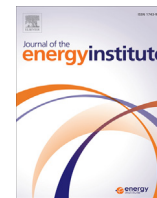




Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: <http://www.journals.elsevier.com/journal-of-the-energy-institute>

Decomposition kinetics of uronic acids obtained from kelp under hydrothermal condition

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ARTICLE INFO

Article history:

Received 24 May 2015

Received in revised form

16 February 2016

Accepted 22 February 2016

Available online xxx

Keywords:

Biomass

Marine macroalgae

Hydrothermal treatment

Uronic acid

Decomposition

Q1 Kinetic parameters

ABSTRACT

The main objective of this study was to obtain guidelines for the hydrothermal pretreatment of kelp for the isolation of uronic acids. This was done by determining the effect of hydrothermal treatment on the kinetic of the decomposition of mannuronic acid (MA) and guluronic acid (GA). These uronic acids were obtained by the hydrolysis of alginic acid originating from kelp. Each uronic acid was treated under hydrothermal conditions using a continuous-flow reactor. The temperature ranged from 170 to 250 °C, the residence time was varied between 5 and 100 s, and the pressure was set at 25 MPa. The decomposed products were analyzed with high-performance liquid chromatography (HPLC). The yields of both uronic acids showed similar trends; they decreased as the temperature was increased. Activation energies for the decomposition of MA and GA were approximately 28.3 and 20.6 kJ/mol, respectively, and pre-exponential factors were determined to be 282 and 40.6 s⁻¹, respectively. Uronic acids were readily decomposed under hydrothermal conditions. Calculations showed the superiority of the continuous reactor over the autoclave reactor, in terms of the recovery of uronic acids.

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1. Introduction

The development of renewable resources, to substitute or reduce our dependency on non-renewable resources, is of essential importance. This is mainly because of environmental problems concerning global warming, fossil fuel depletion, and fluctuations in the price of crude oil. The use of marine macroalgae as a renewable resource has attracted significant attention of researchers in various fields of study. Typically, the growth rate of marine algae is significantly higher than those of terrestrial plants. For example, a study showed that the mass production rate of several species of macroalgae such as kelp is as high as 40 g/m² d¹ [4]. Thus, a relatively small area is required for their cultivation. Furthermore, the considerable amount of carbohydrates contained in macroalgae has a great potential to be used as a feedstock for bioconversion.

Various studies have been conducted on the use of kelp for several applications, including the production of biogas and bioethanol [2,5–7]. Its characteristics as a biofuel also have been extensively studied [15]. Additionally, this type of brown algae has a higher nutritional value, and it is mainly used for human consumption [3]. Others have highlighted the possibility of kelp to be used as a marine bioreactor [14]. Nevertheless, pretreatment of these brown algae is essential for their efficient use. This is because kelp contains a significant amount of carbohydrates such as alginic acid, which is not easily digested. A group of researchers successfully conducted the hydrothermal treatment of kelp for the production of reducing sugars. They demonstrated that the reaction temperature and time significantly affect the decomposition of the sugars [13]. Another study was conducted on the production of organic acids from alginate under hydrothermal conditions.

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The results indicated a significant influence of the reaction conditions on the mechanism of decomposition of alginate [1]. Besides [9], have highlighted the negligible effect of salt on the hydrothermal treatment of kelp using a batch reactor system.

Alginic acid has a complex structure that consists of a sequence of uronic acids, namely, guluronic acid (GA) and mannuronic acid (MA), as illustrated in Fig. 1. The properties of alginic acid, the main component of kelp, have been studied thoroughly. It has been reported that the rate of decomposition of alginic acid is higher than that of sodium alginate because, in alginic acid, the decomposition is intramolecularly catalyzed by carboxyl groups [18]. Furthermore, the rate of degradation also strongly depends on the phenolic content [12,17]. In addition, several researchers have studied the effect of the hydrolysis process on the structure of alginic acid [8,20,22]. Nonetheless, the reaction kinetics of the individual uronic acid constituents of alginic acid have yet to be studied. These characteristics are of importance for determining the hydrothermal pretreatment conditions. Thus, this research was initiated to elucidate the kinetic behavior of GA and MA under hydrothermal conditions.

Hydrothermal treatment is considered to be a clean technology for the conversion of biomass into valuable products. Basically, the process employs water as a solvent at high temperatures and pressures, which changes the structure of biomass [16]. In fact, the change in the structure of biomass is greatly affected by the hydrothermal conditions. Subcritical water is often employed for the pretreatment in order to avoid decomposition of the organic products. Thus, it is desirable to know the decomposition characteristics of uronic acids. The purpose of this study is to obtain guidelines for the hydrothermal pretreatment of kelp for the recovery of uronic acids, by determining the behavior of uronic acids under subcritical-water conditions, so that the use of kelp as a renewable resource can be further explored and commercialized.

2. Material and methods

2.1. Materials

Commercial alginic acid (originating from kelp) was supplied by Sigma–Aldrich; other chemicals were of analytical grade and purchased from Nacalai Tesque.

2.2. Sample preparation

About 1 wt% of alginic acid was heated to 90 °C, and 3 mol/dm³ hydrochloric acid (HCl) was added (approximately 3% of the total volume). After 30 min, the remaining solid was filtered and subjected to another 2 h of heating at the same temperature in 0.3 mol/dm³ HCl. Then, the solid that remained in the hydrolysate was separated by filtration and dissolved in 1 mol/dm³ sodium hydroxide (NaOH) to obtain a homogeneous solution that contained a mixture of GA and MA.

Separation of these uronic acids was performed by adjustment of the pH of the solution. At pH 2.85, the insoluble product was GA, while MA remained dissolved. The recovery of MA as a solid product was conducted by the addition of an equal volume of ethanol to the solution. The uronic acids were kept in closed containers and preserved in a refrigerator prior to their use in the hydrothermal treatment process.

2.3. Hydrothermal treatment of uronic acids

The experimental apparatus employed in this study was a tubular flow reactor, whose detail have been described in a previous paper [21]. The length of reactor was set to 6 m, while its diameter was kept at 1 mm. Water was first pumped into the preheater to reach the desired temperature. The feedstock solution was then supplied and mixed with hot water from the preheater, just at the entrance of the reactor. The ratio of feedstock to water in the supply was fixed at 1:4, and the concentrations of MA and GA in the feedstock were 0.16 and 0.08 mol/dm³, respectively. The reaction occurred inside the reactor at various temperatures, ranging from 170 to 250 °C, and at a fixed pressure of 5 MPa. After a specified residence time, the product stream was cooled in the heat exchanger and then delivered to the back-pressure regulator for depressurization. Finally, the liquid product was collected at the sampling point.

2.4. Product analysis

The liquid product obtained in the experiment was quantitatively analyzed with an high-performance liquid chromatography (HPLC) instrument (Shimadzu) that was equipped with a sugar column (Shodex KS-802). The analysis was performed using distilled water as the eluent, at a flow rate of 0.5 cm³/min, and at an oven temperature of 60 °C. The yields of the uronic acids were calculated by dividing the concentration of uronic acid in the feedstock after the reaction by the initial concentration.

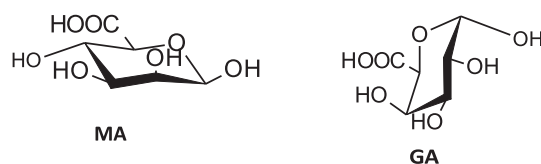


Fig. 1. Chemical structure of GA and MA.

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