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Chapter

Resource Upgrading in Advanced Supercritical Fluid (Supercritical Fluid with Catalyst and Cosolvent): Liquid Fuels from Biomass in Sub and Supercritical Water and Carbohydrate Up-Conversion in Ionic Liquid and Supercritical Fluids Mixtures

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Abstract

Liquid fuels from biomass and up-conversion of biomass in advanced supercritical fluid are reviewed in this chapter. Lignin can be converted into heavy hydrocarbons in subcritical water extraction. Lipid, which is triglyceride, is catalytically converted into straight-chain hydrocarbons of free fatty acid (decarboxylation) formed by hydrolysis. Carbohydrate is also hydrothermally converted into furan ring compound and fatty acids. Protein is converted into amino acids in hydrothermal water and depolymerization of protein is favored with rapid heating and denaturation agency such as alkaline earth metals. Free amino acids are further decomposed into carboxylic acid through deamination and into amine through decarboxylation. To inhibit Maillard reactions, which result in polymerization, the deamination of amino acid at low temperature was favored and a solid catalyst was quite active for deamination of free amino acids at quite low temperature hydrothermal water. Cellulose was dissolved in some ionic liquids with high mass percentages (5–20 wt%) and converted into monomers and useful components such as furan ring compounds and supercritical fluid cosolvent such as hydrothermal water in ionic liquids supported improvement of reaction efficiency. For hydrogenation of biomass, it was confirmed that hydrogen solubility was enhanced with supercritical carbon dioxide and it must be helpful for hydrogen reaction with biomass molecule.

Keywords: liquid fuels, biomass, iso-conversion, ionic liquid, hydrogen solubility

1. Introduction

Renewable carbon resource is only biomass on the earth and its utilization must be enhanced to replace fossil carbon resources into biomass. In particular, among a various energy demands, transport occupies 30% of total carbon footprint in a personal daily life of an American [1]. For short-distance travel at near a house and a town, electrical vehicle such as EV (electric vehicle), HV (hybrid vehicle), PHEV (plug-in hybrid electric vehicle), and so on (so-called xEV) should be spread, but still a long-distance travel with an airplane and a large passenger ship requires liquid fuels such as diesel and heavy oils even though secondary batteries would be further compacted and lightened. For managing of the demands, liquid fuels must be obtained from renewable and sustainable carbon resources, and the only answer is biomass. For transformation of biomass into liquid fuels, one of the useful techniques should be sub and supercritical fluids technique with catalyst and cosolvent, which is called advanced supercritical fluid technology here.

In this chapter, we review our previous studies concerning liquid fuels from biomass and up-conversion of biomass (mainly carbohydrates) in advanced supercritical fluid technology (supercritical fluid with catalyst such as solid aid-base catalyst or cosolvent such as ionic liquid) are introduced.

In a previous study, lignin, which is a major component of woody biomass, can be converted into heavy hydrocarbons in subcritical water (or hydrothermal) extraction [2]. The dimensionless severity number ($k_r \cdot R_o$: k_r [time^{-1}] is kinetic constant at reference condition and R_o [time] is severity factor) can be used to predict conversion of lignin into liquid fuel. The mean molecular weight of the recovered lignin (so-called "hydrothermal lignin" because "lignin" is usually named with the name of solvent, which is used for recovery, such as "alkali-lignin" and "organosolv-lignin") was about 1 kDa, which is 6-mer of syringyl structure. The hydrothermal lignin should be used as heavy oil or source of aromatic structure after post-treatment such as a conventional catalytic cracking and hydrogenation. In this review, the lignin recovery and dissolution into hydrothermal water (obtained lignin is "hydrothermal lignin") is briefly introduced in Section 2, and the importance of dimensionless severity number is emphasized.

Protein-rich biomass can be converted into liquid hydrocarbons through catalytic hydrothermal cracking (CHTC) and conventional hydrogenation/distillation process (total process is so-called "iso-conversion") [3–5]. That is, the first step of "iso-conversion" is CHTC, and the main reaction of CHTC should be catalytic decarboxylation because hydrolyzed lipid is mainly to form free fatty acid, and carboxyl group in the free fatty acid must be detached to form fuel component, such as hydrocarbons. In our previous study, it was found that lipid, which is triglyceride, is catalytically converted into straight-chain hydrocarbons of free fatty acid (decarboxylation) formed by hydrolysis and one of the active materials of catalytic decarboxylation is zirconia [6]. It was also found that zirconia is also active for decarboxylation of small fatty acid such as acetic acid in supercritical water [7]. In "iso-conversion," the remaining components after extraction of lipid from protein-rich biomass, which are carbohydrate and protein, are proposed to be fermented to form small organic acids or olefinic molecules to combine together with unsaturated hydrocarbon (olefin) produced from lipid decarboxylation. Anaerobic fermentation is suggested to get small molecules in "iso-conversion" process, but it requires large space and long time [3]. Then, additional hydrothermal process for carbohydrate and protein conversion into small molecules such as furan ring compounds and fatty acids are proposed by our research group, and a small review of the proposed process is described in Section 3 of this chapter.

Carbohydrate is also hydrothermally converted into furan ring compound [8–13], which is used as liquid fuel, and fatty acids, which are the similar compounds produced from lipid. The furan ring compound such as hydroxymethyl furfural (HMF) was obtained with high yield in hydrothermal water in the presence of appropriate catalyst such as TiO_2 under microwave irradiation [12]. Microwave irradiation affected HMF formation from fructose, and the selectivity of HMF was enhanced under microwave heating in hydrothermal conversion [13].

Protein is converted into amino acids in hydrothermal water, and depolymerization of protein is favored with rapid heating and denaturation agency such as alkaline earth metals [14]. Free amino acids are further decomposed into carboxylic acid through deamination and amine through decarboxylation. However, in high temperature reactions, carbohydrates and protein (and these monomers) are easily combined together to form melanoidins, which inhibit fragmentations of both of the components (such as carbohydrates and proteins), through so-called Maillard reaction, which is a group of amino-carbonyl reactions. The deamination of amino acid at low temperature is favorable because Maillard reaction is not developed. However, deamination requires high temperature in subcritical water. For example, alanine deamination is meaningfully developed over 513 K [15]. To know the favorable acid or basic condition for enhancing amino acid deamination, pH dependence on alanine reaction was investigated. As a result, as introduced in Section 3, lower temperature than 513 K, the amino acid degradation is remarkably slow. By screening of several types of solid acid additives, it was surprisingly found that a type of solid catalyst was quite active for deamination of free amino acids not only alanine but also glycine, leucine, and serine at quite low temperature hydrothermal water.

Further decomposition of small free fatty acid into alkene and CH_4 is favored for iso-conversion because these can be acted as alkane source or hydrogen source for long chain hydrocarbon formation. By integration of each unit reactions/operation (hydrolysis, deamination, decarboxylation, hydrogenation, and distillation), liquid fuels such as straight-chain and aromatic-ring compounds are obtained from woody/protein-rich biomass. One of the images for process integration (process intensification) shows in **Figure 1**.

In Section 3 of this chapter, we briefly introduce protein conversion into small fragments with catalyst in hydrothermal water. Then the effect of acid and alkali on subcritical water conversion of alanine, which is the smallest chiral amino acid, is also roughly explained as the basic knowledge of alanine conversion in advanced supercritical fluid technologies. With a solid acid catalyst, alanine conversion is enhanced and the discussion why the solid acid catalyst can promote alanine conversion in low temperature hydrothermal water is provided.

