Catalysis Today 256 (2015) 302–314

Contents lists available at ScienceDirect

Catalysis Today

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

Kinetic model of homogeneous lignocellulosic biomass solvolysis in glycerol and imidazolium-based ionic liquids with subsequent heterogeneous hydrodeoxygenation over NiMo/Al_2O_3 catalyst

M. Grilc[a], B. Likozar[a,*], 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 10 October 2014
Received in revised form 3 February 2015
Accepted 9 February 2015
Available online 29 March 2015

Keywords:
Solvolysis
Lignocellulose
Liquefaction kinetics
Ionic liquid
Hydrodeoxygenation
Lumped model

ABSTRACT

Solvolysis of wood, cellulose, hemicellulose and lignin in glycerol was investigated in the presence of homogeneous imidazolium-based ionic liquid (IL) catalysts, where the influence of the IL type, reaction time, temperature and mass transfer limitations on decomposition rate was investigated. The selection of anions (acetate, hydrogen sulphate or chloride/metal halide complex to form a Lewis acid) and cations (butyl-, methyl- or allyl-functionalised imidazolium) importantly influenced conversion, which was as high as 64.4 and 91.5 wt% for the beech wood liquefaction at 150 and 200 °C within 60 min. By following the mass of solid particles and their specific surface area (BET method) as a function of time and temperature, a novel kinetic model for the solvolysis of biomass and its components was developed, where reactive surface area is a key parameter that dictates the rate of solid–liquid reaction; kinetic model also considered different depolymerisation reactivity of main three wood components. Liquefied biomass was consequently hydrodeoxygenated at 225–275 °C in the presence of commercially available sulphide-form NiMo/γ-Al_2O_3 catalyst. Rates and selectivity of hydrogenolysis, decarbonylation, decarboxylation, hydrogenation and (hydro)cracking were followed and modelled by using previously developed lumped kinetic model, based on the Fourier transformed infrared spectroscopy (FTIR) analysis. The oxygen content of the oil phase of was less than 1.7 wt%.

1. Introduction

Direct liquefaction of lignocellulosic (LC) biomass by solvolysis showed a promising potential in comparison to other thermo-chemical biomass to liquid (BtL) conversion technologies (e.g. pyrolysis and gasification) as it can be conducted at atmospheric pressure and temperatures below 200 °C [1–3]. Liquefaction by solvolysis involves depolymerisation of LC macromolecules and solubilisation of the resulted products in various acidified organic solvents [4,5]. Lignocellulosic biomass liquefaction by the solvolysis in cheap renewable solvents such as glycerol is promising, since it is a by-product from biodiesel production and its world production is significantly higher than the demand [6]. On the other hand, the use of ionic liquids (IL) has also showed some potential for the LC biomass depolymerisation at surprisingly low temperature with the possibility of their regeneration and reuse, although high prices and high toxicity hinder their wide use [7]. Alkyl-methylimidazolium ionic liquids with chlorine or acetate anions are of particular interest as they are non-derivatising solvents for LC biomass and its constituents [7]. Although acetate ion is larger than chloride and might make it difficult to diffuse into the space between the cellulose layers and cause decrystallisation (that is believed to be the rate limiting step for the solvolysis of the crystalline cellulose), some theoretical and experimental studies showed that acetate anion exhibits superior ability to dissolve cellulose in comparison to the corresponding Cl^- anion due to either stronger hydrogen bonds between acetate ions and OH groups of cellulose in comparison to the Cl^- ion or because of the reactivity of acetate with imidazolium cation in IL to form a highly reactive carbine [7–9]. Solvolysis of wood in pure IL with imidazolium cation and an anion being a complex of chloride and metal halides ($AlCl_3$, $SnCl_2$, $FeCl_3$) resulted in less than 10 wt% of insoluble residue at temperatures lower than 100 °C [10]. The ionic liquids might be therefore used to catalyse the solvolysis of LC biomass in polyols, as a substitute for sulphuric or p-toluenesulphonic acid homogeneous catalysts that are traditionally used. In case that IL could efficiently replace a sulphuric or p-toluenesulphonic acid for the biomass solvolysis in polyols, it would beneficially reduce the

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* Corresponding author. Tel.: +386 1 4760283; fax: +386 1 4760300.
E-mail address: blaz.likozar@ki.si (B. Likozar).

http://dx.doi.org/10.1016/j.cattod.2015.02.034
0920-5861/

sulphur presence in the product, while non-volatile and thermally stable ionic liquid could also be separated from the product and reused. Literature data on this topic could not be found, which was an additional motivation for this work.

