1. Introduction

The use of biomass as a sustainable energy resource has been evaluated by a number of researchers in terms of environmental, economical, and social aspects. Among the various types of biomass, marine macroalgae have been identified as a potential renewable energy resource, mainly due to their composition. Macroalgae are multicellular plants that exhibit characteristics similar to terrestrial biomass. They contain large quantities of carbohydrates, which are essential for their application as an alternative to non-renewable resources in biorefinery processes. In Japan, Laminaria japonica, or kelp, has been recognized as the most common macroalga, and is abundantly available, particularly in the Honshu and Hokkaido Islands.

Kelp is classified as brown algae and contains significant quantities of mannitol. This sugar alcohol is derived from its parent sugar, mannose, by the reduction of the aldehyde group to a hydroxyl group. To recover mannitol and other components from kelp, hydrothermal pretreatment is effective, which involves the treatment of kelp with hot compressed water. However, as the use of severe conditions can result in the decomposition of mannitol, its decomposition characteristics under hydrothermal conditions were investigated. It was found that the decomposition of mannitol under hydrothermal conditions followed first-order kinetics, and that the reaction rate constant followed the Arrhenius equation. As few specific details are known regarding such hydrothermal reactions, it is necessary to determine whether this reaction rate is common for all sugar alcohols.

Sorbitol is widely used in food industries, and its decomposition behavior under hydrothermal condition is needed for its recovery from biomass and processing. In order to elucidate the decomposition behavior of sorbitol under hydrothermal conditions, hydrothermal decomposition of sorbitol was investigated in a flow reactor between 170 °C and 250 °C at 25 MPa. The decomposition was well expressed using a first-order reaction rate, and the rate constant followed the Arrhenius law. The pre-exponential factor and the activation energy were also determined. Compared with the decomposition of the sorbitol isomer mannitol, sorbitol was decomposed more rapidly, likely due to the variation in water molecule accessibility owing to different isomeric configurations. In addition, although activation energies were comparable for both mannitol and sorbitol (29.1 kJ mol⁻¹ and 28.3 kJ mol⁻¹ respectively), the pre-exponential factor of mannitol (6.19 s⁻¹) was an order of magnitude lower than that of sorbitol (42.9 s⁻¹).

Keywords
Biomass, Kelp, Hydrothermal treatment, Sorbitol, Decomposition kinetics
studies have evaluated the effect of temperature on sorbitol dehydration under hydrothermal conditions between 250 °C and 300 °C, revealing that the conversion rate of sorbitol was enhanced at higher temperatures. In addition, Li et al. studied the dehydration of sorbitol using a ZnCl₂ catalyst. However, these two studies targeted the dehydration products of sorbitol, and were therefore conducted in the presence of trace amounts of water and at relatively high temperatures. As our target is to optimize the hydrothermal pre-treatment of algae to recover sugar alcohols without significant decomposition, decomposition characteristics of sugar alcohols should be investigated under higher amounts of water and at lower temperatures. To date, studies into the decomposition characteristics of sorbitol in the presence of water between 170 °C and 250 °C at 25 MPa (required for the direct comparison with the previous study of mannitol hydrothermal decomposition) have not been reported. We therefore aim to determine the decomposition characteristics of sorbitol under these conditions, and to compare our results with the hydrothermal decomposition kinetics of mannitol.

2. Experimental

2.1. Hydrothermal Treatment

A continuous flow reactor was employed for the hydrothermal treatment process. A detailed description of the experimental apparatus can be found in our previous study. The apparatus was composed of a continuous stainless steel reactor with an inner diameter of 1 mm. After mixing with preheated water 4 times in weight at the inlet, the feedstock was delivered to the reactor, and the residence time was varied by changing the reactor length. The feedstock concentration in the reactor was 1 wt%. At the exit of the reactor, the effluent was mixed with cooling water, further cooled by a heat exchanger, and sampled following depressurization using a backpressure regulator. The reaction temperature was varied between 170 °C and 250 °C, and the pressure was fixed at 25 MPa throughout the experiment.

