



Original Article

# Hydrothermal Carbonization of Soybean Milk Residue (Okara) for Nutrient and Energy Recovery

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**Abstract:** Turning agricultural waste and by-products into benefits has always been an environmental and economical goal, especially in soymilk and tofu industries. This study explores the nutrients and energy recovery from soybean milk residue (okara) utilizing hydrothermal carbonization (HTC). The research focused on: i) The optimization of the HTC process; ii) The humic acid and nutrient recovery from HTC liquor; and iii) The effects of HTC conditions on the fuel properties of hydrochars. We found that, at optimal conditions, 90.5% phosphorus and 70.8% nitrogen in the pristine okara were extracted into HTC solution. These led to the recovery of 82% humic acid and 99.9% phosphorus from HTC solution, respectively. Additionally, nitrogen in HTC liquor was recovered as  $(\text{NH}_4)_2\text{SO}_4$  solution of 1026.7 mg N/L. The attained hydrochar exhibited a higher heating value (HHV) (23.04 MJ/kg), equivalent to or greater than hydrochars derived from the raw okara (15.03 MJ/kg) and other agro-wastes (16.20 - 22.30 MJ/kg). This study proves that acid-supported HTC is a promising method for the simultaneous recovery of nutrients and energy from okara, opening the way for its successful valorization.

**Keywords:** Hydrothermal carbonization, Okara, Nutrient recovery, Fuel property, Acid supported extraction.

## 1. Introduction

Vietnam is an agricultural country, where a huge amount of agricultural by-products is

generated annually. Thus, recycling of agro-waste as a source of nutrients helps not only reduce solid waste but also opens the way for nutrient recovery.

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Hydrothermal carbonization (HTC) is a thermochemical process for the conversion of wet biowastes into carbonaceous products for multiple purposes [1]. HTC has several merits, namely: i) Using mild temperature (180-260 °C) and autogenous pressure (2-6 MPa) for a short duration (5 min - 12 h) [2]; ii) Applicability to numerous categories of wet biomass (e.g., agricultural residues, animal manures, food waste, algal residues, sludges, etc.); iii) No requiring intensive energy pre-drying of feedstocks [3]; and iv) generating hydrochars with higher energy density than pristine biomass. The products from HTC process include a coal-like substance called hydrochar, aqueous, and gas phases. While hydrochars can be used to generate energy or nourish the soil as soil amendments, HTC process water is rich in nutrients. The distribution of nutrients between the solid and aqueous phases depends on the HTC conditions and feedstock categories [4].

Concerning factors governing the nutrient extractions, Ekpo et al., (2016) [5] reported that acidic conditions favored phosphorus extraction, particularly when an inorganic acid ( $H_2SO_4$ ) was utilized, thus enabling nutrient recovery. With the escalating HTC temperature, the contents of organic compounds and phosphorus in HTC process water were decreased, whereas that of ammonium was elevated. These are ascribed to re-polymerization of acids, re-adsorption of phosphorus on hydrochar, and better degradation of organic nitrogen, respectively [6, 7].

Regarding the recovery of resources, there have been many studies on nutrient recovery. However, little information can be found on valorization of other chemicals in HTC aqueous solutions [8]. By using the ferric coagulant at pH of 4.5 and the iron to humic molar ratio of 0.6, 70% of humic substances in the thermally treated sludge effluent were harvested, resulting in the solid containing 24.2% humic substances and 6.2%  $P_2O_5$  [9].

In relation to energy recovery, Ding et al. (2022) [10] discovered that recirculation of HTC process water 3 times led to an improvement in hydrochar yield, HHV, and energetic recovery

efficiency by 8.11%, 2.26 MJ/kg, and 17.55%, respectively.

Okara is a by-product of the soymilk and tofu industries. The production of 1,000 L of soy beverage yields 250 kg of okara. Consequently, a vast quantity of okara is produced annually worldwide, especially in Asian countries, such as nearly 2,800,000 tons in China, 800,000 tons in Japan, and 310,000 tons in Korea [11]. This paves the way for recovering resources from okara at an industrial scale. Though okara can also be used as animal feed, the need for special conservation conditions to ensure its good quality as animal feed may restrict this application. Contrarily, HTC can use okara as a feedstock in its original form. This process also favors the simultaneous recovery of nutrients, humic substances, and energy from okara.

So far, numerous studies have been conducted on recovering nutrients or energy from various industrial-agro wastes. Nevertheless, to the best of the author's knowledge, this is the first time, the nutrients, humic substances, and energy were recovered simultaneously from soybean milk residues (okara) using HTC technology.

This study aims at: i) Studying the effect of acid addition, HTC solvent concentration, HTC temperature, and HTC time on nutrient extraction; ii) Investigating the potential of recovery of humic acid and nutrients (including phosphorus and nitrogen) from HTC liquid fraction; and iii) Evaluating the influence of HTC conditions and recirculation of HTC liquor on HHV value of the resultant hydrochar.

The recovery of resources (humic acid and nutrients) and energy from okara is expected to mitigate okara disposal requirements as a solid waste, produce beneficial products (e.g., solid fuels, soil amendments, etc.), and generate added value for enterprises.

## 2. Materials and Methods

### 2.1. Okara Pretreatment

The okara, after being collected from a tofu production facility and washed with tap water to remove residual milk, was dried in an oven at 105 °C for 24 h, then ground and sieved into fine powder (< 425  $\mu$ m) for use. To achieve homogeneity, the okara powder was mixed well prior to extraction experiments.

