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“Enhancement of nutrient recovery from microalgae in hydrothermal liquefaction using activated carbon”

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Abstract

For large-scale biofuel production from microalgae, the following outcomes are needed to reduce environmental impact and biofuel production cost 1) extraction of a large amount of lipid (bio-oil), 2) recovery of almost all nutrients and their reuse for cultivation, and 3) effective utilization of solid residue (char). We investigated the possibility of using activated carbon to enhance recovery of bio-oil and nutrients in hydrothermal liquefaction (HTL). Microalga *Fistulifera solaris* was reacted at 573 K and 10 MPa for 0–60 min with or without commercial activated carbon (0.5 wt% of microalgae) in an autoclave reactor. Results show 0.5wt% activated carbon can substantially promote total nitrogen recovery in the aqueous phase, probably because of catalytic effect of activated carbon on the decarboxylation reactions to produce amines. Larger amount of activated carbon (> 1.0wt%) decreased bio-oil recovery due to adsorption. A apparent kinetic study of nitrogen recovery in the aqueous phase showed the apparent reaction order was 3 and the reaction rates were $1.1 \times 10^{-7} \text{ s}^{-1}$ and $5.6 \times 10^{-8} \text{ s}^{-1}$ with and without activated carbon, respectively. 0.5wt% of activated carbon has an insignificant influence on bio-oil and phosphorus recovery.

Keywords: microalgae, hydrothermal liquefaction, activated carbon, recovery of nitrogen

1. Introduction

Microalgae are a promising energy resource because they can grow much more rapidly than terrestrial plants and also they have a higher photosynthesis efficiency. In addition, microalgae can produce bio-oil, which can be converted to biofuel by chemical reactions such as transesterification and hydrotreating [1–8]. Together, these benefits significantly decrease the land area required to produce a unit of biofuel [9]. However, the growth of microalgae requires a large amount of nutrients; e.g. nitrogen, phosphorus and potassium. For large-scale biofuel production, the recovery and reutilization of nutrients from algal residue is critical because of their high costs [4,10], the scarcity of phosphorus [10] and the large amount of fuel consumption required for fertilizer production [11].

Hydrothermal liquefaction (HTL) using subcritical water (ca. 473–623 K, 5–20 MPa) is a promising technology for producing (extracting) crude bio-oil from microalgae because its bio-oil yield is higher than conventional extraction methods and HTL does not require an energy intensive drying process prior to bio-oil extraction. Many studies have been conducted on production of bio-oil from algae through HTL reactions [5, 12–17].

Recent studies have shown that nutrients can be recovered in the aqueous phase (water) after HTL reaction [12,14,18–24]. Alba *et al.* investigated the nitrogen distribution amongst the solid, gas, water and bio-oil after HTL of *Desmodesmus* sp. with a 60-min reaction [18]. Jena *et al.* reported that HTL of 100 g of dry *Spirulina* resulted in 40% bio-oil

and 49% water soluble components, which had high nitrogen, phosphorous, potassium, secondary and micronutrients [14]. Valdez and Savage *et al.* investigated yields of solids, gas, biocrude and aqueous-phase products from *Chlorella protothecoides*, *Scenedesmus* sp., and *Nannochloropsis* sp. by HTL as a function of reaction time. Based on their experimental results, they developed correlated reaction network and kinetic models that could account for the influence of time and temperature on the yields of gas, solid, biocrude, and aqueous-phase products from isothermal HTL of a 15 wt% slurry [19–21]. Yu *et al.* [22] investigated time profiles of carbon and nitrogen distribution in aqueous products, bio-oil and solid residue from HTL of low-lipid microalgae *Chlorella pyrenoidosa* at various reaction temperatures and retention time. They reported that 65–70% nitrogen and 35–40% carbon in the original material were converted into water soluble compounds when the reaction temperature was higher than 493 K and the retention time exceeded 10 min [22]. Gai *et al.* investigated chemical oxygen demand (COD), total nitrogen and total phosphorus in the aqueous phase from HTL of *Chlorella pyrenoidosa* under various operating conditions, including reaction temperatures, retention time and total solid ratio (i.e. microalgae concentration in the slurry). They found that the total solid ratio was the most dominant factor affecting nutrient recovery efficiencies in the aqueous phase [23]. Jazrawi *et al.* reported high levels of K, Na, Ca and other minor nutrients in the aqueous phase after HTL of *Chlorella* and *Spirulina* [24].

