



Modification of potato peel waste with base hydrolysis and subsequent cationization

Katja Lappalainen, Johanna Kärkkäinen, Päivi Joensuu, Marja Lajunen*

Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 University of Oulu, Finland

ARTICLE INFO

Article history:

Received 27 November 2014
Received in revised form 21 May 2015
Accepted 27 May 2015
Available online 10 June 2015

Keywords:

Potato peel waste
Starch
Cationization
Microwave activation

ABSTRACT

Potato peel waste (PW) is a starch containing biomaterial produced in large amounts by food processing industry. In this work, the treatment of PW by alkaline hydrolysis and cationization in the water phase is reported. In order to improve the cationization of starch, PW was hydrolyzed by heating with alkaline (NaOH) ethanol solution (80%) in a water bath. The impact of variable molar ratios of anhydroglucose unit (AGU):NaOH, heating temperatures and times was studied on the degradation of starch and the molecular size distribution of the product. The hydrolyzed PW was cationized subsequently in water by using glycidyltrimethylammonium chloride and catalyzed by NaOH under microwave irradiation or in an oil bath. The impact of the various reaction conditions on the cationization and degree of substitution of starch was studied. The degree of substitution of the cationized starch varied in the range of 0–0.35.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The present environmental law sets demands to reduce the production of waste or where the reduction is not practicable waste should be utilized. The legislation has also become gradually more restrictive. The EU directive 1999/31/EC on the landfill of waste requires that in 2016, the maximum fraction of the bio-compostable municipal waste, which is allowed to be disposed in landfills, is 25%.

Potato peel waste is a non-edible residue generated considerable amounts by food processing plants. Depending on the peeling process, i.e. abrasion, steam or lye peeling, the amount of waste can range between 15 and 40% of the amount of processed potatoes (Arapoglou, Varzakas, Vlyssides, & Israilides, 2010). Most of the PW is discarded (Chen, Lawton, Thompson, & Liu, 2012) and only a low amount of it is used as a supplementary animal feed, fertilizer or is composted (Israilides et al., 2008). PW from the abrasion peeling process contains a large quantity of starch, e.g. 52% (dry basis) (Camire, Violette, Dougherty, & McLaughlin, 1997). Starch is globally the second most abundant carbohydrate. After various modifications, it is largely used in industrial applications

and is a potential resource for bioenergy production. The use of PW for chemical modifications of starch would promote the material efficiency and the sustainable use of natural resources.

In this work, we have studied the suitability of PW for a starting material of the cationization of starch. Typically, the commercial cationized starch derivatives have a low degree of substitution (DS < 0.2). They are exploited, e.g. as a wet-end chemicals in paper industry and flocculants in raw or wastewater clarification (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Heinze, Haack, & Rensing, 2004). The goal of the study was to produce the cationized material in water starting from the partly hydrolyzed potato peel waste. PW and starch are highly insoluble in water, which leads to a heterogeneous reaction system and potentially reduced reactivity. In order to improve the reactivity of starch, PW was pre-treated by a base hydrolysis with NaOH prior to the cationization step. To the best of our knowledge the direct chemical modification of potato peel waste by alkaline depolymerization or cationization has not been reported earlier.

2. Materials and methods

2.1. Reagents

Potato peel waste produced by the abrasion peeling process was provided by Tervakankaan Peruna Oy, Finland. The composition of PW was very heterogeneous and the colour was brown (Scheme 1). The water content of PW was 80%. PW was dried at 105 °C until a constant weight and stored in a desiccator. The dried PW and

Abbreviations: PW, potato peel waste; HW, hydrolyzed potato peel waste; CW, cationized hydrolyzed potato peel waste.

* Corresponding author. Tel.: +358 294 481632; fax: +358 8 5531629.

E-mail addresses: Katja.Lappalainen@oulu.fi (K. Lappalainen),

Johanna.Karkkainen@oulu.fi (J. Kärkkäinen), Paivi.Joensuu@oulu.fi (P. Joensuu), Marja.Lajunen@oulu.fi (M. Lajunen).



Scheme 1. Dried potato peel waste was hydrolyzed under alkaline conditions.

other solid reaction products were homogenized by powdering with a coffee grinder before the use. All reactions were performed by using the same batch of the potato peel waste produced. The starch content of the dry PW was calculated to be 70% based on the starch content of the wet PW (13%, determined by the supplier, Tervakankaan Peruna Oy) and water. Other reagents were used as received from the suppliers.

2.2. Base hydrolysis of potato peel waste

PW (20 g) was hydrolyzed in alkaline (6.2 M aqueous NaOH, v/v) ethanol (80%) solution (100 ml). The molar ratio of AGU:NaOH was either 1:1, 1:0.5 or 1:0.1, respectively. Each hydrolysis was performed in the water bath at 40 and 60 °C with the reaction time of 1, 2 or 3 h. After the reaction, the pH of the reaction mixture was adjusted to 7 by conc. HCl. The product was precipitated by adding ethanol and filtered through a sintered glass funnel (grade 4, 10–16 μm). The filter cake was washed three times with the water–ethanol (1:1) mixture and dried at 35 °C until a constant weight was obtained.

