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Laser-induced hydrogen generation from graphite and coal

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ABSTRACT

This study presents a simple way of obtaining hydrogen gas from various ranks of coal, coke, and graphite using nanosecond laser pulses under different conditions such as water, air and argon atmosphere. It was observed that 532 nm laser pulses were more effective than 1064 nm pulses in gas generation and both were nonlinearly correlated with respect to the laser energy density. Gas chromatography measurements indicate that mainly hydrogen and carbon monoxide were generated. The hydrogen to carbon monoxide ratio shows that the highest efficiency rank was anthracite coal, with an average ratio of 1.4 due to its high fixed-carbon content and relatively high hydrocarbon amount. Graphite was used as a pure carbon source to study the possible reactions of gas yielded during the irradiation process. In addition, theoretical simulations using a standard finite difference method supported experimental observations. The possible mechanisms of gas generation were explained with chemical reactions.

Introduction

Hydrogen is a promising alternative to replace fossil fuels based on its characteristics such as being non-toxic, having wide inflammability range both in air and in oxygen, high in energy, and the most abundant element in the universe, along with having no adverse effect on the environment. Hydrogen does not exist naturally on Earth in its molecular form, instead it must be produced from other sources such as natural gas, coal and renewable sources with input from renewable energy sources such as solar light, biomass, wind, and hydropower [1–4]. In fact, up to 96% of hydrogen is produced from fossil fuels and the other 4% from water [5].

Thermal, electric, photonic and biochemical energies are mainly used to drive hydrogen production process. Combination of these energies is used for hydrogen production as well.

In electrolytic process, electricity is used to split water into its constituents [6]. This reaction takes place in an electrolyzer and emits zero greenhouse gases depending on the source of electricity [7]. Water electrolysis may play a vital role in future for clean and sustainable energy production due to its easy coupling to hydropower, wind and photovoltaic sources [8].

Photolytic processes use light energy to split water into hydrogen and oxygen [9,10]. This method also includes using biological species ranging from photosynthetic and fermentative bacteria to green microalgae and cyanobacteria in

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combination with light for hydrogen production [11–13]. Although it is still in its infancy, this method has a long term potential in terms of sustainable hydrogen production with minimal environmental impact [14].

Another type of hydrogen production method is thermal processes which uses the coal or biomass to release hydrogen inside the material. In addition, heat in combination with water can produce hydrogen as well. Examples of this methods includes natural gas reforming, bio-derived liquids reformation, coal and biomass gasification, and thermo-chemical production [15,16].

Historically, coal was gasified using early technology to produce coal gas. Most hydrogen today is produced through natural gas reforming at large refineries and by coal gasification, i.e. reacting coal with oxygen and steam under high pressures and temperatures to form synthesis gas, a mixture consisting primarily of carbon monoxide and hydrogen. The direct reaction of carbon with water is called the water-gas reaction and takes place at high temperatures (~1300 K) [17,18]. A photocatalytic system was reported in 1979 in which the carbon was used as the raw material to decompose water and produce hydrogen gas at lower temperatures. This indicates that oxygen produced on the surface of the photocatalyst has a strong oxidizing effect on the carbon [19].

