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Technology

Hydrothermal Treatment of Macroalgae to Produce Substitutes for Fossil Raw Materials and Fuels

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Abstract

As environmental problems such as global warming become more serious, the use of biomass energy as an alternative to fossil raw materials and fossil fuels has been attracting attention. In particular marine biomass is a largely unused resource, and has the advantages of being less competitive with food and having a fast growth rate. Nippon Steel Chemical & Material Co., Ltd. and Shizuoka University have been developing oil, tar, pitch, and carbon materials by the hydrothermal treatment of kelp. This paper describes the results of this hydrothermal treatment.

1. Introduction

In recent years, as one of the countermeasures to deal with climate change, the use of biomass is attracting attention as a sustainable clean energy that can be a substitute for fossil fuel energy. In particular, as compared with wood-base biomass, the macroalgae represented by kelp (marine biomass) has a fast growth rate, does not need land and water, and does not conflict with human life. Therefore, use of the macroalgae is a very important issue for Japan which has the 6th largest exclusive economic zone in the world. This paper describes the overview of the technologies by using the hydrothermal treatment of kelp to obtain various alternative products to fossil raw materials and fossil fuels.

2. Decomposition of Biomass with Subcritical Water

Since the macroalgae represented by kelp (marine biomass) has a very high water content, hydrothermal treatment that uses water as the reaction solvent and does not need pre-drying pretreatment is effective. A number of studies on the hydrothermal treatment of biomass have been reported, covering liquefaction,[1] gasification,[2] carbonization,[3] and fermentation pre-treatment.[4] However, they have been mainly made on woody biomass. Recently, reports on microalgae liquefaction technologies and the application of hydrothermal treatment to the carbonization or liquefaction of the extraction residues after oil extraction from microalgae having high oil content have increased.[5, 6] The hydrothermal treatment of kelp introduced in this paper is a method of obtaining various products by the hydrothermal decomposition treatment of biomass under the subcritical phase water treatment to realize the utilization of the carbon fixed in kelp to the extent possible.

Figure 1 shows the phase diagram of water. The critical temperature of water is 374°C, and the critical pressure is 22.1 MPa. The water in the area exceeding the critical points of temperature and pressure is termed as super critical water. Furthermore, the water in the area wherein either of temperature or pressure lies below the critical points is termed as the subcritical water, wherein various application technologies such as extraction,[7, 8] decomposition reaction,[9, 10] and material synthesis[11, 12] are under study. The subcritical water has the characteristic capability of changing significantly with

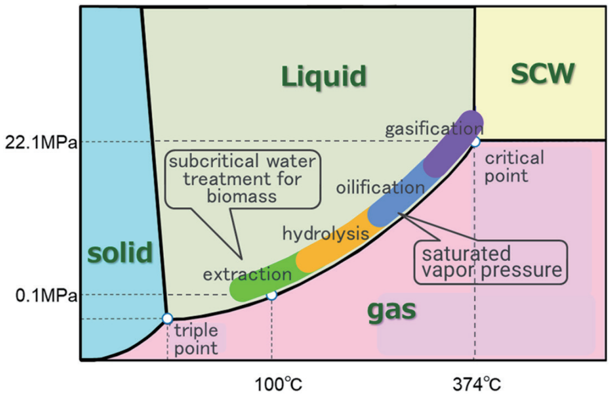

Fig. 1 Phase diagram of water

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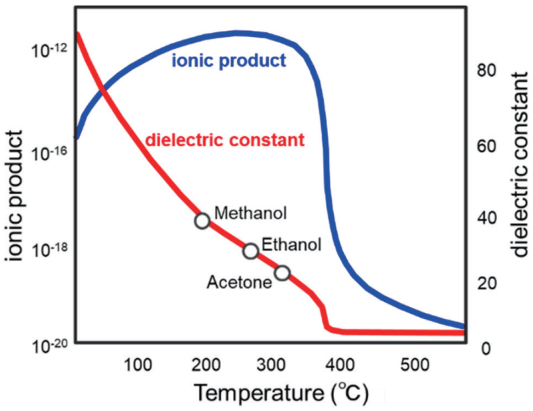

