Catalysis Today 309 (2018) 18–30

Contents lists available at ScienceDirect

Catalysis Today

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

Green catalytic processing of native and organosolv lignins

B.N. Kuznetsov[a,b,*], N.V. Chesnokov[a], I.G. Sudakova[a], N.V. Garyntseva[a], S.A. Kuznetsova[a,b], Yu.N. Malyar[a,b], V.A. Yakovlev[c], L. Djakovitch[d]

[a] Institute of Chemistry and Chemical Technology SB RAS, FRC KSC SB RAS Krasnoyarsk, 660036, Akademgorodok, 50-24, Russia
[b] Siberian Federal University, Krasnoyarsk, 660041, Svobodny prospect, 79, Russia
[c] Boreskov Institute of Catalysis, SB RAS, Novosibirsk, 630090, Pr. Ak. Lavrentieva, 5, Russia
[d] IRCELYON, 2 Avenue Albert Einstein, F-69626, Villeurbanne Cedex, Lyon, France

ARTICLE INFO

Keywords:
Lignin
Depolymerization
Catalysts
Bio-liquids

ABSTRACT

Two ways of catalytic depolymerization of native and isolated wood lignins are described: the peroxide delignification of hardwood (aspen, birch) and softwood (abies) in the medium of acetic acid – water over TiO_2 catalyst and the thermal dissolution of organosolv lignins (ethanol-lignin and acetone-lignin) in supercritical alcohols (ethanol and butanol) over solid Ni-containing catalysts.

The catalyst TiO_2 in rutile modification has the higher activity in wood peroxide delignification at 100 °C as compared to TiO_2 in anatase modification. The results of kinetic studies and optimization of the processes of peroxide depolymerization of hardwood (aspen, birch) and softwood (abies) lignins in the medium of acetic acid – water over catalyst TiO_2 (rutile) at mild conditions (≤100 °C, atmospheric pressure) are compared. The catalyst TiO_2 initiates the formation of OH· and OOH· radicals from H_2O_2 which promote the oxidative fragmentation of wood lignin. In this case, the peroxide depolymerization of softwood lignin, constructed from phenylpropane units of guaiacyl-type proceeds more difficult than the hardwood lignins, mainly containing syringyl-type units.

The solid and soluble products of peroxide catalytic delignification of wood under the optimized conditions were studied by FTIR, XRD, GC–MS and chemical methods. Regardless of the nature of wood the cellulosic products have a structure similar to microcrystalline cellulose. The soluble products mainly consist of monosaccharides and organic acids. Aromatic compounds are present only in a low amount which indicates the oxidative degradation of aromatic rings of lignin phenylpropane units under the used conditions of wood catalytic delignification.

The processes of thermal dissolution of acetone-lignin and ethanol-lignin from aspen-wood in supercritical ethanol and butanol over Ni-containing catalyst ($NiCu/SiO_2$, $NiCuMo/SiO_2$) are compared. The composition, structure and thermal properties of organosolv lignins were studied with the use of FTIR, GPC, ^1H – ^{13}C HSQC NMR, DTA and elemental analysis.

The influence of a composition of Ni-containing catalyst on the thermal conversion in supercritical butanol and ethanol of ethanol-lignin and acetone-lignin was established. The highest conversion of lignins (to 93% wt.) in supercritical alcohols and the highest yield of liquid products (to 90% wt.) were achieved at 300 °C in the presence of catalyst $NiCuMo/SiO_2$.

Scheme of green biorefinery of wood based on the use of non-toxic and low-toxic reagents (H_2O_2, H_2O, acetic acid, ethanol, butanol) and solid catalysts (TiO_2, $NiCuMo/SiO_2$) is suggested.

