



Phase behavior and stabilization of phosphorus in sub- and supercritical water gasification of cyanobacteria



Huiwen Zhang^{a,b,*}, Xiaoman Zhang^a

^a School of Civil Engineering and Architecture, Anhui University of Technology, Maanshan, Anhui 243002, China

^b Engineering Research Center of Biomembrane Water Purification and Utilization Technology, Ministry of Education, Maanshan, Anhui 243002, China

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ABSTRACT

Normalization of cyanobacteria outbreak in shallow lakes yield lots of salvaging cyanobacteria biomass, which dramatically modify phosphorus (P) cycle in water column and the sediments. Based on studies of SCWG reactions, it was expected to solve the dewatering treatment difficulty in engineering issues and realize potential energy use. By way of cyanobacteria biomass SCWG reactions, this paper clarified major existence forms and distribution law of rich phosphorus, evaluated the corresponding roles that reactions parameters and properties of biomass raw materials played in the products' distribution and morphological process. In addition to this, it discussed effects of alkali additions on phosphorus forms and distribution, with a view to providing potential approach for phosphorus stabilization in SCWG products.

1. Introduction

Phosphorus is a crucial nutrient element for all beings [1]. It comes to itself as a significant participant for constituting biological tissue structures, thus phosphorus fertilization in agriculture is an indispensable way of replenishing phosphorus [2]. As phosphate resources have gradually become scarce and there existed series of environmental pollution problems in the production of phosphorous fertilizers, it is a necessary agricultural developing need and trend to look for a sort of recyclable, environmentally-friendly phosphorus resource which can replace traditional ones.

Macroalgal blooms have occurred worldwide frequently in coastal areas in recent decades, which dramatically modify phosphorus (P) cycle in water column and the sediments [3]. Normalized cyanobacteria outbreak in some Chinese shallow lakes, resulted in lots of salvaging cyanobacteria biomass. Due to the characteristics like high moisture content and high dehydration difficulty, pretreatment processes including dehydration, drying were energy-intensive and inefficient, severely restricting bio-safety disposal and resource utilization of cyanobacteria biomass [4]. Studies have proven that cyanobacteria biomass can be employed to produce hydrogen through supercritical water gasification (SCWG) technology and realize energy utilization [5]. Furthermore, cyanobacteria cell itself is rich in large amounts of phosphorus from eutrophic waters [6]. If phosphorus in SCWG products can be recycled further, this can not only help obtain phosphorus from the lake waters needing treatment but also put it into agriculture for

fertilization. In addition to this, it can help get rid of the influence that phosphorus pollution exerted on subsequent safety disposal.

To date, scholars in the SCWG technical research field mainly focused on issues like biomass energy recycling, catalyzing to produce hydrogen and types of biomass including microalgae [7,8], sludge [9,10], sawdust [11] etc. Referring to inorganic salt in SCWG reactions, the majority of research has paid attention to sedimentary congestion issues in treatment [12,13], while barely showing interest in the recycling of phosphate materials rich in reaction products. It has already shown that phosphorus in dewatered sludge can be transformed thoroughly from organic forms to inorganic phosphorus forms and gather around solid products after undertaking SCWG reactions [14]. Only a few would exist in liquid products in the form of dissolved reactive phosphorus (DRP) [15]. In this sense, it can be deemed that solid products composing of phosphorus have created advantageous conditions for phosphorus recycling. In the past, research of phosphorus recycling in solid products focused on biomass perspective, with no clear and systematic awareness of phosphorus distribution, morphology as well as transformation process. For the sake of subsequent phosphorus recycling, it is initially to be aware of binding forms and distribution status of phosphorus in SCWG products, then to have the understanding of in-between transformation process and reaction parameters' influence in the SCWG reactions, and finally to control phosphorus and transform it to the form either in advantage of subsequent recycling or stable product form transformation.

Focusing on the above-mentioned several scientific questions, this

* Corresponding author at: School of Civil Engineering and Architecture, Anhui University of Technology, Maanshan, Anhui 243002, China.
E-mail address: zhw.ahut@qq.com (H. Zhang).

Table 1
Properties of raw Cyanobacteria.

Water content (wt%) ^a	Proximate analysis (wt%) ^b			Carbohydrates (wt%) ^b	Lipids (wt%) ^b	Proteins (wt%) ^b	TOC (mg/L) ^a		
	VM	FC	Ash						
96.15	81.59	3.00	15.41	22.05	4.00	40.54	13320		
TN (mg/L) ^a	NH ₃ -N (mg/L) ^a	TP (mg/L) ^a	DRP (mg/L) ^a	C (wt%) ^b	N (wt%) ^b	S (wt%) ^b	H (wt%) ^b	O (wt%) ^b	HHV (MJ/kg) ^c
3268	619.95	180.63	0.0887	42.635	5.6815	0.9235	6.8775	26.3125	19.687

^a Wet basis measurement.

^b Dry basis measurement.

^c High heating value (HHV) was calculated through Dulong's formula: $HHV \text{ (MJ/kg)} = 0.3383C + 1.443(H-O/8) + 0.0927S$.

paper selected salvaging cyanobacteria biomass from Taihu Lake and conducted phosphorus form distribution experiments in SCWG products under different reaction conditions and parameters, making an attempt to adopt alkali addition Ca(OH)_2 to realize phosphorus forms transformation process during SCWG of cyanobacteria.

