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Use of magnetic nanoparticles to enhance bioethanol production in syngas fermentation

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HIGHLIGHTS

- Nanoparticles were tested to enhance syngas fermentation by mass transfer improvement.
- $CoFe_2O_4@SiO_2–CH_3$ nanoparticles showed better enhancement of syngas fermentation.
- The reusability of $CoFe_2O_4@SiO_2–CH_3$ nanoparticles can improve economic feasibility.

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ABSTRACT

The effect of two types of nanoparticles on the enhancement of bioethanol production in syngas fermentation by *Clostridium ljungdahlii* was examined. Methyl-functionalized silica and methyl-functionalized cobalt ferrite–silica ($CoFe_2O_4@SiO_2–CH_3$) nanoparticles were used to improve syngas–water mass transfer. Of these, $CoFe_2O_4@SiO_2–CH_3$ nanoparticles showed better enhancement of syngas mass transfer. The nanoparticles were recovered using a magnet and reused five times to evaluate reusability, and it was confirmed that their capability for mass transfer enhancement was maintained. Both types of nanoparticles were applied to syngas fermentation, and production of biomass, ethanol, and acetic acid was enhanced. $CoFe_2O_4@SiO_2–CH_3$ nanoparticles were more efficient for the productivity of syngas fermentation due to improved syngas mass transfer. The biomass, ethanol, and acetic acid production compared to a control were increased by 227.6%, 213.5%, and 59.6%, respectively by addition of $CoFe_2O_4@SiO_2–CH_3$ nanoparticles. The reusability of the nanoparticles was confirmed by reuse of recovered nanoparticles for fermentation.

1. Introduction

In recent years, lignocellulosic biomass has been highlighted as a potential raw material for bioenergy production, with advantages including its abundance and the fact that it does not require use of food resources. The primary biological method for the production of bioenergy from lignocellulosic biomass is the saccharification–fermentation process. In this process, biomass is saccharified by hydrolysis to produce monosaccharides, which are then fermented to produce ethanol (Kootstra et al., 2009). Gasification–fermenta tion has emerged as an alternative to this, overcoming a major drawback of saccharification–fermentation by removing the complex saccharification step. In the gasification–fermentation process, lignocellulosic biomass is thermally gasified to produce synthetic gas (syngas) composed of CO, CO_2, H_2, and N_2, which is then fermented to produce biosubstances including bioethanol (Balat, 2011; Liua et al., 2014; Wilkins and Atiyeh, 2011). The gasi fication–fermentation process has another advantage in that organic wastes such as agricultural and municipal wastes can be used as raw materials for syngas production (Arafat and Jijakli, 2013; Nipattummakul et al., 2012). In addition, the use of biological processes has some advantages over the use of a chemical catalytic method. Fermentation does not have high operating costs under ambient temperature and pressure and can be carried out with unpurified reactants (Munasinghe and Khanal, 2010). Some anaerobic microorganisms including *Clostridium ljungdahlii*, *Eubacterium limosum*, and *Clostridium aceticum* have been reported to be able to produce ethanol from syngas (Hurst and Lewis, 2010; Najafpour and Younesi, 2006; Younesi et al., 2005).

The rate-limiting step in syngas fermentation is the gas–liquid mass transfer of the gaseous substrates (CO, CO_2, and H_2) into the fermentation broth (Munasinghe and Khanal, 2010; Zhu et al., 2010), resulting in syngas fermentation having low

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productivity and therefore poor economic feasibility. As the gas–liquid mass transfer rate is affected by reactor geometry, power input, and pressure, previous studies have examined altering reactor design as an approach to improving the performance of syngas fermentation (Bredwell et al., 1999; Younesi et al., 2005; Ungerman and Heindel, 2007; Hurst and Lewis, 2010). However, the effect of the reactor-engineering approach on increasing gas–liquid mass transfer rate is limited, leading some researchers to use electrolytes and small particles to increase the gas–liquid mass transfer rates (Zhu et al., 2009, 2010). The enhancement of the mass transfer coefficient by the adhesion of nanoparticles to the gas–liquid interface can be explained by three mechanisms: a shuttling or grazing effect, hydrodynamic effects at the gas–liquid boundary layer, and changes in the specific gas–liquid interfacial area (Ruthiya, 2005).

In our previous study, the effect of nanoparticles with different surface properties on the gas–liquid mass transfer rate between syngas components (CO, CO_2, and H_2) and water was examined, as was the effect of the introduction of functional groups to the surface of the nanoparticles. Methyl-functionalized silica nanoparticles showed the best enhancement of bioethanol production by improving syngas mass transfer during *C. ljungdahlii* fermentation (Kim et al., 2014). However, a drawback of these nanoparticles is the difficulty of recovering them for reuse. A high-performance centrifuge technique and a complex purification operation is needed to obtain nanoparticles from nanoparticles-culture broth mixture (Nemati et al., 2014). Therefore, a cheap, easy-to-use recovery method is necessary to make the process economically feasible. Magnetic nanoparticles are a candidate to allow easier recovery of the nanoparticles (Khaligh and Shirini, 2013).

In this study, magnetic nanoparticles with methyl functional groups were synthesized, and their effect on gas–liquid mass transfer between syngas components and water was examined. Magnetic nanoparticles were used in a fermentation process with *C. ljungdahlii* to evaluate their influence on bioethanol production. The recyclability of the magnetic nanoparticles was also examined by reuse of recovered nanoparticles.

2. Methods

2.1. Materials

C. ljungdahlii (ATCC 55383), an acetogenic anaerobic strain of bacteria, was supplied by the American Type Culture Collection (USA). The components and composition of the culture medium have been detailed in a previous paper (Kim et al., 2014).