Although conventional hydrogen production involves a mature technology and market applications, the high cost and carbon monoxide pollution limits its application [20]. With the desire of an alternative fast and cost-effective method of hydrogen production, various light sources have been utilized in the search for a sustainable hydrogen production mechanism with low environmental impact. Powdered photocatalysts (such as TiO_2, $Sr_3Ti_2O_7$, and $BaTi_4O_9$) have been used with solar and UV light sources to produce hydrogen by decomposing water. In this process, the photon energy is converted to chemical energy accompanied by a positive change in the Gibbs free energy [21]. Carbon was shown to assist the photocatalytic decomposition of water on TiO_2 and platinized TiO_2 using an intense mercury lamp by suppressing reverse reactions that lead to water [22]. Flower like graphene supported by ZnS composite showed enhanced photocatalytic hydrogen production activity [23]. The structure of graphene was believed to help light absorption, adsorption of sacrificing agents in the solution, and separation of photogenerated carriers. Photocatalytic generation of hydrogen by ZnO nanoparticles have been investigated under UV–Visible light irradiation [24]. Enhanced H_2 activity under UV-Vis light was attributed to the presence of large amount of oxygen defects. Many semiconductor photocatalyst materials have been developed for hydrogen production. However, their wide bandgap, poor carrier mobility, low light absorption, and low separation efficiency of photo-generated electrons and holes impedes their practical applications. As an alternative, quantum dots have been developed in order to enhance the catalytic activity of such materials [25]. The size of the nanoparticles played an important role in determining the relative efficiency hydrogen production from CdSe and CdSe/CdS quantum dots, CdSe quantum rods, and CdSe/CdS dot-in-rods [26]. In addition, the positive correlation were determined between the photoexcited surface charge densities and hydrogen production rate [26]. Hydrogen production significantly increased by tuning the length and size of the platinum-tipped cadmium sulfide rod with an embedded cadmium selenide seed compared to that of unseeded rods [27]. When gallium oxide (Ga_2O_3) was modified with Ag nanoparticles, it was observed that 1% Ag/Ga_2O_3 had higher activity than that of the pure Ga_2O_3 for photocatalytic H_2 evolution due to high separation efficiency of photogenerated carriers [28].

Nanodiamonds dispersed in water and subjected to pulsed laser irradiation were found to generate hydrogen and carbon monoxide [22]. Laser-induced graphitization of nanodiamonds to “onion-like” graphitic layers and the incorporation of various metals (e.g., Au, Pt, Pd, Ag, and Cu), have been shown to be an effective mechanism of hydrogen generation [22]. Several other techniques of hydrogen generation using nanosecond laser pulses have been proposed since the temperature and pressure of the plasma during ns-ablation in liquids are reported to be as high as 4000 K and several GPa, respectively [29–31]. Green laser irradiation has been shown to increase hydrogen production by inducing an additional field to assist conductivity in the water electrolysis [30]. Recently, Akimoto et al. showed that the amount of gas yielded from high-grade carbon powder and Bincho-Tan charcoal powder depends nonlinearly on the laser energy density [31]. However, the energy and wavelength dependence of hydrogen generation amounts and concentrations from different ranks of coal were not analyzed in detail.

In this study, we mainly focus on hydrogen generation and its analysis from various ranks of coal in comparison to the pure carbon source, graphite. We show that anthracite coal is the most efficient rank of coal in terms of H_2/CO ratio due to its fixed carbon and hydrocarbon content. We discuss the possible reactions by analogy from the classic technique of coal gasification, that is, the steaming of coal at high temperature (nearly 1300 K) and high pressure (a few MPa) [32–34].

Experimental

Different ranks of coal, namely anthracite, bituminous, lignite, and coke were used. Coal samples were purchased from Mini Me Geology Inc. and smithing coke from Centaur Forge LLC. Each of these coal and coke rocks were pulverized for 15 min by using a Ring and Puck coal pulverizer. The particle size distribution for each rank was investigated by Scanning Electron Microscopy (SEM) (JEOL 6510LV). The distribution shows that the particles have mean diameters between 1 and 5 μm, which is much smaller than the porous structure of coal [35]. Each of the gas generation experiments was performed under an air atmosphere unless otherwise stated. Additionally, pure carbon (graphite), with or without water, was also analyzed in an argon atmosphere. Component analysis of the SEM Electron Diffraction Spectrum (EDS) (JEOL 6510LV) was performed at the secondary electron imaging (SEI) mode at 15 kV. FTIR analysis was performed to understand the bond structure of the coal samples. The proximate analysis of the coke and coal samples were conducted by the Thermogravimetric analyzer (TGA701, Leco) using method D5142 with accordance to ASTM. Energy analysis of coal and coke powders were analyzed by the calorimeter.