The other advanced supercritical technology is combined utilization of supercritical or hydrothermal water with cosolvent such as ionic liquid in the absence and presence of additives (homogeneous or heterogeneous). To improve reaction efficiency (increase of rate, yield, and selectivity of a target component), catalyst is also used in the ionic liquid-supercritical (hydrothermal) fluid mixture. Cellulose, which is the most abundant biomass on the earth, is dissolved in some ionic liquids with high mass percentages (5–20 wt%) and converted into monomers and further conversion into useful components such as furan ring compounds. In our research group, the combinational utilization of ionic liquid with hydrothermal water (or other solvents with and without catalyst) for cellulose (and its monomer, glucose, and the derivative) conversion into small fragments and useful chemicals were reported [16–25]. There are several merits for use of supercritical fluid technology (not only supercritical region but also subcritical and hydrothermal water) with

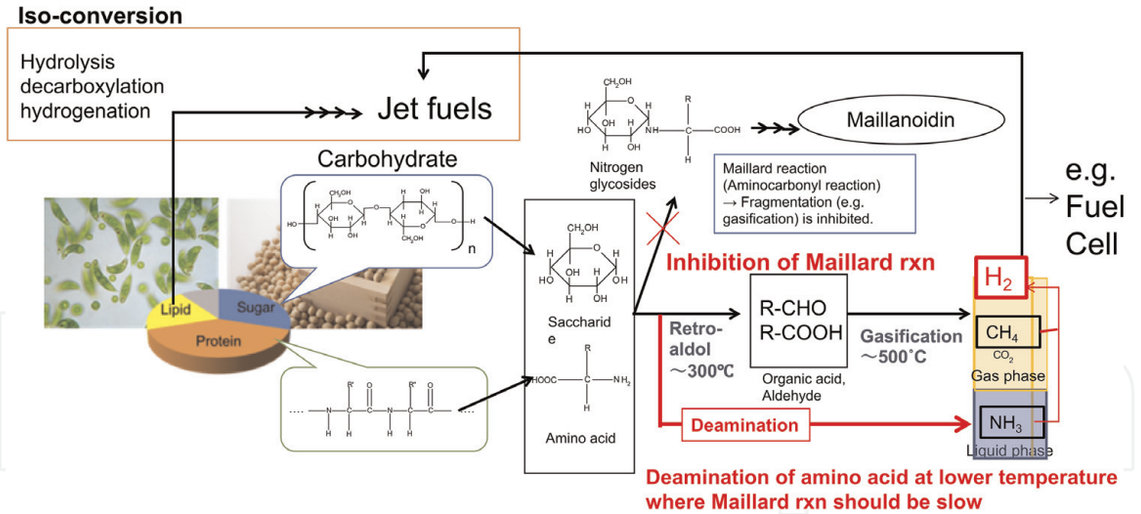


Figure 1.
Proposed process for liquid fuel production from protein-rich biomass by hydrothermal conversion together with "iso-conversion."

ionic liquid as cosolvent: reduction of viscosity of ionic liquid solution [26], control of acidity and basicity of ionic liquid, solubility control of material in ionic liquid, separation of target molecule from ionic liquid into supercritical fluids, and so on. Our research group also progress the study of the separation of some components (biomass molecules or biomass refinery are targeted) from ionic liquid solution with supercritical carbon dioxide [27–30]. Here, we only briefly introduced some research results concerning biomass conversion into useful molecule in ionic liquid-hydrothermal water mixture with additives (Section 4).

In the conclusion of this chapter, we will conclude this chapter and mention outlook in this field.

2. Hydrothermal lignin: aromatic hydrocarbons from woody biomass

2.1 Reducing molecular weight of lignin

Lignin is one of main components of lignocellulosic biomass and a natural phenolic polymer with propyl-phenol groups. One big drawbacks of natural lignin in originally existing woody biomass is large molecular weight (because high molecular weight lignin has high viscosity or it is solid at room temperature and it has a complicated structure), and molecular weight reduction of lignin will provide many advantages in handling and processing as a chemical feedstock. In the paper [2], we proposed an environmental-friendly process for recovery of lignin from woody biomass, and it should have high efficiency with producing simple structure lignin, which is highly desired as a biorefinery feedstock. Here, the brief introduction of the process and the index of the operational parameters (how to know the optimum conditions) is summarized.

2.2 Experimental for hydrothermal lignin preparation

In the paper [2], low-grade wood from Japanese cedar production was provided from a domestic wood manufacturer and had a lignin content of 44.6 wt% (the sample should be mainly bark of the Japanese cedar). The bark was crushed to have a coarse particle size of less than 5 mm. The elemental balance of the Japanese cedar

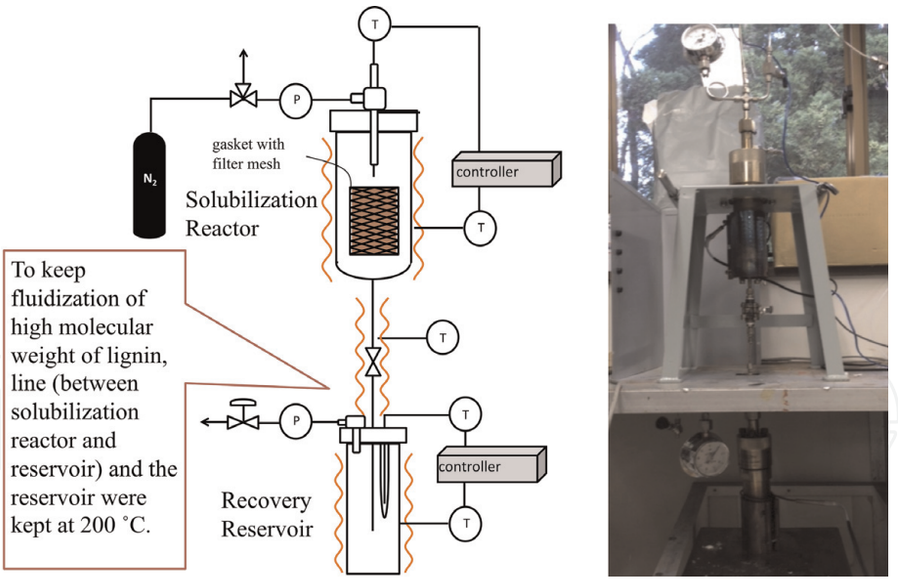


Figure 2.
Coupled system of two batch reactors.

was 49, 5.9, 0.1, 1, and 42.2 wt% for C, H, N, S, and O content, respectively. Ash content was 2 wt%.

A coupled system of two batch reactors was used (the photograph and schematic diagram of the reactor is shown in **Figure 2**, and its detail can be seen elsewhere [2]), and the sample was loaded into the upper reactor. The lower reactor was reservoir and used to recover hydrothermal extracts. The reservoir was maintained at a temperature of 473 K to inhibit the aggregation of lignin because lignin typically is melted into liquid phase at temperatures greater than 423 K in the presence of water [31]. Typically, a 7.5 g sample of bark (covered with stainless mesh) was loaded in the upper reactor along with 150 mL of pure water. After purging air inside the reactor, N_2 gas was loaded. The upper reactor was heated up to 473–573 K. The pressure in the upper reactor (sample-loaded reactor) was close to the saturated pressure of water at the reaction temperature. After the desired treatment time, the valve between the two reactors was opened and the fractionated components in the reactor were recovered in the reservoir. The reservoir was then rapidly cooled with a water bath (ca. 10 min) and was then detached from the sample-loaded reactor. The residue in the upper (sample-loaded) reactor with the stainless mesh was weighed after drying at 333 K overnight. Connection lines between the two reactors were rinsed. The water-insoluble fraction among the recovered solutions was hydrothermal-soluble lignin (namely "hydrothermal lignin"). The soluble Klason lignin (hydrothermal lignin) was quantified, and the molecular characteristics (molecular weight with GPC and molecular structure with NMR) were evaluated.

