



Hydrodeoxygenation and hydrocracking of solvolysed lignocellulosic biomass by oxide, reduced and sulphide form of NiMo, Ni, Mo and Pd catalysts

M. Grilc^a, B. Likozar^{a,b,*}, J. Levec^{a,b}

^a Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

^b Faculty of Chemistry and Chemical Technology, University Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 1 October 2013

Received in revised form

10 December 2013

Accepted 16 December 2013

Available online 24 December 2013

Keywords:

Biomass solvolysis

Hydrotreatment

Hydrocracking

Decarbonylation/decarboxylation

Lumped deoxygenation model

ABSTRACT

Innovative second-generation biofuel was obtained by a low-temperature ultrasonic liquefaction of waste wood biomass in glycerol, diethylene glycol and *p*-toluenesulfonic acid, and its hydrotreatment in the presence of various heterogeneous catalysts and hydrogen donor solvents. Depolymerization and solubilization of cellulose, hemicellulose and lignin by using residual glycerin from biodiesel production make solvolysis process highly sustainable thermochemical biomass to liquid (BtL) route. Solvolytic oil containing 25–33 wt% of liquefied spruce and fir sawdust was upgraded by hydrotreatment utilizing heterogeneous catalysis at 300 °C and 8 MPa of hydrogen pressure. Prior to kinetic experiments, mass transfer and heat transfer resistances were reduced, and activity of catalytic hydrocracking and hydrodeoxygenation (HDO) was investigated for four NiMo/Al₂O₃ bifunctional catalysts in oxide, reduced and sulphide form, Ni/Al₂O₃-SiO₂, MoS₂, Pd/Al₂O₃ and Pd/C. Promoting effects of hydrogen donor solvents were investigated for tetralin, phenol, 2-propanol, pyridine, *m*-cresol, anthracene, cyclohexanol and xylene. Lumped reaction kinetic model was developed to determine kinetics of hydrogenolysis, decarboxylation, decarbonylation and hydrocracking of products of liquefaction, such as levulinic acid, guaiacol and hydroxymethyl furfural (HMF), according to their functional groups and related gaseous products, quantified by Fourier transform infrared spectroscopy. Upgraded liquid product was also characterized for energetic and fuel applications by following its rheological properties and measurements of gross calorific value.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Energy requirements and environmental concerns have led to increased interest in substituting the fossil fuels with the alternatives, derived from biomass, a renewable and sustainable carbon source. The utilization of lignocellulosic waste, such as forest residues and sawdust, is especially sustainable and economically attractive, because the feedstock does not compete with food production or land use. Lignocellulosic biomass can be converted into biofuel by biochemical or thermochemical processes. The latter include technologies such as pyrolysis, gasification, supercritical fluid extraction, and direct liquefaction [1]. Traditional direct biomass liquefaction process operates at high temperature and pressure using reductive atmosphere and heterogeneous catalysts [2]. The high production costs and lack of basic scientific

understanding of the process led to the failure of relatively large demonstration plants in the late seventies [3]. Alternative direct liquefaction process is the solvolysis at mild reaction conditions, using acidified or alkaline polyhydroxy compounds as solvents [4–6]. Although the volumetric energy density of liquefied oil is significantly higher in comparison to original lignocellulosic biomass, there are main drawbacks for its direct use as a transportation fuel, e.g. the low calorific value due to high oxygen content, high viscosity, corrosive effects, and questionable chemical stability.

There are two general routes for upgrading the biomass-derived oils, namely hydrodeoxygenation (HDO) using heterogeneous catalysts and cracking with zeolites [7,8]. The catalytic HDO refers to the oxygen removal through the elimination of water, where the hydrogen content decrease in product is avoided by the high pressure of hydrogen or the presence of hydrogen donor solvent. It is an expensive, but technically and economically feasible route to convert the biomass-derived oil into transportation fuel [8]. Deoxygenation can be also achieved by CO and CO₂ formation; however, this route leads to lower product yields due to the depletion of carbon in liquid phase. The selectivity of deoxygenation reactions depends on the nature of feedstock, reaction conditions

* Corresponding author at: Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia. Tel.: +386 1 4760283; fax: +386 1 4760300.

E-mail address: blaz.likozar@ki.si (B. Likozar).

and catalyst. The most frequently examined HDO catalysts are NiMo/Al₂O₃ and CoMo/Al₂O₃, as these are commercially used for hydrotreatment in petroleum refineries [9,10].

Sulphidation may improve their efficiency, but can be questionable in the industrial scale for the environmental reasons and sulphur compounds in product, therefore the oxide or reduced forms of these catalysts were predominantly investigated [11,12]. Nonetheless, if the activity, selectivity and stability of a sulphide form catalyst greatly surpassed the reduced equivalent, the activation procedure by sulphur-containing components would be justified even on a larger scale. Moreover, by investigating the HDO of the model compounds using these types of bifunctional catalysts, reaction pathways [13,14] and catalytic mechanisms [15] were proposed. In addition to the conventional bifunctional catalysts, catalytic upgrade was also investigated over Fe, Ni [11,16–18], and noble metals, such as Pd, Ru, Rh and Pt, on different supports [19,20].

Some results on the catalytic HDO of the biomass-derived oils liquefied at high pressures are presented in the literature [10,21,22], while the solvolysis of biomass in the acidic or alkaline polar solvents at atmospheric pressure and low temperatures, followed by catalytic upgrade, has not been extensively reported [5,11].

Hydrogen donor solvents enhance HDO by releasing the hydrogen radicals that can stabilize the free radicals, formed by the cleavage of C–O, C–N and C–C bonds, preventing the undesired reactions of charring and polymerization [23]. The effect of hydrogen donor solvents in the liquefied biomass hydrogenation process is not extensively reported as well. Tetralin is the most typical hydrogen donor solvent, used for the biomass-derived oil processing [11,22,23], while 2-propanol [24], *m*-cresol, anthracene and isoquinoline [2] were also reported to have donor effect.

