



# Catalytic upgrading of biopolyols derived from liquefaction of wheat straw over a high-performance and stable supported amorphous alloy catalyst



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## ABSTRACT

Post-refining of crude biomass liquefaction-derived polyols (biopolyols) to remove undesired carbonyl compounds is essential to improve the quality of biopolymers. One of the dominated carbonyl compounds in the crude biopolyols, butyl levulinate (BL), was hydrogenated to  $\gamma$ -valerolactone (GVL) over Cu-modified NiCoB amorphous alloy catalyst to explore a high-efficient hydrogenation upgrading catalyst. Cu<sub>0.5</sub>Ni<sub>1</sub>Co<sub>1</sub>B catalyst with metallic Cu particle size of 10.2 nm and the highest BL conversion of 74.6% was supported on the acid-activated attapulgite (H<sup>+</sup>-ATP) material. The synergistic effect between acidic and hydrogenated active centers in Cu<sub>0.5</sub>Ni<sub>1</sub>Co<sub>1</sub>B/H<sup>+</sup>-ATP catalyst was proved by NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) to promote the conversion of carbonyl compounds compared to unsupported Cu<sub>0.5</sub>Ni<sub>1</sub>Co<sub>1</sub>B catalyst. Reaction temperature also showed a positive effect on the removal of carbonyl compounds especially for the acids and their esters. Under the optimum reaction conditions (140 °C, 1.0 MPa), the relative content of carbonyl compounds in crude biopolyols showed an obvious decrease of 10.3%, while the hydroxyl number of biopolyols increased by 140 mg KOH/g. Gas chromatography–mass spectrometry (GC–MS) analysis results indicated that the conversion of ethylene glycol condensation products and their monoesters or diesters of acetic acid and propionic acid was the major reaction during the process of hydrogenation upgrading of crude biopolyols. Cu<sub>0.5</sub>Ni<sub>1</sub>Co<sub>1</sub>B/H<sup>+</sup>-ATP catalyst also exhibited well stability for the aqueous-phase hydrogenation of crude biopolyols without deactivation in five times run.

## 1. Introduction

Lignocellulosic biomass with low-cost, great availability, and renewable characteristics, has been widely converted into different bio-fuels and biochemicals by thermochemical methods which involve in three main technological routes (gasification, liquefaction and pyrolysis), as showed in Fig. 1 [1,2]. Liquefaction is a more effective method for converting biomass to biochemicals, biopolymer monomers, and etc. compared to pyrolysis or gasification [3]. A large number of lignocellulosic biomass feedstocks have been liquefied to achieve a high-value added application as a matter of course [3–13]. The liquefaction includes solvothermal liquefaction (STL) and hydrothermal

liquefaction (HTL). HTL of biomass is the conversion processing of biomass in a hot, pressurized water environment for sufficient time into synthetic solid, liquid, or gaseous fuels and chemicals [7,10,14]. Typical hydrothermal processing conditions are 200–370 °C of temperature and 2–20 MPa of operating pressure [15,16]. HTL does not require dewatering and drying steps, and therefore, it is suitable for processing aquatic biomass. However, the high temperature and pressure of HTL process results in high energy consumption and capital cost of equipment. STL process is a solvolysis reaction that cleaves various chemical bonds in biomass by using organic solvent (phenols, polyols or cyclic carbonates) under relatively mild conditions (atmospheric pressure, 80–200 °C) [17]. The production of bio-based polyols (biopolyols) by

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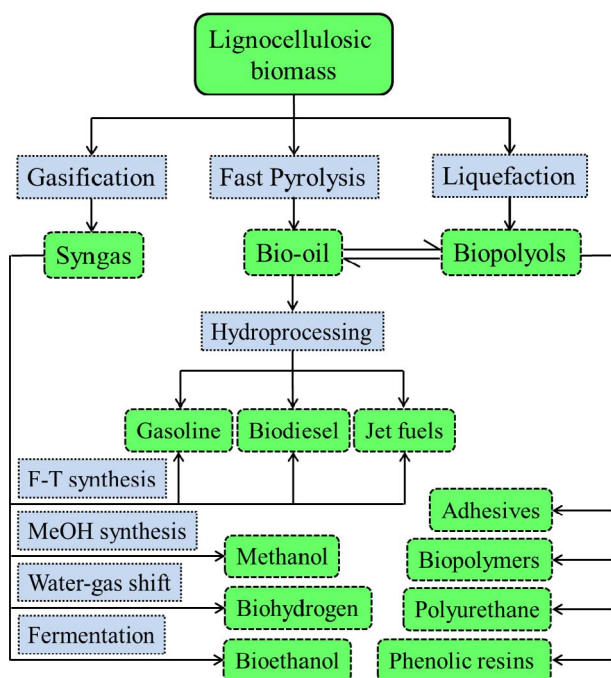


Fig. 1. Scheme of lignocellulosic biomass conversion to biofuels and biochemicals by thermochemical methods.