As a result of the molecular characteristics, the hydrothermal lignin obtained from bark of Japanese cedar by hydrothermal extraction at 523 K under the saturated pressure of water, 3.98 MPa, about was mainly 6-mer (about 1 kDa of mean molecular weight) with syringyl-rich structure [2].

2.3 Dimensionless severity number

The kinetic study for lignin recovery (how much percentage of Klason lignin can be recovered based on the Klason lignin in the raw material, the bark of Japanese cedar) was performed, and severity factor was used for consideration of the effect of reaction temperature and reaction time. The severity factor, R_o [min], is defined as below:

$$R_o = exp\left(\frac{T - T_r}{\omega}\right)t \tag{1}$$

where T [K] is reaction temperature, T_r [K] is the reference temperature (here is 373 K), t [min] is reaction time, and ω is the function of activation energy, E_a [kJ mol^{-1}], gas constant, R = 8.314 J mol^{-1} K^{-1}, and T_r, as shown in the following equation.

$$\omega = \frac{R \bullet T_r^2}{E_a} \tag{2}$$

According to the derivation of the severity model, lignin recovery (LR) can be calculated by the next equation.

$$Lignin\ recovery\ (LR)[wt\%] = \{1 - exp(-k_r \bullet R_o)\} \times 100 \tag{3}$$

where k_r is the rate constants in min^{-1} at reference temperature T_r (373 K), as described in the following equation:

$$k_r = k_o exp\left(-\frac{E_a}{RT_r}\right) \tag{4}$$

where k_o [min^{-1}] is pre-exponential factor of the reference rate constant.

By fitting the equations to the experimental data (as shown in **Figure 3**), all the kinetic parameters were decided as to be 135 kJ mol^{-1} for E_a and 6.8 × 10^{-5} min^{-1} for k_r. The experimental data at the most severe condition ($k_r \cdot R_o$ value is over 1, and these data were obtained at 573 K for 10 min) were far from the calculated value, and the reason why the data are not fitted with the calculated value is because the cellulose in the bark was carbonized and the remained Klason lignin in the residue was estimated to be high.

As shown in **Figure 3**, lignin solubilization (lignin recovery) in hydrothermal water drastically changed between 0.1 < $k_r \cdot R_o$ value <10. The similar trend was seen in the previous reports [2, 32, 33]. From Eqs. (1), (2), and (4), the dimensionless severity number ($k_r \cdot R_o$) is written by the below equation:

$$k_r \bullet R_o = k_o \bullet t \bullet exp\left(\frac{E_a(T - 2T_r)}{R \bullet T_r{}^2}\right) \tag{5}$$

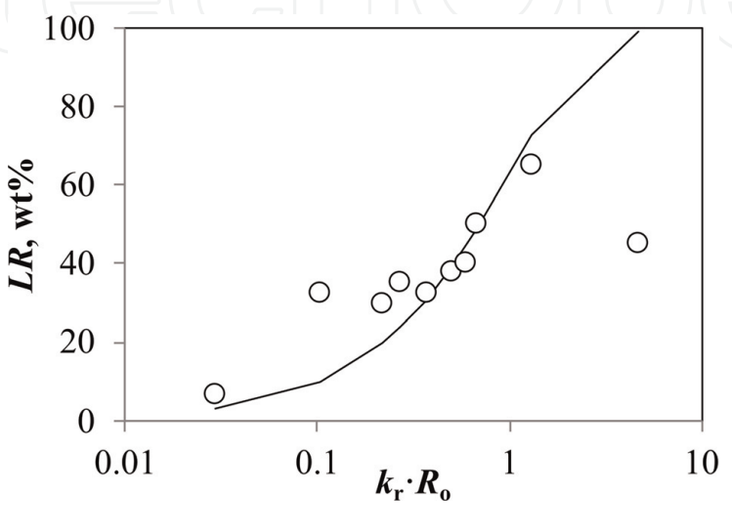


Figure 3.
Dimensionless severity number for lignin recovery from bark of Japanese cedar (473–573 K for 3–40 min).

Eq. (5) shows that the dimensionless severity number ($k_r \cdot R_o$) is also the function of t and T as well as severity factor (R_o) as shown in Eq. (1). While R_o varies a wide range of values and the optimum R_o for the target reaction is not easy to estimate, meaningful transitional change should occur at the range of 0.1 to 10 for the dimensionless severity number $k_r \cdot R_o$, as reported here and in the literatures [2, 32, 33]. Therefore, the dimensionless severity number ($k_r \cdot R_o$) is quite useful, and the severity analysis using $k_r \cdot R_o$ can be adopted to various type of the reactions. Our research group is going to study on utilization of the dimensionless severity number ($k_r \cdot R_o$) for various kind of reactions and its application and usefulness with a variety of the examples will be reported in near future.

3. Protein hydrolysis and amino acid degradation: low temperature catalytic hydrothermal cracking (LT-CHTC) for liquid fuel production

3.1 How to convert protein-rich biomass into liquid fuels

Based on the concept of "sustainable development goals (SDGs)" by UN and "circular economy" by EU, waste materials (by-product of main activity) must be used in effective and useful application and ideally must be back to primary resource production. In our daily life, huge amount of food waste generates and its utilization/valorization is still insufficient. This situation is not only for food waste (including house waste, municipal waste, sewage sludge, which are by-product of our daily life) but also agricultural by-product. One of the big problems of these wastes is to contain high amount of water, which is hard to exclude from the wastes. Water inside the waste (namely wet biomass) assists to cultivate fungi, and some of the wet biomass wastes are easy to rot with a bad odor and toxic component formation. Even with huge amount of energy loss, the large part of the wet wastes is forcedly burned to eliminate without effective utilization as energy or thermal purposes.

Microalgae, which has fast grow rate with CO_2 stabilization through photosynthesis and attracts much attention as renewable resource, is also wet biomass as the same as daily-life wastes with containing a large amount of water mentioned above. The total difference of microalgae from the waste wet biomass is that cultivation and harvesting of microalgae can be controlled to level not only for yield but also composition. Thus, microalgae is a primary and industrial renewable resource. However, problem related to water is to be solved as well as wet biomass waste.

Sub and supercritical water technologies enable water (also in the wet biomass) to eliminate from the structure of the biomass and to use for hydrolysis of the natural polymer in the biomass as reactant. As mentioned above, supercritical water plays the important role in the CHTC for producing olefinic hydrocarbon from lipid and free fatty acid, as solvent and reactant. But, for feeding lipid into the process, extraction of the lipid from microalgae must be done. Typical lipid extraction processes from microalgae are solvent extraction and mechanical press, both of which require dry to improve lipid yield before the extraction. Also, in iso-conversion concept, the residue of the extraction of lipid (protein and carbohydrate are main components) will be treated by anaerobic fermentation to form small molecules such as organic acids. Advantage of the biochemical process is high selectivity, but disadvantage is low reaction rate. For the purpose of liquid fuels production, broad product distribution in the range of small molecular weight is acceptable. Or rather, rapid transformation process has to be necessary for the residue conversion of the residual biomass containing protein and carbohydrate.

