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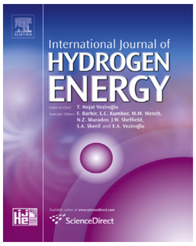

Integrated hydrogen production and power generation from microalgae

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ABSTRACT

An integrated system for hydrogen production, storage, and power generation from microalgae using enhanced process integration technology is proposed. Enhanced process integration has two core technologies: exergy recovery and process integration. Exergy recovery is performed through exergy elevation and heat coupling to minimize exergy destruction. The unrecoverable energy/heat in a single process is recovered and used in other processes through process integration. The proposed integrated system includes supercritical water gasification, hydrogen separation, hydrogenation, and a combined cycle. The microalga *Chlorella vulgaris* is used for modeling and evaluation. Microalgae are converted to syngas, then separated to produce highly pure hydrogen. To store the produced hydrogen, the toluene–methylcyclohexane cycle as a liquid organic hydrogen carrier is adopted. The remaining gas is used as fuel for combustion in the combined cycle to generate electricity. The effects of the fluidization velocity and gasification pressure on energy efficiency are evaluated. From process modeling and calculation, high total energy efficiency (higher than 60%), including electricity generation efficiency of about 40%, can be realized.

Introduction

Microalgae are a high-potential source of biomass for the production of food, industrial materials, pharmaceuticals, and energy [1]. Microalgae have very high photosynthetic fixation capability for CO_2 that can be utilized in generating various algal cell components, energy, and molecular oxygen [2]. Furthermore, microalgae have characteristics superior to those of terrestrial biomasses including a higher growth rate, more efficient solar energy conversion, higher nutrient acquisition, and the ability to grow under severe conditions [3]. Microalgae are rich in lipids and can thus be potentially used as an energy source and converted to different biofuels including bio-hydrogen, bio-diesel, biogas, and bio-oil [4]. The heating value of microalgae that are grown under optimum conditions usually ranges from 17 to 23 GJ per ton of dried microalgae [5].

As microalgae grow in an aqueous environment, they are generally cultivated remotely, possibly a far distance from their demand sites. Hence, the fuel produced from microalgae needs to be stored and transported. Among the secondary energy resources, hydrogen is highly versatile and efficient, has a wide variety of production and utilization technologies,

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and is clean [6]. Hydrogen is widely used and its use is increasing. It is used in reciprocating combustion engines, combustion in a combined cycle, and fuel cells. It is also mixed with other fuels. Furthermore, water is produced during hydrogen oxidation, thus leading to clean energy utilization.

Under ambient conditions, hydrogen has a relatively high energy density by weight of 33 kWh $kg \cdot H_2^{-1}$. Unfortunately, the energy density of hydrogen by volume, 3 Wh per liter of gaseous H_2, is very low compared with that of other hydrocarbons. This leads to difficulty in storing and transporting the produced hydrogen. Recently, storage and transportation methods for hydrogen, including compression, liquefaction, and chemical and physical storage have been developed and applied. Among them, compressed and liquid hydrogen are considered established forms for storage and transport. However, these methods require high energy consumption and have a relatively low safety level. Hydrogen storage utilizing a liquid organic hydrogen carrier (LOHC) is considered promising because of its high safety level, high storage capacity, excellent reversibility, longer storage time, and lower CO_2 emission [7–9]. Ammonia is another promising liquid hydrogen carrier, but unfortunately, it is toxic and corrosive, has a strong odor, and must be carried by a specially designed tanker.

In the LOHC, the hydrogen is covalently bonded through hydrogenation. When the hydrogen is needed, it can be released from the LOHC through dehydrogenation. Available LOHC cycles include cyclohexane–benzene, decalin–naphthalene, and toluene–methylcyclohexane (MCH) cycles. In this study, a toluene (C_7H_8)–MCH (C_7H_{14}) cycle is adopted to store and transport hydrogen because toluene and MCH are cheap, stable, and easy to transport. In addition, both toluene and MCH exist as a liquid over a wide temperature range, which is favorable for long-term storage. Additionally, their applicability has been demonstrated in a large-scale test conducted by Chiyoda Corporation in Japan [10].