## 2.2. Experimental Setup

The experimental setup is illustrated in the following Figure 1.

### 2.2.1. Hydrothermal Carbonization

The HTC experiments were performed using stainless steel autoclaves with an inside diameter of 3.5 cm and a height of 9.5 cm and a furnace (CFW1200, Carbolite, England). After homogenization, 5 g of okara was placed in an HTC reactor containing 30 mL solution (the solid/liquid weight/volume ratio of okara to water/acid was 1:6). The reactor was kept at an unchanged temperature for 6 h. To separate the solid product from the liquid product, a vacuum filtration apparatus, and 0.45  $\mu$ m pore-size filter paper were used. The liquid samples were analyzed for the determination of total phosphorus (TP), orthophosphate ( $\text{PO}_4^{3-}$ ), and ammonia ( $\text{NH}_4^+$ ).

Effect of HTC solvent category: 5 g of okara after pretreatment was added into an autoclave containing 30 mL of distilled water or an acid solution (0.1 M  $\text{H}_2\text{SO}_4$ , HCl, citric acid), which was placed in a furnace (CWF12/13, Carbolite, UK) at 180 °C for 6 h. After that, the furnace was turned off and cooled down to room temperature. The solid was separated from the liquid fraction using the 0.45  $\mu$ m pore-size filter paper. The solid fraction was dried in a drying oven (PR305220 M, Thermo Scientific, USA) at 105 °C until the constant weight was reached. The liquid fraction was collected for analyses of TP,  $\text{PO}_4\text{-P}$ , and  $\text{NH}_4\text{-N}$ .

Experiments investigating the effects of the solvent concentration, HTC temperature, and HTC contact time were conducted in the same way as those examining the effect of HTC

solvent but varying some specific conditions as follows:

Effect of HTC solvent concentration: 5 g of pretreated okara was added in an autoclave containing 30 mL  $\text{H}_2\text{SO}_4$  solution of varying concentrations (0.1, 0.3, 0.5 and 1 M). The HTC experiment was carried out at 180 °C for 6 h.

Effect of HTC temperature: 5 g of pretreated okara was added in an autoclave containing 30 mL of 0.3 M  $\text{H}_2\text{SO}_4$ , which was placed in a furnace (CWF12/13, Carbolite, England) at 170, 180 and 200 °C for 6 h.

Effect of HTC contact time: 5 g of pretreated okara was placed in an autoclave containing 30 mL of 0.3 M  $\text{H}_2\text{SO}_4$ , which was placed in a furnace (CWF12/13, Carbolite, England) at 170 °C for different HTC contact time (4, 6 and 8 h) for the optimal P extraction. Another HTC experiment, which was carried out at the same conditions as mentioned above but at 200 °C, was utilized for the optimal N extraction.

### 2.2.2. Humic acid Nutrient Recovery

Humic acid (HA) and phosphorus (P) recovery: The coagulation test was conducted in a 250 mL beaker with a coagulation mixer. A certain amount of ferric chloride ( $\text{FeCl}_3$ ) was added to 200 mL of HTC solution (solution A), and then the pH was adjusted using 1 M hydroxide (NaOH) or 1 M hydrochloric acid (HCl). The solution was first stirred at a speed of 300 rpm for 30 min, then 50 rpm for 10 min to allow the floc formation. The flocculated materials were collected using a centrifuge (PLC-012E, GEMMY, Taiwan) with a speed of 8000 rpm for 10 min. After being dried at 40 °C to the constant weight, the recovered materials were placed in a bag and kept at 4 °C in a refrigerator.

Nitrogen (N) recovery as  $(\text{NH}_4)_2\text{SO}_4$  solution: After the humic acid and phosphorus recovery from HTC aqueous product, 80 mL of the remaining solution (solution B) was utilized for nitrogen (N) recovery using the Kjeldahl distillation method with the Kjeldahl distillation unit (UDK129, Velp, Italy). Accordingly, an excessive amount of sodium hydroxide (NaOH)

solution was added to solution B to release N as  $\text{NH}_3$ , which was reacted with  $\text{H}_2\text{O}$  vapor to form an  $\text{NH}_4\text{OH}$  solution (solution C). The solution C was conveyed into a conical flask containing 10 mL of 0.05 M  $\text{H}_2\text{SO}_4$  solution for 3 min. Then, the collected solution (solution D) was titrated using 0.05 M  $\text{H}_2\text{SO}_4$  until the color of phenolphthalein was changed from red to no color, indicating that all residual  $\text{NH}_4\text{OH}$  was converted into  $(\text{NH}_4)_2\text{SO}_4$  solution.

### 2.2.3. HTC Liquor Recirculation

This experiment was performed to evaluate the influence of recirculation of HTC liquid fraction on HHV value of hydrochar and composition of HTC liquor. 15 g of pretreated okara was added into an autoclave containing 30 mL of 0.3 M  $\text{H}_2\text{SO}_4$ , which was placed in a furnace at 200 °C for 8 h. At the end of HTC experiment, the solid fraction was separated from the liquid fraction by utilizing 0.45  $\mu\text{m}$  pore-size filter paper. The liquid fraction was employed as a part of the HTC solvent for the next HTC cycle. The volume ratio of the HTC liquid fraction to the new 0.3 M  $\text{H}_2\text{SO}_4$  solution was 2:1 (20 mL: 10 mL). The HTC experiments were continuously carried out for 3 consecutive cycles. After separation, the solid fraction (hydrochar) was used to determine the HHV value, whereas the liquid fraction was employed for measurement of COD,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , TP, and  $\text{PO}_4^{3-}$  concentrations.

