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From biomass waste to biofuels and biomaterial building blocks

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ABSTRACT

Concerns about the earth's sustainable management and the reduction of greenhouse gas emissions have become an important issue in the world. One of the alternative solutions is producing biofuels and biomaterial building blocks from biomass waste. Biomass wastes, which include solid waste of agricultural residues (rice straw, wet birch pulp), agro-industrial wastes (mushroom waste, cotton cellulose) and liquid waste of food and related industrial wastewater are abundant feedstock for renewable biohydrogen, biomethane and biochemicals productions etc. This technology of waste to energy and biochemicals includes the pretreatment of biomass, subsequently converted to sugars (hydrolyzate). Sugars are thereafter transformed into biofuels such as hydrogen, methane, ethanol, and the biomaterial building blocks such as volatile fatty acids: Lactic acid, Acetic acid, Propionic acid, and Butyric acid etc.

This study proposes an integrated two-stage continuous system to produce biohydrogen and biomethane at higher yields, whilst removing more COD from the wastewater.

1. Introduction

In recent years, global warming and climate changes has affected human life. To alleviate this problem, one of the promising alternatives of renewable energy is hydrogen from biomass. Biological processes from lignocelluloses biomass can produce hydrogen via cellulose hydrolysis to sugars, and further fermentative process.

According to Taiwan's Executive Yuan statistics, the food industry wastewater is 180,000 ton/per year in 2013. If not properly handled these high organic concentration of wastewater, it will discharge large amount of pollutants into rivers caused serious water pollution. Hence, solving the wastewater problems are vital issues to the environment. Rice straw is one of the common and abundant agricultural wastes which can be converted to sugars (hydrolyzate) through the hydrolysis process in Asia. It is estimated that about 650–975 million tons of rice straw produced per year globally and a large part of this goes to cattle feed while the rest is treated as waste [5]. Every year, approximately 2.35 million tons of the rice straw is produced in Taiwan and most of them are burned or buried on-site causing environmental problems [7]. These agricultural residues, agro-industrial wastes and high concentration of wastewater streams, if not properly treated will create problems since they are discharged in to various rivers and causes environmental pollution issues. Therefore, we try to use that to produce bioenergy and high value added products.

The biohydrogen production from lignocellulose hydrolysates obtained more attractions since 2006. Previous studies of biohydrogen production, they are normally by using pure cultures in the batch mode [10,36,31,34,38,28,29,6,30]. Biohydrogen production by lignocellulosic feedstock hydrolysates is a biological process, which include several parameters, such as different hydrolysis method, substrate source, substrate concentration, operating temperature, pH etc. The feedstock hydrolysates from biomass is quite similar to the process of bioethanol [3]. The performances of biohydrogen production in previous investigations were reviewed, and shown in Table 1 for a batch process and Table 2 for a continuous process. Dark fermentative hydrogen production has received increasing attention in recent years, due to its high hydrogen production rate (HPR) [15]. The proposed three-phase fluidized bed bioreactors showed promising H_2 producing performance and may have a potential to apply in practical biohydrogen production processes [41]. The fluidized-bed bioreactor holds the advantage of being flexible to operate and easy to scale up and it seems to have the potential to be practically applied in large-scale biohydrogen

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Table 1
Literature comparison of bio-hydrogen production by batch processes from lignocellulose hydrolysate.

Bacteria	Substrate	Hydrolysis method	Temp. (°C)	Initial pH	H_2 production yield	References
C. butyricum TISTR 1032	Sugarcane bagasse	Acid hydrolysis (0.5% H_2SO_4, 121 °C, 60 min)	37	5.5	1.73 mol H_2/mol total sugar	[36]
Cow dung compost	Wheat straw	Acid hydrolysis (2.0% HCl, microwave 8 min)	36	7.0	68.1 mL H_2/g TVS	[12]
Clostridium pasteuianum	Carboxymethyl cellulose	Cellulose hydrolytic bacteria	35	7.0	0.22 mol H_2/mol R-sugar	[28]
Hot spring sediment	Oil palm trunk hydrolysate	Acid hydrolysis and microwave (1.56% H_2SO_4, 450 W, 7.50 min)	55	6.03	0.71 mol H_2/mol sugar consumed	[16]
Seed sludge	Corn stover	Acid hydrolysis (0.3 N H_2SO_4, 45 min)	55	7	8.5 mmol H_2/g-glucose	[24]
Thermoanaerobacterium thermosaccharolyticum W16	Corn stover	Acid hydrolysis (2.13% H_2SO_4, 121 °C, 105 min)	60	7.0	12.44 mmol H_2/g-sugar	[6]
Sewage sludge	Cotton	Acid hydrolysis (55% H_2SO_4, 40 °C, 2 h)	37	8.4	0.99 mol H_2/mol R-sugar	[9]
Activated sludge	Starch flour	Heated (100 °C, 30 min)	35	–	1.94 mol H_2/mol glucose	[4]

Table 2
Literature comparison of bio-hydrogen production by continues processes from lignocellulose hydrolysate.