It was reported and confirmed that the nutrient-rich aqueous phase of HTL can

subsequently be used for microalgae cultivation after dilution and addition of other minor nutrients although the growth rates achieved were dependent on the microalgae strain [10, 14, 25–28]. These results indicate that the integration of nutrient recovery in the aqueous phase after HTL and its recycle for subsequent culturing is very promising and that nutrient recovery should be promoted to reduce fertilizer consumption in the culturing section.

In a large-scale algal biofuel production plant, the solid residue (char) produced after the HTL reaction should also be utilized. In most cases, anaerobic digestion is **considered to be** a feasible technology to convert **remaining** algae or solid residue. **However**, post-treatment of solid residue is still required. We believe that activated carbon production from algal residue [29–32] is an alternative, feasible option because activated carbon can be used as an adsorbent in gas and liquid phases, for energy storage and as a catalyst-support material. Activated carbon will be a further chemical product of this algal biofuel production plant. **Furthermore**, there is **a** possibility that **activated carbon** can function as an adsorbent **and/or catalyst** to promote nutrient and bio-oil recovery from algae during HTL reaction. **However**, to the best of our knowledge, there has been no study published describing an investigation of adsorption **and/or catalytic** characteristics of activated carbon **during HTL reaction**.

This study attempted to promote nutrient recovery in the **aqueous** phase and increase bio-oil yields from the HTL reaction using commercial activated carbon, which is an alternative to microalgae char, as an adsorbent **and/or catalyst**. Concentrations of nitrogen and

phosphorous in the aqueous phase and bio-oil from the marine microalga *Fistulifera solaris* at 573 K and 10 MPa in subcritical water were measured with an autoclave reactor at various retention times.

2. Experimental

2.1.1 Microalgae

A marine diatom, *Fistulifera solaris* JPCC DA0580 [33], was used. The algal cells were maintained in a flask (100 mL) containing 60 mL 2f medium (2-fold concentrated f medium) [34] dissolved in artificial seawater. The algal cells were grown photoautotrophically at 298 K on a rotary shaker. The algae were then pre-cultured in a flat 1.5-L oblong culture vessel in the 2f medium for 7 days, then cultured in a 10-L flat-panel photobioreactor with 2f medium at 298 K for 12 days [35], in which cultures were aerated with sterile air under continuous illumination. Algal growth was evaluated by measuring differences in dry weight.

After culturing, the concentration of the culture fluid was about 1.0 g-dry-algae/L. The culture fluid was then centrifuged to produce a 10-g-dry-algae/L slurry. This microalgal slurry was used as the feedstock for the subsequent HTL reaction. Note each cultivation batch produced a microalgae sample was sufficient for four HTL experiments.

2.1.2 Activated Carbon

Commercial activated carbon (Kanto Chemicals, Co. Ltd, Tokyo, Japan) was used and its specific surface area was measured using the BET method (BELSORP-max, MicrotracBEL Corp.) with liquid nitrogen.

The surface functional groups were measured by the Boehm method [36–39]. Prior to each measurement, 100 mg activated carbon was mixed with approximately 30 mL distilled water in a pycnometer and deaerated under vacuum for 20 min. The deaerated activated carbon was mixed with NaOH (Kanto Chemical Co., Ltd., Tokyo, Japan), NaHCO₃ (Wako Pure Chemical Industries, Ltd, Osaka, Japan), and Na₂CO₃ (Kanto Chemical Co., Ltd., Tokyo, Japan) separately and stirred for 24 h to measure phenolic, carboxyl and lactone/lactol groups, respectively. The concentration of the alkali solutions was 0.02 mol/L. The amount of each functional group was then quantified by titration with 0.02 mol/L HCl (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Each measurement was repeated three times.