For the synthesis of the nanoparticles, reagent-grade tetraethyl orthosilicate, ammonium hydroxide solution, triethoxymethylsilane, trimethoxy(octadecyl)silane, cobalt(II) nitrate hexahydrate, polyoxyethylene nonylphenylether, iron(III) nitrate nonahydrate, and dioctyl ether were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA).

Custom-made artificial syngas composed of 20 vol% CO, 20 vol% CO_2, 5 vol% H_2, and 55 vol% N_2 was provided by MS Dongmin Gas Co. (Gyeonggi-Do, Korea). Tedlar bags for gas sampling were purchased from Top Trading Eng. Inc. (Product No. 208-1001-01; vol: 1 L; 250 × 150 mm; Seoul, Korea).

2.2. Methods

2.2.1. Nanoparticle synthesis and surface modification

Methods for silica nanoparticle synthesis and surface modification with methyl groups were fully explained in a previous paper (Kim et al., 2014), a brief methods are as follows. Four hundred milliliters of ethanol and 3 mL of tetraethyl orthosilicate were mixed for 1 h. Thirty milliliters of an ammonium hydroxide solution was added to this mixture, which was then stirred for 2 h. Then, 10 mL of the mixture was poured into a conical tube and centrifuged at 3000 rpm for 15 min. The supernatant was discarded, and the precipitated silica nanoparticles were washed with an ethanol solution to remove impurities. Then, the precipitate was resuspended in 2 mL of ethanol and centrifuged again at 3000 rpm for 5 min. After the supernatant was removed, the precipitate was washed 3 times and then dried at 80 °C for 1.5 h to obtain the silica nanoparticles. In order to modify the silica nanoparticles with methyl groups. One gram of prepared silica nanoparticles was added to 450 mL of 20 vol% triethoxymethylsilane ethanol solution. After stirring for 12 h, the mixture was washed with ethanol 3 times and dried at 80 °C for 1.5 h to obtain silica nanoparticles with methyl groups.

In order to fabricate cobalt ferrite-silica core/shell nanoparticles ($CoFe_2O_4@SiO_2$), first mesoporous SiO_2 nanoparticles were prepared. Distilled water (20 mL), ethanol (150 mL), and ammonium hydroxide solution (6 mL) were mixed using a magnetic stirrer for 10 min. Next, 12 mL of tetraethyl orthosilicate was added to the mixture, which was then stirred for 2 h. Then, 10 mL of tetraethyl orthosilicate and 4 mL of trimethoxy(octadecyl)silane were added and the mixture was stirred for 1.5 h. After this, 25 mL of the mixture was poured into a 50 mL conical tube and centrifuged at 3000 rpm for 10 min. The supernatant was discarded, and the precipitate was washed 3 times with an ethanol to remove impurities. The precipitate was then dried at 80 °C followed by calcination at 550 °C for 6 h to obtain the mesoporous silica nanoparticles.

In order to disperse cobalt ferrite around the mesoporous silica nanoparticle cores, 1 g of silica nanoparticles and 10 mL of ethanol were mixed and sonicated for 1 h. Next, 0.0975 g of cobalt(II) nitrate hexahydrate and 0.2705 g of iron(III) nitrate nonahydrate were added and mixed to ensure complete dissolution. After this, 1 mL of IGEPAL® CO-520 and 30 mL of dioctyl ether were added to the mixture, followed by sonication for 10 min. The mixture was poured into 100 mL three-necked flask and heated at 100 °C until the ethanol was completely evaporated, and then a center neck of the flask was equipped with a reflux condenser and the side necks were blocked, and the mixture was refluxed at 300 °C for 6 h. The mixture was then poured into a conical tube and centrifuged at 3000 rpm for 10 min. The supernatant was discarded, and the precipitate was washed 3 times with an ethanol. The precipitate was dried at 80 °C and then calcined at 500 °C for 3 h to obtain $CoFe_2O_4@SiO_2$ core/shell nanoparticles.

The $CoFe_2O_4@SiO_2$ nanoparticles were modified with methyl groups as follows: The as-prepared nanoparticles (1 g) were added to a mixture of 400 mL of 95% (v/v) ethanol and 40 mL of triethoxymethylsilane. After sonicating for 1 h, the reaction mixture was poured into a conical tube and centrifuged at 3000 rpm for 10 min. The precipitate was then washed 3 times with ethanol and dried at 80 °C to obtain $CoFe_2O_4@SiO_2$ nanoparticles that had been surface modified with methyl groups ($CoFe_2O_4@SiO_2–CH_3$).

2.2.2. Measurement of syngas mass transfer in aqueous solutions containing magnetic nanoparticles

Distilled water (200 mL) in a 250 mL glass bottle was purged with nitrogen to give an oxygen-free environment. Syngas was then injected into the bottle until the internal pressure reached 121.6 kPa, after which the inlet was closed. The experimental setup and conditions have been explained in a previous paper (Kim et al., 2014). Mixing was performed with a magnetic stirrer at a rate of 300 rpm for 20 min. In a previous paper (Kim et al., 2014), nonporous silica nanoparticles modified with methyl groups ($SiO_2–CH_3$) at a concentration of 0.3 wt% were the best at enhancing syngas mass transfer in a range of 0.1–0.5 wt%. Therefore, $CoFe_2O_4@SiO_2–CH_3$ and $SiO_2–CH_3$ nanoparticles concentrations of 0.3 wt% were used in the experiments for comparison at a same condition.