Dissertation

Hydrogen Production from n-Dodecane using Steam Reforming in-Liquid Plasma Method

液中プラズマを用いた水蒸気改質による
n-ドデカンからの水素製造

Andi Amijoyo Mochtar

Ehime University

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Chapter 1: Introduction

1.1 Research background

The main cause of energy problem is the world's dependency on fossil fuels as primary energy source. All fossil fuels used today are formed from plants and animals that lived up to hundreds of millions of years ago, during the same time period when dinosaurs lived. The time span required to make fossil fuels therefore exceeds the relatively short time scale of the human race. As a result, fossil fuels are considered non-renewable natural resources. On the other hand, economic growth and population increase necessitate an even higher energy demand in the future. The energy challenge is to address the future energy demand with limited supplies of fossil fuels.
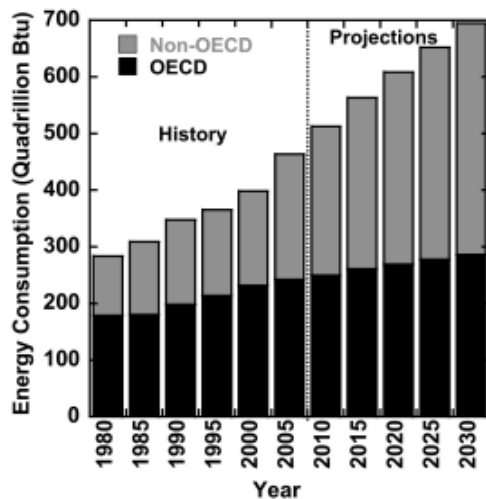
Fig. 1.1 World energy consumption, 1980-2030 [1]
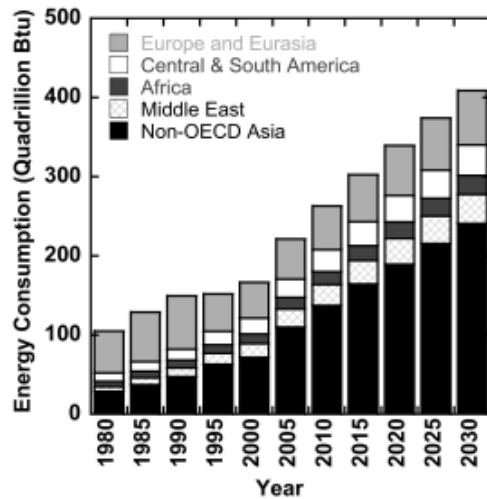
Fig. 1.2 Total non-OECD energy, 1980-2030[1]

Despite a limit in fossil supplies, its demand is expected to grow. Currently, 85% of the world's energy consumption comes from fossil fuels, and this dependency is expected to continue in the next several decades [1]. **Fig. 1.1** shows the total energy consumption from 1985 to 2030 in quadrillion (10^{15}) Btu per year (1 Btu = 1054 J) [1]. In 1980, the energy consumption was below 300 quadrillion Btu, but it expected to reach 700 quadrillion Btu in 2030. These data substantiate the energy problem-the world continues to depend on non-renewable fossil fuel supplies.

In addition to population growth, economic growth also contributes in the increasing energy demand. In **Fig. 1.2**, the histogram, is divided into two groups: countries in the Organization for Economic Co-operation and Development (OECD) and those outside of OECD. The rate of energy consumption increase for non-OECD countries for the past several decades and this trend is expected to continue in the next several decades.

These predictions of significant increase in energy demand as shown in **Fig. 1.1** and **Fig. 1.2** will likely occur unless countries around the world drastically alter their energy consumption habits. However, primary energy sources still remain finite. **Fig. 1.3 − 1.5** show proven reserves of oil, natural gas, and coal as of 2015 [2]. Even though finding more fossil fuel reserves is a possibility, the fact remains that fossil fuels are limited to finite quantities. This calls for urgent actions to reduce global energy consumption, to become less dependent on fossil fuels, and to find alternative sources of energy. This figures of proven reserves further illustrate an uneven distribution of current global energy supplies. The Middle East has most of the oil reserves and a large part of the natural gas reserves. Europe has a large share of the natural gas and coal. North America and Asia Pacific has a large share of coal. For

