Behavior of Organics in Kelp during Hydrothermal Pretreatment: Fundamental Characteristics and Effect of Salt

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Kelp (Laminaria japonica) was treated in a batch reactor under hydrothermal conditions over a temperature range of 150-190 ℃, and the resulting liquid and solid products were analyzed. The effect of salt on the hydrothermal pretreatment of kelp was also investigated. We found that more than 80 % of total organic carbon moved into the liquid phase, leaving only about 10 % in the solid phase. Thus, the effectiveness of the hydrothermal pretreatment on the dissolution of organic compounds was studied. Mannitol, the primary monosaccharide present in kelp, was extracted into the liquid phase; however, the high target temperature resulted in a slight decrease in the yield of mannitol. Formic acid and acetic acid were also produced. The effect of salt was not observed, which indicated the effectiveness of direct treatment of kelp under hydrothermal conditions without the need for desalination.

Key Words
Marine biomass, Hydrothermal pretreatment, Batch reactor, Kelp, Mannitol

1. Introduction

Japan has the sixth largest exclusive economic zone in the world; thus, utilization of marine resource is predictable 1). The production of renewable energy using such widely available sea based resources, especially marine biomass production followed by proper conversion, is attracting attention. Because the domestic biomass availability is only 5 % of the total energy supply in Japan, it is important to develop the marine biomass conversion technology for sustainability purposes 2). However, marine biomass is more expensive than land biomass making the economic feasibility of the former challenging. To circumvent this problem, we have proposed a marine biomass utilization system wherein both energy and value-added oil are produced along with mineral recovery 3). In this system, kelp is employed as feedstock, and some amount of kelp is fermented to produce value-added oil production. The remaining amount of the kelp is fermented to produce methane. To enhance the system efficiency, proper pretreatment of marine biomass is essential. In this regard, it would be worthwhile to examine the usefulness of hydrothermal pretreatment 4-8). In order to efficiently recover energy from marine biomass, it is imperative that fat production and salt-tolerant methane fermentation proceed rapidly, thereby necessitating the pretreatment of the marine bio-resources. Marine biomass has high water content; therefore, the hydrothermal pretreatment

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is effective as it destroys the cellular structure\(^{9, 10}\) and releases nutrients such as sugars, which are expected to be utilized as substrates for the microorganisms in fat production and methane fermentation.

Among the various marine biomass species, kelp is the most common macroalgae in Japan, and would be the best choice of feedstock. Mannitol and alginic acid are its main components as well as the target materials to be used as the substrates. Mannitol and alginic acid constitute 26 % and 20 % of the kelp, respectively, but they cannot be effectively used without the pretreatment because they are intracellular materials. Thus, hydrothermal pretreatment serves to release these components from kelp by destroying the cell structure, thereby allowing the microorganisms to gain easy access to the nutrients\(^{11}\). Studies on the hydrothermal treatment of marine biomass have been reported previously but the behavior of the nutrients has not been elucidated. Further, the effect of salts (essential for commercial applications) has also not been reported earlier. In order to determine the optimum conditions, it is necessary to know the behavior of the components extracted from the hydrothermally pretreated kelp. Therefore, the purposes of this study were to treat kelp under hydrothermal conditions and to analyze the behavior of the constituents of kelp as well as to determine the effect of salt on it.

2. Experimental

2.1 Apparatus and procedure

Fig. 1 shows the experimental apparatus, which was the same as that used in the previous study\(^{1, 2}\). The autoclave reactor had an inner diameter of 90 mm and a depth of 125 mm (inner volume: 800 cm\(^3\)), and was placed in an electric furnace for temperature control. A ceramic beaker, containing the feedstock and salt, was placed inside the autoclave to prevent the corrosion of the reactor wall due to salts. The use of silicon oil outside the ceramic beaker facilitated the heat transfer. After closing the lid, the autoclave was heated using the electric furnace until it reached the target temperature, and then it was cooled down to room temperature. The product was taken out of the autoclave and filtered to separate out the liquid and solid products for the analyses described below. The experimental conditions are shown in Table 1. Solid to liquid weight ratio is 0.04 kg/kg. The time required to reach the reaction time was 100 min for 150 ℃, and 200 min for 190 ℃.

2.2 Analytical methods

The liquid product was analyzed using a total organic carbon (TOC) analyzer to quantify the total carbon present in the liquid phase (non-purgeable organic carbon) and dissolved carbon dioxide (inorganic carbon). The organic components (mannitol, formic acid, acetic acid, and propionic acid) were quantified using high performance liquid chromatography (HPLC) with a Shim-Pack SCR-102H (Shimadzu) column under the following analytical conditions: 0.7 mL/min as flow rate, 0.005 M HClO\(_4\) as eluent, 40 ℃ as oven temperature, and a refractive index detector (RID).

The solid product was dried overnight in an oven at 105 ℃. The elemental analysis of the solid product was conducted using a Perkin Elmer Series II CHNS/O Analyzer 2400. The total carbon balance (solid + liquid) in this study was higher than 91 % in all of the experimental results discussed below.

2.3 Materials

Kelp (Laminaria japonica) was used as feedstock because they are found abundantly in Japan, and its carbon content was higher compared with other marine algae\(^{3}\). It was dried at 105 ℃ for 1 d and was pulverized to obtain a particle size of < 63 μm before use. Sodium chloride was added by 3 wt% to water to simulate sea water.