Since high oxygen content in the LC feedstock results in a low calorific value of the biomass-derived oils, the progressive removal of chemically bonded oxygen by hydrodeoxygenation (HDO) is required to provide a competitive alternative fuel [11,12]. Elevated temperature and hydrogen pressure are required for a successful deoxygenation, as well as a presence of a heterogeneous catalyst either based on transition metals (Mo, W, Ni, Co) in their sulphide, metal, oxide, nitride or carbide form or noble metals (Pt, Ru, Pd) on different supports [13]. Various catalysts were tested for HDO of the biomass-derived solvolysis oil in our previous studies, the reaction pathway network was proposed and lumped kinetic model was developed for the deoxygenation and (hydro)cracking reactions that take place during the hydrotreatment [14–16].

There were several kinetic models reported in the literature for an acidic solvolysis of biomass and their main components; however in most models kinetic rates of the solvolysis only depend on the mass of the material [17–19], although the reaction takes place on the solid–liquid interphase and the specific surface area should be considered as well, since it can change dramatically during the solvolysis as will be later shown in this work. The importance of reactive solid–liquid interphase during the wood solvolysis of rather large wood cylinders (diameter 10–15 mm) was investigated and modelled by Ammar et al. [20]. Models also often neglect the influence of different reactivity of cellulose, hemicellulose and lignin. Zhang et al. investigated the kinetics of the liquefaction of wood and its main three components in acidified polyhydric alcohols [17], but did not simulate the solvolysis of wood from results independently obtained for cellulose, hemicellulose and lignin.

The aim of this work is: (i) to perform a screening of five different imidazolium-based ionic liquids (IL) as potential homogeneous catalysts for the biomass solvolysis in glycerol, (ii) to study the kinetics of wood solvolysis with best performed IL catalyst, (iii) to propose a kinetic model for batch solid–liquid reaction of wood, cellulose, hemicellulose and lignin solvolysis, which includes the reactive surface area as a key parameter of the solid–liquid reaction. Furthermore, the aim of this work is also to perform a catalytic upgrade of the solvolysed oil by the liquefaction of biomass in IL-catalysed glycerol by mild hydrotreatment over commercially available NiMo/γ-Al_2O_3 catalyst and to determine the kinetic rates of hydrodeoxygenation.

2. Materials and methods

2.1. Biomass and ionic liquids preparation

Before the solvolysis, a thin layer (approximately 2 mm) of sawdust from debarked European beech (*Fagus sylvatica*) was placed on a metal tray (dimensions 200 × 200 mm), dried at 80 °C under N_2 atmosphere for 20 h and kept in a desiccator at room temperature.

Three main components of wood were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification, specifically; high purity cellulose fibres (Sigma-Aldrich reference number C6288), alkali lignin with low sulphonate content (Sigma-Aldrich reference number 471003) and xylan from beech wood (≥90% purity, Sigma-Aldrich reference number X0502). Glycerol (≥98.7 wt%, Pharmachem Sušnik, Ljubljana, Slovenia) was used as solvent for solvolysis, while five different ionic liquids were used as homogeneous catalysts. 1-Butyl-3-methylimidazolium hydrogen sulphate ($[BMIM^+][HSO_4^-]$) and 1-butyl-3-methylimidazolium acetate ($[BMIM^+][CH_3COO^-]$) were purchased (≥98 wt%, Solvionic, Toulouse, France) and used as received, while $[BMIM^+][Cl^-/AlCl_3]$, $[EMIM^+][Cl^-/AlCl_3]$ and $[AMIM^+][Cl^-/AlCl_3]$ ionic liquids were prepared from anhydrous $AlCl_3$ (≥98 wt%, Sigma-Aldrich, St. Louis, MO, USA) and equimolar amount of 1-allyl-3-methylimidazolium chloride (≥98 wt%, Solvionic, Toulouse, France), 1-ethyl-3-methylimidazolium chloride (≥95 wt%, Iolitech, Heilbronn, Germany) or 1-butyl-3-methylimidazolium chloride (99 wt%, Iolitech, Heilbronn, Germany).