Table 1 shows the BET surface area and the amount of surface functional groups in the activated carbon. Similar results of amount of the carboxyl and phenyl groups were observed compared with the literature [38, 40, 41]. Lactone groups were not detected.

2.2 Determination of weight of lipid in algae

Part of the algal slurry was freeze-dried and the dried alga was ground using a pestle and mortar. The dried alga was then mixed with hexane to extract lipid. The

lipid/hexane/algae mixture was poured into a test tube and centrifuged for approximately 10 min at $200 \times g$. The lipid/hexane solution was removed from the test tube and the hexane was evaporated at 353 K and the weight of the obtained lipid (W_{oil}) measured.

2.3 HTL Reactor and Procedure

The HTL experimental apparatus is shown in Figure 1. One hundred milliliters of the feedstock slurry was loaded into an autoclave HTL reactor (TPR-1, 300 mL, Taiatsu Techno® Corporation, Osaka, Japan). In the case of addition of activated carbon, the 100 mL of the algal slurry was poured into a vial and mixed with the activated carbon prior to loading into the autoclave reactor. The mixture of the activated carbon and slurry was shaken and then poured into the autoclave reactor. The autoclave reactor was sealed and purged with Ar several times until the N_2 concentration in the reactor was below 1%. The initial pressure was then set to approximately 2.5 MPa by adding Ar gas. The reactor temperature was measured with a Type-K thermocouple. The reactor was stirred at 300 rpm and heated to 573 K (reaction temperature) with an electric heater. The reaction temperature and pressure were maintained at 573 K and 10 MPa, respectively, for 0, 10, 20, 30, 40 and 60 min. The electric furnace was then turned off and the reactor was cooled to room temperature.

After the reactor was cooled, products were separated by the procedure shown in Figure 2 [42]. Gaseous products were collected with a gas bag by opening stop valve (2) and adjusting a needle valve (Figure 1). The flow rate of the gaseous products was measured with

a digital mass flow meter. After opening the lid of the reactor, the water soluble fraction was separated from the bio-oil and solid products by filtration. The remaining bio-oil was also extracted from the solid products with acetone for 30 min and the solid product and bio-oil then separated by filtration with a nylon-mesh. Acetone was evaporated using a hot plate at 353 K. Hereafter, this solid product is referred to as “char”.

The bio-oil recovery ratio (R_B [wt%]) was calculated using eq. (1).

$$R_B[\text{wt}\%] = \frac{\text{weight of recovered bio-oil [g]}}{\text{weight of lipid in algae (Woil) [g]}} \times 100 \quad (1)$$

2.4 Decomposition of algal feed

Dry algal feed was decomposed to analyze N and P compositions. Three milliliters of HF and 3 mL HNO_3 were added to 10–40 mg of dry algal feed and sealed in a Teflon vessel. The vessel was heated at 413 K for 3 h, then cooled to room temperature. After opening the lid, the remaining solution was evaporated at 353 K until the residue was completely dry. The dried residue was dissolved with 2 mL HCl solution and 48 mL distilled water was then added to the solution.

2.5 Analyses of Products

2.5.1 Phosphorus in the Water-Soluble Fraction

The total amount of P in the water-soluble fraction was determined using the molybdenum blue method. Fifty milliliters of the water-soluble fraction recovered after HTL reaction was mixed with 10 mL potassium peroxodisulfate in a Teflon vessel. The solution

was heated to 393 K for 1.5 h in an autoclave to convert P-containing components into PO_4^{3-} by hydrolysis. The solution was mixed with reagent solution A (1.5 g L(+)-ascorbic acid, 1.0 g sodium dodecyl sulfate and 1 L distilled water) and reagent solution B (67 mL hydro sulfuric acid, 5.48 g ammonium molybdate 4-hydrate, and 0.25 g potassium antimony tartrate and 1 L of distilled water) and this was then analyzed using a flow injection analyzer (FIA-300, Mitsubishi Chemical Analytech Co., Ltd., Kanagawa, Japan). The P recovery ratio in the aqueous phase (R_P [wt%]) was calculated using eq. (2).

