(第3号様式) (Form No. 3)

学 位 論 文 要 旨
Dissertation Summary

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論　文　名:Hydrogen Production from n-dodecane using Steam Reforming in-Liquid Plasma Method

(Dissertation Title)

Fossil fuels are still the most used until today where they are formed from plants and animals that lived up to hundreds of millions of years ago. By the time, the fossil fuels reserve have been reduced drastically since the industrial revolution era that consume the most of fuels. As a result, fossil fuels are considered non-renewable natural resources. Since the highest demand on the fuels, the alternative energy is needed to anticipate the limited supplies of fossil fuels. Currently, 85% of the world's energy consumption comes from fossil fuels, and this dependency is expected to continue in the next several decades.

In addition to the energy challenge, the world also currently faces problem on the climate challenge which caused by the pollution affect. The recent observed global warming shows that the increased CO_2 emissions as the exhaust gas has influenced the greenhouse affects. As the earth's surface radiates long wavelength radiation back to space, CO_2 and other greenhouse gases (H_2O, O_3, CH_4, NO, etc) absorb the infrared radiation and become vibrationally excited. Approximately 31% of the incoming solar radiation-mostly long wavelength in the infrared range is reflected by clouds, aerosol, atmospheric gases, and the surface. The radiation of 19% and 49% of the solar radiation have absorbed in the atmosphere and the earth's surface, respectively.

Hydrogen is one of the most abundant elements in the universe and can be found nearly everywhere including in waste materials. It is an energy source that could provide for the energy needs in countries with low carbon fuel resources and solve the environmental problems in those with high energy usage. However, fundamental issues such as storage and transportation must be addressed. Hydrogen is not a primary energy source like coal, oil, and natural gas that exist in nature. Rather, it is an energy alternative that can be obtained by processing a primary energy source. Hydrogen can be a viable alternative energy source if its production costs can be reduced to a competitive level. In-liquid plasma is created by the application of microwaves or other high-frequency waves. The gas temperatures of in-liquid

plasma can exceed 3000 K at atmospheric pressure. Under these conditions, nearly all organic and non-organic materials can be decomposed and any existing hydrogen in the processed materials (e.g., hydrocarbons) can be extracted. It has already been determined that hydrogen with a purity of 66% to 81% can be created by using plasma to decompose organic solvents and waste oils.

Synthesis gas (Syngas), a mixture of carbon monoxide and hydrogen, is important intermediate for various synthesizing chemicals and environmentally clean fuels, such as ammonia, methanol, methyl formate, acetic acid, dimethyl ether (DME), and methyl-tert-butyl ether (MTBE) and for the increasingly important production of synthesis liquid fuels. There are several processes available for syngas production depending on the feed stock, such as steam reforming, partial oxidation, autothermal reforming (ATR), gasification and a combination of them, which result in different H_2/CO ratio. Steam reforming is the conversion of hydrocarbons (HCs) with steam into a mixture of carbon monoxides, hydrogen, methane and unconverted steam. On the other hand, partial oxidation occurs while the hydrocarbons feed and oxidant are mixed in an inlet zone upstream the catalyst bed. The ATR was used to produced synthesis gas for ammonia production and methanol where combined combustion and catalytic process in an adiabatic reactor. Another syngas method is gasification which is one of the most promising technologies for converting coal and biomass into an easily transportable and usable fuel. The main gasification reactions are endothermic and the heat required to sustain the gasification is typically supplied by combustion of part of the carbonaceous material. During biomass gasification, several parameters such as gasifiers type, reaction temperature, biomass fuels properties, bed materials and gasifying agent have a substantial influence on product gas composition, carbon conversion efficiency and tar formation.

Recently, plasmas reforming have been investigated for their potential to exhibit catalytic effects primarily because of complex interactions of their excited species (electrons, ions, radicals) in fuel conversion reactions. Different paths have been investigated for the last two decades using various plasma technologies such as gliding arc, dielectric barrier discharge (DBD), corona and microwave (MW) to reform HCs such as methane, diesel and bio fuels.

