Bioresource Technology 119 (2012) 48–54

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Hydrothermal decomposition of glucose and fructose with inorganic and organic potassium salts

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HIGHLIGHTS

- The effect of inorganic and organic salts on hexose decomposition was studied.
- The decomposition rate constants and impact factors of hexoses were calculated.
- Anions influence the decomposition of hexose via different mechanisms.
- The relationship between impact factor and physical properties was demonstrated.

ARTICLE INFO

Article history:
Received 5 February 2012
Received in revised form 22 May 2012
Accepted 22 May 2012
Available online 1 June 2012

Keywords:
Hydrothermal decomposition
Anion
Glucose
Fructose
5-Hydroxymethylfurfural

ABSTRACT

The effects of 15 inorganic and organic acid potassium salts on hydrothermal decomposition of glucose, fructose and 5-hydroxymethylfurfural (5-HMF) were investigated at 180 °C. The rate constants for glucose, fructose and 5-HMF decomposition with anions were calculated by a pseudo first-order equation, and the impact factors of the rate constants were calculated, to demonstrate the catalytic effect of the different anions. Compared to the results without added salts, chloride, bromide, iodide and nitrate anions did not significantly accelerate the decomposition rate of glucose or improve the selectivity for 5-HMF, but increased the decomposition rate of fructose from 19% to 44%, and improved the selectivity for 5-HMF by 4–29%. Phosphate, fluoride, sulfate and all organic acid anions increased the decomposition rate of glucose and fructose by 23–2781%, but lowered the selectivity for 5-HMF from 36% to 100% as compared to the results without added salts. These findings provide insights on the reactivity and mechanism of the hydrothermal decomposition of glucose and fructose with inorganic and organic salts.

1. Introduction

The hydrothermal decomposition of cellulose or its constituent, glucose, to produce platform chemicals, such as 5-hydroxymethylfurfural (5-HMF) and levulinic acid is impacted by the presence of inorganic salts. For example, Fe^{3+}, La^{3+}, Zn^{2+} and Cu^{2+} are able to catalyze the decomposition of cellulose and glucose, and improve the selectivity for 5-HMF (Bicker et al., 2005; Lu and Lu, 2009; Rasrendra et al., 2010; Seri et al., 2002). A role of sulfate and chloride anions in the formation of humin from glucose has also been reported (Tyrlik et al., 1996). The current study was carried out to investigate the impact of a wider range of anions on the decomposition of glucose and fructose and to elucidate possible mechanisms by which these anions influence their decomposition. Glucose and fructose were selected as model compounds, and the hydrothermal decomposition of these sugars in the presence of 15 types of potassium salts was conducted. The stability of 5-HMF in the presence of these salts was also investigated. The decomposition rate constant and impact factor of the rate constants were also calculated.

2. Experimental section

2.1. Materials

Glucose, fructose, and potassium fluoride, chloride, bromide, iodide, nitrate, sulfate, phosphate, formate, acetate, oxalate and citrate were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Potassium propionate, trifluoroacetate, benzoate and sorbate were obtained from Tokyo Chemical Industry Co. LTD, Japan. 5-Hydroxymethyl-2-furaldehyde (5-HMF) was purchased from Sigma, USA.

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http://dx.doi.org/10.1016/j.biortech.2012.05.113