$$R_P[\text{wt}\%] = \frac{\text{weight of total P in water soluble fraction [g]}}{\text{weight of P in dry algae [g]}} \times 100 \quad (2)$$

2.5.2 Nitrogen in the Water-Soluble Fraction

The total amount of N in the aqueous phase was determined by an ultraviolet spectrophotometric method. Fifty milliliters of the water-soluble fraction recovered after HTL reaction was mixed with 10 mL potassium peroxodisulfate and sodium hydroxide solution in a Teflon vessel. The solution was heated to 393 K for 1.5 h in an autoclave to convert nitrogen-containing components into NO_3^- . After 5 mL of the supernatant was mixed with 1 mL (1+16) HCl solution, NO_3^- concentration in the solution was analyzed with an absorption spectrophotometer (UVmini-1240, Shimadzu Corporation, Kyoto, Japan) at a wavelength of 220 nm. Total nitrogen recovery ratio (R_N [wt%]) in the aqueous phase was calculated using eq. (3).

$$R_N[\text{wt}\%] = \frac{\text{weight of total N in water soluble fraction [g]}}{\text{weight of N in dry algae [g]}} \times 100 \quad (3)$$

The amounts of NO_2^- and NO_3^- in the water phase were measured using an ion chromatograph (LC-20ADSP, Shimadzu Corporation, Kyoto, Japan) with a detector (CDD-10AVP). A TSKgel IC-Anion-PW column, and a TSKgel eluent IC-Anion A (1.2 mL/min) borate buffer with glucose/methanol/acetonitrile/distilled water solution were used. The amount of NH_4^+ in the aqueous phase was also measured using the same ion chromatograph and detector. An IC-C4 column and oxalic acid solution eluent were used.

2.5.3 Gaseous Products

Gases collected in the gas bag were analyzed using a gas chromatograph (GC, GC-2014, Shimadzu Corporation, Kyoto, Japan) with a thermal conductive detector (TCD). H_2 , O_2 , N_2 , CH_4 and CO were measured with an MS-5A column and He carrier gas. H_2 was measured using the same column, with an Ar carrier gas. CO_2 was measured with a Porapak Q column and He carrier gas.

3. Results and discussion

3.1 Bio-oil recovery and reaction rate

Figure 3a shows the bio-oil recovery ratio (R_B) as a function of activated carbon amount compared with the amount of microalgae in dry basis when residence time was 30 min at 573 K. The residence time was defined as the reaction time after the reactor temperature reached 573 K. No significant effect of activated carbon was observed on bio-oil

recovery at 0.5wt%. More than 0.5wt% of activated carbon decreased bio-oil recovery. This is due to adsorption of bio-oil by the activated carbon. Figure 3b shows R_B as a function of residence time with (i.e. 0.5wt%) or without activated carbon. The error bars represent standard errors at each residence time. At 0 min (i.e. the heater was turned off without maintaining the reaction temperature at 573 K), R_B was $47.9 \pm 15.9\%$ (no activated carbon) and $43.8 \pm 9.6\%$ (with 0.5wt% activated carbon). The R_B peaked at $72.1 \pm 22.7\%$ and $72.9 \pm 19.9\%$ in the absence and presence of activated carbon at 30 min. This implies that bio-oil is formed by HTL reaction up to 30 min and some of the produced bio-oil is subsequently decomposed at longer residence times. No clear effect of activated carbon on bio-oil recovery was observed at any residence time when the amount of activated carbon was 0.5wt%.

Figure 4 shows CO_2 evolution ratios as a function of residence time when activated carbon amount was 0.5wt%. CO_2 evolution was observed mainly at the beginning of the HTL reactions. CO , H_2 , N_2 and CH_4 were not produced. The effect of activated carbon on gas production was insignificant.