2.2. Product Analysis

The liquid product obtained following the hydrothermal process was quantitatively analyzed using high-performance liquid chromatography (HPLC) (Shimadzu, Japan). Analysis was performed using a Showa Denko K. K. column (Shodex KS-802). Deionized water was used as the eluent at a flow rate of 0.7 cm³ min⁻¹, and the oven temperature was 60 °C. Decomposition of the feedstock sugar alcohol was evaluated using the residual ratio, which was defined as the ratio of undecomposed feedstock concentration, C, to initial feedstock concentration, C₀.

2.3. Materials

The feedstock (sorbitol) was supplied by Sigma-Aldrich, while the other analytical grade chemicals were purchased from Nacalai Tesque.

3. Results and Discussion

3.1. Effect of Residence Time

Figure 1 shows the effect of residence time on the residual ratio of sorbitol at 210 °C. As can be seen in this figure, a good linear relationship was obtained, demonstrating that the thermal decomposition of sorbitol is a first-order reaction under hydrothermal conditions. This is in agreement with the studies of Yamaguchi et al. and Li et al., which also reported first-order reactions. It is possible that both the dehydration of sorbitol and the reaction between sorbitol and water are taking place under these conditions. For the former reaction, sorbitol molecules with sufficient temperature-dependent energy can decompose, thus accounting for the first-order reaction. The latter reaction, however, would be second order in total, i.e., first order for sorbitol and first order for water. When the sorbitol concentration is varied, the water concentration is affected accordingly, and thus a first-order relationship cannot be observed. However, due to the presence of excess amounts of water, the reaction is pseudo-first order, and can therefore appear to be a first-order reaction.

3.2. Effect of Reaction Temperature

Figure 2 shows the residual ratio of sorbitol for each reaction temperature with a residence time of 15 s, demonstrating that the residual ratio of sorbitol decreased at higher temperatures. This result was in part expected, as reaction rates generally increase with an increase in reaction temperature, and thus the Arrhenius law is expected to hold. However, compared to the results of Yamaguchi et al. and Li et al., the conversion reported herein is significantly higher. Li et al. employed a ZnCl₂ catalyst in their reaction, and reported complete conversion at 220 °C, with a reaction time of
However, in our experiments, complete conversion was achieved at 210 °C with a residence time of ~120 s. They did however report the use of a titanium batch reactor, but this would not be expected to affect the reaction rate. It is therefore possible that a different reaction, possibly reaction between sorbitol and water, is taking place here compared to those observed in previous studies.

3.3. Determination of Reaction Rate Parameters

By applying the first-order rate equation, the reaction rate constant \(k\) of sorbitol decomposition could be determined, as shown in Table 1. The first-order reaction rate determined by Yamaguchi et al.\(^8\) (see Table 1), was determined by the authors of this paper by fitting their data to the model using the least squares method. As expected, the decomposition rates observed herein were significantly higher than those reported by Yamaguchi’s group.

The temperature dependence of the reaction rate constant was evaluated using the Arrhenius equation as represented in Eq. (1).

\[
k = A \exp\left(-\frac{E_a}{RT}\right)
\]

where \(k\), \(A\), \(E_a\), \(R\), and \(T\) are the reaction rate constant, pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively. The Arrhenius plot of sorbitol is shown in Fig. 3, where the difference between the decomposition rate constant obtained in this study and that reported by Yamaguchi et al.\(^8\) can be clearly seen. This suggests that the reaction taking place in this study differs from that observed by Yamaguchi et al.\(^8\), where the dehydration of sorbitol was examined (also Li et al.\(^9\)). When a limited amount of water was used, isosorbide was obtained as the decomposition product\(^8,9\). Similar results were obtained by Birta et al.\(^7\), who examined the use of non-hydrothermal conditions. In the study reported by Yamaguchi et al.\(^3\), a sorbitol concentration of 1 mol dm\(^{-3}\) was used. A rough calculation showed that only 50 water molecules were distributed to each sorbitol molecule. It should be noted that sorbitol is not a small molecule, being composed of 6 carbon atoms, 6 oxygen atoms, and 14 hydrogen atoms. Thus, placing 50 water molecules around the sorbitol molecule will allow only 2 to 3 layers of water molecule shells. Furthermore, in the study reported by Li et al.\(^9\), a 70 wt% ZnCl\(_2\) aqueous solution was employed, suppressing the movement of water molecules in the bulk phase, thus retarding the reaction between the water molecules and sorbitol. In contrast, in our study, a large amount of water was supplied for the hydrothermal pretreatment of kelp, thus leading to reaction between the water molecules and sorbitol, with the reaction being first order due to the excess amount of