Thus, the whole biomass including lipid, protein, and carbohydrate should be treated by sub and supercritical water technologies in the presence of an appropriate catalyst (so it should be advanced supercritical technology). Here, we focus on effective conversion of carbohydrates and protein into small fragments, and low temperature catalytic hydrothermal cracking (LT-CHTC) must be designed with the concept of inhibition of Maillard reaction, which is undesired reaction because complex nitrogen-containing components are produced and these will be repolymerized into non-decomposable materials like char or coke.

3.2 Carbohydrate conversion into precursors of liquid fuels

Our research group has studied protein and carbohydrate conversion in hydrothermal water (subcritical water) condition with some catalysts.

It has been revealed that hydrolysis of cellulose, which is main component of carbohydrate in biomass, is rapid in sub and supercritical water without additive [34, 35]. The hydrolysis product of cellulose, glucose, is converted into furan ring compounds [8–13] and further small molecules (including hydrogen gas) in hydrothermal and supercritical water in the presence and absence of catalyst/additive [34, 36–43].

3.3 Protein conversion into small fragments

Protein-rich biomass, defatted soybean meal, was converted into oligopeptides with the advanced supercritical technology (catalytic hydrothermal conversion) [14]. Protein is easily denatured to aggregate into brownish compound, which is hard to be hydrolyzed, with heat. To alter the reactivity of peptide under the heat, rapid heating technique is helpful [14, 44]. In addition, denaturation agent is also useful to improve and accelerate hydrolysis rate of protein into small fragments [14]. The effectiveness of the denaturation agent is known as Hofmeister series, which tells that alkaline earth metal ion such as Ca^{2+} and Mg^{2+} is a strong denaturation agent [45, 46]. Further, pH of the protein solution is important factor for keeping solubility in water, and alkali condition is favor for soy protein solubilization in water [47]. In our previous study, the multiple techniques (microwave technique for rapid heating, Mg^{2+} addition for Hofmeister series and alkali condition) for keeping reactivity and solubility of soy protein were employed for improving the yield of oligomer (over 70% of oligopeptide yield based on the soy protein in the defatted soy bean meal) from defatted soy bean meal at 190°C under saturated pressure of water for 1 h [14]. The oligopeptide obtained from the advanced supercritical technology for protein conversion (rapid heating with high Hofmeister additive in subcritical water) shows high foaming ability, antioxidant activity, and high inhibitory activity on angiotensin I converting enzyme (ACE) [14]. We also confirmed that the oligopeptide can be converted into free amino acid with over 80% yield at an advanced supercritical fluid technology (patent application and data are not shown), and it will be reported in near future elsewhere.

3.4 Alanine degradation in subcritical water

In the concept of the total protein-rich biomass conversion into liquid fuel with advanced supercritical fluid technology (new “iso-conversion” for total protein-rich biomass), free amino acid produced through hydrolysis of protein and oligopeptides is further degraded into small molecular weight components such as organic acids and aldehydes (**Figure 1**). To know the optimum condition of amino acid degradation in subcritical water at a wide range of reaction temperature, alanine is selected

as a standard amino acid. In a literature [48], it was found that the rate of thermal decomposition of amino acids were correlated with Taft rule, which allows the prediction of the rate of different amino acid based on a reaction rate of standard amino acid with substituent parameter, σ^*, and reaction parameter. It is expected that the same relation of degradation rate of amino acid in subcritical water can be found (it will be revealed in near future by our research group) and alanine is appropriate as the standard.

3.4.1 pH dependence of rate constant of alanine degradation

Here, pH dependence of the reaction rate of alanine was investigated because an appropriate additive for improvement of alanine conversion will be looked for. For the objective, an overall rate constant for 1st order alanine degradation at a wide range of pH condition [49] was considered:

$$k_{\mathrm{Ala}} = \frac{k_{\mathrm{Ala}^+}[\mathrm{H}^+]^2 + k_{\mathrm{Ala}^\pm} Ka_1[\mathrm{H}^+] + k_{\mathrm{Ala}^-} \bullet Ka_1 Ka_2}{[\mathrm{H}^+]^2 + Ka_1[\mathrm{H}^+] + Ka_1 Ka_2} \tag{6}$$

where k_{ala} is the rate constant of 1st order overall alanine degradation, $k_{\mathrm{ala}+}$ is the rate constant of 1st order overall cationic alanine (Ala^+) degradation, $k_{\mathrm{ala}\pm}$ is the rate constant of 1st order overall zwitterion alanine ($\mathrm{Ala}^\pm$) degradation, and $k_{\mathrm{ala}-}$ is the rate constant of 1st order overall anionic alanine (Ala^-) degradation. $[\mathrm{H}^+]$ is the concentration of proton in the system. Ka_1 is the dissociation constant between cationic (Ala^+) and zwitterion alanine ($\mathrm{Ala}^\pm$), and Ka_2 is the dissociation constant between zwitterion ($\mathrm{Ala}^\pm$) and anionic alanine (Ala^-), as shown in the below equation:

$$\mathrm{Ala}^+ \overset{Ka_1}{\leftrightarrow} \mathrm{Ala}^\pm \overset{Ka_2}{\leftrightarrow} \mathrm{Ala}^- \tag{7}$$

In the literature [49], the rate of decarboxylation (which is main reaction at sub and supercritical water over 573 K [15]) was measured with monitoring CO_2 formation by in situ FTIR. Here, in Eq. (6), it is considered that pH dependence of the 1st order rate constant of alanine evaluated from the rate of decarboxylation was almost the same as the rate of overall alanine degradation (k_{ala}). The dissociation constant of Ka_1 and Ka_2 in subcritical condition can be calculated by revised HKF model with the reported parameters [50]. We performed the alanine degradation in subcritical water (260∼360°C at 20 MPa) not only neutral condition but also acid (5 mmol dm^{-3} of H_2SO_4 solution) and alkali (20 mmol dm^{-3} of NaOH solution) conditions to know the intrinsic first-order rate constant of degradation for all kinds of alanine species ($k_{\mathrm{ala}+}$ for cationic, $k_{\mathrm{ala}\pm}$ for zwitterion and $k_{\mathrm{ala}-}$ for anion). **Figure 4** shows the alanine species distribution in the reaction conditions.

Here, the dissociation constant of H_2SO_4 was correlated by the equation proposed by Oscarson et al. [51]. For NaOH, the dissociation constant was calculated by the revised HKF (Helgeson-Kirkham-Flowers) model [52].

In the alkali condition (**Figure 4C**), only the anionic alanine (Ala^-) is present. At the neutral condition (**Figure 4B**), the composition of zwitterion alanine ($\mathrm{Ala}^\pm$) is major. With increasing temperature, the composition of anionic alanine (Ala^-) is drastically increased and the composition of anionic alanine (Ala^-) is higher than that of zwitterion alanine ($\mathrm{Ala}^\pm$). In the acidic condition (**Figure 4A**), the composition of cationic alanine (Ala^+) is major species and its composition becomes higher with increasing temperatures.