Fig. 2 Temperature dependence of ionic product and dielectric constant of water

temperature and/or pressure the physical properties which influence greatly the reactivity of water such as dielectric constant and/or ionic product (**Fig. 2**). In the subcritical water at 300 to 360°C wherein there are many studies on the biomass liquefaction reaction, since the dielectric constant becomes about 10 to 20 similar to those of the organic solvents having weak polarity, the subcritical water dissolves the organic substance having a low dielectric constant. Furthermore, the ionic product indicates the degree of ionic dissociation of water. The ionic product of water is 10^{-14} mol^2/kg^2 at room temperature under atmospheric pressure; however, in the subcritical water of saturated vapor at 250 to 300°C, it increases to about 10^{-11}. Namely, in the subcritical water region, water is dissociated, and the hydrogen cations and the hydroxyl ions which act as acid and alkali catalysts are produced in large amounts, and ionic reaction like hydrolysis is promoted.

3. Result of Hydrothermal Treatment Experiment of Kelp

3.1 Type of kelp used for experiment

There are various kinds of macroalgae, and their compositions and their ratios vary significantly depending on their type, habitat, and post-treatment after harvest from sea water. For example, the chlorophyceae-like monostroma nitidum contains an abundance of rhamnan sulfate, a polysaccharide, while brown algae such as wakame seaweed and konbu (kelp) contains copious amounts of a polysaccharide of alginate and a sugar alcohol of mannitol. The kelp employed for the experiment described in this paper was harvested off the Sanriku Coast. The kelp was frozen and stored, and then thawed, aqueous-cleaned, crushed coarsely, and then dried. **Figure 3** shows the underwater kelp off the Onagawa Coast.

The result of the elemental analysis and the contained saccharides together with their ratios are shown in **Table 1**, and the structural formulae of the main compositions of kelp, namely alginate, mannitol, and glucose, are shown in **Fig. 4**. Low molecular weight organic matter like mannitol which is normally contained in great amounts and the water-soluble nonorganic matter have flowed out through the aqueous-cleaning after freezing and then thawing. Furthermore, glucose remains characteristically as the monosaccharide in the greatest quantity after the acidic cleavage of the constituent polysaccharide.

Fig. 3 Underwater photos of Onagawa

Table 1 Elemental analysis values and composition of organic matter

Elemental analysis values		Composition of organic matter	
Carbon	35.1	Fucose	2.9
Hydrogen	4.0	Rhamnose	–
Nitrogen	1.5	Arabinose	–
Oxygen	38.7	Galactose	1.4
Chlorine	4.4	Glucose	18.1
Sulfur	0.79	Xylose	0.4
Sodium	4.6	Mannose	0.7
Magnesium	1.3	Fructose	–
Phosphorus	0.12	Ribose	–
Potassium	2.7	Glucuronic acid	–
Calcium	1.6	Galacturonic acid	–
Overall composition		Alginate	65.3
Water	7.0	Mannitol	1.3
Organic	70.1	Others	9.8
Inorganic	22.9		

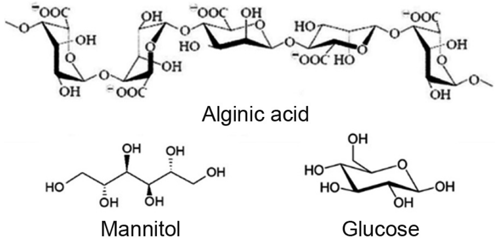

Fig. 4 Structural formulas of alginic acid, mannitol, and glucose

3.2 Hydrothermal treatment experiment

The experiment of hydrothermal treatment described in this paper was conducted using the equipment of Shizuoka University, and the analysis and the evaluation of the products were conducted unitedly by Nippon Steel Chemical & Material Co., Ltd. and Shizuoka University. The hydrothermal treatment was conducted as shown in **Fig. 5**; the predetermined amounts of kelp and water were enclosed in a stainless steel batch-type reactor with an inner volume of 9 cm^3 equipped with a valve, and sealed, raising the internal temperature and the internal pressure of the reactor to the predetermined values by immersing the reactor tube in the salt bath heated to the reaction temperature. After the elapse of a predetermined time, the reactor was rapidly cooled, suspending the reaction. Soon after, the produced gas was recovered, and the components soluble in hexane and tetrahydrofuran, the water layer containing water-soluble organic matters, and the solid residue containing unreacted matter and semicarbides were separately recovered. The solvent-soluble matter includes light oil, heavy oil, and some of tar and pitch. In this paper,