| Temperature [°C] | Mannitol\(^6\) | Mannitol\(^11\) | Sorbitol | Sorbitol\(^8\) |
|------------------|----------------|----------------|-----------|----------------|
| 170              | 2.79E-03       | 2.73E-03       | 3.78E-02  | 4.20E-05       |
| 190              | 2.73E-03       | 4.60E-03       | 4.13E-02  | 3.23E-04       |
| 210              | 5.58E-03       | 5.58E-03       | 6.15E-02  | 5.35E-04       |
| 230              | 7.78E-03       | 1.67E-05       | 4.27E-02  | 5.35E-04       |
| 250              | 9.49E-05       | 9.49E-05       | 1.84E-04  |                |
| 275              | 1.81E-04       | 1.81E-04       | 3.23E-04  |                |
| 287              | 3.53E-04       | 3.53E-04       | 5.35E-04  |                |
| 300              |                |                |           |                |

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water.

3. 4. Comparison with Mannitol Decomposition

Figure 3 also shows the Arrhenius plot of mannitol decomposition under hydrothermal conditions reported in our previous study\(^6\), demonstrating that sorbitol decomposed significantly faster than its isomer, mannitol, at the same reaction temperatures (170-250 °C). This is disappointing, as it suggests that there is no general decomposition rate constant for sugar alcohols under such hydrothermal conditions. Thus, reaction rate has to be determined for each of the sugar alcohol. Yamaguchi et al.\(^8\) recently published a study on mannitol decomposition under hydrothermal conditions, but using a high concentration of mannitol to achieve a dehydration reaction. The Arrhenius plot for their work is also shown, and the reaction rate constants were determined by the authors of this paper by fitting the data to the model using the least squares method. The calculated reaction rate constants differ significantly from those determined from the work of Matsumoto et al.\(^6\).

In both cases, sorbitol decomposed faster than mannitol. However, the differences were less significant than when a large amount of water available.

Sorbitol is more reactive than mannitol when both large and small amounts of water are present. This difference in decomposition rate between sorbitol and mannitol implies that chemical configuration has a great impact on decomposition characteristics. Considering the difference between these molecules, the orientation of the C2 hydroxyl group may be responsible for this difference. The model shown in Fig. 4 demonstrates this configuration effect.

Where large amounts of water were present, the water molecules can attack the carbon atoms. In the case of sorbitol, hydroxyl groups on carbon atoms C3 to C5 are on the same side of the molecule, thus allowing water molecules to attack from the other side. In contrast, the hydroxyl group attached to C5 in mannitol prevents attack from water molecules, thus slowing the reaction rate.

Where only trace amounts of water were present, dehydration likely takes place through interactions between the hydroxyl groups. In the case of sorbitol, Yamaguchi et al.\(^8\) reported 1,4-anhydroxysorbitol and 2,5-anhydroxysorbitol as the major products, while for mannitol, Yamaguchi et al.\(^11\) reported 1,4-anhydromannitol and 2,5-anhydroxymannitol as the major products. These results indicate the importance of the interaction between the C1 and C4 hydroxyl groups and between the C2 and C5 hydroxyl groups in the formation of a 5-membered ring. While configuration for the C1 and C4 hydroxyl groups is common in both sorbitol and mannitol, the relationship between the C2 and C5 hydroxyl groups is different. When a chair conformation is adopted to allow interaction between these atoms as shown in Fig. 5, the hydroxyl groups in the C2 and C5 positions of sorbitol are in the axial conformation, while the hydroxyl group attached to the mannitol C2 atom is equatorial. Therefore, as a greater distance exists between these two hydroxyl groups, the dehydration reaction is retarded.

Although both reactions are affected by hydroxyl group configuration, the inhibition mechanism is different for each. Thus, the ratio of reaction rate constants for the sorbitol and mannitol reactions varies depending on the quantity of water present.

3. 5. Reaction Rate Parameters

Reaction parameters, namely the pre-exponential factor (\(A\)) and the activation energy (\(E_a\)), were calculated for both compounds as summarized in Table 2. Similar activation energies were obtained for sorbitol (28.3 kJ mol\(^{-1}\)) and mannitol (26.5 kJ mol\(^{-1}\)), while the pre-exponential factor of sorbitol (42.9 s\(^{-1}\)) was significantly higher than that of mannitol (3.23 s\(^{-1}\)), indicating faster decomposition. This is in agreement with the mechanism shown in Fig. 4, where attack of water...