## 2.3. Analysis of HTC Products

### 2.3.1. Analysis of HTC Aqueous Product

The pH values of HTC solvent and HTC aqueous product were monitored using a pH meter (SevenCompact S220, Mettler Toledo, China). The chemical composition of HTC liquors was analyzed with UV-VIS Spectrophotometer (S2150UV, Unico, India) according to the following methods: TP and  $\text{PO}_4\text{-P}$ : TCVN6202:2008 (ISO6878:2004);  $\text{NH}_4\text{-N}$ : TCVN6179 -1:1996 (ISO7150-1:1984). The wavelength numbers for measurement of COD, TP,  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , and humic acid (HA)

were 600, 710, 710, 640, 415, and 254 nm, respectively.

### 2.3.2. Analysis of HTC Solid Product

The TP and HA contents in the recovered solid were determined according to the TCVN 8940: 2011 and the method adapted from [9].

HHV values of the okara-derived hydrochars were measured using a Calorimeter (Parr 6200 Automatic Isoperibol Oxygen Bomb). The proximate analyses to determine ash, volatile matter, and fixed carbon were carried out according to methods adapted from [12].

## 2.4. Data Statistical Analysis

All experiments were triplicated. Microsoft Office Excel 2010 (Microsoft, USA) was applied to analyze all data with one-way analysis of variance (ANOVA). A significant difference was considered at the level  $p < 0.05$ .

## 3. Results and Discussion

### 3.1. Effect of HTC Solvent and HTC Conditions for Nutrient Extraction into the HTC Liquor

This study aimed at the recovery of resources (nutrients, humic substances, and energy) from okara. To do that, the effects of various HTC process parameters, including acid categories ( $\text{H}_2\text{SO}_4$ , HCl, citric), acid concentrations (0.3, 0.5, and 1.0 M), and HTC temperatures (170, 180, and 200 °C) on the nutrient extraction were investigated. By comparing the nutrient contents extracted into HTC process water at different HTC conditions, the optimal HTC conditions for P extraction and N extraction into HTC process water were determined.

#### 3.1.1. Effect of HTC Solvent and HTC Conditions on Nitrogen Extraction as $\text{NH}_4\text{-N}$

Effect of HTC solvent category: The  $\text{NH}_4\text{-N}$  extraction capacity into HTC liquor using different solvents is displayed in Figure 2(a). Of which,  $\text{H}_2\text{SO}_4$  exhibited the highest  $\text{NH}_4\text{-N}$  extraction capacity ( $2.27 \pm 0.21$  mg/g), followed

by HCl ( $1.13 \pm 0.08$  mg/g), citric acid ( $0.68 \pm 0.08$  mg/g), and distilled water ( $0.51 \pm 0.09$  mg/g). The difference in  $\text{NH}_4\text{-N}$  extraction capacity by  $\text{H}_2\text{SO}_4$  and other solvents was significant ( $p < 0.001$ ). Therefore,  $\text{H}_2\text{SO}_4$  was selected as the HTC solvent in other HTC experiments.

Effect of HTC solvent concentration: Figure 2(b) shows that the  $\text{NH}_4\text{-N}$  extraction capacity in HTC liquor declined in the following order, depending on the  $\text{H}_2\text{SO}_4$  concentration: 0.5 M ( $3.79 \pm 0.12$  mg/g) > 0.3 M ( $3.78 \pm 0.17$  mg/g) > 1 M ( $2.96 \pm 0.04$  mg/g) > 0.1 M ( $2.27 \pm 0.21$  mg/g). The statistical analysis indicated that the difference in  $\text{NH}_4\text{-N}$  extraction capacity between 0.3 M  $\text{H}_2\text{SO}_4$  and 0.1 M and 1 M  $\text{H}_2\text{SO}_4$  solutions was significant ( $p < 0.001$ ). Contrarily, the difference in this capacity between 0.3 M  $\text{H}_2\text{SO}_4$  solution and 0.5 M  $\text{H}_2\text{SO}_4$  solution was insignificant ( $p > 0.05$ ). Hence, the concentration of 0.3 M was considered the optimal concentration of  $\text{H}_2\text{SO}_4$  solution as the HTC solvent. The above results are consistent with those by Ekpo et al., (2016) [5], suggesting that the nitrogen extraction was not significantly influenced by pH.

Effect of HTC temperature: It is clear from Figure 2(c) that the highest  $\text{NH}_4\text{-N}$  concentration ( $4.54 \pm 0.14$  mg/g) in HTC liquor was achieved with the HTC temperature of 200 °C. It was significantly different ( $p < 0.001$ ) from  $\text{NH}_4\text{-N}$  concentrations,  $3.78 \pm 0.17$  and  $3.67 \pm 0.18$  mg/g, which were attained with two other HTC temperatures, 180 and 170 °C, respectively.