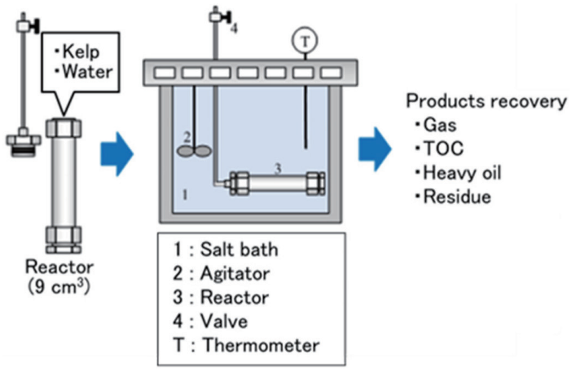

Fig. 5 Experimental apparatus and hydrothermal treatment procedure

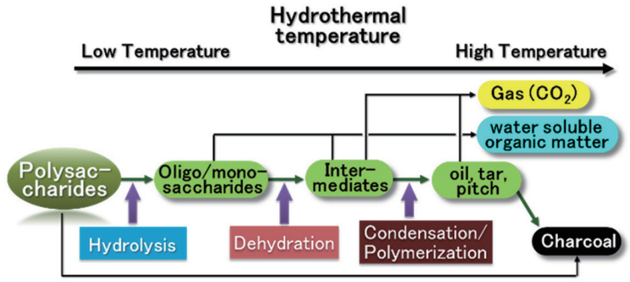

Fig. 6 Reaction pathway of formation of charcoal from polysaccharides by hydrothermal treatment

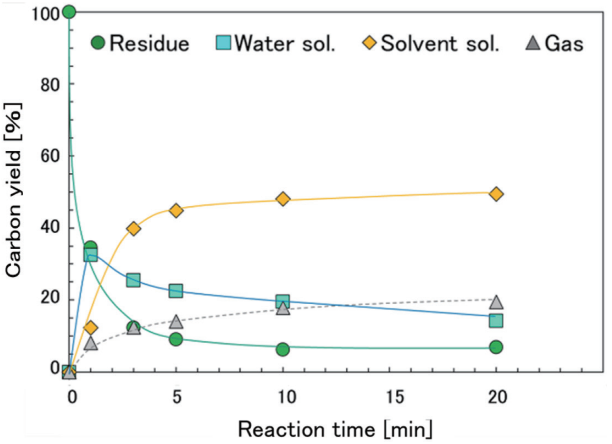

Fig. 7 Dependence of carbon yield on reaction time for 350°C

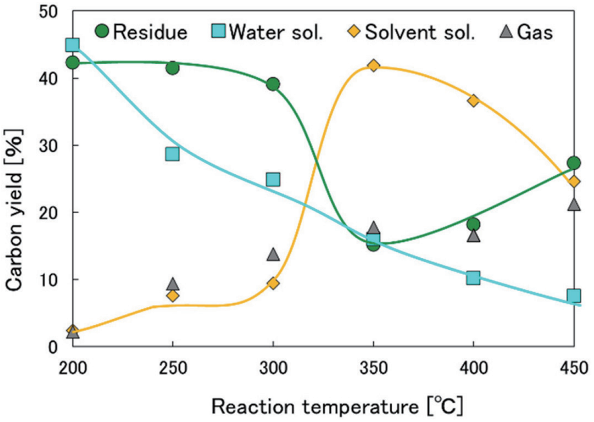

Fig. 8 Dependence of carbon yield on reaction temperature for 5 min

they are treated as solvent-soluble matter (heavy matter) in the same way as the matter soluble in hexane and tetrahydrofuran. Hereafter, we will classify the compositions more in detail during the massive synthesizing stage, and will conduct further qualitative and quantitative analysis. The formed gas was analyzed qualitatively and quantitatively by a gas chromatography unit having a thermal conductivity detector (GC-TCD). The amount of water-soluble organic carbon (TOC) in the water layer containing water-soluble matter was measured. The weights of the solvent-soluble matter (heavy matter) and the residue were measured, and based on the result of the elemental analysis, the carbon yield and the calorific value of higher order were calculated.

