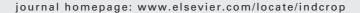
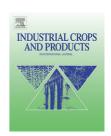


available at www.sciencedirect.com







Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues

El-barbary M. Hassan*, Nadia Shukry

Cellulose & Paper Department, National Research Center, El-Behoos Street, Dokki, 12622-Cairo, Egypt

ARTICLE INFO

Article history: Received 13 December 2004 Accepted 2 July 2007

Keywords: Lignocellulosic agricultural residues Liquefaction Polyhydric alcohols

ABSTRACT

Liquefaction of bagasse and cotton stalks was conducted by using polyhydric alcohols (polyethylene glycol PEG#400 and glycerin) in the presence of sulfuric acid (SA) as a catalyst. The effects of different liquefaction conditions, such as ratio raw material/liquefying solvent, effect of PEG#400/glycerin, acid concentration, liquefaction temperature and time on the liquefaction yield have been investigated. The hydroxyl and acid numbers for some liquefied samples were also determined. The results showed that the minimum residue content was obtained at 1/5 raw material to liquefying solvent. PEG#400 alone is not favoured as liquefying solvent as it gives $\sim\!19\%$ residual content for bagasse and $\sim\!22\%$ for cotton stalks at the optimum studied reaction conditions. Replacing 10% of PEG#400 with glycerin as well as increasing the SA concentration, liquefaction temperature or time, decreased the amount of residue for both bagasse and cotton stalks to less than 10%. The hydroxyl number of the produced polyols slowly decreased from 253 to 223 mg KOH/g on extending the reaction time till 120 min and the residual polyols prevented re-condensation of the liquefied components. It seems that this system can be applied on various types of lignocellulosic agricultural residues.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Agricultural crop residues, such as sugar cane bagasse, rice straw, wheat straw and cotton stalks are the potential source of lignocellulosic raw materials in many countries, e.g. Egypt, India, China, ..., etc., where the wood supplies are limited or non-existent. A little amount of these lignocellulosic residues is used in pulp and paper industry and the remaining are generated as waste by-product in huge quantities every year, creating disposal problems in absence of its proper utilization. Such ligonocellulosic crop residues contain appreciable quantities of cellulose, hemicelluloses and lignin, therefore, an effective utilization creates a renewable source for production of several beneficial products (Majumdar and Chanda, 2001). The main reason for the ineffective utilization of these lignocellulosic residues was the lack of techniques by which

these wastes can be converted into materials with high additional values (Lin et al., 1994).

In recent years, a promising new approach of liquefying the whole lignocellulosic materials was developed; this technique opened the door for utilizing the huge amounts of biomass unused (Shiraishi et al., 1985). Through liquefaction, lignocellulosic components, cellulose, hemicelluloses and lignin are brought to low molecular weight compounds with high reactivity that can be used in many useful potential applications. Liquefaction technique can be done in the presence of organic solvents (phenols or polyhydric alcohols) using acidic or alkaline catalyst (organic or inorganic) at temperatures ranging from 120 to 180 °C, or without catalyst at higher temperatures ranging from 180 to 250 °C (Pu and Shiraishi, 1993; Kato et al., 1990; Kurimoto et al., 1992; Maldas and Shiraishi, 1997; Alma et al., 1996). Recently, many solvents, such as cyclic carbonates,

^{*} Corresponding author.

lower alcohols and dioxane were examined and used successfully for the liquefaction of woody biomass (Yamada and Ono, 1999; Hassan and Mun, 2002; Mun and Hassan, 2004). The products of phenol liquefaction are rich in phenolic units and, therefore, can be utilized for preparation of phenolic resins, moldings and adhesives (Kato et al., 1990; Lin et al., 1995). The products of polyhydric alcohol liquefaction (biomass-based polyols) could be used directly without any additional reaction or treatment for making polyurethane foams with comparable properties to conventional polyurethane foams (Yao et al., 1995, 1996).

In the literature, very little studies have been found focusing on the liquefaction of agricultural residues by using organic solvents. Therefore, the aim of this work was studying the liquefaction of bagasse and cotton stalks using PEG#400/glycerin blended solvents and evaluating the produced polyols as starting material for the preparation of polyurethanes. Liquefaction conditions, such as raw material to solvent ratio, solvent type, catalyst concentration, liquefaction temperature and time have been investigated. The composition of liquefied products was characterized using FTIR spectroscopy. The hydroxyl groups and acid number, which are important parameters in the preparation of polyurethanes, were also determined for the resulted polyols.