1. Introduction

Wood biomass is constructed from polysaccharides and lignin [1]. The lignin content depends on the type of tree: about 28% for softwood and 20% for hardwood. The cellulose content is approximately 45% in the wood of both types, while the hemicelluloses content is roughly 17% in softwoods and 25% in hardwoods. Lignin is a polymer of aromatic nature [2]. The principal monomer for softwood lignins is coniferyl alcohol. Hardwood lignins have two main monomers: coniferyl and sinapyl alcohols. The aromatic rings in lignins are presented by guaiacyl units with the one aryl-OCH_3 group, which derived from coniferyl alcohol, by syringyl units with the two aryl-OCH_3 groups,

* Corresponding author at: Institute of Chemistry and Chemical Technology SB RAS, FRC KSC SB RAS Krasnoyarsk, 660036, Akademgorodok, 50-24, Russia.
E-mail addresses: bnk@icct.ru, inm@icct.ru (B.N. Kuznetsov).

https://doi.org/10.1016/j.cattod.2017.11.036
Received 3 April 2017; Received in revised form 8 November 2017; Accepted 29 November 2017
Available online 15 December 2017
0920-5861/

which derived from sinapyl alcohols and by p-hydroxyphenyl units without the OCH_3-groups, which derived from p-coumaryl alcohol.

The huge amounts of waste lignin are produced by pulp and hydrolysis plants. But the high-tech methods of lignin valorization are lacking to date. The variable composition and structure of native and technical lignins complicate the choice of their utilization strategy.

With its unique structure and chemical properties a wide variety of bulk and fine chemicals, particularly aromatic and phenolic compounds are potentially obtainable from lignin. At present the different processes are used for lignin conversion: pyrolysis, catalytic hydrogenation, catalytic oxidation, alkaline depolymerization in supercritical fluids [3–5].

The studies, directed on catalytic processing of biomass and lignin into biofuels and chemicals are intensified in the last decade [4–7]. Application of catalysts allows to speed up the reactions of lignin depolymerization and to increase the yield of liquid products [8–11].

Promising directions of lignocellulosic biomass processing are connected with the use of solid catalysts which have a number of technological advantages in comparison with the dissolved catalytic systems [12–14].

Catalysts based on noble metals (Pd, Ru, Pt) and on the less expensive metals (Ni, Mo, etc.) supported on Al_2O_3, SiO_2 and carbon carries are used in the different processes of lignin valorization [8,15,16]. In particular, the catalyst Ni/C shows the comparable with catalysts Pt/C, Pd/C, Ru/C activity in organosolv lignin depolymerization in supercritical butanol with obtaining of alcylated phenols [17]. In alcohol medium the catalyst Ni/C is active in the rupture of β−O−4 bonds between lignin structural fragments with the formation of monomeric phenols, mainly 4-propyl-4-propenyl-phenol [18].

Catalytic depolymerization of birch-wood organosolv lignin was studied in supercritical ethanol at 260 °C [19]. Different acid-basic materials, namely sepiolite, zeolite ZSM-5 supported on Al_2O_3 and Sibunit graphite-like mesoporous carbon, Ru-containing catalysts based on these supports were used in lignin depolymerization process. The catalyst Ru/Sibunit allows to avoid coke formation, increases the amount of aromatic monomers and the total yield of liquid products up to 76%.

The promising catalytic processes in wood biorefinery include, as a key stage, biomass fractionation on polysaccharides and lignin and their subsequent transformation to various chemicals and liquid biofuels.

The known ways of lignocelluloses biomass fractionation can be united into two groups. In one of them the cellulose and hemicelluloses are removed and the lignin remains as a rest, another includes methods in which the lignin is removed.

Reductive catalytic fractionation is an effective way to separate lignocellulosic biomass into lignin-based soluble mono-, di- and oligomers while retaining most of the carbohydrates in the pulp [20–22].

Single-stage processes of wood fractionation on cellulose and soluble lignin, based on the oxidative depolymerization of lignin in “hydrogen peroxide-acetic acid-water” medium at 120–130 °C in the presence of different catalysts were suggested [23]. At optimum conditions of wood peroxide delignification in the presence of H_2SO_4 catalysts (2 wt%) and TiO_2 (0,5 wt%) the cellulosic products containing less than 1 wt% of residual lignin can be obtained with an acceptable yield (44–48 wt% on abs. dry wood) along with soluble products from lignin and hemicelluloses.