2.3. Cationization of hydrolyzed potato peel waste in microwave reactor or oil bath

The cationization of the hydrolyzed potato peel waste (HW) was performed according to the literature (Bendoraitiene, Kavaliuskaite, Klimaviciute, & Zemaitaitis, 2006; Heinze et al., 2004). The powdered HW (1 g) was weighed into a flask or microwave reactor tube (size 10–20 ml) equipped with a magnetic stirring bar. Distilled water (9 ml) and NaOH (57 μl, 6.2 M aqueous solution) were added. Glycidyltrimethylammonium chloride (70% aqueous solution, Sigma–Aldrich, Germany) was added dropwise into the stirred reaction mixture. The molar ratio of AGU:GTAC was either 1:1 or 1:2. The reaction vessel was set into the oil bath or irradiated in the microwave reactor (Biotage Initiator with a single-mode microwave unit). The stirred mixture was heated at 60 or 80 °C for 2 and 4 h. The cooled crude product was precipitated by adding ethanol (60 ml) and filtered through a sintered glass funnel (grade 4). The filter cake was washed three times with ethanol and dried at 35 °C.

2.4. Water-solubility determinations

The water-solubility of dry PW, HW or cationized potato peel waste (CW) was determined by suspending a sample (15 mg) of each material into distilled water (1.5 ml) in a weighted Eppendorf tube. The suspension was centrifuged (Eppendorf Minispinner) for 3 min with the speed of 13,200 rpm. The supernatant was decanted and the remaining solid was dried at 35 °C until a constant weight was obtained.

2.5. Characterization of hydrolyzed and cationized products with ¹H NMR and HPLC-ELSD

A sample (10 mg) was taken from the product of each hydrolysis and cationization reaction for ¹H NMR measurement. D₂O (1.5 ml) was added and the mixture was carefully shaken. The mixture was

centrifuged at 13,200 rpm for 3 min. The supernatant was decanted and its ¹H NMR spectrum was recorded with a Bruker DPX 200 MHz spectrometer at ambient temperature. The solvent peak was used as a reference.

The supernatants of the water-solubility determinations were used to estimate molecular size distribution of PW and CW with the HPLC-ELSD method (Kärkkäinen, Lappalainen, Joensuu, & Lajunen, 2011). Dextrans (BioChemika Dextran 5, 25, 50, and 150 kDa) were used as standards (Lappalainen, Kärkkäinen, & Lajunen, 2013). The samples were analyzed with a Shimadzu HPLC-ELSD instrument, which consisted of three isocratic pumps (LC-10AD), a degasser (DGU-14A) and an automatic sampler (SIL-10AD) and was equipped with a guard column (PolySep–GFC–P 35x7.80 mm, Phenomenex, Macclesfield, Cheshire, UK) and an analytical column (Poly Sep–GFC–Linear 300x7.80 mm, Phenomenex, Macclesfield, Cheshire, UK). The temperature of the column oven (Shimadzu, CTO-10AS) was maintained at 40 °C. The ELS detector (Polymer Laboratories PL-ELS 2100) was optimized for the analytes and the following parameters were used: 80 °C for an evaporative temperature, 50 °C for a nebulizer and 0.90 ml/min for a nitrogen gas flow. Distilled-deionized water passed through in-line membrane filters (0.45 μm Millipore, Bedford, MA) was used as a mobile phase with the flow rate of 0.4 ml/min. The system was controlled and data was handled by using LC Solution program (LabSolutions 1.03 SP5 Shimadzu).

3. Results and discussion

3.1. Base hydrolysis of potato peel waste

In order to improve the water-solubility and reactivity of PW for cationization, PW was pre-treated by basic ethanol (Scheme 1). Conventionally, alkaline hydrolysis is performed in water. In this study, ethanol (80%, v/v) was a more suitable reaction media because it also inhibited the gelatinization of starch (Heinze et al., 2004) and thus facilitated the work-up of the subsequent cationization. Additionally, basic ethanol dissolves phenolic compounds, a minor constituent of PW (Mohdaly, Sarhan, Smetanska, & Mahmoud, 2010; Wan Ngah & Hanafiah, 2008). The removal of these compounds is preferred since they can interfere the cationization reaction. Furthermore, the phenolic compounds of potato are also nutritionally and pharmacologically beneficial compounds, which justifies their recovery (Schieber & Saldana, 2009; Singh et al., 2011).

The conditions of the hydrolysis reactions are given in Table 1. Visible differences between the separate reactions or their products were not detected. Ethanol dispersed the reaction components and thus ensured the efficient mixing. After the depolymerization, the crude product was precipitated by ethanol and separated by vacuum filtration yielding a brown sand-like product. The filtrate was dark brown in colour, which indicated that alkaline ethanol dissolved the coloured compounds of PW. Those compounds were not in the focus of this study and hence the filtrates were not analyzed.

In order to study the effect of the alkaline treatment on PW, the molecular size distribution of the hydrolysis products was estimated with HPLC-ELSD and the water-solubility of the products was studied. According to the HPLC-ELSD study, the molecular

Download English Version:

<https://daneshyari.com/en/article/7787458>

Download Persian Version:

<https://daneshyari.com/article/7787458>

[Daneshyari.com](https://daneshyari.com)