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**Fig. 4** Possible Reaction Mechanism to Explain the Experimental Results (a) Sorbitol; (b) Mannitol
molecules to the chain carbon atoms takes place in both molecules, but access to these carbon atoms is limited in mannitol. Therefore, although the similar transition states result in comparable activation energies, steric issues result in a lower pre-exponential factor.

### 4. Conclusion

Hydrothermal decomposition of sorbitol was investigated. The decomposition characteristics of sorbitol were evaluated in a flow reactor between 170 °C and 250 °C at 25 MPa. The reaction rate was expressed using the first-order rate equation, with the reaction rate constant being in agreement with the Arrhenius law. The calculated rate was significantly faster than that reported in previous studies, likely due to the amount of water. Decomposition rates differed between sorbitol and mannitol, which is expected owing to the configuration of the hydroxyl groups in the two structures. Indeed, mannitol was less susceptible than sorbitol to degradation under the same experimental conditions. This was the case when water was in excess and when only trace amounts of water were available, although the reaction mechanism was expected to differ. When water was in excess, decomposition was favored, but when trace amounts of water were available, dehydration was favored. Finally, the pre-exponential factor and activation energy of sorbitol decomposition were determined to be 42.9 s⁻¹ and 28.3 kJ mol⁻¹, respectively.

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### References

1) Sadamichi, Y., Kudoh, Y., Sagisaka, M., Chen, S. S., Elauria, J. C., Gheewala, S. H., Hasanudin, U., Romero, J., Shi, X., Sharma, V. K., *J. Jpn. Inst. Energy*, 91, 960 (2012).
2) Kim, N. J., Li, H., Jung, K., Chang, H. N., Lee, P. C., *Bioresour. Technol.*, 102, 7466 (2011).
3) Levine, R. B., Pinnarat, T., Savage, P. E., *Energy & Fuels*, 24, 5235 (2010).
4) Radiarta, I. N., Saitoh, S., Yasui, H., *ICES J. Mar. Sci.*, 68, (4), 773 (2011).
5) Hricovíniová, Z., *Tetrahedron: Asymmetry*, 22, 1184 (2011).
6) Matsumoto, R., Aki, T., Nakashimada, Y., Okamura, Y., Tajima, T., Matsumura, Y., *J. Jpn. Petrol. Inst.*, 58, (4), 252 (2015).
7) Birta, N., Doica, N., Vlase, G., Vlase, T., *J. Therm. Anal. Calorim.*, 92, (2), 635 (2008).
8) Yamaguchi, A., Hiyoshi, N., Sato, O., Shirai, M., *Green Chem.*, 13, 873 (2011).
9) Li, J., Spina, A., Moulijn, J. A., Makkee, M., *Catal. Sci. Technol.*, 3, 1540 (2013).
10) Yong, T. L., Matsumura, Y., *Ind. Eng. Chem. Res.*, 51, 11975 (2012).
11) Yamaguchi, A., Sato, O., Mimura, N., Shirai, M., *RSC Advances*, 4, 45575 (2014).
要 点

水熱条件下におけるソルビトールの分解速度

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食品工業で広く用いられているソルビトールは水熱分解によってバイオマスからの回収可能であるが、その過程における分解挙動を把握することは必要不可欠である。水熱条件下におけるソルビトールの分解挙動を解明することを目的として、ソルビトールの水熱分解を170～250 ℃の温度範囲、25 MPa で流通反応器を用いて行った。分解は一次反応速度で表され、その速度定数はアレニウスの法則に従った。頻度因子および活性化エネルギーも決定した。ソルビトール異性体であるマンニトールと比較すると、ソルビトールの分解の方が急速で、構造の違いにより分子の近づきやすさが異なるためと考えられた。マンニトールとソルビトールの活性化エネルギーはそれぞれ29.1 kJ mol$^{-1}$と28.3 kJ mol$^{-1}$で同等であったが、頻度因子は6.19 s$^{-1}$と42.9 s$^{-1}$で、マンニトールがソルビトールよりも高い値であった。