分类号：X705　　　　　　　　　　单位代码：10335
密　级：公 开　　　　　　　　　　学　　号：11813057

浙江大学

博 士 学 位 论 文

中文论文题目：大豆加工剩余物预处理及厌氧消化提高氢气和甲烷产量的研究

英文论文题目：Study on Enhancing Biohythane Production from Tofu (Soybean) Processing Residue via Pretreatment and Anaerobic Digestion

申请人姓名：**MAHMOUD MOHAMED AHMED HUSSEIN ALI**

指导教师：盛奎川　教授

学科(专业)：农业生物环境与能源工程

研究方向：生物质能工程

所在学院：生物系统工程与食品科学学院

论文提交日期　2022 年 6 月

中国 • 杭州

ABSTRACT

Biofuel generation from biomass has received more attention as an alternative, renewable, sustainable, and clean energy source that replaces fossil fuel, alleviating energy demand and environmental concerns. Among biomass, tofu processing residue (TPR), which is a by-product of the tofu and soymilk production industry, is rich in carbohydrates (50-60%), proteins (20-30%), and fats (10-20%), as well as contain high moisture content (≥85%), posing it as a suitable substrate for biofuels production through anaerobic digestion (AD) technology. TPR deteriorates rapidly and is thus mainly disposed of in landfills, causing environmental concerns. Therefore, how to efficiently treat TPR is a big concern for soybean processing plants. AD is the most sustainable and cost-effective method to treat organic wastes along with energy recovery as well as it reduces the emission of greenhouse gases, generated during the self-decomposition of biowastes. In this research, energy recovery from TPR was improved by the production of biohythane from one-stage and two-stage AD through controlling the operational conditions, pretreating TPR using ultrasonic pretreatment, dilute sulfuric acid (H_2SO_4) pretreatment, and the simultaneous combination of ultrasonic and dilute H_2SO_4 pretreatments, as well as adding molybdate (MoO_4^{2-}) and ferric chloride ($FeCl_3$). The main results are as follows:

1) Two-stage AD of TPR was investigated considering the impacts of operational conditions on microbial community diversity and biohythane production. The results showed that the optimal conditions were dark fermentation (DF) operated at the substrate to inoculum ratio (SIR) of 8 and 37 ℃ for 36 h, followed by methanogenic fermentation (MF) performed at the SIR of 1 and 37 ℃ for 13 d, which produced 324.4 ml/g-VS_{fed} of biohythane along with 103 mmol/L acetic acid and 38 mmol/L propionic acid. Two-stage AD improved specific energy recovery by 41.5% compared to one-stage AD, producing a biogas yield of 189.6 ml/g-VS_{fed}. SIR and temperature affected microbial community diversity of DF system, where high SIR of 8 speciated hydrogen producers such as *Mobilitalea* and *Clostridium sensu stricto 1* at thermophilic and mesophilic temperatures, respectively, whereas low SIR of 0.5 stimulated methane generation by the speciation of *Methanoculleus thermophilus*. Likewise, hydrogenotrophic methanogens (*Methanomassiliicoccus*) enriched MF reactors operated at low SIR. Overall, this study demonstrated two-stage AD as an efficient technology for producing clean energy and value-added products using TPR.

2) TPR has received more attention as a source of bioenergy. However, their low solubility has hindered biohythane generation. Consequently, the ultrasonic and H_2SO_4 pretreatments were combined and compared for the first time to improve the hydrolysis of organic matter and carbohydrates as well as to increase free amino nitrogen generation from TPR. Besides, the impact of pretreatments on biohythane generation via one-stage AD was also investigated. Under the optimal conditions of 7.54% substrate level, 8% H_2SO_4 concentration, 80 ℃, and 50 min, the coincident ultrasonic-H_2SO_4 pretreatment enriched the contents of soluble chemical oxygen demand, reducing sugar, and free amino nitrogen to 49675 mg/L, 26 g/L, and 1721 mg/L, respectively, greater than individual pretreatments. Also, Biohythane yield increased by 4.20-12.58% over control (389.39±23.8 ml/g-VS_{fed}). Furthermore, the highest hydrogen yields of 42.5±2.08 and 28.1±1.07 ml/g-VS_{fed} and the sulfate removal efficiencies of 93 and 92% were achieved with ultrasonic-H_2SO_4 and H_2SO_4 pretreatments, respectively, indicating the enhancement of acidogenic and sulfidogenic activity.

3) Biohythane production through one-stage AD of sulfate-rich hydrolyzed TPR has been hampered by high H_2S production. Herein, two-stage AD was investigated with the addition of MoO_4^{2-} (0.24-3.63 g/L) and $FeCl_3$ (0.025-5.4 g/L) to the DF stage to improve biohythane production. DF supplemented with 1.21 g/L MoO_4^{2-} increased hydrogen yield by 14.6% compared to the control (68.39 ml/g-VS_{fed}), while $FeCl_3$ had no effective effect. Furthermore, the maximum methane yields of MF were 524.75 ml/g-VS_{fed} with 3.63 g/L MoO_4^{2-} and 521.60 ml/g-VS_{fed} with 0.6 g/L $FeCl_3$ compared to 466.07 ml/g-VS_{fed} of the control. The maximum yields of biohythane and energy were 796.7 ml/g-VS_{fed} and 21.80 MJ/kg-VS_{fed} with 0.6 g/L $FeCl_3$ when the sulfate removal efficiency was 66.71%, and H_2S content was limited at 0.08%. Therefore, adding 0.6 g/L $FeCl_3$ is the most beneficial in improving energy recovery and sulfate removal with low H_2S content.

Keywords: Sulfuric acid pretreatment, Ultrasonic pretreatment, Anaerobic digestion, Biohythane, Ferric chloride, Molybdate

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD: Anaerobic digestion

ACE: Abundance coverage-based estimator

CH_4: Methane

CO_2: Carbon dioxide

C/N: Carbon to nitrogen

COD: Chemical oxygen demand

CH_2O: Formaldehyde

Chao1: Species richness estimator

COA: Coenzyme A

DF: Dark fermentation

FAN: Free amino nitrogen

$FeCl_3$: Ferric chloride

GHGs: Greenhouse gases

H_2: Hydrogen

H_2S: Hydrogen sulfide

H_2SO_4: Sulfuric acid

HCl: Hydrochloric acid

H_3PO_4: Phosphoric acid

KOH: Potassium hydroxide

MF: Methanogenic fermentation

MoO_4^{2-}: Molybdate

NH_4-N: Ammonium nitrogen

NaOH: Sodium hydroxide

NMDS: Non-metric multidimensional scaling analysis

POME: Palm oil mill effluent

SIR: Substrate to inoculum ratio

SRB: Sulfate-reducing bacteria

SLR: Solid loading ratios

SCOD: Soluble chemical oxygen demand

SO_4^{2-}: Sulfate

SO_3^{2-}: Sulfite

$S_2O_3^{2-}$: Thiosulfate

SEM: Scanning electron microscopy

TPR: Tofu processing residue

TS: total solid

VFAs: Volatile fatty acids

VS: Volatile solid

5-HMF: 5-hydroxymethylfurfural