those countries that have direct access to reserves of fossil fuels from their own land mass or within their water boundary, finding alternative energy sources will ensure future energy security. For countries without a direct access to reserves of fossil fuels and therefore have to import them, finding alternative sources of energy has immediate economic and political benefits.
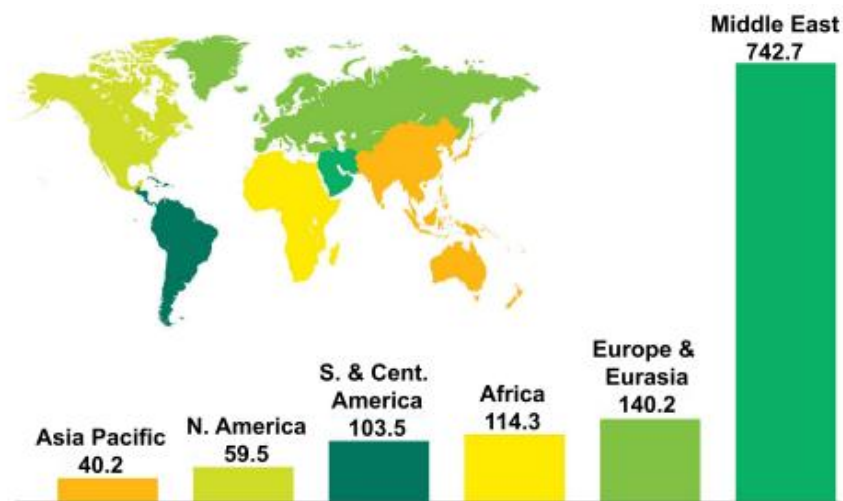
Fig. 1.3 Distribution of proven reserves of oil at the end of 2015 in billion barrels [2]
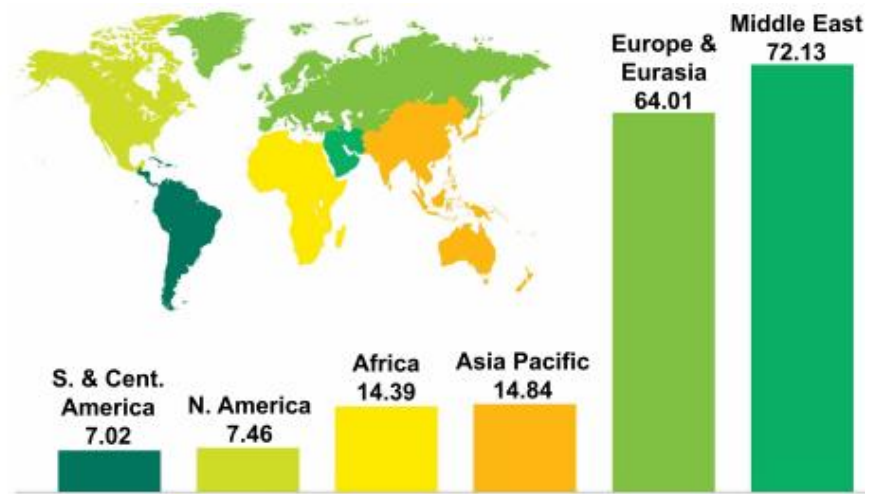
Fig. 1.4 Distribution of proven reserves of natural gas at the end of 2015 in trillion cubic meters [2]
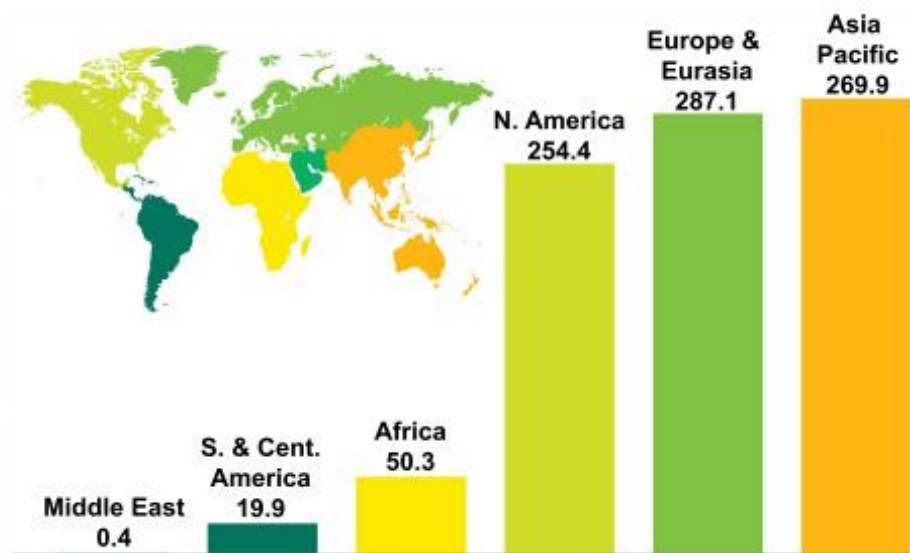
Fig. 1.5 Distribution of proven reserves of coal at the end of 2015 in billion tons [2]

1.2 Greenhouse effect

In addition to the energy challenge, the world also currently faces an equivalently grave problem-the climate challenge. There is still a few skeptics who attribute the recent observed global warming to the climate's natural cycle, but ample evidence has linked climate change to increased anthropogenic (man-made) CO_2 emissions. To understand this link, the greenhouse gas effect is examined.