Effect of HTC contact time: As shown in Figure 2(d), the longer the HTC contact time was, the greater the  $\text{NH}_4\text{-N}$  extraction capacity in HTC liquor was observed. Specifically, the  $\text{NH}_4\text{-N}$  extraction capacities for the HTC contact time of 4, 6 and 8 h were  $3.25 \pm 0.12$ ,  $4.54 \pm 0.14$ , and  $5.22 \pm 0.2$  mg/g, respectively. The difference in  $\text{NH}_4\text{-N}$  extraction capacity into HTC liquor at different HTC contact times was significant ( $p < 0.001$ ). Thus, among three HTC contact times, 8 h was regarded as the best one.

Based on the obtained results, the best HTC solvent for N extraction into HTC liquor was 0.3

M  $\text{H}_2\text{SO}_4$ , the optimal HTC temperature and contact time were 200 °C, and 8 h, respectively. At these conditions, 81.2% of the total N in okara was extracted into HTC aqueous phase, which was considerably higher than in cow manure (60%) [13]. This can be attributed to the nature of two biomasses.

### 3.1.2. Effect of HTC Solvent and HTC Conditions for Phosphorus Extraction as TP and $\text{PO}_4\text{-P}$

Phosphorus is a finite natural resource, a vital element for all living creatures, and an important mineral fertilizer for agricultural production. Agricultural residues generally contain high levels of nutrients, including phosphorus. As a result, seeking a technology that can facilitate the extraction and recovery of phosphorus is crucial.

Effect of HTC solvent category: As indicated by Figure 3(a), the TP and  $\text{PO}_4\text{-P}$  extraction capacity into HTC liquor by the distilled water as HTC solvent were  $0.67 \pm 0.14$  and  $0.61 \pm 0.1$  mg/g, respectively. They increased substantially as acid solutions replaced the distilled water. The  $\text{PO}_4\text{-P}$  extraction in HTC liquors with different solvents was declined in the following order:  $\text{H}_2\text{SO}_4$  ( $0.87 \pm 0.03$  mg/g) > HCl ( $0.88 \pm 0.13$  mg/g) > citric acid ( $0.76 \pm 0.11$  mg/g) > the distilled water ( $0.61 \pm 0.1$  mg/g). A similar trend occurred with TP concentrations:  $\text{H}_2\text{SO}_4$  ( $0.99 \pm 0.05$  mg/g) > HCl ( $0.79 \pm 0.04$  mg/g) > citric acid ( $0.85 \pm 0.13$  mg/g) > distilled water ( $0.67 \pm 0.14$  mg/g). It can be seen that the maximum TP and  $\text{PO}_4\text{-P}$  extraction capacities were attained when  $\text{H}_2\text{SO}_4$  was utilized as the HTC solvent. The elevated level of P in HTC solution at the acidic condition can be explained as follows: Firstly, a high concentration of  $\text{H}^+$  ions in HTC solution enabled the extraction of P from okara into HTC liquor. According to Dai et al., (2015) [14] and Zhu et al., (2011) [15], HTC of biomass converted all phosphorus species to orthophosphates. Secondly, low pH increased the solubility of Ca- and Fe-P minerals, thus hindering the P complexation and retention of P in the solid hydrochar [13]. The above result is in harmony with that reported by Ekpo et al.,

(2016) [5], indicating that organic acid was less effective than mineral acid in P extraction from swine manure. However, it is different from the finding in a previous study by Qaramaleki et al., (2020) [13] showing that inorganic (HCl) acid was less effective than organic (citric) acid in solubilization of P into HTC liquor.

Effect of HTC solvent concentration: Figure 3(b) shows the TP and PO<sub>4</sub>-P extraction capacities into HTC liquors of H<sub>2</sub>SO<sub>4</sub> solution with various concentrations. The statistical analysis showed that there was a significant difference ( $0.001 \leq p < 0.05$ ), in PO<sub>4</sub>-P extraction capacity between 0.3 M H<sub>2</sub>SO<sub>4</sub> ( $1.04 \pm 0.01$  mg/g) and 0.1 M H<sub>2</sub>SO<sub>4</sub> ( $0.87 \pm 0.03$  mg/g). On the contrary, the difference in PO<sub>4</sub>-P extraction capacity between 0.3 M H<sub>2</sub>SO<sub>4</sub> ( $1.04 \pm 0.01$  mg/g) and 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $1.05 \pm 0.03$  mg/g) as well as 1 M H<sub>2</sub>SO<sub>4</sub> ( $1.08 \pm 0.03$  mg/g) was insignificant ( $p > 0.05$ ). Similarly, TP extraction capacity in HTC liquor increased from  $0.99 \pm 0.05$  to  $1.18 \pm 0.05$  mg/g as the H<sub>2</sub>SO<sub>4</sub> concentration was elevated from 0.1 to 1 M. Nevertheless, the TP extraction capacity attained with 0.3 M H<sub>2</sub>SO<sub>4</sub> ( $1.12 \pm 0.05$  mg/g) was insignificantly different from those achieved with 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $1.15 \pm 0.02$  mg/g) và 1 M ( $1.18 \pm 0.05$  mg/g). For those reasons, 0.3 M H<sub>2</sub>SO<sub>4</sub> was selected as the best solvent concentration for TP and PO<sub>4</sub>-P extraction in HTC liquor. These results agree well with those revealed by Dai et al., (2017) [16], showing that the P extraction was better at greater acid concentrations. Similar results were reported by Qaramaleki et al., (2020) [13]. The level of phosphate in HTC liquor elevated significantly from 339 to 1018 mg/L when the H<sub>2</sub>SO<sub>4</sub> concentration increased from 0.1 to 0.3 M. However, a further increase in H<sub>2</sub>SO<sub>4</sub> concentration from 0.3 to 0.5 M did not show a significant change in the level of phosphate in the HTC liquor.

