



# Pretreatment of cheese whey for hydrogen production using a simple hydrodynamic cavitation system under alkaline condition



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## HIGHLIGHTS

- Hydrodynamic cavitation (HC) system gives heating and sonication effects.
- HC satisfies the commercialization requirements such as low energy and scale-up.
- Combination of HC with alkaline makes more advantages including production rate.

## ARTICLE INFO

### Article history:

Received 29 September 2014  
Received in revised form 27 January 2015  
Accepted 28 January 2015  
Available online 9 February 2015

### Keywords:

Cheese whey  
Hydrodynamic cavitation  
Hydrogen production  
Alkaline pretreatment

## ABSTRACT

A simple hydrodynamic cavitation (HC) system was newly employed as a pretreatment method for H<sub>2</sub> production from cheese whey. This system offered not only the sonication effect but also an increase in the temperature of the solution. With HC pretreatment for 15 min, a higher H<sub>2</sub> production yield (1.89 mol H<sub>2</sub>/mol lactose) was obtained than with other conventional pretreatment methods such as heating and sonication. HC pretreatment efficiency was synergistically increased when combined with alkaline conditions. In this way, the amount of solubilized nutrient was greatly increased and methanogens were completely removed, leading to H<sub>2</sub> gas of higher purity (48%) and a yield of 3.30 mol H<sub>2</sub>/mol lactose. HC pretreatment under alkaline conditions can be used to efficiently pretreat organic-rich wastewater, including cheese whey, without any scale-up problem, and is an excellent pretreatment option for H<sub>2</sub> production.

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## 1. Introduction

The exploration of alternative renewable energy has been greatly stimulated in recent years by rising concerns over environmental and energy crises. Among various alternatives, hydrogen (H<sub>2</sub>) is strategically important due to its high energy content (122 kJ/g) [1].

Currently, over 90% of H<sub>2</sub> is made from natural gas, which is a fossil fuel and thus a finite resource. The use of this resource generates large quantities of carbon dioxide (CO<sub>2</sub>), a major player in global warming. Biological H<sub>2</sub> production via anaerobic fermentation is an environment-friendly alternative. In light of the current levels of efficiency and cost, it is true that this biological approach is far from economic viability at the moment. However, it will become appealing if appropriate ways to utilize cheap substrates such as carbohydrate-rich wastes and wastewater [2].

Cheese whey, a major waste from the cheese-making process, is a good candidate for this purpose. In fact, some researchers have already had some success [3,4]. This form of bio-waste typically contains 5–8% (w/w) of dry matter, of which lactose is roughly 60–80%, protein 10–20%, and the rest minerals, vitamins, fat, lactic acid and trace elements [5]. The exceptionally high organic content of cheese whey, with a biological oxygen demand (BOD) of about 50,000 mg/L, and chemical oxygen demand (COD) of up to 80,000 mg/L, is problematic from the waste-treatment perspective [6], but could serve as a rich resource for biological processes such as hydrogen generation [7].

The production of bio-H<sub>2</sub>, particularly from bio-waste, requires some kind of pretreatment to suppress contaminating microbes (e.g., methanogens) and to enrich only the H<sub>2</sub>-producing bacteria [8]. To this end, various physical pretreatments such as heat and sonication, as well as chemical pretreatment using acid/base, have been used to inactivate background microbes and leave active spore-forming, H<sub>2</sub>-producing bacteria such as *Clostridia* [9]. However, the conventional physical methods are energy-intensive, and the problems related to scale-up have become a critical issue.

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For example, the heating equipment cannot make a uniform increase of temperature for a large volume, and the sonication system distributes the cavitation effect over a very limited area due to its horn structure [10].

Here, we introduce a more effective physical means of pretreatment, namely hydrodynamic cavitation (HC) system, that is known for its exceptional ability to disrupt cells and inactivate microorganisms [11,12]. The HC system has a simple structure, consisting of only a pump and an orifice plate, and the cavities are effectively formed by the circulation of fluid through an orifice plate. This phenomenon is explained by the Bernoulli equation, which is a theory that relates fluid pressure (Eq. (1)) and cross sectional area (Eq. (2)). The terminologies were defined as followed:  $P$  = pressure of fluid,  $\rho$  = density of fluid,  $V$  = velocity of fluid,  $A$  = cross sectional area

$$P_1 + \frac{1}{2}\rho V_1^2 = P_2 + \frac{1}{2}\rho V_2^2 \quad (1)$$

$$A_1 V_1 = A_2 V_2 \quad (2)$$

At the orifice plate, where the cross-sectional area is very small, local pressure is low, and cavities are generated if the fluid pressure falls below a threshold level. Subsequently, the pressure recovers after the fluid passes through the orifice plate, and the cavities collapse. At the instant of collapse, the temperature within the micro-bubble reaches several thousand kelvins and a pressure of several atmospheres, theoretically. With the HC system, cavities and heating effects are efficiently distributed throughout the fluid and scale-up is not an issue. This system has already been utilized in cell disintegration, depolymerization, hydrolysis, and as a heating source without any scale-up problem [13–15]. However, the HC system has not previously been applied in the pretreatment of biowastes for H<sub>2</sub> production.

