CHEMICAL ENGINEERING TRANSACTIONS Volume 18, 2009
Editor Jiří Klemeš
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DOI: 10.3303/CET0918158

An Overview Of Solar Thermochemical Hydrogen, Carbon Nano-Materials And Metals Production Technologies

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This paper gives an overview of the solar thermochemical technologies for the production of hydrogen, marketable grade carbon black and metals with zero or near zero emission footprint. The paper also discusses carbon nanotubes (CNT) production from direct solar-cracking of methane. Process heat that is necessary to drive endothermic reactions for the production of hydrogen, carbon nanotubes and metals can be obtained from concentrated solar radiation, which eliminates or reduces green house and toxic gas emissions.

1. Introduction

The impending shortage of fossil fuels and environmental consequences of fossil fuel consumption for mainly power generation are two of the most imperative problems of the world. If we consider the solar radiation reaching our planet, although the intensity is not equally allocated, the majority of the world has solar energy as a consumable and accountable energy source. Since the fossil fuel resources is limited whereas the solar energy reserve is unlimited, the most logical way of searching an alternative source of energy before the fossil fuels are ran out is to go through an intermediate path by combining limited energy sources with unlimited ones until we find a permanent way of utilizing the unlimited solar energy.

Thermochemical hydrogen generation processes by means of active solar energy can be categorized under five main pathways: ***(1)*** Solar thermolysis, ***(2)*** Solar thermochemical cycles, ***(3)*** Solar reforming, ***(4)*** Solar cracking, and ***(5)*** Solar gasification (Steinfeld and Meier, 2004). The main difference between these processes is the source that they use to generate hydrogen. In solar thermolysis and solar thermochemical cycles, water is the source of hydrogen. As for solar reforming, solar cracking, and solar gasification, the feedstock is fossil fuels. Utilization of water as feedstock to solar thermally crack water molecules into hydrogen and oxygen requires a much higher process temperature than solar cracking of fossil fuels. For example, direct thermal splitting of water needs a process temperature higher than 2500K (Kodama, 2003), whereas methane

Please cite this article as: Ozalp N., Epstein M. and Kogan A., (2009), An overview of solar thermochemical hydrogen, carbon nanomaterials and metals production technologies, Chemical Engineering Transactions, 18, 965-970 DOI: 10.3303/CET0918158

decomposition starts about 700K and approaches to completion at about 1300K (Trommer et al., 2005). Although the high temperature need of thermochemical water splitting can be overcome in some processes, there are still application problems preventing them to be practical, such as the use of corrosive materials that lead into difficulty finding suitable reactor construction material (Kodama, 2003). As for the other low temperature water splitting processes, although hydrogen production is achieved at about less than 1200K, either the kinetics of the process was slow, or the amount of hydrogen production is very limited (Kodama, 2003). On the other hand, direct cracking of methane into hydrogen and solid carbon requires high temperatures to reach reasonable chemical conversion efficiency. Such high temperatures in the order of 2200K can be obtained by concentrating solar energy using heliostats and parabolic dishes.

2. Solar Radiation Concentration

The majority of the world receives more than 1500kWh/m^2 a year which can be concentrated up to the ratios of 10,000 suns (kW/m^2) with the current solar concentrating systems for steam and power generation (Kreith and Krieger, 1978). Considering that the solar energy reserve is unlimited, an intermediate path by combining fossil based energy sources with solar energy would be the best transition route on the way towards a permanent new energy economy. Concentration of solar energy for high temperature has been extensively studied since 1960s (Trombe, 1963; Klein et al., 1975; Beattie et al., 1983; Mills and Monger, 1992; Melchoir et al., in press). Concentrated solar energy is focused towards a solar reactor, where chemical reactions take place. High chemical conversion efficiencies are achievable with the advancement in solar reactor design and mode of operation.

There are mainly three optical configurations that can concentrate intermitted solar radiation for the required high temperature process heat: trough, tower, and dish. On the other hand, receivers depend on the optical configuration of choice. For example, a receiver could be a boiler or a reactor for the case of tower systems, whereas it could be a pipe as in the case of trough systems. It should be noted that the benefits of concentrating solar power are not only limited by their compelling environmental protection, but also diversity of fuel supply and global potential for technology transfer and innovation. Since the solar energy is abundant and free, this is basically the major advantage of the solar concentrating systems over conventional power generating systems relying on fuels that are neither free, nor abundant. However, developments in the field of energy storage are of particular importance to the maturation of solar power technologies.