Bacteria	Substrate	HRT (h)	Temp. (°C)	Initial pH	H_2 production rate	H_2 production yield	References
Seed sludge	Food waste	–	35	–	–	1.04 mol H_2/mol hexose	[17]
Mixed culture	Oat straw hydrolysate	12	–	5.5	1.92 L/L/d	2.9 mol H_2/mol hexose	[2]
Clostridium butyricum CGS2	Starch hydrolysate	12	37	7.5	26 L/L/d	10.01 mol H_2/g starch	[8]
Seed sludge	Rice straw hydrolysate	8	40	5.71 ± 0.16	5.52 L/L/d	0.72 mol H_2/mol hexose	[26]
Seed sludge	Rice straw hydrolysate	4	40	5.60 ± 0.18	16.32 L/L/d	1.02 ± 0.03 mol H_2/mol hexos	[26]

production from organic wastes [40]. For the sugary wastewater, enrichment in the presence of 2-bromoethanesulfonic acid resulted in lower H_2 yields due to increased propionate production and decreased butyrate/acetate ratio [19–21]. Adding Fe^{2+} helps improve the H_2 production by 105% and speeds up the reaction. Adding L-cysteine enhances the H_2 production by nearly 50% [4]. Adding proper concentration of calcium ion could enhance bioH_2 producing [19–21]. Using activated carbon to remove bio-toxic inhibitors can improve the hydrogen yield [19–21]. The rice straw hydrolysate mixing the feeding substrate with another high strength organic wastewater could enhance the productivity of biohydrogen in the continuous system [25]. Sulfate concentration has a negative effect on biohydrogen production [27]. An analysis of the economic benefits of this innovative reference commercial model prove its feasibility by using beverage wastewater and agricultural waste as feedstock which will enable a hydrogen-producing system to gain a maximum annual profit with an annual return rate of approximately 60% and 39% with Aspen Plus; 81% and 30% with local price evaluation [19–21]. Some of the example from different sources, performance, and its operating conditions are reviewed and shown in Table 3.

In this study, we will recommend the optimum integration system, which take into account for various feedstock, pre-treatment processes, and fermentative and/or physical chemistry method to produce high value added products. Especially this technology of waste to energy and biochemicals include pretreatment of biomass that converted the biomass to sugars (hydrolyzate) via the cellulose hydrolysis process, and produced biofuels such as H_2, CH_4, ethanol, and the biomaterial building blocks such as volatile fatty acids: Lactic acid, Acetic acid, Propionic acid, and Butyric acid etc. The biomass convert to biofuels and biochemical are shown in Fig. 1.

2. Materials and methods

2.1. Feedstock and pre-treatment

The substrate of dark fermentation mainly from biomass wastes, which include solid waste of agricultural residues, agro-industrial wastes, and liquid wastewater. The solid waste generally contents cellulose, hemicellulose and lignin. Except of the lignin, cellulose and hemicellulose can be hydrolysed to hexose and/or pentose in a monomer or oligomer type of sugars.

There are several raw material of lignocellulose was easily available, such as cotton-based waste was sourced from Terng Wang Surgical Dressings Co., Ltd (Taiwan). Mushroom farm waste was collected from a mushroom farm in Shinshou, Taichung County, where located in central Taiwan. Lignocellulose raw materials of mushroom farm waste were pretreated by air dryer for 24 h, then milled by a high-speed grinder, and sieved through a no. 40–65 sieve. The particle size of the mushroom farm waste varied from 65 to 497 μm. Rice straw was collected from Wurih East Garden, Taichung City. The rice straw shredded and crushed to get its powder (particle size of 200 μm).

The cotton was hydrolyzed with a high concentration of sulfuric acid (55%). The prepared sulfuric acid (55%) was first put in the 250 mL flask and mixed well using a magnetic stirred mixer, then cotton of 30, 40, 50, 60 and 70 g/L, was added individually to the

Table 3
Literature comparison of bio-hydrogen production from wastewater.

Substrate	HRT (h)	Influent (g COD/L)	pH	Temp. (°C)	Hydrogen production rate (L/L/d)	H_2 yield (mol H_2/mol hexose)	References
Dairy wastewater	24	4.7	4.5	28	0.03	–	[33]
Molasses	16	28.2 (g VS//L)	–	55	3.97	–	[18]
Coffee drink manufacturing wastewater	4	20	5.5	35	4.64	0.96	[14]
Beverage wastewater	2	20	5.5	40	44.06	1.81	[23]