Effect of HTC temperature: The effects of HTC temperature on TP and PO<sub>4</sub>-P extraction in HTC liquor are shown in Figure 3(c). It is observed that the PO<sub>4</sub>-P extraction in HTC liquor was highest at 170 °C. There was a significant

difference ( $p < 0.001$ ) between the P extraction capacity at 170 °C ( $1.08 \pm 0.02$  mg/g) and that at 200 °C ( $0.94 \pm 0.02$  mg/g). In contrast, the difference in the PO<sub>4</sub>-P extraction into HTC liquor between 170 and 180 °C was insignificant ( $p > 0.05$ ). The trend for TP extraction was the same as that for PO<sub>4</sub>-P extraction: 170 °C ( $1.23 \pm 0.1$  mg/g) > 180 °C ( $1.12 \pm 0.05$  mg/g) > 200 °C ( $0.97 \pm 0.04$  mg/g). Based on the obtained results, 170 °C was considered as the most appropriate for TP and PO<sub>4</sub>-P extraction in HTC liquors. This result matches well with the finding by Qaramaleki et al., (2020) [13], showing that the maximum P concentration (847 mg/L) was detected in HTC solution at 170 °C, and lower HTC temperature induced a positive influence on P extraction into HTC solution.

Effect of HTC contact time: As illustrated in Figure 3(d), the PO<sub>4</sub>-P extraction into HTC liquor at the HTC contact time of 4, 6, and 8 h was found to be  $0.98 \pm 0.05$ ,  $1.08 \pm 0.02$  and  $1.08 \pm 0.001$  mg/g, respectively. The statistical analysis suggested that the difference between 6 h and 4 h was significant ( $p < 0.001$ ), whereas the difference between 6 h and 8 h was insignificant ( $p > 0.05$ ). A similar trend occurred with the TP extraction. For these reasons, 6 h was chosen as the best HTC contact time. The lower P level in HTC aqueous phase at a shorter HTC duration suggested that the P solubilization was relatively slow [12, 17].

Based on the achieved results, the best solvent and most appropriate HTC conditions for P extraction into HTC liquor were 0.3 M H<sub>2</sub>SO<sub>4</sub>, 170 °C, and 6 h. At these conditions, 90,5% of the total P in okara was solubilized in HTC aqueous product. The obtained results match well the finding by Qaramaleki et al., (2020) [13], reporting that the highest P extraction percentage (up to 98%) into HTC liquor was achieved at 170 °C with citric acid addition.

### 3.2. Acid Humic and Nutrient Recovery from HTC Process Water

Effect of Fe to humic acid (HA) mass ratio on HA recovery: The effect of Fe/HA mass ratio on HA recovery is presented in Table 1. It was

shown that the HA recovery efficiency elevated from 47 to 85% as the Fe/HA ratio was increased from 0.7 to 6. Therefore, the Fe/HA ratio of 6 was used for HA and P recovery from the HTC liquors at the optimal conditions for P and N extraction from okara.

Table 1. Influence of Fe/HA mass ratio on the HA recovery percentage (%)

Fe/HA	Initial HC concentration (mg/L)	HA concentration after precipitation (mg/L)	HA recovery (%)
6	14110	2142	85
4.5	14110	3144	78
2.5	14110	4247	70
2	14110	4939	65
1.5	14110	6179	56
0.7	14110	7496	47

HA and P recovery from okara-based HTC liquors: Table 2 shows the P and HA recovery from okara-based HTC liquors at optimal conditions for phosphorus and nitrogen extraction. It was found that at optimal conditions for P extraction, P and HA recovery efficiencies were found to be 99.9 and 81.7%, respectively. At the optimal conditions for N extraction, P and HA recovery efficiencies were reported to be 99.9 and 84.8%, respectively.

Table 2. Phosphorus and humic acid recovery efficiencies at the optimal phosphorus and nitrogen extraction conditions

Properties of the recovered precipitate	P optimal extraction conditions	N optimal extraction conditions
P recovery efficiency (%)	99.9 ± 0.01	99.9 ± 0.01
P amount in the precipitate (mg)	4.99	4.71
P percentage in the precipitate (%)	0.88	0.09
HA recovery efficiency (%)	81.7 ± 0.6	84.8 ± 0.9
HA amount in the precipitate (mg)	289	255

HA percentage in the precipitate (%)	4.62	4.64
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At optimal extraction conditions, the extracted HA and nutrient contents in the HTC process water were relatively high. Though the recovery percentages of HA and P from HTC process water were high, their contents in the recovered solid product were still low. This may be resulted from the utilization of a large amount of FeCl<sub>3</sub> in an attempt to recover a majority of HA in the HTC process water. Since high Fe content in the recovered solid product may have undesirable effects on the crop's growth, it is recommended to seek another method to successfully recover HA in advance, enabling the recovery of P and N later.