3. Hydrogen Production Via Concentrated Solar Power

Currently, the primary means of hydrogen production in industry is the steam reforming of natural gas (Padro and Keller, 2005; Muradov and Veziroglu, 2005; Baade et al., 2001). The process is using natural gas combustion with air to obtain necessary high temperature to break the covalent chemical bonds between the carbon and hydrogen atoms involved in the methane molecule. Steam reforming of methane emits global and toxic emissions at the first step of the process from the boiler and ends up with CO_2 as a byproduct. It occurs via the following reaction:

$CH_4 + H_2O \rightarrow CO + 3H_2$, $\Delta H_{298}^0 = 206.25\ kJ/mol$ (1)

The syngas in (2) can be shifted via water-shift reaction to produce more hydrogen via:

$CO + H_2O \rightarrow CO_2 + H_2$, $\Delta H_{298}^0 = -41.03\ kJ/mol$ (2)

Solar thermochemical technology combines fossil fuels with solar energy for hydrogen generation. In traditional thermochemical technology, fossil fuels are combusted with air, which emits not only green house gases but also gases that contribute on the ozone layer depletion and acid rains. On the other hand, solar thermochemical technology offers either zero or lower hazardous gas emissions.

Solar reforming and solar gasification of hydrocarbons for hydrogen generation are basically the same processes as conventional steam reforming and gasification of fossil fuels, which occur via the following reaction:

$$C_xH_y + xH_2O \rightarrow xCO + \left(\frac{y}{2} + x\right)H_2 \quad (3)$$

Traditional hydrogen production, e.g. steam reforming of methane, is given as:

$CH_4 + H_2O \rightarrow CO + 3\ H_2$ (4)

In order to produce more hydrogen, the syngas (CO and H_2) is shifted via water-shift reaction, where water reacts with CO in the syngas generating carbon monoxide and hydrogen as in the following reaction:

$CO + H_2O \rightarrow CO_2 + H_2$ (5)

Then the carbon monoxide is released to the atmosphere or sequestrated. The CO_2 sequestration is an expensive and difficult process that involves multi process steps. Once the CO_2 is sequestrated, then it either has to be stored onsite or needs to transport to a location where it can be stored.

If steam reforming of methane is done via solar energy, then the CO_2 emissions from the first step of the process are eliminated. Because, in traditional steam reforming, the first step of the process is burning of fossil fuels with air to create high temperature heat necessary for splitting the methane molecule. However, the follow up steps of the process are exactly same as the traditional steam reforming. Therefore, although CO_2 emissions are omitted in the first step, it is not omitted at the last step.

In direct solar cracking of methane, high temperature process heat is obtained by concentrating solar energy. This avoids the toxic and global warming emissions. Direct cracking of methane is occurs via the following moderate endothermic reaction:

$CH_4 \rightarrow C\ (\text{solid}) + 2\ H_2$, $\Delta H_{298}^0 = 75\ kJ/mol$ (6)

Solid carbon produced by direct solar-cracking of methane is a high-grade industrial commodity (Dahl et al., 2004). High-grade carbon black is used in batteries, automotive tires, polymers, rubber etc. Since 0.75 kg carbon black is produced per kg natural gas cracked, solar cracking of natural gas is rewarded by carbon black production.

Methane dissociation requires high temperatures, e.g. starts around 700°C and completes around 1500°C (Hirsch et al., 2001). On the other hand, with the use of catalysts, methane decomposition can be achieved at lower temperatures.

For example, injection of micro-size carbon particles into the feedstock gas (methane) creates a high temperature core inside the reactor while the reactor walls and tubing are maintained at moderate temperatures compatible with present materials. Once the chemical bonds in methane molecule are broken, hydrogen gas can be easily separated from solid carbon. However, temperatures of above 1800 K are desirable to get reasonable kinetics and high-grade carbon, minimizing other organic byproducts. In order to obtain such high temperatures without emitting any hazardous gases, solar radiation concentrating technologies can be used.

To summarize, "endothermic processes that use fossil fuels exclusively as chemical reactants and solar energy as process heat yield cleaner fuels with a solar-upgraded calorific value. Thus, the mixing of solar and fossil energies could substantially reduce greenhouse gas emissions and become an important intermediate solution towards a sustainable energy supply system" (Hirsch et al., 2001).

