



Production of biomaterials from cork: Liquefaction in polyhydric alcohols at moderate temperatures



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ARTICLE INFO

Article history:

Received 6 November 2013

Received in revised form 10 January 2014

Accepted 16 January 2014

Available online 22 February 2014

Keywords:

Cork
Suberin
Liquefaction
Glycerol
Polyethylene glycol

ABSTRACT

The aim of this study was to develop polymers in a liquid solution, from renewable bio-resources, usable as intermediate materials in the preparation of plastics, adhesives or coatings. The liquefaction of cork with glycerol was investigated at 150 °C, 180 °C, and 200 °C under acidic (sulphuric acid) or alkaline conditions (sodium hydroxide). Cork appears as a two-component material, containing suberin and lignocelluloses. In the presence of sulphuric acid, only the liquefaction of the lignocellulosic components was achieved, leading to liquefaction yield of less than 47% at all investigated conditions. The inverse phenomenon was observed with sodium hydroxide. Suberin was almost completely liquefied, but an increase of temperature and/or sodium hydroxide content was necessary to improve the liquefaction of lignocelluloses. Addition of polyethylene glycol to glycerol to a certain extent caused the conversion of suberin under acid conditions leading to liquefaction yield up to 93%. Therefore, it was demonstrated that it is possible to use cork dust, a less valuable by-product, for the production of various basic chemicals and/or polymers with a high added value.

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1. Introduction

Thermochemical liquefaction of renewable bio-resources for the production of polymers has attracted much attention in recent years, driven by the global need for new technologies with reduced environmental impact and increased long-term productivity (sustainability). The use of biomass-derived chemicals in the synthesis of materials traditionally made of petroleum-based ones could reduce the current dependency upon fossil resources and environmental problems related to their exploitation, and add value to agro-forestry by-products (e.g. wood residues, bark, bagasse, wheat, and corncob) and end-live woody materials (recycling). Biomass materials are composed of polymers such as cellulose, lignin, starch or suberin that can be converted under specific conditions into liquid mixtures of monomers, oligomers and polymers, and subsequently can re-condensate to produce plastics, adhesives or coatings via conventional polymerisation techniques, involving either hydroxyl groups (self-crosslinking, polycondensation with diisocyanates, diacids or their anhydrides, reaction with

epichlorohydrine, etc.) or phenolic-benzene rings (reaction with formaldehyde systems). There are many encouraging reports on liquefaction processes (Honglu and Tiejun, 2006; Lee and Ohkita, 2003; Shiraishi, 1997) as well as on the application of liquefied products (Lee et al., 2001; Tohmura et al., 2005).

Liquefaction of biomass can be performed using different techniques. Direct liquefactions at high temperatures (350–500 °C) and high pressures (5–20 MPa) without a catalyst or with weak bases as a catalyst have been applied mainly for the purpose of recovering heavy oil that can be used as biofuel (Balat, 2008; Demirbaş, 2001). Biomass liquefaction has also been achieved in sub- and super-critical solvents, carbon dioxide, phenol, water, or methanol (Lee and Ohkita, 2003; Minami and Saka, 2003; Qian et al., 2007) or in ionic liquids (Honglu and Tiejun, 2006; Kilpelainen et al., 2007; Li et al., 2010; Mäki-Arvela et al., 2010). Biomass has finally been liquefied by using an appropriate reactive solvent and a catalyst, the solvent being part of the liquefied-end products. Numerous solvents have been successfully applied: cyclic carbonates (ethylene carbonate, propylene carbonate) (Yamada and Ono, 1999), phenol (Alma et al., 2001; Lin et al., 1994) or polyhydric alcohols (ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, glycerol...) (Briones et al., 2011; Budija et al., 2009; Kobayashi et al., 2004; Kurimoto et al., 1999; Ugovšek et al., 2011). Phenol

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has been for example preferred as a liquefaction reagent when the end-objective was the preparation of phenol-formaldehyde like resins. The liquefaction methods with polyhydric alcohols have been widely used for the production of bio-polymer materials (polyurethanes).

Cork, bark from *Quercus suber* L., has been used for many centuries in many industrial applications such as stoppers, insulation boards, furniture and shoes insoles. Cork industry consumes worldwide about 280,000 tons of raw cork annually, and processes about 70–80% of this amount; approximately 20–30% of the cork entering the mill being rejected mainly as dust (Cordeiro et al., 1998; Gandini et al., 2006; Silva et al., 2005). This by-product could be potentially more efficiently used for the production of bio-polymers, instead of for example being burned for the production of energy. Several efforts have already been done in this direction. Suberin, the major component of cork, has been extracted and used for preparation of polyurethanes (Cordeiro et al., 1998, 1999). Liquefaction of cork has also been performed using cyclic carbonate methods (oxypropylation) and the obtained polyols used for preparation of polyurethanes (Costa Cruz Pinto et al., 2010; Evtiouguina et al., 2001, 2002).