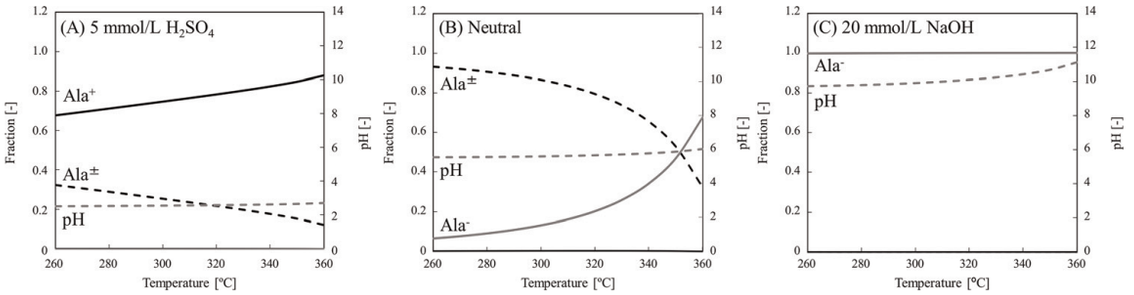


Figure 4.
Alanine species distribution in subcritical water at (A) acid, (B) neutral, and (C) alkali conditions at 20 MPa.

In this part, pH dependence of the overall rate constant of alanine degradation at a wide range of reaction temperature and pH condition is explained. To correlate the rate constant, a correlation was performed:

i. At alkali condition, $k_{\text{ala}-}$ was measured and it was the same as the overall rate constant, k_{ala}.

ii. The apparent rate constant was measured at neutral condition as k_{ala}, which includes both contribution of anionic and zwitterion alanine as below.

$$-\frac{d[\text{Ala}]}{dt} = k_{\text{Ala}}[\text{Ala}]_0 = k_{\text{Ala}^-}[\text{Ala}^-] + k_{\text{Ala}^\pm}\left[\text{Ala}^\pm\right] \tag{8}$$

By using $k_{\text{ala}-}$ measured in alkali condition and the concentration of each species ($\text{Ala}^\pm$ and Ala^-) calculated as shown in **Figure 4B**, $k_{\text{Ala}\pm}$ was obtained by the below equation.

$$k_{\text{Ala}^\pm} = \frac{k_{\text{Ala}}[\text{Ala}]_0 - k_{\text{Ala}^-}[\text{Ala}^-]}{\left[\text{Ala}^\pm\right]} \tag{9}$$

where $[\text{Ala}]_0$ was the initial concentration of alanine. All brackets, [X], are correspondent to concentration of species X in mole m^{-3}.

iii. For $k_{\text{Ala}+}$ was obtained as the same manner of $k_{\text{Ala}\pm}$ mentioned above.

3.4.2 Experimental for alanine conversion in subcritical water

Figures 5 and **6** show a photograph and schematic diagram of a flow apparatus that used for subcritical water decomposition of alanine, respectively. The reactor consisted of two pumps, preheater, reactor, cooler, and back-pressure regulator. The preheater was made of SUS316 stainless steel (length 40 m., id: 1 mm, od: 1/16 inch) and placed in a GC oven (HP6890, Agilent Technologies). The reactor was also made of SUS316 stainless steel (length 100 m, id: 1 mm, od: 1/16 inch, volume of reactor: 81.2 cm^3) placed in another GC oven (6890N, Agilent Technologies). The shell tube heat exchanger for cooling made of SUS316 stainless steel (length 30 m., id: 1 mm, od: 1/16 inch) was located in a chiller (LE-600, Advantec). The pressure was controlled at 20 MPa by the back-pressure regulator (TESCOM). The sample solution and water were supplied by pumps (PU-2100S, Jasco and NP-KX-500, Nihon Seimitsu Co., Ltd.). For rapid heating, water was fed to mixing part with flow ratio of 1:9 or 1:3 (sample solution:water) and preheated. The preheater temperature was decided by consideration of enthalpy balance to reach the mixing temperature to the targeted temperature, which was in the range of 260–360°C.

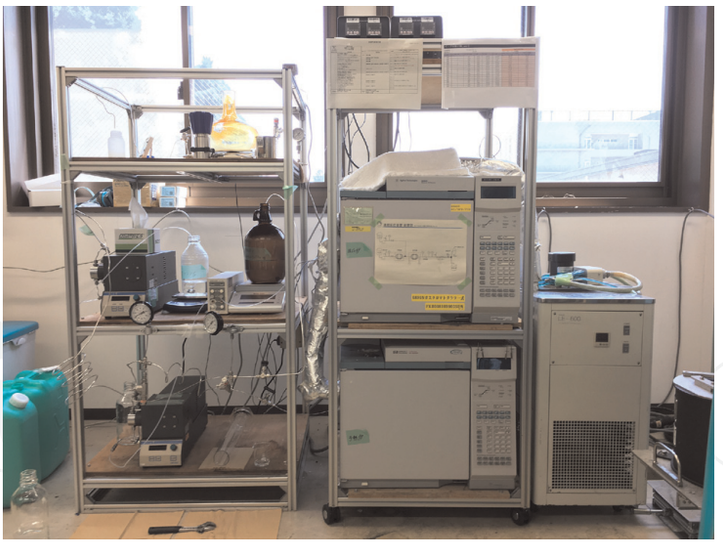


Figure 5.
Photograph of continuous flow reactor.

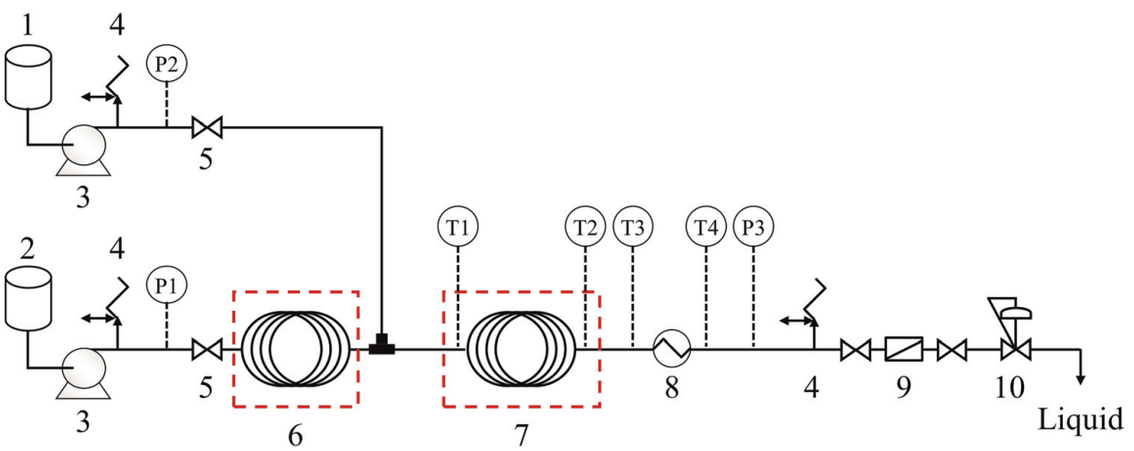


Figure 6.
Schematic diagram of continuous-flow system (1: alanine solution, 2: water, NaOH, or H_2SO_4, 3: pump, 4: relief valve, 5: valve, 6: preheating unit, 7: reaction unit, 8: cooling unit, 9: filter, 10: back-pressure regulator).

The effluent was cooled down in the cooler and collected. Reaction time was varied in the range of 60–300 s by changing flow rates of the reaction fluids and calculated based on the water density at reaction temperature (260–360°C) and pressure (20 MPa).