2.2. Characterisation of wood, cellulose, hemicellulose, lignin and insoluble residue

The particle size distribution of wood samples before the solvolysis was determined by sieve analysis of 40 g a sample using 1.00, 0.71, 0.50, 0.25, 0.10, 0.08 and 0.02 mm sieve sizes. Particle size distribution of beech wood, cellulose, hemicellulose, lignin and their solid residue after the solvolysis was also determined by a field emission scanning electron microscopy (FE-SEM) (SUPRA 35 VP, Carl Zeiss, Jena, Germany) and subsequent image processing. SEM operated in a high-contrast acquisition mode, where particles were well spread over the graphite tape, while high acceleration voltage and secondary electron detector was used. This allowed automatic determination of particle sizes for representative population by using image processing and analysis software (ImageJ, Bethesda, MA, USA). 100 to 250 particles were digitally measured on SEM images for each sample and their minimal Ferret diameters (characteristic dimension for the sieve analysis) were determined, assuming that 2D projection is representative for the size and shape of a 3D object. The specific surface area of a solid material was measured by BET (Brunauer–Emmett–Teller) method using the ASAP 2020 (Micrometrics, Norcross, GA, USA) instrument for gas adsorption. The sample chamber with 0.5 g of tested material was evacuated at 50 °C to hold the pressure below 0.40 Pa for 60 min. The adsorption isotherm was determined at −196 °C by gradually increasing the nitrogen pressure in the sample chamber (2 kPa steps) from 6 to 30 kPa and monitoring the amount of the adsorbed nitrogen. The Fourier transform infrared (FTIR) spectra of solid materials were recorded by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) method, by averaging 16 scans with resolution of 4 cm^{-1} using DiffusIR (Pike Technologies, Madison, WI, USA) environmental chamber, flushed with nitrogen, and installed in the spectrometer (Spectrum 100, Perkin Elmer, Waltham, MA, USA). KBr background was recorded before solid samples were diluted with KBr in 1:2 mass ratio, placed in a sample cup (10 mm diameter, 2.3 mm deep) and analysed.

2.3. Solvolysis

Solvolysis was investigated in a 300 mL stainless steel autoclave, equipped with electric heating mantle (Autoclave Engineers). Cylindrical reactor vessel had an inner diameter of 45 mm and height of 185 mm, while the magnetically driven stirrer contained three four-blade impellers with 30 mm diameter, mounted 20, 60 and 100 mm above the reactor's bottom. The reactor was filled with 150 mL of cold reaction mixture that contained 15 wt% of dry wood, cellulose, hemicellulose or lignin, the rest being solvent, prepared from 90 wt% of glycerol and 10 wt% of homogeneous catalyst (IL). The reaction mixture was intensively stirred using the agitation speed of 500 min^{-1}, while the headspace of the reactor was continuously purged with constant (250 mL min^{-1}) nitrogen flow (5.0, Messer, Bad Soden am Taunus, Germany) and the gaseous phase was analysed online as described in Section 2.5. The reactor configuration in actual proportions and the progress of the lignocellulosic biomass solvolysis reaction is symbolically visualised in Video 1 (e-component). To establish a constant nitrogen purge, the pressure in the reactor was set to 1 bar above the ambient pressure. Experiment started at room temperature; consequently, the reaction mixture