4. CNT And Metal Production Via Concentrated Solar Power

Multi-walled carbon nanotubes were discovered in 1991 by Sumio Iijima using an arc-discharge evaporation method (Iijima, 1991), whereas single-walled carbon nanotubes were first observed in 1993 by (Iijima and Ichihashi, 1993) and (Bethune et al., 1993). Since their discovery, carbon nanotubes have attracted many researchers and considerable progress has been made using various production techniques. Currently, the CNTs are produced by different catalytic processes at moderate temperatures of a few hundreds degrees Celsius with poor production rates due to the limited surface coverage of the catalyst.

Recent comprehensive research works report nanotubes and other filamentous carbon production on supported catalyst in CH_4 cracking reactors. Iron (Takenaka et al., 2004), nickel and cobalt (Qian et al., 2004; Reshetenko et al., 2005) have been implemented as catalysts. Reported processes are carried out at moderate temperatures of 650-800°C and result in poor quantities of carbon products due to catalyst consumption from single layer coverage and its attachment to the product. On the other hand, volumetric production on spread carbon particles in the solar reactor with the aid of homogenous catalyst can be achieved by injecting catalysts laden with methane and decompose on the seeding particles. Recent research works show efforts to shift CNT production from methane cracking towards enhanced production modes while improving controllability of the processes and the quality of the CNT product. A pioneer work including implementation of catalyst floating technique was already published by Ci et al. on 2000, Lin et al. (2004) and Kuo et al. (2005) developed the technique of spreading the volatile iron pentacarbonyl ($Fe(CO)_5$) catalyst in a methane cracking reactor operated at about 1100-1150°C. The recent efforts at Weizmann Institute use a solar reactor and carbon fluidized particles as a basis for the metal catalyst and the growth of the CNT on this pioneering approach. The fluid dynamics simulations developed for our reactor prototype provide the residence time needed for the growth rate of the CNT. The reactor quartz window is protected from contact with incandescent carbon particles by maintaining inside the reaction chamber a certain flow pattern akin to the natural tornado phenomenon.

Thermochemical reduction of metallic oxides using concentrated solar energy can be performed with the methane feed resulting in carbon monoxide, hydrogen and metal according to:

$$ZnO + CH_4 \rightarrow Zn + 2H_2 + CO \qquad (7)$$

As a consecutive step, metal can be re-oxidized with water resulting with additional hydrogen or the metal can be utilized as a commodity. Alternatively, solid carbon from the solar cracking process can be used as a reducing agent in solar carbo-reduction of ZnO to produce the zinc metal and hydrogen via the following overall stoichiometric reaction:

$$ZnO+C \rightarrow Zn+CO+2H_2O \rightarrow ZnO+CO_2+2H_2 \qquad (8)$$

Therefore, solar cracking of methane and solar carbo-reduction of ZnO yield with valuable products, namely, additional hydrogen and zinc. Zinc can be used as long term storage of solar energy in the chemical form.

5. Summary and Conclusions

Utilization of fossil fuels as feedstock to solar thermally crack hydrocarbon molecules into hydrogen and other reaction products is achieved by reforming, cracking, and gasification processes, where concentrated solar radiation is used as high temperature process heat. The main difference between conventional fossil fuel decomposition by combustion and solar decomposition of fossil fuels is the source of process heat. Making use of concentrated solar radiation as process heat produces an environmentally favourable impact on the product composition of the decomposed fossil fuels by eliminating or reducing green house and toxic gas emissions. Therefore, consumption of fossil fuels and concentrated solar energy in hybrid fashion for hydrogen generation would help prolong available fossil fuel sources without further jeopardizing the current seriousness of the combustion related environmental problems.

Among the five thermochemical pathways of hydrogen generation from concentrated solar energy, solar cracking appears to be the most suitable candidate to take a role during the course of transition from today's fossil fuel energy economy to tomorrow's sustainable energy economy. Although solar reforming and solar gasification processes release carbon dioxide in the product gas composition, the hydrogen amount produced via these processes is more than that of solar cracking. Therefore, the solar cracking of natural gas is a compromise from hydrogen production amount to avoid carbon dioxide release. However, the advantage of solar cracking is the replacement of solid carbon as a product instead of carbon dioxide. Considering the fact that the world market for high grade black carbon is 0.6 million tonnes/year, then we can conclude that the solar cracking process offers two very valuable products that bring up the possibility of economical competition with the unit price of gasoline.

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