In this study, the novel use of a simple HC system for bio-waste pretreatment is proposed, then the advantages of HC, compared to other conventional physical pretreatment methods (e.g., heating and sonication), are demonstrated. Finally, a chemical phase using an alkaline condition is used to enhance the pretreatment efficiency of the HC process.

## 2. Material and methods

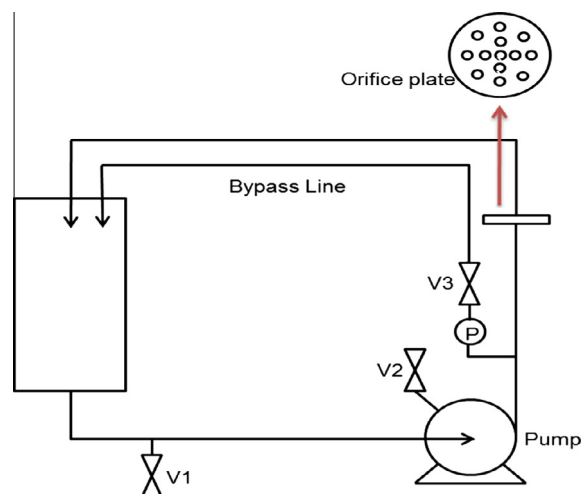
### 2.1. Inoculum and feedstock preparation

Seeding anaerobic sludge was obtained from a sewage treatment plant in Daejeon, Republic of Korea. Cheese whey was provided by a Nonghyup cheese processing plant located in Imsil, Republic of Korea. The compositions of the anaerobic sludge and cheese whey were given in Table 1. For pretreatment, a mixture of anaerobic sludge and cheese whey (1:9 v/v) was used.

**Table 1**

Composition of cheese whey, anaerobic sludge, and waste mixture (T: total, S: solubilized, N: nitrogen, and P: phosphorus).

	Values (mg/L)		
	Cheese whey	Anaerobic sludge	Waste mixture (Cheese whey:Anaerobic sludge = 9:1, v/v)
T-COD	88,000	15,300	80,730
S-COD	30,000	340	27,030
Lactose	40,000	–	36,000
T-Protein	22,000	4238	20,200
S-Protein	1500	427	1400
T-N	1088	975	1075
S-N	15	117	25
T-P	810	441	770
S-P	8	98	15



**Fig. 1.** Schematic diagram of Hydrodynamic cavitation system (P: pressure gauge, V1, V2, V3: valves).

As a physical pretreatment method, HC system made of stainless steel was connected to a water pump (TPH2TK6KS; Walrus Pump – Taiwan; Fig. 1). Capacity of the system was 1.5 L, and the inner diameter of pipe line was 20 mm. Orifice plate having 27 holes of 1 mm diameter was used in this system. As a physico-chemical pretreatment method, potassium hydroxide (KOH, 5 M) was added to obtain pH 10. Conventional methods were done using 100 mL of waste mixture under four conditions as control: (1) without pretreatment, (2) with heat (90 °C) using water-bath (DAIHAN, WB-11) for 15 min, (3) with ultrasonication (VCX-750, S&M, USA, 20 kHz frequency with Maximum power of 750 W) for 15 min, and (4) with alkaline pretreatment (pH 10) for 15 min.

### 2.2. Batch fermentation

A pretreated sample was then examined for H<sub>2</sub> productivity, after being mixed with deionized water containing trace metals (v/v = 1:1). The trace metal solution contained the following ingredients in 1 L of deionized water: NH<sub>4</sub>Cl – 3.5 g, KH<sub>2</sub>PO<sub>4</sub> – 0.25 g, FeCl<sub>2</sub> – 35 mg, NaHCO<sub>3</sub> – 1.25 g, CoCl<sub>2</sub> 6H<sub>2</sub>O – 2.5 mg, NiCl<sub>2</sub> 6H<sub>2</sub>O – 2.5 mg, ZnCl<sub>2</sub> – 2.5 mg, CaCl<sub>2</sub> – 250 mg, MgCl<sub>2</sub> – 100 mg, MnCl<sub>2</sub> – 5 mg, Na<sub>2</sub>MoO<sub>4</sub> – 10 mg, CuCl<sub>2</sub> – 5 mg, yeast extract – 100 mg, L-cysteine – 100 mg.

A batch test was performed to produce H<sub>2</sub> gas in a 250 ml-flask with 100 mL of working volume. The pH was initially adjusted to 8.0 using 1 M KOH, and then the flask was purged with N<sub>2</sub> gas to ensure an anaerobic condition. All batch digestions were conducted in a shaking incubator at 36 ± 1 °C and 150 rpm. These conditions were described by Jeong et al. [8], and experiments were done in triplicate.

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