It was shown that the use of small particles of wood, high liquid to wood ratio (LWR) and the intensive mixing of the reaction solution allows to reduce the external diffusion limitations and to provide a high rate of aspen wood peroxide delignification under mild conditions (70–100 °C, atmospheric pressure) in the presence of 2% H_2SO_4 catalyst [24].

In this paper the two ways of catalytic depolymerization of native and isolated wood lignins are described: the peroxide delignification of hardwood (aspen, birch) and softwood (abies) over the catalyst TiO_2 in the medium of acetic acid − water at mild conditions (≤100 °C, atmospheric pressure) and the thermal dissolution of organosolv lignins (ethanol-lignin and acetone-lignin) in supercritical alcohols (ethanol and butanol) over solid Ni-containing catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation of TiO_2

The synthesis of titanium dioxide was carried out by hydrolysis of ammonia solution of titanium tetrachloride with the subsequent calcination of a titanium (IV) hydroxide according to [25].

The necessary amount of $TiCl_4$ was slowly added to a chemical glass with distilled water and the mixture was boiled within 10 min. Then a solution was cooled up to the temperature of 70–80 °C and NH_4OH was added up to full sedimentation of $Ti(OH)_4$. Precipitate was filtered on Buchner funnel and washed out by hot water from chlorine ions. Obtained paste of titanium hydroxide (IV) was then transfered to Petri's dish and dried up in muffler at 110 °C up to the constant weight. The dried-up precipitate was placed to the porcelain boat and calcinated in the muffle furnace at various temperatures within one hour.

For obtaining TiO_2 samples in the rutile modifications, the dried-up precipitate was calcinated at 800 °C within one hour, then crushed in an agate mortar, washed out by water from chlorine ions and calcinated at 1000 °C within 1,5 h.

2.1.2. Preparation of $NiCuMo/SiO_2$

Catalysts $NiCuMo/SiO_2$ were obtained from nickel (II) carbonate basic hydrate $NiCO_3 \cdot mNi(OH)_2\ nH_2O$, copper(II) carbonate basic $CuCO_3 \cdot mCu(OH)_2$, molybdenum(VI) oxide MoO_3, and an alcohol solution of ethyl silicate-32 in the presence of ammonia water (25%), using the sol–gel technique described in [26]. The resulting viscous paste was then dried at 100 °C and calcined at 500 °C. The samples were heated to 500 °C in the H_2 (flow) in a quartz reactor, kept at this temperature for 1 h, and then cooled and passivated with a mixture of $O_2(2\%)/N_2$ [27].

2.2. Initial wood materials

Air dry sawdust (fraction 0.5–2.0 mm) of birch-wood, aspen-wood and abies-wood were used in experiments. The contents of cellulose, lignin and hemicelluloses in wood were defined by analytical methods, common in wood chemistry [28]. The cellulose content in wood was defined by Kurschner method. The lignin content was determined by hydrolysis of the sample with 72 wt% of sulfuric acid at 20 °C for 2.5 h, followed by dilution of a solution with water and boiling for 4 h. The hemicelluloses content was defined by McKein and Shoorly method using the hydrolysis by 2 wt% HCl at 100 °C during 3 h.

The composition of wood samples is given in Table 1.

Samples of acetone-lignin and ethanol-lignin were isolated from aspen-wood by methods described in [29,30].

For isolation of acetone-lignin the treatments of aspen-wood sawdust (fraction less

0.5 mm.) at first by water at 180 °C during 1 h and then by boiling acetone (high purity, EKOS-1, Russia) during 1 h were used. Yield of acetone-lignin was 29.5 wt% from content of Klason lignin in the wood.

Table 1
Composition of wood samples.

Wood	Composition, wt%		
	Cellulose	Hemicelluloses	Lignin
Aspen-wood	46.3	24.5	21.9
Birch-wood	46.5	27.2	21.8
Abies-wood	45.7	17.7	25.3