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Overall evaluation of microwave-assisted alkali pretreatment for enhancement of biomethane production from brewers' spent grain

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ABSTRACT

In this study, microwave-assisted alkali pretreatment for brewers' spent grain (BSG) waste was comprehensively investigated using Box-Behnken design under varying operating parameters, *i.e.* microwave power, pretreatment time and alkali/biomass (A/B) ratio. Both quantitative and qualitative characterization analysis such as crystallinity index (CrI), specific surface area (SSA), morphology and compositional analyses were conducted on pretreated samples. Standard biomethane potential (BMP) tests were performed for each pretreated sample to observe the biomethane enhancement after pretreatment. Under optimized conditions, it was observed that the pretreatment technique has facilitated removal of 46% of lignin and 38% of hemicellulose and improved the SSA of samples from 9.55 to 161.98 m^2/g, contributing to 52% increase in BMP value. Meanwhile, mathematical models with correlation coefficients of 97.9% and 98.2% respectively were built to predict both the soluble chemical oxygen demand (COD) yield and BMP after pretreatment. Furthermore, a simplified concept of overall evaluation mechanism for pretreatment has been introduced, taking into account waste-removal, energetic and economic indices. Under the proposed evaluation mechanism, the caustic soda price was found to play a more important role than the prices of industry electricity and wholesale natural gas.

1. Introduction

In the world context of fossil fuel depletion, rapid increase in population and global warming issue, anaerobic digestion (AD) has been widely recognized as a green technology to generate biofuel from organic solid wastes, due to its advantages of low energy consumption, limited environmental impacts and high potential for energy recovery [1]. AD is a bioconversion process in the absence of oxygen, through which the biodegradables of the organic wastes can be digested, resulting in the production of high-quality combustible biogas, composed primarily of methane (~60 vol%) and carbon dioxide (~40 vol%) [2]. In the brewing industry, AD is commonly used to treat brewers' spent grains (BSG), acting as a promising method to cover energy demand in the plant from thermal application of produced biomethane [3].

There are four main steps involved in AD process, including hydrolysis, acidogenesis, acetogenesis and methanogenesis. It has been reported by many researchers that the hydrolysis is the rate limiting step for lignocellulosic biomass, since the substrates possess low biodegradable content such as lignin [4–6]. The nondegradable lignin content of the cell wall for the particulate substrate is the major limiting factor. Specifically, the long-chain lignin polymer reduces the accessibility of microorganisms to biodegradable contents (holocellulose: cellulose and hemicellulose) which are enclosed by lignin, resulting in low biodegradability of the microbes [7]. Therefore, pretreatment is recommended to break down the cell wall to release the biodegradable cellulose and hemicellulose contents locked inside, in order to boost the hydrolysis step of the AD process. However, the energetic and economic evaluation for the pretreatment system have rarely been discussed in previous studies, which are important for overall evaluation of the pretreatment technology. Wang et al. [8] studied ultrasound-assisted alkaline pretreatment to enhance enzymatic saccharification of grass clipping, in which the performance was mainly evaluated through the reducing sugar yield after pretreatment. Li et al. [9] conducted research about chemical–biological pretreatment of corn stalks on the bio-oils produced by hydrothermal liquefaction, with their focus on reduction of lignin and hemicellulose, concentrations of ethanol and remaining reducing sugar and the lower heating value after pretreatment. Zou et al. [10] aimed at enhancement of biogas production in anaerobic co-digestion of maize straw and dairy manure by ultrasonic pretreatment. To summarise, the evaluation of the pretreatment was largely done by the yield of desired chemical products, e.g. glucose, biomethane and biohydrogen, depending on different reaction

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Nomenclature

A/B	alkali/biomass, –
AD	anaerobic digestion, –
AIL	acid insoluble lignin, wt%
ANOVA	analysis of variance, –
ASL	acid soluble lignin, wt%
BMP	biomethane potential, $Nm^{3}*kg^{-1}VS$
BSG	brewers' spent grain, –
COD	chemical oxygen demand, –
CrI	crystallinity index, %
f_d	degradability extent, $Nm^{3}*kg^{-1}VS$
HHV	higher heating value, –
I	evaluation index, –
I_{002}	maximum intensity diffraction near 22.5°, –
$I_{18^{\circ}}$	intensity diffraction located near 18°, –
k_{hyd}	lumped apparent first order coefficient, day^{-1}
m_{BSG}	weight of the raw sample, kg
P	calibrated microwave power, W
Pr_{alkali}	price of caustic soda, USD/ton
Pr_{CH4}	price of wholesale natural gas, USD/kWh
Pr_{elec}	price of wholesale industry electricity, USD/kWh
R	ratio, –
RSM	response surface method, –
SSA	specific surface area, m^2/g
T	pretreatment time, min
t	anaerobic digestion time, day
TCD	thermal conductivity detector, –
TS	total solids, wt%
VS	volatile solids, wt%
w	weighting factor, –
Y_{BMP}	predicted biomethane potential, $Nm^{3}*kg^{-1}VS$
$Y_{BMP,ref}$	reference BMP value, $Nm^{3}*kg^{-1}VS$
Y_{CH4}	cumulative specific methane yield, $Nm^{3}*kg^{-1}VS$
Y_{COD}	predicted soluble chemical oxygen demand, gCOD/gVS
$Y_{economy}$	total economy gained, USD CH_4/USD alkali and electricity
$Y_{economy,net}$	net economy gained, USD CH_4/USD alkali and electricity
Y_{energy}	extra amount of energy produced, kWh CH_4/kWh electricity
α	model coefficient, –
η_M	electricity to heat efficiency, –

pathways in the existing literature. Thus, an overall evaluation mechanism for the pretreatment method has been brought up in this study, considering various indices, *i.e.* waste-removal, energetic and economic performance.