3.2 Nitrogen recovery

3.2.1 Total nitrogen, NH_4^+ , NO_3^- , and NO_2^- recovery in the aqueous phase

Figure 5a shows the total nitrogen recovery ratio in the aqueous phase (R_N) as a function of activated carbon amount at 573 K when the residence time was 30 min. The R_N

increased up to 1.0wt%. No increase in R_N was observed with 2.5wt% and 5.0wt% of the activated carbon. Figure 5b shows the total nitrogen recovery ratio in the aqueous phase as a function of residence time at 573 K with (i.e. 0.5wt%) or without activated carbon. The error bars represent standard errors at each residence time. It can clearly be seen that in the absence of activated carbon, R_N increased with time, except at 40 min. R_N was $50.0 \pm 10.3\%$ at 30 min and $57.1 \pm 4.9\%$ at 60 min. By adding 0.5wt% of activated carbon, R_N was increased to $60.8 \pm 14.2\%$ at 30 min and to $65.2 \pm 3.1\%$ at 60 min. It was found that total nitrogen recovery ratio was significantly increased through addition of 0.5wt% of activated carbon in all cases.

Table 2 shows the ratios of NH_4^+ , NO_3^- , and NO_2^- recovered in the aqueous phase measured with the ion chromatograph and the pH of the aqueous phase measured with a digital pH meter. The recovery ratio of NH_4^+ in water substantially increased up to 30 min and was slightly decreased in the presence of activated carbon. No NO_3^- peak was observed at residence times of 0–30 min. A small NO_2^- peak was observed at 30 min; however, the concentration could not be quantified because the peak area was below the detection limit of the ion chromatograph. These results show that no significant amounts of NO_3^- or NO_2^- were present in the aqueous phase. The solution was around pH 7 in all conditions.

3.2.2 Mechanism of enhancement of total nitrogen recovery by activated carbon

It is considered the enhancement of total nitrogen recovery is due to i) chemisorption with the organic functional groups on activated carbon surfaces, ii) physisorption of

N-containing ions within the pores of activated carbon, or iii) catalytic effect of activated carbon on thermal decomposition of microalgae in HTL.

It has been reported that amino acids and organic acids are produced by hydrolysis of proteins under subcritical water conditions, in which the water ion product (K_w) was maximal [43–45]. At higher temperatures (above 523–573 K), thermal decomposition of amino acids occurred, producing 1) amines (i.e. CH_3NH_2 , $\text{C}_2\text{H}_5\text{NH}_2$), carbonic acids and CO_2 by decarboxylation reactions, and 2) ammonia and organic acids by deamination reactions. Sato *et al.* investigated the decomposition of glycine in water at 30 MPa and 533–613 K [46]. They reported more than 87% of nitrogen was converted to CH_3NH_3^+ or NH_4^+ at 573 K and that the ratio of CH_3NH_3^+ to NH_4^+ was 1.95–0.92 after 90–360 s. These authors also investigated the decomposition of five amino acids (aspartic acid, serine, phenylalanine, leucine and alanine) in high-pressure (20 MPa) and high-temperature (473–613 K) water [47]. They reported that about 90% of the nitrogen is in the form of ammonia or ethylamine and proposed a reaction network for amino acid decomposition. Klingler *et al.* investigated the decomposition of the alanine and glycine as model amino acids in a continuous high-pressure plant with a feed solution of 1.0 and 2.0% amino acid at 523–723 °C, 34 and 24 MPa, and residence times of 2.5–35 s [48]. They formulated reaction networks with the main reactions amino acid decarboxylation and deamination and reported the activation energies are for the alanine and glycine decomposition. Based on these studies [43–48], the reaction mechanism of amino

acid decomposition in subcritical water is summarized in Figure 6. It is considered that most of the N-containing species produced after HTL of microalgae are NH_4^+ and R-NH_3^+ , derived from proteins in the microalgae and that the NH_4^+ is not oxidized into NO_2^- or NO_3^- in subcritical water.