In this work, liquefaction of cork using polyhydric alcohols (glycerol or glycerol/polyethylene glycol #400 co-solvent mixtures) was investigated with the aim to propose a relatively soft alternative approach to oxypropylation method widely applied. Liquefaction of cork was studied in pure glycerol. Glycerol as a by-product of various vegetable oil processing has a promising future as a chemical. Its production is set to increase significantly with the increasing perspectives of biodiesel production (Pachauri and He, 2006; Stelmachowski, 2011). Because of the low liquefaction yield measured in pure glycerol under sulphuric acid conditions, polyethylene glycol #400 (PEG #400) was increasingly added to glycerol and its influence on the liquefied yield recorded. Liquefaction of cork was studied as a function of catalyst type (acid or base), temperature and reaction time using liquefaction yield (percentage of cork dissolved), chemical analyses (chemical composition of original cork and liquefaction residues) and FT-IR.

2. Experimental

2.1. Materials

Cork from *Q. suber* L. was kindly provided by the Amorim Revestimentos (Amorim, Portugal) in the form of fine powder. The powder (cork) was oven-dried at 103 °C for 24 h before each liquefaction experiment. All the chemicals were reagent grade and were used without further purifications.

2.2. Methods

2.2.1. Cork liquefaction

The liquefaction experiments were performed using a classical reflux setup, an oil bath equipped with a thermometer, a glass flask, and a condenser. Two types of catalyst were tested: sulphuric acid (H₂SO₄) for acid catalysis and sodium hydroxide (NaOH) for base catalysis. Glycerol and respective catalyst were at first mixed and pre-heated to the predetermined liquefaction temperature (150 °C, 180 °C, or 200 °C, respectively). When sodium hydroxide was used, this mixture was kept at the selected temperature until the complete dissolution of the catalyst. Subsequently, the dried cork powder was added. After a preset reaction time, about 2–3 g of the reaction mixture was picked-up and cooled down to quench the reaction, diluted with methanol and filtered under vacuum through a filter disk (Sartorius filter disks 388 grade/12–15 μm particles retention). The residual solid was washed with methanol,

oven-dried (103 °C, 24 h) and weighed. The liquefaction yield (LY) was calculated on the basis of the part which was insoluble in methanol, using the Equation (1):

$$LY(\%) = \left(1 - \frac{W_R}{W_C}\right) \times 100 \quad (1)$$

W_R is the mass fraction of the solid residue in the reaction mixture at time t and W_C is the mass fraction of solid cork in the starting mixture.

2.2.2. Chemical analyses

The chemical composition of initial cork and residues of liquefaction were determined in order to identify the susceptibility of the different components of cork to liquefaction. All experiments were conducted with oven-dry samples (103 °C, 24 h). The samples were Soxhlet extracted with a mixture of toluene/ethanol (2:1) for 6 h, and then with water for 6 h. After each extraction, the extraction solvents were evaporated using a rotavapor, the extracts were dried (60 °C, 24 h) and weighed.

The solid residues obtained after water extraction were dried (103 °C, 24 h) and used for the determination of suberin content, using alkaline ethanol–water method (Ekman, 1983). The samples were treated under reflux at (75 °C, 1.5 h) with 0.5 mol/L potassium hydroxide in ethanol–water (9:1) solution. Suberin was depolymerised and solubilised in alkaline ethanol–water mixture, and the obtained liquid filtered under vacuum through a filter disk (Sartorius filters disks 388 grade/12–15 μm particles retention). The de-suberinated residues were dried at 103 °C and used for the analyses of lignin and polysaccharides.

The content of lignin was determined using acid hydrolysis (Rowell et al., 2005). De-suberinated residues were treated with sulphuric acid (72%, 30 °C, 1 h), the mixture diluted to 3% sulphuric acid and boiled under reflux (120 °C, 1 h). Acid-insoluble lignin (Klason lignin) was recovered after filtration using a crucible N°4 (Intos Pula B-4), washed with hot water, dried and weighed.

The content of holocellulose (total carbohydrates) was determined by acid chlorite method (Rowell et al., 2005). The samples were mixed with water, acetic acid and sodium chlorite, and heated at 70 °C. Additional amount of acetic acid and sodium chlorite was added until the complete discoloration of the residue (white residue) was achieved, indicating the complete dissolution of lignin. Treatment for 6 h was sufficient to complete the reaction. The residue was filtered with a crucible N°4 (Intos Pula B-4), dried, and weighed.

2.2.3. FT-IR analyses

FT-IR analyses were performed with a Perkin-Elmer Spectrum One FT-IR Spectrometer using KBr technique. All the spectra were recorded at a 4 cm⁻¹ resolution, and were the averages of 40 scans. KBr and the samples were oven-dried (103 °C, 24 h) before the measurements.

3. Results and discussion

3.1. Liquefaction of cork in glycerol

3.1.1. Effect of catalyst type

Two model catalysts were tested: sulphuric acid (H₂SO₄) for acid and sodium hydroxide (NaOH) for base catalysis. Liquefaction of cork dust was performed at 150 °C, 180 °C or 200 °C using a cork to glycerol mass ratio 1:10 and catalyst/glycerol mass ratio 3:100. The advancement of the reaction (liquefaction yield LY) after 1 h and 3 h are shown in Table 1. LY was generally higher under alkaline (64.5–85.1%) than under the acidic conditions (43.2–50.2%). It was significantly sensitive to temperature range under alkaline, but not under the acidic conditions. The increase of reaction time from 1 h

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