### 3.3. Effects of HTC Solvent and Process Water Recirculation on HHV Value of Hydrochar

#### 3.3.1. Effect of HTC Solvent on HHV Value of the Resultant Hydrochar

Table 3 presents the HHV values of acid-supported okara-derived hydrochars produced at the optimal conditions for P and N extraction, which hereinafter referred to as hydrochar P and hydrochar N, together with their proximate analysis results. It was found that the hydrochar N exhibited a slightly higher HHV value (24.15 MJ/kg) than the hydrochar P (23.48 MJ/kg). This can be ascribed to the greater percent of the fixed carbon (35.54%) and lower percent of volatile matter (60.95%) of the hydrochar N as compared to those (24.30 and 73.02%) of hydrochar P. This could yield from the higher HTC temperature (200 °C) and longer HTC contact time (8 h) at the optimal N extraction conditions, as compared with those (170 °C and 6 h) at the optimal P extraction conditions. In addition, the HHV values of acid-supported okara-derived hydrochars were markedly enhanced (35.95 - 37.72%) as compared to that of the pristine okara. The clearly lower HHV value of the pristine okara can be attributed to its considerably lower percent of fixed carbon (11.05%) and substantially higher percent of volatile matter (85.96%) than those of the acid-supported okara-

derived hydrochars [16]. Similarly, Yang et al., (2015) [18] reported an enhancement of 52.4 - 127.6% in HHV of the *Carya cathayensis sarg* (PCCS) derived hydrochar as compared to the

pristine PCSS. Results indicated that HTC with acid addition can be another pathway for improving the HHV of lignocellulosic biomass in addition to the increase in HTC temperature.

Table 3. The proximate analysis of pristine okara and acid-supported okara-derived hydrochars

Hydrochar	HHV (MJ/kg)	Proximate analysis		
		Ash content (%)	Volatile matter (%)	Fixed carbon (%)
Pristine okara	15.44	2.99	85.96	11.05
Acid-supported hydrochar P*	23.48	2.68	73.02	24.30
Acid-supported hydrochar N**	24.15	3.51	60.95	35.54

Note: \* Hydrochar produced at the optimal P extraction conditions;

\*\* Hydrochar produced at the optimal N extraction conditions.

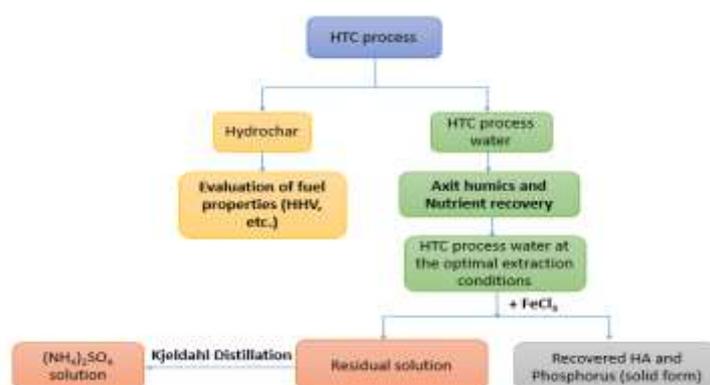
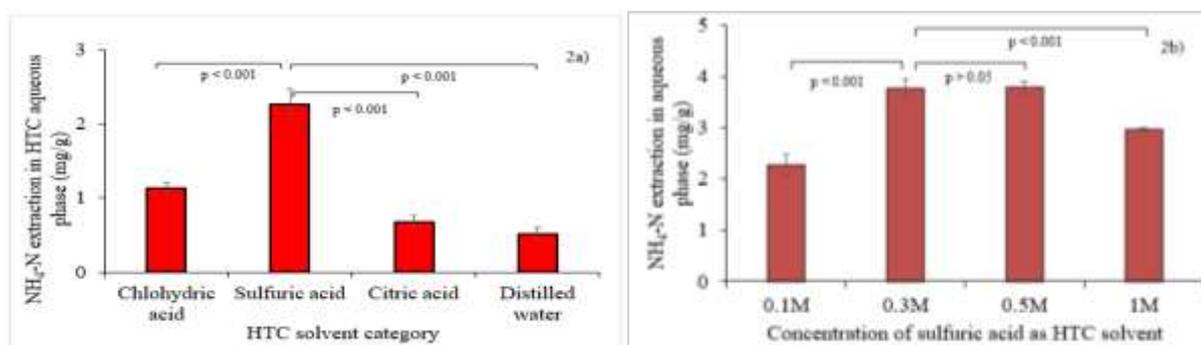


Figure 1. Hydrothermal carbonization and resource recovery experiment setup.