As previously mentioned, carboxyl and phenol groups exist on the surfaces of the activated carbon (cf. Table 1). The total amount of these groups is

$$2.54 \times 10^{-4} + 3.08 \times 10^{-4} = 5.62 \times 10^{-4} \text{ mol/g-activated carbon} \quad (4)$$

In the case that 0.5wt% (i.e. 5.0 mg) of activated carbon was used for each HTL experiment of 0.100 L microalgal slurry, the maximum amount of N-containing species chemisorbed by the functional groups is calculated to be $2.8 \times 10^{-6} \text{ mol-N} = 0.039 \text{ mg-N}$. This value is only 0.21wt% of nitrogen in the raw microalgae. Thus, the effect of chemisorption is insignificant.

Next, we carried out blank test of adsorption of HTL products in the aqueous phase at room temperature. After HTL reaction, the products were cooled down to room temperature and the aqueous phase was separated from other products by filtering. We added activated carbon, of which amount was 1.0, 2.5 and 5.0wt% of the raw microalgae, into the separated aqueous solution. Then, the aqueous solution was mixed with a stirrer at 300 rpm and kept for 1 h (i.e. longest residence time in the HTL reaction) at the room temperature. The results show about 7.2–7.6%, 13.6–14.2%, 15.0–15.7% of nitrogen was adsorbed on the 1.0wt%, 2.5wt% and 5.0wt% of the activated carbon, respectively, at room temperature. Thus, the

effect of adsorption, including chemisorption and physisorption in pores, of the activated carbon is small when the amount is 1.0wt%. However, the adsorption effect becomes larger when 2.5wt% or 5.0wt% of activated carbon is used.

Based on the above results (cf. Figure 5, Table 2 and the blank test), it can be concluded the enhancement of total-N recovery by small amount of activated carbon (< 1.0wt%) is due to catalytic effect of the activated carbon in subcritical water and that the decarboxylation reaction to produce amine groups is facilitated by activated carbon. Larger amount ($\geq 2.5\text{wt}\%$) of activated carbon may cancel this catalytic effect by adsorption effect. In our next study, the detailed mechanism of enhancement of amine groups recovery by catalytic effect of activated carbon will be investigated.

3.2.3 Kinetic analysis of total nitrogen recovery

The kinetic analysis was conducted on total nitrogen recovery (i.e. algae or char). The apparent overall reaction rate of total nitrogen recovery can be represented by eq. (5):

$$\frac{dC}{d\tau} = -kC^n, \quad (5)$$

where τ is the residence time, k is the rate constant, and n is the reaction order. By solving eq. (5), we obtain the following eqs. (6) and (7).

$$\left(\frac{C}{C_0}\right) = \{1 + (n-1)kC_0^{n-1}\tau\}^{\frac{1}{1-n}} \quad (n \neq 1) \quad (6)$$

$$\ln\left(\frac{C}{C_0}\right) = -k\tau \quad (n=1) \quad (7)$$

In this calculation, we defined the concentration of N remaining in the solid phase C and its

initial value (C_0) by eqs. (8) and (9):

$$C = (1 - X_{N,\tau}), \quad (8)$$

$$C_0 = (1 - X_{N,0}), \quad (9)$$

where $X_{N,\tau}$ and $X_{N,0}$ [g-bio-oil/g-bio-oil-in-dry-biomass] are the ratio of nitrogen remaining in the microalgae or char during the HTL reaction at residence times τ and 0, respectively.

The results are shown in Figure 7. When no activated carbon was added, the reaction order (n) calculated using the least-squares method was 3.16. Thus, the apparent reaction order of nitrogen extraction was considered to be 3. Note that the deviation between the experimental and calculated values was smaller than those of an apparent reaction order of 2 or 1. By using this apparent reaction order of 3, the apparent rate constant (k) was calculated using the least-squares method. The calculated rate constants at 573 K were 5.6×10^{-8} and $1.1 \times 10^{-7} \text{ s}^{-1}$ in the absence and presence of activated carbon, respectively.