3.3 Hydrothermal treatment condition and product

In the hydrothermal treatment of biomass, since products are formed via complicated reaction pathways, the details of how products are formed have not yet been clarified; however, it is considered that the formation of products progresses generally in line with the scheme shown in **Fig. 6**.[13] Firstly, at a relatively low temperature, monosaccharide and/or oligosaccharide are formed by the hydrolysis of polysaccharides. Along with the rise of temperature, the dehydration reaction progresses, the products become heavier via condensation reaction and/or polymerization reaction, and oil, tar, pitch, and carbon are formed.

In the research in this paper, in order to estimate the reaction pathway of the hydrothermal treatment of kelp, the dependence of carbon yields of respective products on the reaction time and the reaction temperature were studied. Firstly, the timewise change of the carbon yields of respective products of kelp treated in the subcritical water under the saturated vapor pressure at 350°C is shown in **Fig. 7**. The decomposition of kelp progresses along with the reaction time, the yield of the solid residue rapidly decreases, and the solvent-soluble matter (heavy matter) is already formed at the initial stage of the reaction. In the meantime, since the water-soluble matter increases in the initial stage, and then tends to decrease along with the reaction time, in addition to the hydrolysis and/or the growth to the low molecular mass of the polysaccharide contained in kelp occurring in the formation of the solvent-soluble matter (heavy matter), the possibility of the progress of the dehydration and/or polymerization of the matter once decomposed to water-soluble is suggested.

Secondly, the dependence of the carbon yield on the reaction temperature by changing the hydrothermal treatment temperature was studied. **Figure 8** shows the dependence of the carbon yield on the reaction temperature. In the low temperature region up to 300°C, the decrease in the residue and the increase in the solvent-soluble matter (heavy matter) are relatively moderate, and the progress of the hydrolysis of the polysaccharide to form water-soluble low molecular matter is suggested. Above 300°C, a rapid increase in the solvent-soluble matter (heavy matter) is observed, and the yield of the carbon of the solvent-soluble matter (heavy matter) becomes highest at 350°C. In this temperature region, there is a possibility that the dehydration of the water-soluble low molecular matter and the growth to heavy matter by the following polymerization are taking place simultaneously. At 400°C and above, increase in the residue due to carbonization, increase in the gaseous matter due to decomposition, and the decrease in the solvent-soluble matter (heavy matter) are observed.

3.4 Analysis of product formed by hydrothermal treatment

The analysis of the products of the hydrothermal treated kelp was conducted by nuclear magnetic resonance (NMR), gas chromatography-mass spectrometry (GC-MS), and a gas chromatography unit having a thermal conductivity detector (GC-TCD). In the measurement by proton nuclear magnetic resonance (1H-NMR), the olefin-originated proton in the neighborhood of the chemical shift 4 ppm to 6 ppm overlaps the proton adjacent to the oxygen of the saccharide chain; however, in the measurement by 13C nuclear magnetic resonance (13C-NMR), the carbon which forms the ring structure of the saccharide emerges in 60 to 100 ppm, and therefore becomes distinguishable from the olefin-originated carbon. Therefore, both were measured and compared. As a result, in the solvent-soluble matter (heavy matter) hydrothermally treated at the low temperature of about 200°C, the ring structure of the saccharide chain was not observed, and the structure was on average close to that of unsaturated fatty acid. This trend does not change significantly even when the reaction temperature is raised. In the low temperature region, the yield is small; however, the double bond formed by the dehydration decreases through polymerization and growth to heavy matter are suggested.