2. Materials and methods

2.1. Raw materials

Depithed bagasse – delivered from Edfo mill by Aswan, Egypt – and cotton stalks (Giza 75) obtained from cotton farms were used in this study. The cotton stalks were cut into pieces about 2.5–4.0 cm in length by hand without debarking. Bagasse and cotton stalks were ground by a Wiley mill, sieved and particles of mesh size 20–80 μm were used in this study. Some of the characteristics of these raw materials are shown in Table 1. The analysis of the raw materials was determined according to the following methods:

- Lignin content (Institute of paper chemistry, Appleton, Wisconsin 428, 1952).
- Hemicellulose content (Jayme and Sarten, 1941).
- α-Cellulose content (Zellcheming Merkblatt IV/29 A).
- Ash content (T 211-om 93).

2.2. Liquefaction

Liquefaction experiments were carried out in a 100 ml reaction flask. The flask was charged with the liquefying solvent and

Table 1 – Some characteristics of bagasse and cotton stalks Cotton stalks Bagasse 23.3 Lignin content (%) 20.1 21.7 17.4 Hemicellulose content (%) α-Cellulose content (%) 49.2 48.8 Ash content (%) 1.55 1.84

catalyst (SA). Then, it was immersed for about 1 min in an oil bath preheated to the reaction temperature to allow for complete mixing of chemicals. After that 3 g o.d. raw material was added to the flask. The flask was immersed again in the oil bath and this time is considered to be the starting reaction time. After ending liquefaction time, the flask mixture was diluted with 80% 1,4-dioxane and immersed in a cold-water bath to quench the reaction. The diluted resultant was filtered in a G4 glass filter to separate the residue and filtrate. The residue was washed with 100% 1,4-dioxane, dried at 105 °C for 12 h in an oven and then weighed.

$$Residue\ content\ (\%) = \frac{Residue\ (g)\times 100}{Weight\ of\ raw\ material\ (o.d.)}$$

Liquefaction yield (%) = 100 - Residue content (%)

2.3. FTIR analysis

Infrared spectra of bagasse and cotton stalks liquefied wood were investigated by using Fourier Transform Infrared Spectrophotometer (FTIR-3000 E). All measurements were carried out using the KBr disc technique.

2.4. Measurement of hydroxyl number of liquefied materials (LM)

The hydroxyl numbers of LM was determined as follows: a mixture of $1\,\mathrm{g}$ LM and $25\,\mathrm{ml}$ of a phthalation reagent was heated for 20 min at $110\,^\circ\mathrm{C}$. This was followed by addition of $50\,\mathrm{ml}$ of 100% 1,4-dioxane and $25\,\mathrm{ml}$ of distilled water, and the mixture was titrated with a $1\,\mathrm{M}$ sodium hydroxide solution to the equivalence point using a pH meter. The phthalation reagent consisted of a mixture of $150\,\mathrm{g}$ phthalic anhydride, $24.2\,\mathrm{g}$ imidazol and $1000\,\mathrm{g}$ dioxane. The hydroxyl number in $100\,\mathrm{m}$ mg KOH/g of sample was calculated by the following equation:

$$\label{eq:Hydroxyl number (mg KOH/g) = } \frac{\left(B-A\right)N\times56.1}{W} + \text{Acid number}$$

where A is the volume of the sodium hydroxide solution required for titration of LM sample (ml); B is the volume of blank solution (ml); N is the normality of the sodium hydroxide solution and W is the weight of LM (g).

2.5. Measurement of acid number of LM

A mixture of 8 g LM sample, 80 ml 100% 1,4-dioxane and 20 ml water was titrated with 1 M sodium hydroxide solution to the equivalence point. The acid number in mg KOH/g of sample was calculated by the following equation:

Acid number (mg KOH/g) =
$$\frac{(C - B)N \times 56.1}{W}$$

where C is the titration volume of the sodium hydroxide solution at the equivalence point (ml); B is the volume of blank solution (ml); N is the normality of the sodium hydroxide solution and W is the weight of LM.

Download English Version:

https://daneshyari.com/en/article/4515321

Download Persian Version:

https://daneshyari.com/article/4515321

Daneshyari.com