Fuel 113 (2013) 340–346

Contents lists available at SciVerse ScienceDirect

Fuel

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

Hydrothermal decomposition of rapeseed straw in subcritical water. Proposal of three-step treatment

Hanna Pińkowska *, Paweł Wolak

Department of Industrial Chemistry, Wrocław University of Economics, ul. Komandorska 118/120, 53-345 Wrocław, Poland

HIGHLIGHTS

- Utilizing of rapeseed straw-rich in lignocellulosic components waste product.
- Three-step hydrothermal treatment of rapeseed straw as a new method of its conversion.
- Investigation of the effects of the temperature and time on the composition of the reaction products.
- Saccharides and phenolics as a valuable products of studied reaction.

ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form 28 May 2013
Accepted 28 May 2013
Available online 11 June 2013

Keywords:
Rapeseed straw
Subcritical water
Hydrolytic depolymerization
Saccharides
Phenolics

ABSTRACT

We have investigated the three-step hydrothermal decomposition of rapeseed straw, rich in lignocellulosic components, as a batch process. The effects of the reaction temperature and holding time on the composition of the reaction products were studied. After the first step of the treatment there prevailed products of the hydrolytic depolymerization of hemicellulose. The highest yield of xylose (5.87% (w/w)) was obtained at a temperature of 210 °C and a holding time of 10 min. In the second step of the process as a result of depolymerization of cellulose, glucose was obtained, with the largest yield (17.4% (w/w)) at a temperature of 270 °C after 5 min. Unreacted lignin was used in the third step of the treatment. Its decomposition was performed at a temperature of 330 °C. The highest yield of guaiacol (11.56% (w/w) and catechol (5.61% (w/w)), was obtained after a holding time of 0 min and 60 min, respectively, whereas the highest yields of phenol (4.11% (w/w)), *m*,*p*-cresol (4.09% (w/w)) and *o*-cresol (2.71% (w/w)), were obtained after 150 min. The solid residue obtained in the third step of the process consisted mainly of phenolic biochar.

1. Introduction

In recent years, there has been growing interest in using subcritical water as an environmentally friendly reaction medium. The valuable properties of subcritical water are exploited in, e.g., the conversion of waste plant biomass into useful bioproducts [1–4].

Rapeseed straw – raw material, rich in hemicellulose, cellulose and lignin components, produced from rapeseed (*Brassica napus L.*) during the manufacture of rapeseed oil for consumption and in the fuel industry (production of biodiesel) – is an example of waste biomass that can be successfully utilized in hydrothermal conditions.

Until now, only a few attempts have been made at using rapeseed straw as a base material in processing in subcritical water without the catalyst [5] and with the use of H_2SO_4 [6,7]. After hydrothermal pretreatment the solid postreaction residue containing unreacted cellulose was subjected to enzymatic hydrolysis [5,7,8] and fermentation which resulted in bioethanol production [7].

The present research was undertaken to study the hydrothermal decomposition of 5% (w/w) rapeseed straw suspension in subcritical water under batch conditions, leading to the production of valuable bioproducts. The use of subcritical water is believed to have a positive effect on the decomposition of rapeseed straw to saccharides and phenolic compounds, as the main reaction products. The hydrothermolysis was performed as a three-step process, without adding a catalyst. The effect of the reaction parameters – temperature and holding time – on the degree of conversion of the components contained in the rapeseed straw was investigated. The composition and yield of the compounds in the water product fractions was determined, and solid postreaction residues produced by the rapeseed straw hydrothermal decomposition, were examined.

* Corresponding author. Tel.: +48 71 36 80 879; fax: +48 71 36 80 275.
E-mail address: hanna.pinkowska@ue.wroc.pl (H. Pińkowska).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.05.088

2. Materials and methods

2.1. Materials and chemicals

For all experiments, rapeseed straw was used harvested on a farm in Opolskie Province (Poland). Saccharides and carboxylic acids (acetic, glycolic, lactic and levulinic), were purchased from Fluka, while water, aldehydes including furfurals, 1,2,4-benzenetriol (BTO) and dihydroxyacetone (DHA), and also catechol, guaiacol, *o*-cresol, *p*-cresol and phenol were purchased from Sigma–Aldrich. *m*-Cresol was derived from Roth GmbH. Formic acid, oxalic acid and other reagents used in chromatographic determinations were purchased from POCh (Poland). Analytically pure and HPLC-grade reagents were used without further purification.

2.2. Reactor and experimental procedure

The grain size rapeseed straw, dried at 103 °C for 24 h and ground below 1-mm was decomposed in a 4576A-type batch reactor (Parr Instrument Company, USA).

Preliminary experimental results with hydrothermal decomposition of model substances for waste plant biomass and with rapeseed straw (data not shown) allowed to set the initial reaction parameters: the reaction temperature and time.

In the first step of the experiments (series 1) the hydrothermal decomposition of the rapeseed straw was conducted at a temperature of 210 °C. The second set of experiments (series 2) was performed at a temperature of 270 °C and as raw material the postreaction residue obtained in the series 1 was used. The reaction would be stopped once the intended temperature was reached (zero holding time) or after a holding time of 5, 10, 15, 20 and 30 min. In the third step of experiments (series 3) the solid postreaction residue obtained in the series 2 was used as raw material. The series 3 was conducted at a temperature of 330 °C and a holding time of 0, 30, 60, 90, 120 and 150 min.