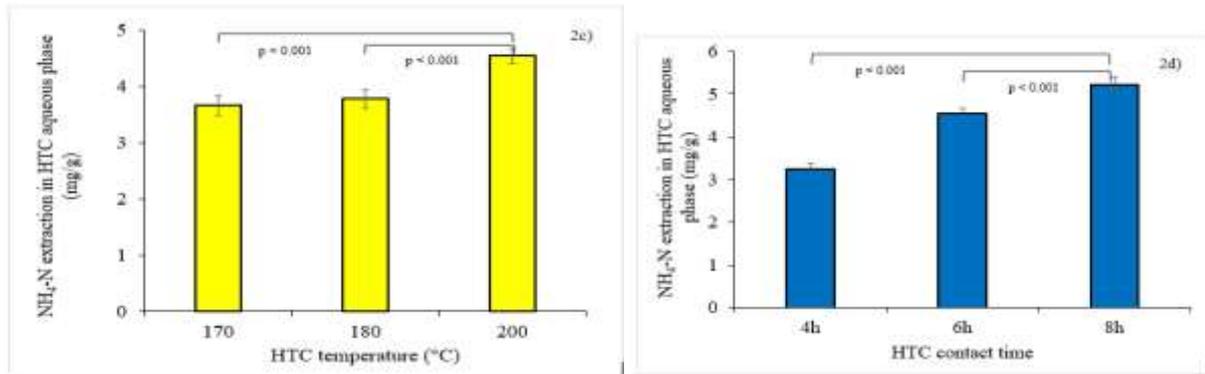


Figure 2. Effect of 2a) solvent category, 2b) solvent concentration, 2c) HTC temperature, and 2d) HTC time on N-NH<sub>4</sub> extraction into HTC aqueous phase.

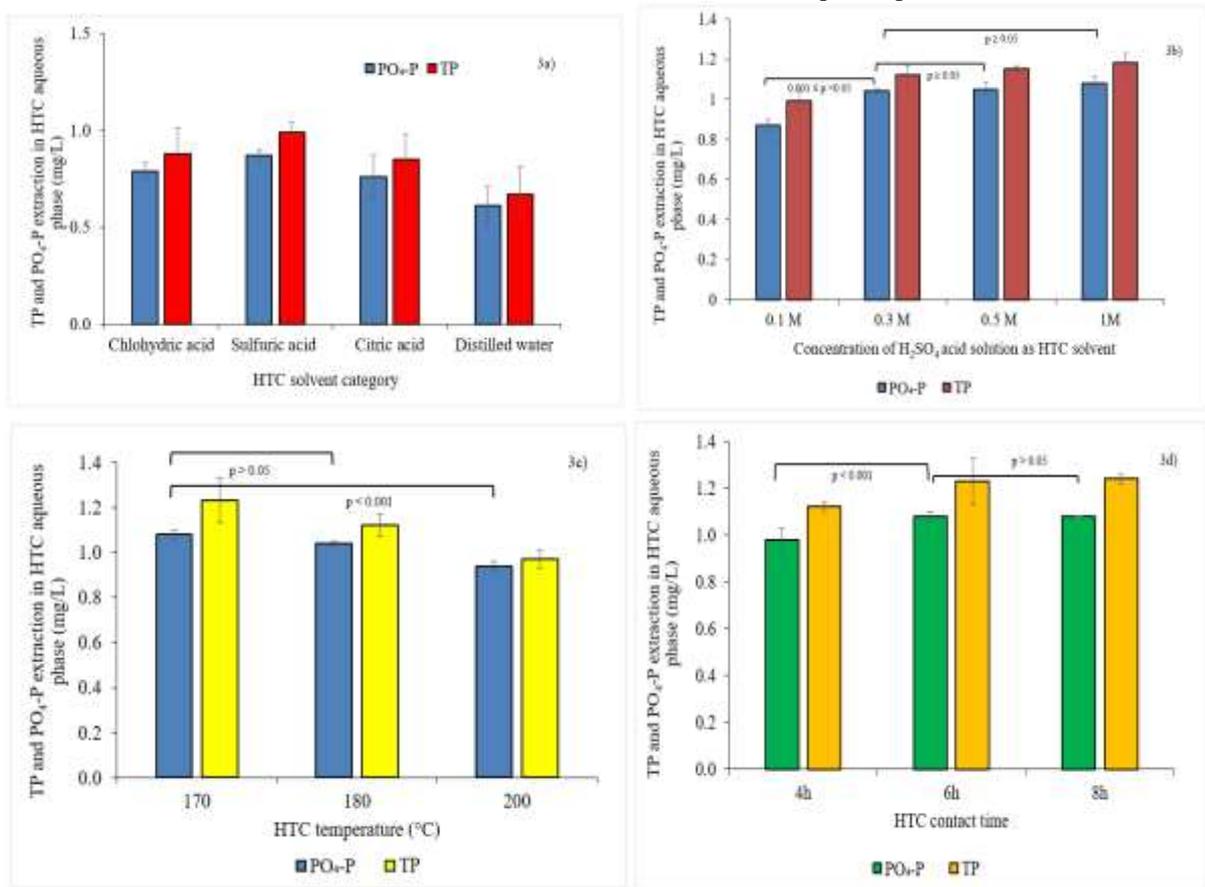


Figure 3. Effect of 3a) solvent category, 3b) solvent concentration, 3c) HTC temperature, and 3d) HTC time on TP (total phosphorous) and PO<sub>4</sub>-P (orthophosphorous) extraction into HTC aqueous phase.

Table 4 shows that the HHV values of acid-supported okara-based hydrochars (23.48 and 24.15 MJ/kg) were still lower than those of conventional solid fuels (24.39 - 45.70 MJ/kg).

However, they were greater as compared to HHV values of many agro-waste-based hydrochars (16.69-22.3 MJ/kg). Results indicate

that the acid-supported okara-derived hydrochar can be a potential solid fuel.