The DBD is well known type of non-thermal plasma discharge. Two metal electrodes are separated by a thin layer of dielectric material in the DBD device which acts to limit current flow once the plasma discharge is ignited. DBD plasmas typically operate with either an AC frequency (0.5-500 kHz) or in a pulsed DC mode and most often have a non-uniform, filamentary structure consisting of a series of micro discharges. The next plasma method is corona discharge which usually involve two asymmetric electrodes, one high curvature, such as a plate or a cylinder. The electron temperature of corona plasma is in the range of 3.5 to 5 eV while the gas temperature is less than 400 K and the electron density is about 10^{15} to 10^{19} m^{-3}. However, high electron density mainly occupies the region around the high curvature electrode. Microwave discharge is another plasma method where it characterized by high density of electrons and active spices, such as ions and free radicals. Microwave plasmas can be operated in a wide range of pressure from milliTorr to near atmospheric; however, at high pressures, the discharge tends to contract and behave similar to thermal plasma. Thus, gliding arc method is constructed by two knives and the electrical are formed between them. The arc disappears at the end of the knives and a new discharge immediately re-formed at the initial locations.

The most mature technologies are reforming and gasification. Electrolysis coupled with renewable energy is near term low emission technology. Longer term technologies include biohydrogen, thermochemical water splitting, and photoelectrolysis. While significant progress has been made in development of these alternative hydrogen production systems, more technical progress and cost reduction needs to occur for them to compete with traditional large scale reforming technologies at this time. However, for smaller scale hydrogen production at distributed facilities the technologies, particularly electrolysis, may be cost competitive. In addition, it is important to note that hydrogen can be produced from a wide variety of feed stocks available almost anywhere. There are many processes under development which will have a minimal environmental impact.

Meanwhile, Plasma was generated within the bubble in-liquid. Two types of microwave in-liquid plasma apparatus are adopted for hydrogen production. One is a conventional MW oven, the other is a microwave generator with a waveguide to apply the in-liquid plasma steam reforming method in n-dodecane. A conventional microwave (MW) oven is used to irradiate at 2.45 (GHz) within liquid. The conventional MW oven has an output of 1260 W with only 750 W being used by the magnetron to generate plasma. Furthermore, in a separated system, 150 – 330 W of energy power was used by the steaming reforming method to generate plasma in the vessel reactor. For the experimental results of the MW oven, the hydrogen proportion of the generated gas was affected by the graphite concentration. Hydrogen was dominant in the gas produced, with the ratio around 58 to 90% of the total gas. By using a bubble control plate, the gas production rate could be increased up to 1.3 times. The gas production rate using steam reforming could be increased up to 1.4 times over that without using steam reforming. This indicates that steam reforming method was effective in producing hydrogen gas since the rate of hydrogen gas production is higher than that of using a conventional MW oven.

Finally, the steam feeding method when using in liquid plasma for decomposition of *n*-dodecane oil to produce hydrogen was significantly effective in increasing the hydrogen production rate over the method without steam. A single electrode positioned in the bottom center of a reactor vessel was utilized to generated plasma at its tip. The produced gas was measured and the composition of the produced gas was analyzed. The gas production rate using plasma by injecting steam at the same power consumption showed an increase of 1.4 times over that without using steam. Hydrogen production was dominant in the experimental results and amounted to 73 to 82% of the product gas. The maximum hydrogen production efficiency determined by the ratio of the enthalpy difference of the chemical reactions to the input energy was approximately 12%. The optimal EPR_{H2} is found to be 47% when the input power reaches 225 W and 250 W as well as when the gas generation rate reaches 10.5 cm^3/s and 12.5 cm^3/s. The hydrogen production efficiency using 2.45 GHz of microwave plasma can provide an improvement of 59% over that by alkaline water electrolysis for the same power consumption. This indicates that at present, the manufacturing costs remain high when used solely for hydrogen production.