In each run the reagents were used at a water/raw material mass ratio of 95:5. The liquid and solid product fractions were collected by washing the reactor vessel with water. Detailed description of the reactor equipment, as well the experimental procedure is given in Supplementary material. Fig. 1S (is given in Supplementary material) shows the temperature profile of a typical runs. The heating profile showed three zones, i.e. heating up, maintenance after the target temperature was reached, and cooling down.

2.3. Separation of the reaction products

As a result of the hydrothermal decomposition of rapeseed straw and solid postreaction residues obtained from subsequent steps (series 1 and 2) of the conversion, a liquid product containing water-soluble substances (the WS fraction) and pretreated solids (the WN fraction) were obtained. Each time, the WS fraction was separated from the WN fraction by vacuum filtration using PTFE membrane filters (Sartorius, SRP 15, 0.45 μm).

The yield (% w/w) of reaction products was defined as the weight of the product to the initial weight of raw material loaded into the reactor vessel.

2.4. Analysis and analytical methods

Except for moisture content determinations, raw rapeseed straw and pretreated rapeseed straw dried to constant mass were investigated. The chemical composition of rapeseed straw and solid postreaction residues (obtained from successive steps of the process) was determined using typical chemical analysis methods for plant biomass [9,10]. All the analytical determinations were performed in triplicate and the mean values were calculated.

The composition of rapeseed straw and WN fractions was determined by elemental analysis and Fourier transform infrared spectroscopy (FTIR). The elementary composition of rapeseed straw and other raw materials loaded into the reactor vessel was determined with a Vario EL III analyzer (Elementar Analysensysteme GmbH), while their Fourier transform infrared spectra (FTIR) were recorded using a Perkin Elmer System 2000 spectrometer (2 mg sample in 200 mg KBr).

The WS fractions were directly analyzed by high performance liquid chromatography (HPLC) [11–13]. These determinations were made by using a Merck-Hitachi chromatograph equipped with a gradient pump (SmartLine 1000, Knauer).

The saccharides (arabinose, fructose, galactose, glucose, mannose and xylose) contents were determined with an experimental error of ±5% at a temperature of 85 °C on a Biorad Aminex HPX-87P column, equipped with a precolumn. Water flowing at a rate of 0.6 $cm^3 \times min^{-1}$ was used as the mobile phase. Saccharides were detected using a refractometric (RI) detector K-2300 (Knauer).

The carboxylic acids (acetic, formic, glycolic, lactic and oxalic) contents were determined with an experimental error of ±3% using a Eurospher C18 column (Knauer), 25 mM KH_2PO_4 (pH correction up to 2.5 with 85% H_3PO_4) as the mobile phase, a mobile phase flow rate of 1.5 $cm^3 \times min^{-1}$ and a Merck-Hitachi L7455 diode array detector (DAD) at a wavelength of 210 nm.

The 2-furfural and the 5-hydroxymethylfurfural contents were determined at a temperature of 35 °C in a Eurospher C18 column. A solution consisting of acetonitrile and solution A (2 cm^3 acetic acid + 0.2 cm^3 phosphoric acid, diluted with water up to 1 dm^3) at a ratio of 18:82 v/v was used as the mobile phase. The flow rate of the mobile phase was 1.2 $cm^3 \times min^{-1}$. The DAD detector was used and measurements were performed at a wavelength of 280 nm. Experimental errors were about 5%.

A Shodex KC-811 column was employed to determine the aldehydes (glyceraldehyde, glycolaldehyde and pyruvaldehyde), 1,2,4-benzenetriol, dihydroxyacetone and levulinic acid contents. The analytes were separated and identified using a 5.0 mM solution of H_3PO_4 as the mobile phase, a phase flow rate of 1 $cm^3 \times min^{-1}$, the DAD detector (210 nm wavelength) and a RI detector. Experimental errors were about ±3%.

The contents of catechol, guaiacol, *m, p*-cresols, *o*-cresol and phenol with an experimental error of ±5% were determined at a temperature of 40 °C on an Inertsil ODS-3 column (Bujno Chemicals). As the mobile phase, an acetonitrile and water solution at an acetonitrile: water ratio of 95:5 v/v was used. The mobile phase flow rate was 1.0 $cm^3 \times min^{-1}$. A DAD detector was used, with the detection wavelength of 280 nm.

Moreover, WS fractions obtained in the third step of hydrothermal decomposition of rapeseed straw were identified by gas chromatography mass spectroscopy (GC–MS). The GC–MS analyses were predated by extraction of the components contained in the studied WS fractions with diethyl ether. 0.5 cm^3 samples and 1 cm^3 of ether were shaken and separated. The chromatographic analysis was performed using a Hewlett-Packard 6890 gas chromatograph coupled with a HP5973 mass selective detector. A DB1701 capillary column (30 m × 0.25 mm i.d., 0.25 mm film thickness, cross-linked 14%-cyanopropyl–phenyl)–methylpolysiloxane was used with He as the carrier gas at a constant rate of 0.7 $cm^3 \times min^{-1}$. The temperature of the column was programmed from 45 °C to 260 °C at 10 °C × min^{-1} after an initial 1 min isothermal period and kept at the final temperature for 10 min. The inlet was maintained at 260 °C. Sample injection was made in the split mode (1:10). The mass spectrometer was set at an ionizing voltage of 70 eV with mass range *m/z* 25–350. The identification of rapeseed straw hydrothermal decomposition components in the WS fractions