Alanine in the outlet solution was measured by HPLC with an ODS column (Shim-pack VP-ODS, Shimazu) and PDA detector (L-7455, Hitachi) at wavelength of 200 nm. The column oven was 60°C. The carrier were sodium 50 mM of sodium phosphoric acid with 7.2 mM of hexane sulphonate set to pH 2.5 (solution A) and HPLC grade acetonitrile (solution B) with flow ratio of 96:4 (A:B) and the flow rate was 1.0 mL/min.

Conversion of alanine was calculated from the concentration of alanine before and after the reaction and the rate constants (k_{Ala-}, $k_{Ala\pm}$ and k_{Ala+}) by already mentioned protocol: (i) k_{Ala-} was measured at alkali condition, (ii) $k_{Ala\pm}$ was correlated from k_{Ala} measured in neutral condition, and (iii) k_{Ala+} was obtained at acidic condition by correlation with the measured k_{Ala} measured and $k_{Ala\pm}$.

3.4.3 Rate constant of alanine at wide temperature and pH conditions

Figure 7 shows the Arrhenius plots of the intrinsic rate constant of each alanine species degradation in subcritical water at 20 MPa. The data for k_{Ala+} and k_{Ala-} were

largely scattered, and the correctness of the data must further be investigated. Here, we analyzed the trend of the rate constant for each species as the order and the temperature dependence (namely activation energy) should be correct. The activation energy of the rate constant of zwitterion, $k_{Ala\pm}$, was the highest among all the rate constants shown in **Figure 7**. Thus the reactivity of zwitterion alanine becomes higher than the others. **Figure 8** shows the simulation of pH dependence of the overall rate constant of alanine degradation in subcritical water at 20 MPa and various temperatures.

At the range of reaction temperatures from 340 (**Figure 8A**) to 280°C (**Figure 8D**), the simulation of pH dependence of the overall rate constant of alanine degradation, k_{Ala}, (drawn with the bold line) well explained the experimental data (plots in the figures). As shown in **Figure 8**, over 300°C, zwitterion alanine is the most active species and surprisingly an acid or alkali catalyst is not useful for enhancing degradation rate. Below 280°C, alanine degradation should be enhanced by an acid or alkali catalyst. But lower temperature, the reaction rate is so low and decomposition of alanine requires long time. For the pretreatment of protein-rich biomass to produce the precursor of hydrocarbons such as organic acids, the enhancement of the reaction rate must be necessary. To seek an appropriate additive, some types of solid acid additives were screened.

3.5 Amino acid deamination with solid acid additives in hydrothermal water

3.5.1 Previous studies on solid catalytic reaction of amino acid in hydrothermal (subcritical) water

Since amino acid is monomer unit of protein and key compound in life, amino acid reaction in hydrothermal system is highly motivated to know the origin of life because protein is basic molecule for life and polypeptide formation, namely protein synthesis, should be the first step. Hydrothermal vent under deep sea is seemed to be one of the spaces where is the original place of life. To form protein, survivability of amino acid at such severe condition (hydrothermal water is partially higher than 200°C) is crucial for the origin of life, and the stability of amino acid at hydrothermal water condition is important. In the origin of life point of view, amino acid touches on the surface of inorganic materials at the deep sea near the hydrothermal vent and the effect of the inorganics on the stability of amino acid has

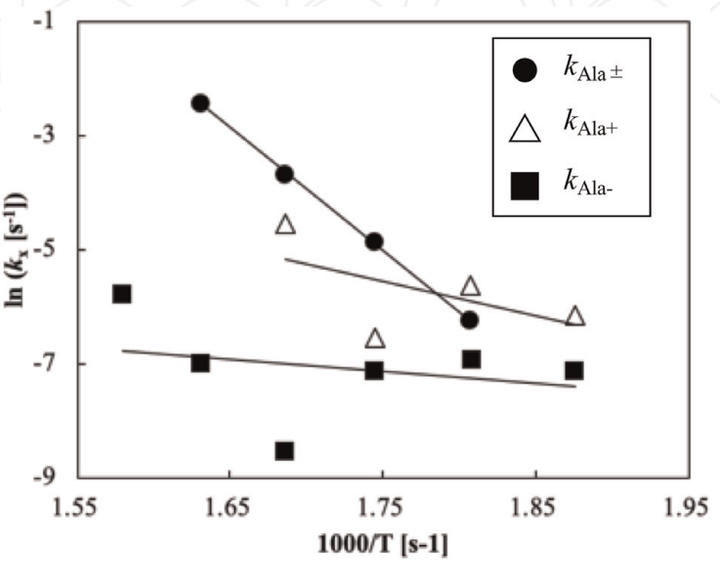


Figure 7.
Intrinsic rate constant of each alanine species at 20 MPa.

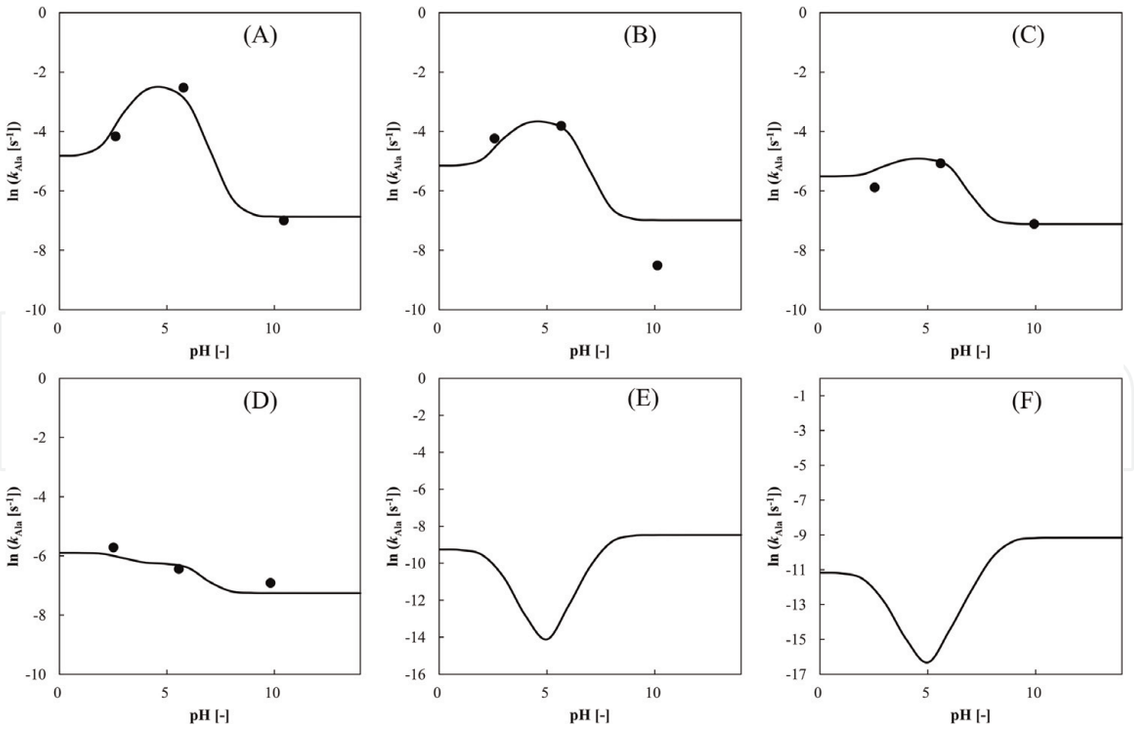


Figure 8
pH dependence of the overall rate constant of alanine degradation, k_{Ala}, at 20 MPa: (A) 340°C, (B) 320°C, (C) 300°C, (D) 280°C, (E) 150°C, and (F) 100°C.

been studied. It was reported that iron compounds enhance dimerization to form alanyl-alanine and diketopiperazine at hydrothermal condition [53]. Glycine and alanine are reacted at 100°C for 35 days with metal ferrites such as $NiFeO_4$ to obtain 30% of yield of dimerization products [53].

