally based on two main approaches: *oxidation* and *hydrotreating* (hydrogenolysis) related protocols [2,3]. In some cases, degradation with enzyme cocktails have also been described [4]. However, depolymerisation processes are often not well understood. Taking a look at general methodologies and recently reported protocols, there are two main considerations that should be taken into account for lignin valorisation purposes, which most of the literature reports have generally overlooked to date. These include (1) a maximisation of the activity of the catalyst under the chosen conditions (as mild as possible), bearing in mind the bulky nature of this recalcitrant biomass source and (2) most importantly repolymerisation and self-condensation capability of lignin under processing conditions (due to the formation of radicals [5] and/or C—C bond forming self-condensation reactions in acidic media [6]) which may eventually lead to a complex pool of poorly

---

[*] Corresponding author. Tel.: +34 957211050; fax: +34 957212066.
[**] Corresponding author. Tel.: +34 943017178; fax: +34 94301714.
E-mail addresses: q62alsor@uco.es (R. Luque), jalel.labidi@ehu.es (J. Labidi).

0926-3373/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2012.10.015

controllable re-condensed aromatics as demonstrated by several groups worldwide [2,5–7]. In other cases, depolymerisation is more or less achieved giving a series of relatively simple aromatics under generally harsh reaction conditions (high hydrogen pressures, temperatures >400 °C) with low yields to products (<50%) [2,3,6,8,9]. Another important aspect to consider is the addition of hydrogen in the systems, which is generally not avoided or controlled in most cases and could lead to an undesirable partial or complete hydrogenation of the aromatic rings in the presence of metal sites [10]. This will contribute not only to a poor hydrogen economy of the methodology but also to less interesting and low value compounds [11].

The use of oxidants and/or oxidising protocols is in principle totally undesirable as the presence of radicals will lead to partial re-polymerisation of lignin and thus to more complex structures. In contrast, reactions under hydrotreating conditions may favour quenching and recombination of radicals, minimising lignin repolymerisation side reactions while maximising C—O bond cleavage. Previous work and results in this field point to a general consensus in catalytic hydrogenolysis methodologies as a valuable approach to unravel structural features of lignin through the production of lignin degradation products [12].

In any case, the design of a system able to work under mild reaction conditions without the addition of molecular hydrogen (e.g. the use of hydrogen donating solvents) will offer a significant advantage to improve the green credentials of the process. The hydrogen-donating effect of certain solvents (e.g. tetralin) in the hydrocracking of kraft lignin was established by Connor et al. in the early 80s [13]. The advantages of tetralin as hydrogen-donor solvent included a high boiling point as well as the swift and efficient generation of hydrogen under hydrocracking conditions which leads to the formation of naphthalene, a relatively stable compound. In Thring's proposed approach, phenols, guaiacols, syringols, catechols and aldehydes were obtained as major products from lignin [14].

In this work, we disclose a novel microwave-assisted mild hydrogenolytic methodology to depolymerise organosolv lignin from olive tree pruning into simple phenolic compounds. With this purpose, a range of catalysts based on metal supported nanoparticles on mesoporous acidic aluminosilicate supports (Al-SBA-15) with typical metal loadings of 2 wt.% have been prepared using a novel mechanochemical approach developed in our group [15]. Nickel catalysts were also tested at higher concentrations (5 and 10 wt.%).

The bifunctional catalysts were rationally designed from a fundamental understanding point of view to maximise lignin depolymerisation under the investigated conditions. These include (1) the maximisation of the accessibility and activity of the metal sites (supported metal nanoparticles synthesised by ball milling have been proved to predominantly deposit in the external surface of a support being highly active and accessible even at very low loadings [15]) as well as (2) the minimisation of repolymerisation and related side reactions (by using a mild hydrogenolytic approach under reducing conditions that can in principle quench radicals and unstable intermediates formed during depolymerisation) which avoids, at the same time, the addition of hydrogen in the systems. Al-SBA-15 was chosen as support due to its good (hydro)thermal stability, large surface area (useful for the deposition of nanoparticles) and most importantly combination of moderate Brönsted and Lewis acidity which is a pre-requisite to promote dealkylations, deacylations and related chemistries involved in the production of simple aromatics generated in lignin valorisation practises [6].

2. Materials and methods

2.1. Lignin isolation

Olive tree pruning (*Olea eurpoea*, variety Arróniz) was utilised as feedstock to isolate lignin. The treatment for lignin extraction consisted on the digestion of the feedstock in a mixture of ethanol–water (70 wt.%) at 200 °C for 90 min (previous optimised conditions [16]) in a pressure reactor. The liquid fraction (where lignin was dissolved) was separated from the solid fraction by filtration. Dissolved lignin was isolated by precipitation with two acidified portions of an aqueous solution (pH around 2). The suspension was centrifuged at 4000 rpm for 20 min to recover lignin which was then dried at 50 °C. Organosolv olive tree pruning lignin possessed the following composition: acid insoluble

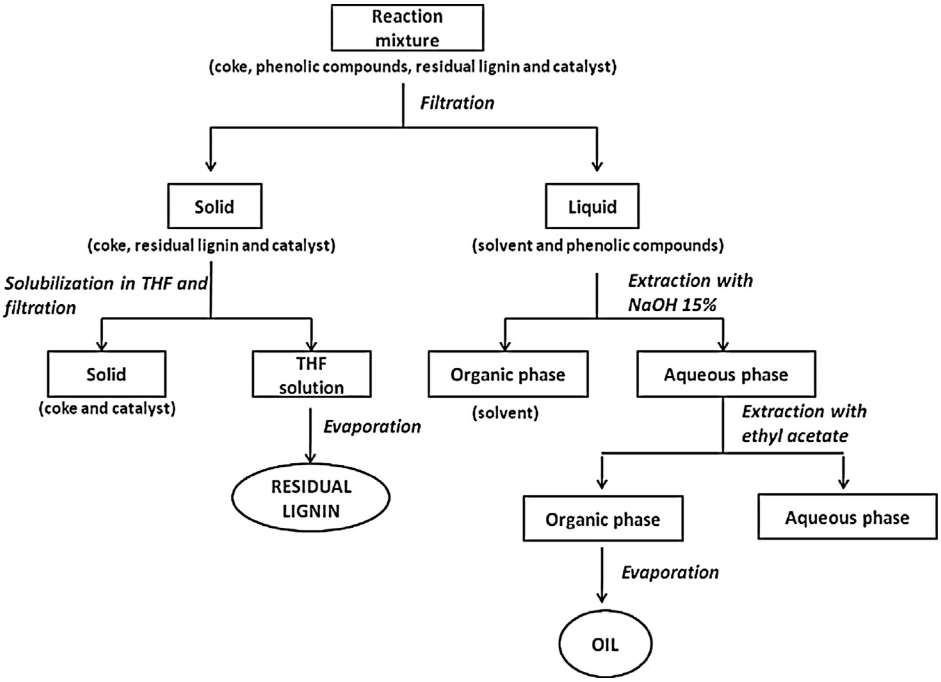

Fig. 1. Reaction mixture separation procedure.