Figure 9 shows the result of the analysis by GC-MS of the solvent-soluble matter (heavy matter) obtained at the reaction temperature of 350°C. An intermediary body and the saturated/unsaturated fatty acid of alginate origin formed by the hydrolysis and the cleavage of the ring were detected. This detection agrees with the result of analysis by NMR. However, the low molecular matter detected by GC-MS was only about 10% of the whole solvent-soluble matter, and the majority of the solvent-soluble matter was the heavier tar and pitch. Furthermore, seaweed contains a very small amount of fat, and the evaluation separate from that of the product formed by hydrothermal treatment is necessary.

As shown in **Fig. 10**, in the components of the decomposed gas analyzed by GC-TCD, a phenomenon specific to hydrothermal treatment is observed. In the pyrolysis decomposition of cedar, various types of gas are detected, and hydrogen and CO are major components. In the meantime, in the hydrothermal treatment, regardless of the types of biomass, CO_2 occupies most of the formed gas. In particular, the components of the decomposed gas when kelp is hydrothermally treated at 350°C for 5 min are 95 mol% of CO_2 and 4.6 mol% of hydrogen.

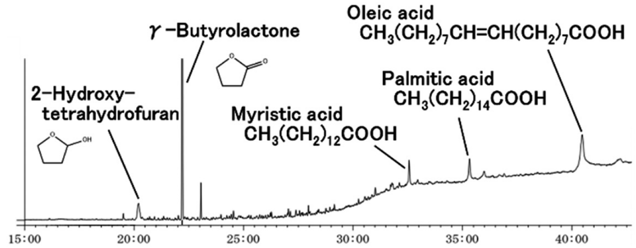

Fig. 9 Analysis of solvent-soluble matter (heavy matter) by GC-MS (Reaction temperature 350°C, reaction time 5 min)

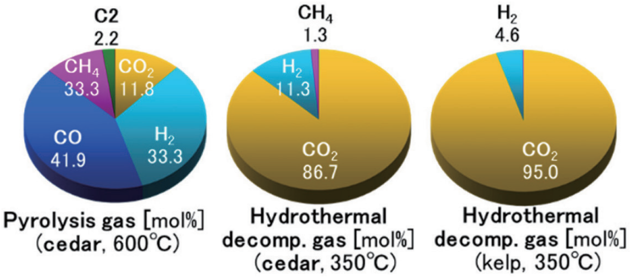

Fig. 10 Analysis of gas components by GC-TCD

3.5 Hydrothermal treatment of respective constituent composition of kelp

Each of the organic compositions of kelp is considered to have different reactivity to hydrothermal treatment. The compositions of kelp used in the study described in this paper are shown in Table 1. Alginate, mannitol, and other organic compositions were separately hydrothermally treated, and the carbon yields of the respective products were examined. Since alginate exists in the form of salt combined with the cations contained in the sea water in a large quantity, calcium alginate which is insoluble in water was also employed as the model matter. As the kelp employed in the study described in this paper was aqueous-cleaned after being thawed, a significant amount of mannitol is lost. However, the mannitol was employed as a typical water-soluble low molecular matter generally contained in kelp. As for other organic matters, after treating the alginate with 2% hydrogen peroxide solution and 2% sodium carbonate, the obtained solid component was dried, and was taken as the alginate-extracted residue. The residue is considered to contain as major compositions polysaccharide other than alginate, other protein in small quantities, and fat.

Figure 11 shows the carbon yields of the products of alginate, calcium alginate, mannitol and the alginate-extracted residue obtained when hydrothermally treated at 350°C for 10 minutes in the subcritical water under the saturated vapor pressure. It is found that, from the facts that the decomposition of alginate, calcium alginate, and the alginate-extracted residue progresses by the subcritical water treatment and that, as compared with alginate, calcium alginate yields more gaseous composition, solvent-soluble composition, and water-soluble composition, decomposition tends to progress more readily when cations are coordinated. Large amounts of alginate residue are possibly attributed to the carbonization promoted by acid. Furthermore, mannitol is water-soluble; however, under the subcritical water treatment at 350°C, the formation of gas is not recognized, and the formation of solvent-soluble matter (heavy matter) is recognized. From these facts, it is observed that, in the subcritical water, the formation of high molecular matter and oily matter possi-