As amino acids to be key compounds in biomass refinery, there have also been some reports concerning conversion of amino acids into chemicals with solid additives. It was reported that Pt/TiO_2 promotes the reductive deamination of glutamic acid derivatives to form organic acids at 225°C for 24 h [54]. By the same research group of [54], decarbonylation of amino acids was attempted by Ru-based catalyst [55]. Reductive (hydrogenation) decarbonylation of valine to isobutylamine was developed in the presence of Ru-catalyst with isobutylamine yield of 87% in hydrothermal water at 150°C for 2 h.

3.5.2 Sulfonyl solid acid catalytic reactions of alanine in hydrothermal (subcritical) water

As described above, there have been several papers concerning some solid catalytic reactions of amino acids in hydrothermal water; however, solid acid or base reactions on hydrothermal (subcritical water) reaction of amino acids was not investigated so far.

Based on the analysis of the pH dependence of degradation of alanine, solid acid or base catalyst must be effective. The batch experiments were performed with microwave hydrothermal small reactor (**Figure 9**). The detail of the apparatus and procedures are found elsewhere [13]. Here, conversion of alanine was investigated in hydrothermal water with and without sulfonyl solid catalyst at 150°C for 1–60 min. Basically, 5.0 g of 110 mmol dm^{-3} of amino acid solution was loaded in a glass reactor with 0.5 g of solid sulfonyl additive such as sulfonyl carbon (detail is not shown because of the patent application) and cationic (having sulfonyl group) ionic exchange (Amberlyst 45) resin. As shown in **Figure 10**, alanine is decomposed



Figure 9.
Microwave hydrothermal small reactor.

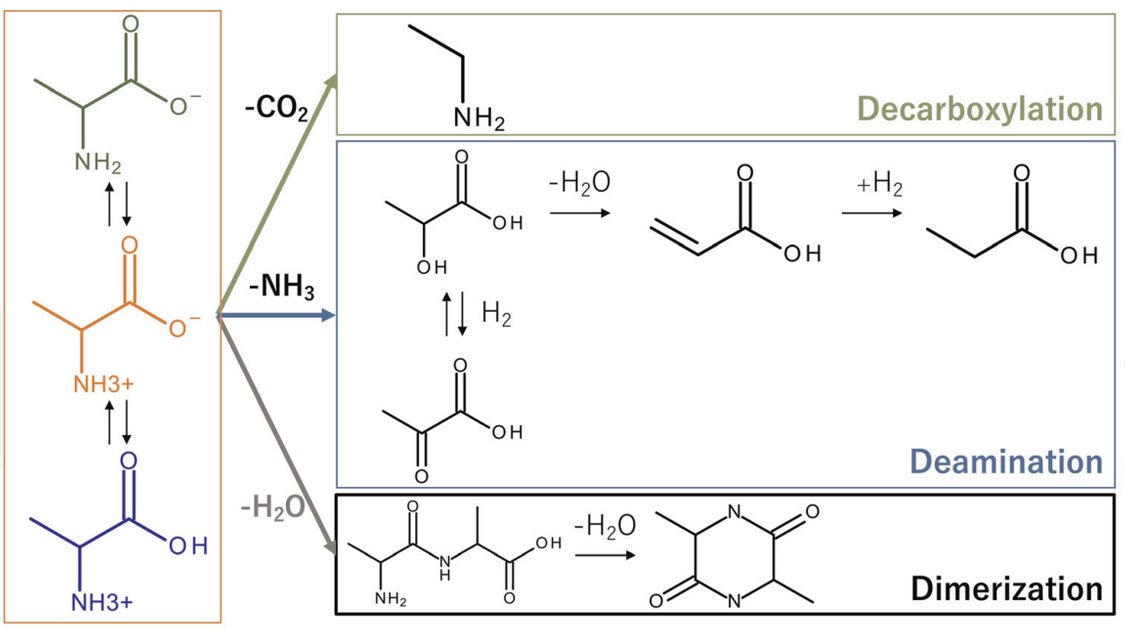


Figure 10.
Main pathways of alanine degradation in hydrothermal water.

through decarboxylation, deamination, and dimerization. To know which pathway is developed, decarboxylation product, CO_2, was detected by CO_2 meter and fingerprint of deamination, NH_3, was analyzed by an ion chromatography.

Figure 11 shows the results. Amberlyst 45 was inert for deamination of amino acids at hydrothermal water at 150°C. In the presence of the sulfonyl carbon, deamination of alanine was progressed. Not shown here, the other pathways of alanine degradation were not found for all the cases in these experiments.

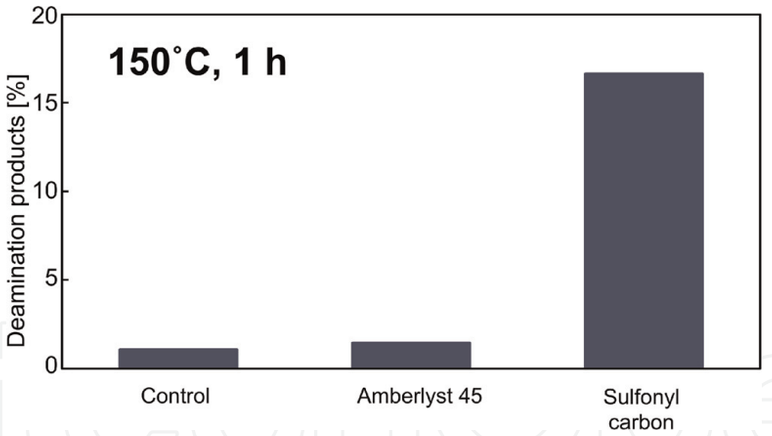


Figure 11.
Yield of deamination product, NH_3, of alanine in hydrothermal water with and without sulfonyl solid additive at 150°C for 1 h (under saturated pressure of water, 0.48 MPa).

On Amberlyst 45, 2.95 eq kg^{-1} of sulfonyl group is bearded, while 1.90 eq kg^{-1} of sulfonyl group is attached on the surface of sulfonyl carbon. The catalytic activity for deamination of alanine is probably related to oxygenated function group (OFGs) such as hydroxyl and carboxyl because the sulfonyl carbon has 2.40 mmol g^{-1} of OFGs (Amberlyst 45 has no OFG except for sulfonyl group). More detail study for amino acid deamination on the sulfonyl carbon catalyst is now on-going and it will be reported in near future.

3.5.3 Sulfonyl carbon reactions of okara in hydrothermal (subcritical) water

Through the experiments, it was revealed that sulfonyl carbon was active for deamination of amino acids. It must be resulted in the activation of alanine at strong acid condition (not only by sulfonyl group but also by OFGs) as predicted (**Figure 8**). The LT-CHTC, mainly for deamination, is favored as liquid fuel pretreatment as proposed in **Figure 1**. Here, to know the usefulness of the reaction for a real biomass, "okara," which is a residue of soy bean cake ("Tofu") production, was deaminated in the presence of the sulfonyl carbon. The elemental composition of okara used in this study is C:H:N:S:O (wt%) = 47.2:7.29:5.85:0.43:39.2 (the weight percentage of oxygen atom was subtraction of total weight % of C, H, N. and S from 100 and it should include ash, which will be analyzed by TGA). As a result, a large portion of amino group in okara was detached as ammonia, NH_3, (detail is not shown at this moment because of the reason for patent application). Thus, the sulfonyl carbon catalytically assisted NH_2-group abstraction as NH_3. It means that Maillard reaction during okara conversion was less happened and much organic acids were formed. For this study, now the detail is being studied and it will be also reported in near future.