**Table 1**  
Chemical and elemental composition of wheat straw feedstock and liquefaction residue.

Component or element	Samples (%)	
	Wheat straw feedstock	Liquefaction residue <sup>a</sup>
<i>Chemical composition</i>		
Cellulose	36.2	8.4
Hemicellulose	25.4	0
Acid-soluble lignin	11.5	1.4
Acid-insoluble lignin	17.1	71.3
Ash	5.4	13.8
Others	4.4	5.2
<i>Elemental composition</i>		
C	42.5	51.2
H	5.7	4.9
N	0.5	0.2
O	51.4	43.7

<sup>a</sup> Obtained from the liquefaction of wheat straw in EG (liquefaction conditions: mass ratio of EG/WS = 5/1, H<sub>2</sub>SO<sub>4</sub> 3%, 160 °C, 2 h).

catalytic STL of biomass using the polyols, such as ethylene glycol (EG), glycerol (G), polyethylene glycol (PEG 200 or PEG 400) and their mixture as the solvent in the presence of an acidic or alkaline catalyst (organic or inorganic) has been cognized as a promising technology for substituting the production of petroleum-derived polyols [18–20]. On the one hand, the multiple hydroxyl groups in its structure is suitable for the synthesis of a variety of polymers such as epoxy, polyurethane (PU), polyester, polycarbonate, and phenolic resin [4,21–23]. On the other hand, the PU foams derived from biopolyols present better biodegradability than the PU foams produced from petroleum-derived polyols [24–27].

As we all known, lignocellulosic biomass is composed of cellulose, hemicellulose and lignin. Because of their different structures and morphologies, biomass components are usually liquefied at different stages of the liquefaction process [28]. During the early stages, the liquefaction of hemicellulose, lignin, and amorphous cellulose occurs rapidly because they have amorphous structures that are easily accessible to liquefaction solvents. However, the liquefaction of crystalline

cellulose is typically slower and continues until the later stage of the liquefaction process because it has a well-packed structure that is less accessible to the solvents [24,25,29]. For this reason, the process of biomass liquefaction is extremely complex: a large number of chemical reactions occur and compete against each other simultaneously [28]. Zhang et al. [6] qualitatively analyzed the products formed during the acid-catalyzed liquefaction of bagasse in EG. Results showed the obtained water soluble fraction after separation of crude liquefaction products mainly contained EG and its derivatives, saccharides, other alcohols, aldehydes, ketones, phenols, especially some acids such as formic acid, levulinic acid, acetic acid, oxalic acid and 2-hydroxy-butyric acid and their esters, which was similar to our previous report [5]. During the process of PU foams preparation from biopolyols, these carbonyl compounds, especially ketones, carboxylic acid and their esters, are liable to react with isocyanate to generate some stable by-products as a blocking agent of isocyanate [30]. As a result, the quality of PU foams will decline significantly, such as deeper color and non-uniformly distributed foam pore. Therefore, the post-refining of crude biopolyols is essential to upgrade the biopolyols-based products. One promising method to achieve the goal is the catalytic hydrogenation that allows selective removal of undesirable carbonyl compounds in the biopolyols over noble metal or copper-based catalysts [31,32]. However, though they have high activity, the high cost of noble metal and the high toxicity of industrial copper chromite (Cu-Cr) based catalysts have promoted the development of free-Cr supported Cu-based catalysts in green and sustainable bio-refinery technology, for example furfural (FUR) hydrogenation to furfuryl alcohol (FA) [33–36].

Due to the unique chemical and structural properties of metal-metalloid amorphous alloys including broadly adjustable composition, structural homogeneity, and high concentration of coordinately unsaturated sites [37], the NiB-based amorphous alloy catalysts modified with different metallic promoter, like Fe [38], Co [39,40], Ce [41], La [42], etc., have also been broadly applied in the hydrogenation of unsaturated carbonyl compounds [43]. For example, the NiCoB amorphous alloy catalyst with Ni/Co molar ratio of 1/1 exhibits a stable hydrogenation activity of C=C bond and C=O bond on the same FUR molecule [44]. Unfortunately, because of the poor thermal stability and low surface area, it is necessary to deposit them on a support with high surface area. Bai et al. [42] reported that a SiO<sub>2</sub> supported Ni-La-B amorphous alloys catalyst showed better initial activity and selectivity for the liquid phase selective hydrogenation of benzophenone to benzhydrol compared to a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalyst due to the dispersion of active Ni centers on the surface of SiO<sub>2</sub> with a planar structure while in the internal channels of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with porous structure. In contrast, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Ni-La-B catalyst showed better stability due to the exposure of more acidic Al<sub>2</sub>O<sub>3</sub> species. It was indicated that the chemical and physical properties of support materials are of great influence to the activity and stability of catalysts [45]. The crude biopolyols has similar composition characters with the water insoluble fraction of bio-oil which has been extensively upgraded by hydrodeoxygenation (HDO), in-situ hydrogenation, esterification and one step hydrogenation-esterification (OHE) [46]. The metal/acidic zeolite dual-functional catalyst is an efficient catalyst in HDO of bio-oil due to a synergetic effect. The acid centers promote isomerization/cracking reactions, and metallic centers improve hydrogenation of oxygenated compounds such as acids and aldehydes compounds [47]. However, to our best knowledge, the acidic zeolite was mostly synthesized to increase the preparation cost of catalyst. In addition, few studies use a dual-functional catalyst for hydrogenation upgrading of biopolyols.

Attapulgite (ATP, also known as palygorskite) is a naturally available hydrated magnesium aluminum silicate clay mineral [48]. Suitable acidification treatment of attapulgite could increase its surface area and pore volume [49] and adjust the surface acidity [50]. Accordingly, the acid-activated attapulgite (H<sup>+</sup>-ATP) has attracted much attention for its application in the catalyst supports [51–53]. From another perspective,

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