In order to understand, describe and scale-up the hydrotreatment of biomass-derived oils, chemical kinetic modelling may be considered to play a crucial role in devising the activity, selectivity and stability of a catalyst. The kinetic studies of real bio-oil HDO are rare and always simplified by lumping. Zhang et al. [25] used a power law kinetic expression to evaluate the HDO of a pyrolysis oil using the CoMo catalyst in a batch reactor. Additionally, Sheu et al. [26] also used a simple power law model for the wood-derived pyrolysis oil HDO using Pt, NiMo, CoMo catalysts. The rate of oxygen removal was represented as a function of the oxygen content and partial pressure of hydrogen, while the temperature dependence of rate constant was given by the Arrhenius law.

In this work, hydrodeoxygenation of biomass, liquefied at 160 °C in acidified glycerol and ethylene glycol mixture, was carried out using 18 different catalysts and 8 hydrogen donor solvents, at the temperature of 300 °C and 8 MPa of hydrogen pressure. The influence of other parameters (i.e. temperature, pressure, process gas, heat-up rate, stirring speed, mass fraction of NiMo catalyst and

tetralin) on hydrotreatment of the same feedstock was reported in previous study [27]. The aim of this work was to determine the influence of various catalysts and donor solvents on the rate and selectivity of upgrading-associated reactions (e.g. hydrodeoxygenation, decarbonylation, decarboxylation, hydrocracking), to propose the most suitable option for a large-scale process. The novelty of this work is the advanced reaction pathway network and lumped kinetic model for the upgrading-associated reactions of the real biomass-derived oil, based on the oxygen-containing functional groups, followed by Fourier transform infrared (FTIR) spectroscopy, and their corresponding gaseous oxygen carriers. This method allows for a simple, but an advanced insight into the complex reaction system in comparison to kinetic models, based on elemental analysis.

2. Experimental

2.1. Liquefied biomass preparation and characterization

For this study, liquefied wood samples were provided by the company that runs the pilot plant for the liquefaction of the lignocellulosic biomass in polyols, following the procedure, presented in literature [28,29]. Dry sawdust from debarked European spruce (*Picea abies*) and European silver fir (*Abies alba*) was used as a feedstock, while the mixture of glycerol and diethylene glycol (1:1 by mass) was used as the liquefaction solvent, containing 3 wt% of *p*-toluenesulfonic acid as a homogeneous catalyst. The approximate mass fractions of cellulose, hemicellulose and lignin in the sample of sawdust were 41, 25, and 29%, respectively.

Two sample grades, treated in this study, consisted of the biomass to solvent ratios of 1:3 and 1:2 (by mass). The first sample had the gross calorific value (GCV) of 21.9 MJ kg⁻¹, viscosity of 4 Pa s at 25 °C, and the elemental composition as follows; 47.6 C, 8.0 H, 43.3 O, 0.2 N and 0.9 S (wt%). Water content was below 2 wt%. The second sample had the same GCV and elemental composition (within experimental error), while the viscosity at 25 °C was significantly higher (13 Pa s).

2.2. Catalyst preparation and characterization

Four types of producer-provided commercially available bifunctional nickel–molybdenum catalysts on γ -Al₂O₃ support were studied (Table 1). They were all extrudates (quadrilobe-shaped) of different dimensions, Ni and Mo content and specific surface area. In the present study each NiMo catalyst was tested in oxide/calcination-treated (as received), reduced and sulphide form.

Palladium-based catalysts, tested in this study, were supported on 2–4 mm Al₂O₃ spheres (G-68 C and G-68 G, Süd – Chemie, Munich, Germany) or on activated carbon powder (Nikki-Universal, Tokyo, Japan and Sigma–Aldrich, St. Louis, MO, USA). All

Table 1
Catalysts used for hydrotreatment process tests.

Supplier	Catalyst	Active metal	Content (wt%)	Form ^a	Pre-treatment ^b	Surface area (m ² g ⁻¹)
Industrial #1	NiMo/Al ₂ O ₃ #1	Ni/Mo	Standard/standard ^c	1.3 mm Q	O, R, TS	Standard ^c
Industrial #1	NiMo/Al ₂ O ₃ #2	Ni/Mo	Standard/highest ^c	1.5 mm Q	O, R, TS	Standard ^c
Industrial #2	NiMo/Al ₂ O ₃ #3	Ni/Mo	Highest/standard ^c	1.0 mm Q	O, R, TS	Highest ^c
Industrial #2	NiMo/Al ₂ O ₃ #4	Ni/Mo	Lowest/lowest ^c	1.0 mm Q	O, R, TS	Lowest ^c
Süd-Chemie	Pd/Al ₂ O ₃ #1	Pd	<1	2–4 mm S	R	118
Süd-Chemie	Pd/Al ₂ O ₃ #2	Pd	<1	2–4 mm S	R	93
Sigma–Aldrich	Pd/C #1	Pd	5	P	R	1558
Nikki-Universal	Pd/C #2	Pd	5	P	R	1201
Sigma–Aldrich	Ni/SiO ₂ –Al ₂ O ₃	Ni	65	P	R	149
Riedel de Haën	Bulk MoS ₂	Mo	100	P	None	2

^a Q – quadrilobe extrudates; S – spheres; P – powder.

^b O – used as received in oxide form; R – reduced form; TS – sulphide form by TOTSUCAT process.

^c Among industrial NiMo catalysts.

Download English Version:

<https://daneshyari.com/en/article/45932>

Download Persian Version:

<https://daneshyari.com/article/45932>

[Daneshyari.com](https://daneshyari.com)