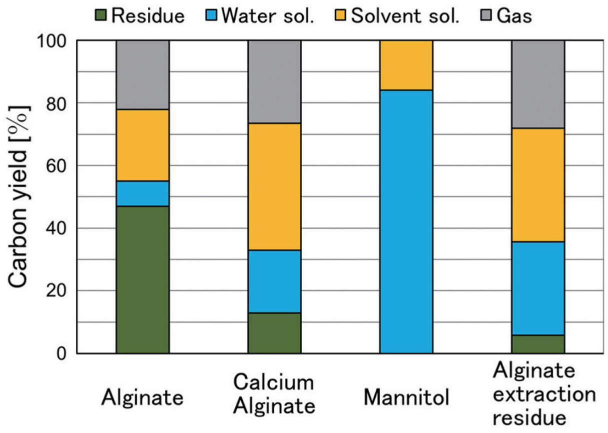

Fig. 11 Product yield from kelp components (350°C, saturated water vapor pressure, 10 min)

bly progresses through dehydration and polymerization of the water-soluble matter. The yield of the product of the alginate-extracted residue is roughly close to the results of kelp and calcium alginate, and it is suggested that even after alginate is unitized as a useful composition of kelp, the use of the energy of the residue by hydrothermal treatment is possible.

4. Characteristics and Applicability of Product of Hydrothermal Treatment

The applicability of using the solvent-soluble matter (heavy matter) and the residue obtained by the hydrothermal treatment of kelp as oily fuel and solid fuel was evaluated from the viewpoint of combustibility.

The relationships between the H/C molar ratio and the O/C molar ratio of the solvent-soluble matter (heavy matter) and the residue obtained by the hydrothermal treatment of kelp are shown in **Fig. 12**. The figure shows that, by the hydrothermal treatment of kelp, deoxygenation progresses, and the oily compositions having an O/C molar ratio and an H/C molar ratio close to those of light oil and/or heavy oil are formed. The higher calorific value obtained from the elemental analysis values of the oily composition and the Dulong formula is about 32 to 35 MJ/kg for the oily composition obtained at the hydrothermal treatment temperature of 250°C to 400°C. However, since the fluidity of the oily composition thus obtained is still problematically low, we are going to promote our future verification, not only aiming at a higher yield of oily composition, but also taking upgrading of the formed oily composition into consideration.

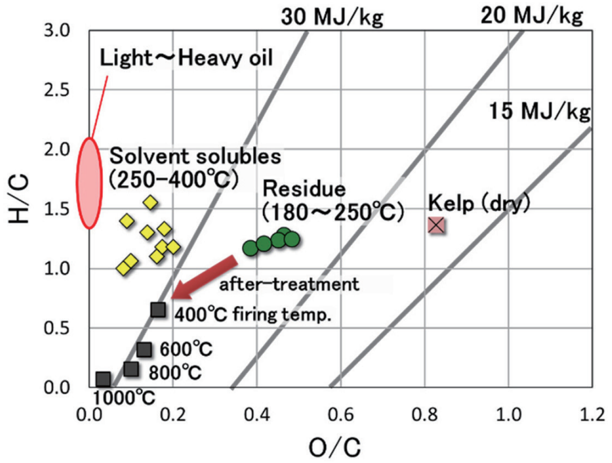

Fig. 12 H/C and O/C molar ratios of components obtained by hydrothermal treatment of kelp

Furthermore, the O/C molar ratio of the residue obtained by the hydrothermal treatment at 180°C to 250°C is half that of raw material kelp, and the residue is considered to be in an insufficiently carbonized state with insufficient hydrolysis. It is possible to further reduce the H/C molar ratio and the O/C molar ratio of the residue by post baking. Figure 12 shows the H/C molar ratio and the O/C molar ratio when fired at 400°C to 1000°C. Although there are still issues like ash not being removed, applicability to the usage as solid fuel is suggested.

5. Conclusion

Since the experiment described in this paper is of a laboratory scale batch type, the amount of the sample is insufficient to obtain detailed data of the product. Hereafter, we will realize the reliable evaluation for the utilization as energy through the batch test of an enlarged scale and the introduction of continuous flow apparatus. Furthermore, we will promote the extraction of issues concerning the process, and the collection of engineering data for the practical application in future.

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