3. Results and Discussion

Fig. 2 shows the weight of the solid product obtained from the hydrothermal pretreatment of kelp in the presence and absence of salt. The solid yield was about 10 %. Table 2 shows the elemental composition of the
solid products. The elemental composition of the original kelp is also shown. After the hydrothermal pretreatment, the carbon content increased, whereas the ash content decreased. This suggested that pyrolysis had occurred, possibly releasing carbon dioxide and water while leaving the carbon structure behind. The decrease in the ash content might be due to the dissolution of a certain portion of the ash. However, the ash content in the solid product increased with increasing temperature. Possibly, more carbon dioxide was produced at higher temperatures, which precipitated the alkaline earth metal ions as carbonate salts. Further investigation is required for the elucidation of this phenomenon. We did not observe any effect of salts.

Fig. 3 shows the TOC yield in the liquid product obtained from the hydrothermal pretreatment in the presence and absence of salt. Table 3 shows the corresponding carbon balance calculation. The total carbon balance (solid + liquid) in this study was higher than 90% in all of the experimental results. We believe that this represented a decent carbon balance closure considering that we did not collect gas products. A low carbon balance at high temperatures implied that the gasification was enhanced at such temperatures. Also, the color of the silicone oil in the reactor changed to pale yellow after the completion of the hydrothermal treatment. Probably, a portion of the organic products evaporated, followed by reabsorption by the silicone oil. Again, we did not observe any effect of the salts.

Fig. 4 shows the effect of target temperatures on the pH of the liquid phase after the hydrothermal pretreatment of kelp in the presence and absence of salt. The pH under

<table>
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<tr>
<th>Temp. [℃]</th>
<th>Original kelp</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ash</th>
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<tr>
<td>150</td>
<td>30.7</td>
<td>4.9</td>
<td>1.5</td>
<td>2.3</td>
<td>27.9</td>
<td>32.7</td>
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</tr>
<tr>
<td>160</td>
<td>49.7</td>
<td>7.6</td>
<td>17</td>
<td>11</td>
<td>31.6</td>
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<tr>
<td>170</td>
<td>48.5</td>
<td>7.3</td>
<td>19</td>
<td>11</td>
<td>35.2</td>
<td>6.0</td>
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<tr>
<td>180</td>
<td>48.1</td>
<td>7.2</td>
<td>16</td>
<td>1.0</td>
<td>34.1</td>
<td>8.0</td>
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<tr>
<td>190</td>
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<td>6.6</td>
<td>16</td>
<td>1.0</td>
<td>33.3</td>
<td>10.5</td>
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Table 3 Total carbon in liquid and solid

<table>
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<tr>
<th>Temp. [℃]</th>
<th>Solid yield [mg]</th>
<th>C in solid phase [mg]</th>
<th>TOC in liquid phase [mg]</th>
<th>C in solid + liquid [mg]</th>
<th>C balance [%]</th>
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<td>150</td>
<td>236.5</td>
<td>107.4</td>
<td>100.8</td>
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<td>101.2</td>
<td>104.9</td>
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<td>102.0</td>
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<td>190</td>
<td>275.9</td>
<td>128.7</td>
<td>106.5</td>
<td>452.9</td>
<td>581.6</td>
</tr>
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</table>
The pH increased at higher temperatures. No effect of salt was observed.

Fig. 5 shows the effect of target temperature on the recovery weight of mannitol in the liquid phase, which was released as a result of the hydrothermal pretreatment in the presence and absence of salt. The effect of temperature was negligible, resulting in a recovery of about 0.7-0.9 g of mannitol from 2 g of dry kelp. A slight decrease in the recovery with temperature may be due to the decomposition of mannitol. No effect of salt was observed.

Fig. 6 shows the recovery weight of formic acid produced as a result of the hydrothermal pretreatment in the presence and absence of salt. Formic acid recovery has been reported previously. Under all conditions, the recovery weight was between 0.06 g and 0.08 g. The thermal decomposition of formic acid into a gas at high target temperatures was also observed in our study. This is in good agreement with the increase in pH over this high target temperature range. No effect of salt was observed.

Figs. 7 and 8 show the weights of acetic acid and propionic acid produced as a result of the hydrothermal pretreatment in the presence and absence of salt, respectively. The recovery weight of acetic acid was between 0.02 g and 0.04 g, and that of propionic acid was about 0.06 g. The effect of salt was negligible. No other acids were found in this study. Considering that the main components of kelp were mannitol and algic acid (both C6 sugar derivatives), organic acids might have been produced from other minor components rather than from mannitol.
and alginic acid. Analogous to glucose decomposition, C2-C4 scission and C3-C3 scission occur; therefore, C4 acid should be obtained if C6 sugar derivatives were used as the reactants.

Interestingly, the effect of salt was negligible in all the experiments performed in this study. The effect of salt was expected to increase the stability of ions and reduce the osmotic pressure. Over the temperature range studied here, which was far below the critical temperature, the stability of ions should not be significantly affected. As for osmotic pressure, once the cell structure was broken, no effect should have been observed. Possibly, owing to the foregoing reasons, no effect of salt was observed in this study. This suggested that desalination was not needed as a precursor for hydrothermal pretreatment. This potentially simplifies the process of kelp treatment, and is important from a practical viewpoint. This emphasizes the requirement for the development of microorganisms for methane fermentation and value-added oil production especially because the hydrothermal pretreatment without desalination results in products containing salt.

4. Conclusions

The behavior of organic compounds in kelp during hydrothermal pretreatment was experimentally investigated in the presence and absence of salt. It was found that more than 80% of the organic compounds were transferred to the liquid phase, leaving only 10% of the solids behind. Thus, the hydrothermal pretreatment was effective in releasing the organic compounds present in kelp into the liquid phase. The effect of salt was also studied and was found to be negligible. This indicated that the process of kelp treatment could be potentially simplified by excluding the desalination step.

Acknowledgment

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References

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