There are numerous techniques of pretreatment available for treating lignocellulosic biomass which can be categorized as mechanical, thermal, chemical, biological, *etc.* The general principle of these pretreatment methods is to remove or alter the hemicellulose or lignin content, decrease the crystallinity of cellulose and increase the surface area of the biomass [11]. Among all pretreatment techniques, alkaline pretreatment has been regarded as one of the front runners attributed to its advantages over other pretreatment methods [12]: (1) alkaline methods utilize mostly non-polluting and non-corrosive chemicals such as ammonia (aqueous, liquid, and gaseous), sodium hydroxide, sodium carbonate, and calcium hydroxide (lime); (2) alkaline pretreatment is carried out under milder conditions than those needed for acid pretreatment; (3) alkaline reagents interact primarily with lignin making itself more efficient for lignin removal than acid pretreatment. In addition, it was reported that alkali pretreatment is preferred to the other chemical pretreatment methods for biomass intended for AD [13], since AD process under high organic loading generally has acidification issue and requires an adjustment of the pH to maintain its optimized pH range of 6.8–7.2 for methane production, which can be accomplished by slightly increasing the alkalinity of the substrate. To further enhance the effectiveness of the chemical pretreatment, microwave heating can be used as an alternative approach to replace conventional heating, e.g. convection oven heating. When lignocellulosic biomass substrates are subjected to microwave radiation, the polar molecules, e.g. water, are selectively heated and 'hot spot' within the inhomogeneous materials are formed which results in an 'explosion' effect among the particles, improving the disruption of recalcitrant structures of lignocelluloses [14]. Compared with conventional heating, for which heat is transferred by means of convection, conduction and radiation from the surfaces to the inner areas of the materials, microwave heating is much faster and more effective in breaking down the complex lignin structure [15]. Moreover, the microwave systems dissipate heat uniformly and are highly effective, easy to operate, highly selective and easy to start-up and stop instantly [16]. Moodley et al. [17] compared two different pretreatment methods for sugarcane leaf waste, *i.e.* steam salt-alkali and microwave salt-alkali, with the conclusion that the required pretreatment time of microwave salt-alkali was 83% lower. Dai et al. [18] conducted a comparative study on microwave and conventional hydrothermal pretreatment of bamboo sawdust and observed that microwave hydrothermal pretreatment removed more acetyl groups in hemicellulose compared to conventional hydrothermal pretreatment. Furthermore, the advantages of microwave heating over conduction and convection heating have also been confirmed by Alejandra et al. [19], e.g. faster heat transfer and shorter reaction time, dielectric and volumetric (around all material) heating, more energy-efficient and cost-effective route, and limited overheating on surface. Several research works have indeed confirmed the positive synergistic effect of the combined pretreatment methods for different biomass wastes [14,15,20–22]. Nonetheless, the earlier studies generally presented the trend of desired chemical yield under varying operating parameters, with lack of quantifying the relationship between the operating parameters and the chemical yield using some explicit formulas, which can be further used for prediction of the pretreatment performance [14,22].

In this study, a combined pretreatment method, *i.e.* microwave-assisted alkali pretreatment, was employed to treat BSG waste. Parametric study on the effects of the microwave power, treatment time and the alkali/biomass (A/B) ratio has been investigated comprehensively using Box-Behnken design. Simultaneously, two second-order polynomial mathematical models with good accuracy were built based on experimental results to predict both the soluble chemical oxygen demand (COD) yield and BMP value of pretreated samples under different operating conditions. Furthermore, a comparison between conventional and microwave heating has been made. Last but not least, an overall evaluation mechanism for the pretreatment method has been introduced, taking account of various indices, *i.e.* waste-removal, energetic and economic performance.

2. Materials and methods

2.1. Samples source and pretreatment design

2.1.1. Substrate and inoculum sources

The raw BSG samples, typical lignocellulosic biomass wastes, were collected from local BSG processing company, Bioplas Energy Pte. Ltd., and stored in a refrigerator maintained at −4 °C before pretreatment. The inoculum (seed sludge) for BMP test was collected from the effluent of a large-scale mesophilic anaerobic digester from a local municipal wastewater treatment plant, Ulu Pandan Water Reclamation Plant, Singapore. Inoculum was sealed and stored in a cold ambience of 4 °C. It was tempered at 35 °C for 4 days before AD experiments.