Microalgae can be biochemically and thermochemically converted to hydrogen. Unfortunately, biochemical conversion, including fermentation, has a slower conversion rate and lower conversion efficiency than thermochemical conversion. Hence, for large-scale energy conversion, thermochemical conversion, including gasification and pyrolysis, is generally adopted. Among forms of thermochemical conversion, gasification is considered to have the highest conversion efficiency [11]. Two gasification methods are currently available: conventional thermal gasification and supercritical water gasification (SCWG). In the former, the harvested microalgae need to be dried to quite a low moisture content to achieve a stable conversion with high efficiency. Unfortunately, the moisture content of microalgae is very high, ranging from 70 to 90 wt% on a wet basis (wb), leading to huge energy consumption for drying [12]. In contrast, supercritical water gasification can be performed without drying because gasification is performed under an aqueous state. However, the energy demand required to bring the microalgae to a supercritical condition is high, resulting in lower total energy efficiency. Hence, a novel system that resolves this problem is urgently required.

To the author's knowledge, there has been no study focusing on the effort to effectively integrate the conversion of microalgae to hydrogen and storage of the produced hydrogen. Many studies focusing on the application of SCWG to microalgae did not pay further attention to system development [13–15]. Furthermore, some researchers studied the production of hydrogen through SCWG using biomass including microalgae [16,17]. Fiori et al. [18] and Haiduc et al. [19] proposed a design for hydrogen and methane production from biomass including microalgae with SCWG. Unfortunately, no notable effort was made to realize energy/heat recirculation in their proposed systems; hence, what was still large exergy destruction was generated. In addition, the systems included no storage process for the produced hydrogen. In the present study, a novel integrated system consisting of gasification, hydrogen separation, hydrogenation, and a combined cycle is proposed on the basis of enhanced process integration (EPI). EPI is a technology that combines exergy recovery and process integration with the purpose of minimizing the exergy destruction throughout the system. Therefore, high energy efficiency can be achieved.

Integrated system for hydrogen production, storage, and power generation

To minimize the exergy destruction throughout the system, the concept of EPI has been developed and applied to several materials including coal and biomasses [20–23]. EPI consists of two core technologies: exergy recovery and process integration. The former relates to the idea of heat circulation throughout a single process. Fig. 1 shows the concept of exergy recovery and two possible methods of exergy elevation. The dotted and solid lines represent streams with a high and low exergy rate, respectively. To realize the proposed exergy recovery, exergy elevation of the stream and heat coupling among the streams are performed (Fig. 1(a)). In exergy elevation, the exergy rate of the cold stream is raised, creating a hot stream by means of compression and heat combination (Fig. 1(b)). The stream is then used as the heat source and is paired with the cold stream through heat coupling (self-heat exchange). In heat coupling, the heat of the hot stream and the heat of the cold stream exchanged. Additionally, considerations are made of the heat type, heat amount and exergy rate to achieve an optimum balanced heat exchange. It is thus important to note that the idea of exergy recovery is different from that of conventional pinch or heat recovery technologies, which are essentially based on heat cascade utilization.

Although heat recovery throughout a single process has been optimized through exergy recovery, there is still unrecoverable energy/heat relating to the minimum temperature approach during heat exchange, the imbalance of heat following a change in stream properties, and heat loss. To minimize the amount of unrecoverable energy/heat, a process integration is introduced where the unrecoverable energy/heat from any process is used in other processes. As a result, exergy throughout the integrated systems can be further minimized, leading to high total energy efficiency.

Fig. 2 shows a diagram of the basic schematic material and energy flows of the proposed integrated system. Solid and dotted lines represent material and energy flows, respectively.

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