4. Up-conversion of carbohydrate in ionic liquid and supercritical fluids mixtures

Cellulose and chitin are abundant biomass and these up-conversion (valorization) into useful compounds are aggressively being investigated. Our research group has studied cellulose and chitin conversion with advanced supercritical technologies. As one of advanced supercritical technologies, ionic liquid utilization together with supercritical fluid technologies (including subcritical and

hydrothermal water) has been studied. Here, two biomass conversion process are focused on: furan ring compound formation from cellulose and hydrogenation.

4.1 HMF formation from cellulose

HMF is a platform compound that can be derived from cellulose in coming biomass society [23, 24]. It is known that the formation of HMF from cellulose is three-step reaction: (1) hydrolysis of cellulose into glucose, (2) glucose isomerization to fructose, and (3) fructose dehydration to HMF, as shown in **Figure 12**. Step 1 and step 3 are acid-catalyzed reactions, and step 2 is a base-catalyzed reaction. To increase the yield of HMF, optimization of each reaction step is necessary.

For step 1, selective glucose production by cellulose hydrolysis with sequential water addition in the presence of solid acid catalysts in 1-butyl-3-methyl imidazolium chloride ([bmIm][Cl]) under microwave irradiation was investigated at 120°C, where water is hydrothermal condition [23]. It revealed that the large amount of water added in the initial stage was inhibited to form homogeneous phase among three components (cellulose-water-[bmIm][Cl]) and some amounts of cellulose was precipitated. The precipitation of cellulose was resulted in the low yield of glucose because hydrolysis of cellulose was stopped. To keep the cellulose dissolution and improve hydrolysis of cellulose into glucose, sequential water addition where water is added in steps as the reaction proceeds was investigated. Glucose yields in the presence of Amberlyst-15 in [bmIm][Cl] were 75.0 mol% by three step of water addition [23].

Step 2 (glucose isomerization, which requires basic catalyst) was also optimized in the presence of hydrothermal water with [bmIm][Cl] at 120°C, and the effect of water on step 3 (glucose into HMF) was investigated [24]. For isomerization of glucose in the presence of 35 wt% of hydrothermal water in [bmIm][Cl], $MgCO_3$ was the most effective base additives (23.1 mol% of fructose yield with 85.3 mol% selectivity was obtained at 120°C for 30 min). For dehydration of fructose into HMF with Amberlyst 15 (Step 3), the rate of dehydration of fructose was slightly reduced by adding water but not so large effect was confirmed. Also in the paper [24], continuous HMF production process via three-step reaction is proposed with separation of HMF from [bmIm][Cl] and water mixture. It was found that dimethyl ether was a good separation solvent and almost 100% of HMF was recovered. Finally, virtual integration of the three-step process tells us that the yield of HMF from cellulose is estimated to be 32 mol%.

4.2 Hydrogen solubility in ionic liquid with supercritical CO_2

The other important reaction routes from biomass into useful material are hydrogenolysis and hydrogenation of biomass [56]. Ionic liquid media has advantage of biomass conversion because solubilization of cellulose and chitin in some types of ionic liquid is high. One of drawbacks of the ionic liquid process is high viscosity. Supercritical CO_2 assists reduction of viscosity of ionic liquid-cellulose mixture [26]. For the process of hydrogen addition (such as hydrogenolysis and

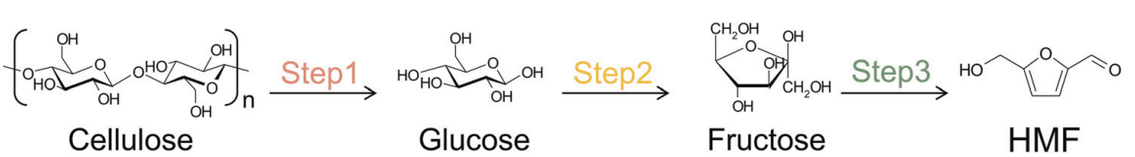


Figure 12.
HMF formation from cellulose.

hydrogenation), the synergetic effect of hydrogen and supercritical CO_2 coexistence must be revealed.

Hydrogen solubility was experimental measured and a simple correlation for hydrogen solubility in ionic liquids in the presence of CO_2 was developed from available binary/ternary data. The correlation could provide reliable estimation of hydrogen solubility enhancement by CO_2 for six ionic liquids at 313–453 K [56]. In the study [56], a definition for enhancement ratio (ER) based on molality and applied it to available hydrogen-CO_2-ionic liquid systems were proposed. It was found that the ER was convenient for examining the trends of solubility change of hydrogen in an ionic liquid with CO_2 concentration or temperature. Also in the study [56], hydrogen solubility in the presence of CO_2 was estimated for biomass soluble ionic liquids.

5. Conclusions

In this chapter, the concept of liquid fuels from biomass in advanced supercritical fluid is firstly explained. To know the optimum condition for various kind of biomass, dimensionless severity number should be useful and the application for lignin recovery in hydrothermal and subcritical water was shown. Then, as the application of one of the advanced supercritical fluid technologies, hydrothermal water with catalyst process for carbohydrate and protein performed by our research group was briefly reviewed. For total biomass utilization as liquid fuel production, protein fragmentation is a key process and some of experimental research results were shown. Particularly, alanine conversion with and without additive was deeply considered. To inhibit Maillard reactions, the deamination of amino acid at low temperature was quite important, and it was found that a sulfonyl carbon was quite active for deamination of alanine at 150°C in hydrothermal water. Cellulose conversion in ionic liquid with supercritical fluid (hydrothermal water) to furan ring compound (HMF) was introduced. For hydrogenation of biomass, hydrogen solubility was controlled in the presence of supercritical carbon dioxide and it shows that ionic liquid with supercritical CO_2 is favored hydrogenolysis and hydrogenation reaction field for up-conversion of biomass.

Conflict of interest

The authors declare no conflict of interest.

Nomenclature

$[Ala]$	concentration of alanine, mol m^{-3}
$[Ala]_0$	initial concentration of alanine, mol m^{-3}
$[Ala^-]$	concentration of anionic alanine, mol m^{-3}
$[Ala^{\pm}]$	concentration of zwitterion alanine, mol m^{-3}
E_a	Activation energy, kJ mol^{-1}
$[H^+]$	concentration of proton, mol m^{-3}
K_{a1}	dissociation constant between cationic and zwitterion alanine
K_{a2}	dissociation constant between zwitterion and anionic alanine
k	rate constant, min^{-1}

k_o	pre-exponential factor, min^{-1}
k_r	rate constant, min^{-1}
LR	lignin recovery, wt%
R	gas constant, 8.314 J mol^{-1} K^{-1}
R_o	severity factor, min
T	temperature, K
t	reaction time, min
T_r	reference temperature, 373 K

Greek letters

σ^*	substituent parameter for Taft rule

Subscripts or superscripts

Ala	alanine
ala+	cationic alanine
ala_	anionic alanine
ala±	zwitterion alanine

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