3.3 Phosphorus recovery

Figure 8 shows the total phosphorus recovery ratio in the aqueous phase (R_P) as a function of residence time. Most of phosphorus in the aqueous phase was considered to be free phosphate (PO_4^{3-}) [5, 19, 23]. At 0 min, R_P was about 10%, without activated carbon. The R_P increased with the residence time and peaked at 30 min. As mentioned, the bio-oil recovery (R_B , cf. Figure 3b), total nitrogen recovery in the aqueous phase (R_N , cf. Figure 5b) and R_P peaked at 30 min, implying that 30 min is an optimal residence time to effectively recover

bio-oil and nutrients from the aqueous phase.

No significant effect of 0.5wt% activated carbon on R_P was observed. Thus, it is considered that addition of small amount of activated carbon does not have a significant effect on PO_4^{3-} recovery in HTL, indicating PO_4^{3-} does not interact with functional groups on the surfaces or adsorbed in pores of the activated carbon during HTL reactions. Note that the phosphorus content in the bio-oil fraction was under 1wt%. Thus, more than half of phosphorus remains in the char during HTL. Further study is necessary to clarify the reaction mechanism for phosphorous from microalgae to the aqueous phase and to develop a feasible phosphorus recovery technology in HTL.

4. Conclusions

Hydrothermal liquefaction of microalga *Fistulifera solaris* was conducted in subcritical water at 573 K and 10 MPa in an autoclave reactor. The effect of activated carbon on the recovery of bio-oil, nitrogen and phosphorus from the aqueous phase was investigated. The following conclusions were drawn:

- 1) 0.5wt% activated carbon significantly enhances total nitrogen recovery in the aqueous phase in HTL. This is probably due to catalytic effect of activated carbon to promote decarboxylation reaction, producing larger amount of amines.
- 2) Larger amount of activated carbon (>1.0wt%) does not have positive effect on total

nitrogen recovery. This indicates adsorption effect cancels catalytic effect on nitrogen recovery in the aqueous phase.

3) 0.5wt% of activated carbon does not have a significant influence on bio-oil recovery in HTL. Larger amount of activated carbon reduces bio-oil recovery due to adsorption.

4) 0.5wt% activated carbon does not have a significant influence phosphorus (PO_4^{3-}) recovery from the aqueous phase during HTL reactions.

5) The apparent overall reaction order (n) for nitrogen recovery from the water phase during HTL reaction is 3. The apparent rate constants (k) of nitrogen recovery, calculated by the least-squares method, are 5.6×10^{-8} and $1.1 \times 10^{-7} \text{ s}^{-1}$ in the absence and presence of activated carbon, respectively.

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Appendix

Supplementary data are given in Table S1.

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Table 1 Characteristics of activated carbon

BET Surface area	Carboxyl groups	Phenyl groups	Lactone groups
m ² /g	mol/g	mol/g	mol/g
1019	2.54×10^{-4}	3.08×10^{-4}	n.d.
n.d.: not detected			

Table 2. Amounts of NH_4^+ , NO_3^- and NO_2^- and the pH of the aqueous solutions

Retention time [min]	10		20		30	
	No A.C.	With A.C.	No A.C.	With A.C.	No A.C.	With A.C.
NH_4^+ recovery ratio [w%]	82.0	64.9	73.3	66.5	87.0	84.8
NO_3^- recovery ratio [w%]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NO_2^- recovery ratio [w%]	n.d.	n.d.	n.d.	n.d.	n.d.	u.d.
pH [–]	7.10	7.32	7.06	7.06	7.18	7.02

A.C.: activated carbon

n.d.: no peak detected

u.d.: under the detection limit

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Figure 4 CO₂ evolution ratio

Figure 5 Total nitrogen recovery ratios (R_N) in water as a function of a) activated carbon (a.c.) amount (residence time=30 min), and b) residence time (a.c. amount=0.5wt%)

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Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4

Figure 5a

Figure 5b

Figure 6

Figure 7

Figure 8