Table 4. Comparing HHV values of agro-waste-based hydrochars and conventional fuel materials

No	Hydrochars	HHV (MJ/kg)	Reference	No	Hydrochars	HHV (MJ/kg)	Reference
A	Agro-waste-based hydrochars			B	Conventional solid fuels		
1	Eucalyptus sawdust	16.69	[19]	7	Methanol	22.70	[18]
2	Barely straw	17.34	[19]	8	Lignite coal	24.39	[22]
3	Coconut fiber	18.4	[20]	9	Pyrolytic oil	24.70	[18]
4	Rice husk	21.97	[10]	10	Raw coal	25.37	[23]
5	Maize silage	22.3	[21]	11	Heavy fuel oil	42.90	[18]
6	Okara	23.48	This study	12	Diesel oil	45.70	[18]

Table 5. Variations in the HHV value of the acid-supported okara-derived hydrochar and composition of HTC liquor as a result of HTC liquor recirculation

Cycle	Okara derived hydrochar				pH of HTC solvent	HTC liquor composition				
	Ash (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)	HHV (MJ/kg)		COD (mg/L)	NO <sub>3</sub> -N (mg/L)	NH <sub>4</sub> -N (mg/L)	PO <sub>4</sub> -P (mg/L)	TP (mg/L)
HC-R0	3.03	71.36	25.61	27.63	0.16	121666	64.03	913.31	335.78	347.24
HC-R1	7.81	68.41	23.78	25.30	0.46	198333	114.14	1031.06	473.30	477.88
HC-R2	8.27	69.69	22.04	23.75	0.50	233333	208.80	1388.73	528.31	552.37

### 3.3.2. Effect of Recirculation of HTC Liquor on HHV of the Resultant Hydrochar and Composition of HTC Liquor

In an attempt to enhance the HHV value of the resulting hydrochar and concentrations of substances in HTC liquor for resource recovery, the HTC liquor was recirculated as a portion of the HTC solvent for the next HTC cycle. The HHV values of the acid-supported okara-derived hydrochars and the composition of HTC liquors after 3 cycles are presented in Table 5.

It was observed that the HHV value of the resultant hydrochar was slightly declined from 27.63 to 23.75 MJ/kg as the number of cycles increased from 1 to 3. This can be attributed to the increase in the final pH value from 0.16 to 0.50, which reduced the percent of fixed carbon from 25.61 to 22.04% and the increase in the percent of ash from 3.03 to 8.27%. In HTC

experiments, H<sub>2</sub>SO<sub>4</sub> solvent played an important role in dissolving some organic matter, enhancing the percent of the fixed carbon. Therefore, the increase in pH of the HTC solvent may result in a decline in the percent of the fixed carbon. Consequently, the HHV value of the resulting hydrochar was reduced. Similarly, Dai et al., (2017) [16] reported that the HHV value of cattle manure-derived hydrochar was elevated from 15.45 to 17.04 MJ/kg when HCl concentration was increased from 0 to 2%, respectively. Contrarily, Ding et al., (2022) [10] revealed that as a result of HTC process water recirculation, HHV of hydrochar was enhanced from 19.71 to 21.97 MJ/kg in the first 3 cycles. The possible reason was that the study utilized water rather than the acid solution as HTC solvent. Since the HTC process water contained higher organic carbon than pure water, the HHV values of the hydrochars in the next cycles were

improved. In contrast, when acid solution was employed as HTC solvent, the HHV values of hydrochars in the next cycles depended on the final pH value. In this work, since the final pH value was increased due to the acid consumption in the previous cycle, the HHV value of hydrochar in the next cycle declined. The obtained result showed that while recirculation of HTC liquor helped to save the acid consumption, the HHV value of the resultant hydrochar may be reduced. To avoid this, the pH of the HTC solvent should be maintained by acid addition to compensate for the utilized acid.

The concentrations of COD and all nutrients were increased thanks to the recirculation of HTC process water. This may pave the way for the successful recovery of resources from HTC liquid fraction.

#### 4. Conclusion

Hydrothermal carbonization of okara using 0.3 M H<sub>2</sub>SO<sub>4</sub> was conducted for resource recovery from HTC process water and hydrochar's HHV upgradation simultaneously. Results showed that the optimal conditions for P and N extraction from okara were 0.3 M H<sub>2</sub>SO<sub>4</sub>, 170 °C, 6 h and 0.3 M H<sub>2</sub>SO<sub>4</sub>, 200 °C, 8 h, respectively. The extracted amounts of P and N accounted for 90.5 and 70.8% of their total contents in the pristine okara. HA and P contents in the HTC process solution were recovered as the solid product, whereas N was recovered as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> liquid. At the optimal P extraction conditions, the recovery percentages of HA and P were 81.7 and 99.9%, respectively. At the optimal N extraction conditions, the recovery percentages of HA and P were 84.8% and 99.9%, respectively. Nitrogen concentrations in the recovered (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solutions were 554.9 and 1026.7 mg N/L at optimal P and N extraction conditions, correspondingly. The HHV value of the acid-supported okara-derived hydrochar (27.63 MJ/kg) is comparable to those of some conventional fuel materials (22.70 - 25.37 MJ/kg). The acid-assisted HTC of okara is an efficient pathway for the simultaneous recovery

of organic matter, nutrients, and energy from okara. However, the environmental risks of chemical uses and the economic feasibility of the whole HTC process at a larger scale should be addressed in the future.

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