2. Material devices and method

2.1. Experimental materials

The cyanobacteria included *Microcystin aeruginos*, *Microcystin ichthyoblabe*, *Microcystin viridis*, *Microcystin novacekii* and *Microcystin wesenbergii* [16] and mainly consisted of proteins, nucleic acids and polysaccharides, as well as a small amount of fat. The cyanobacteria biomass used in this study was collected from a water–algae separation station at Lake Taihu, China. Floating cyanobacteria were removed in May 2015. The collected cyanobacteria biomass was stored in a refrigerator at $-20\text{ }^\circ\text{C}$ from Yangwan water–algae separate plant. Samples were thawed at room temperature for the SCWG reaction. The characteristics of the cyanobacteria biomass are shown in Table 1. The feedstock was used without any pretreatment.

2.2. Experimental procedures

The adopted reaction kettle was made of 316L stainless steel and designed to possess $600\text{ }^\circ\text{C}$ temperature, 30 MPa pressure, with effective volume 100 ml. Salt-bath furnace was employed as its heating device. The corresponding bath salt took $334\text{ }^\circ\text{C}$ as its melting point, $400\text{ }^\circ\text{C}$ as the boiling point and used $370\text{--}550\text{ }^\circ\text{C}$ KNO_3 , according to *Heat Treatment Manual*. Temperature conditions in the reaction kettle were controlled by the thermocouple placed in the salt bath furnace and different reaction pressure can be achieved by way of adjusting moisture content through water-temperature-pressure curve. Experimental conditions were obtained as follows: reaction temperature $350\text{--}450\text{ }^\circ\text{C}$, reaction time 0–60 min, pressure 23 MPa. During the reaction process, it was supposed to heat up salt bath furnace to the preset temperature and placed the reaction kettle into it which was equipped with samples. After heating rapidly and reaching preset temperature stably, it was ready to keep time. Took out the reaction kettle from salt-bath furnace after a period of retention time, Natural cooling ($5\text{ }^\circ\text{C}/\text{min}$), forced air cooling ($20\text{ }^\circ\text{C}/\text{min}$) and circulating water cooling ($50\text{ }^\circ\text{C}/\text{min}$) were applied respectively to reduce the reaction kettle room temperature. Gas products received gas yield on the basis of saturated NaHCO_3 solution method. At this moment, the reaction kettle was opened and solid-liquid residues were gathered: liquid products were separated in $0\text{--}4\text{ }^\circ\text{C}$ centrifuge tube for measurement which was experiencing 5-min-separation by high-speed refrigerated centrifuge under 10000rpm; solid products were dried and collected under $80\text{ }^\circ\text{C}$. It was later to wash the oil sticking to the kettle wall by CCl_4 solution and acquire oil content when centrifugalized and distilled.

2.3. Analytical methods

Gas composition was determined using a gas chromatograph (Nanjing Kejie GC5890A) equipped with a thermal conductivity detector (TCD). Nitrogen served as the carrier gas, and the flow rate and the pressure were 30 ml/min and 0.5 MPa, respectively; the column temperature was maintained at 353 K; the temperature of both the injector and detector temperature were 393 K. According to water and wastewater monitoring and analytical standard, GB/T11894-1989, HJ535-2009, GB/T11893-1989 were used to determine the total nitrogen (TN), ammonia nitrogen ($\text{NH}_4\text{-N}$), total phosphorus (TP) and DRP in the liquid phase respectively, using a Shimadzu UV-2450 system. A Shimadzu TOC-VCPH analyzer and an SSM-5000 analyzer were applied to detect the total carbon (TC) and total organic carbon (TOC) of the liquid and solid phase. GB/T 2001-1991 was used to determine the volatile matter (VM), fixed carbon (FC) and ash, the proteins and lipids were determined on previous research [17].

It was acceptable to adopt ammonium molybdate spectrophotometric method to measure TP and DRP in liquid products. Research on phosphorus morphology distribution stemmed from different phosphorus forms in agronomy and effective discussions, hence gradually established clear awareness of its circulation in natural environment. Phosphorus in solid products existed in either organic form or inorganic form, the latter of which can be further divided into exchangeable phosphorus (Ex-P), aluminum-combined phosphorus (Al-P), iron-combined phosphorus (Fe-P), occluded phosphate (Oc-P), self-ecological phosphorite (Ca-P), debris phosphorus (De-P). In terms of measuring method, the most mature and desirable one to date was continuous chemical extraction. Inorganic phosphorus (Ino-P) form grading method possessing foundation meaning was established initially in 1957; separation methods of protogenic debris phosphorus and autogenic calcium-combined phosphorus were distinguished and undergone detailed standard tests in 1992 [18]; based upon this, Y. Li and G. Zhu et al. further improved extracting liquid and corresponding steps for upgrading extraction effect and experimental accuracy [19]. This paper mainly adopted the upgraded phosphorus form extraction method, the steps of which were improved slightly. The core part of this improved method was divided into Ca-P and De-P through 1 M NaAc-HAc ($\text{pH} = 4.0$) extraction and 1 M HCl extraction, and the divided P forms would be provide evidence for assessment of plant bioavailability.

3. Results and discussion

3.1. Effects of reaction conditions on phosphorus distribution

In order to realize subsequent recycling of phosphorus in cyanobacteria biomass, it was necessary to firstly clarify its distribution law in SCWG products. Fig. 1 demonstrated reaction parameters' influence on dry weight distribution and phosphorus distribution in solid, gas and liquid products correspondingly. Due to high moisture content of

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