Fig. 1.6 shows Kiehl and Trenberth's estimate of the energy balance [3]. 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 atmosphere absorbs 19% of the radiation and earth's surface absorbs the rest of the 49% of the solar radiation, mostly short wavelength in the visible spectrum. Earth maintains an energy equilibrium by radiating infrared radiation. Without greenhouse gases, the radiation would be lost to space and earth's temperature would be approximately 30K colder [4]. Therefore, greenhouse gases have a vital role in nature to maintain a comfortable range of temperature on this planet, making it a habitable place for human beings.

Since the industrial revolution, an increased use of fossil fuels has resulted in a significant increase in CO_2 emission in the atmosphere. In fact, CO_2 makes up the largest portion of anthropogenic greenhouse gas. The sharp increase in the world's CO_2 emissions from fossil fuels is shown in **Fig. 1.6**. Even though greenhouse gases exist in nature and are needed to maintain a comfortable temperature range on earth, an increased concentration creates an energy imbalance and causes climate change.
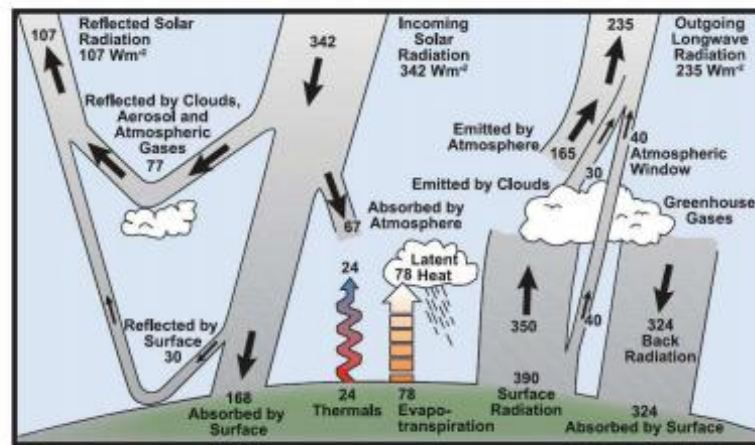
Fig. 1.6 Annual global energy balance [3]

In addition to CO_2, other greenhouse gases include H_2O, O_3, CH_4, NO and a trace amount of other gases [5]. In any combustion process of fossil fuels (hydrocarbon), the reaction takes place [6]:

$$C_nH_m + (n+\frac{m}{4})O_2 \rightarrow {}_nCO_2 + \frac{m}{2}H_2O + \text{heat} \qquad (1)$$
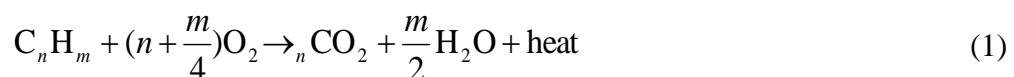
The burning of fossil fuels necessarily emits CO_2, which explains why CO_2 is the largest anthropogenic greenhouse gas emissions. As the earth's surface radiates long wavelength radiation back to space, CO_2 and other greenhouse gases absorb the infrared radiation and become vibrationally excited. When they relax, the total energy absorbed is released as infrared radiation in all directions, some is lost to space and some is directed back to earth, thus warming it.

In conclusion, the world's dependence on fossil fuels as the primary energy source presents a problem that two points. Firstly, fossil fuels are available in finite

supplies, and they cannot address increasing future energy demand. Secondly, burning of fossil fuels has an indirect consequence of causing climate change through the emission of CO_2. Therefore, to solve both the energy and climate challenges, the world must alter our energy consumption habits and must get rid of our dependency on fossil fuels.

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 [7–9]. 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 [10, 11].

Recycling of waste from organic and non-organic materials such as garbage, waste oil, or plastics can protect the environment by reducing waste, pollution, and green house effects. Processing organic and non-organic materials to produce hydrogen gas is a challenging task and has been the focus of much research [12–14]. In the past, clean hydrogen was mostly produced through electrolysis of water. However, since water is an extremely stable material, creating hydrogen from it requires a large amount of energy. Steam reforming of natural gas is another method that has been commercially used for generating large amounts of hydrogen [15–17]. This method, though, has the drawback of carbon dioxide being released in the final stage of the steam reforming reaction, which requires methods for capturing and

storing of the CO_2 [18, 19]. If the energy required to solidify the carbon is taken into consideration, this method may actually require as much, if not more, energy as the electrolysis method. Thermal plasma decomposition of methane gas is another method that has been developed to extract hydrogen without carbon dioxide emission. However, this method is not efficient because the amount of energy required for thermal cracking is approximately the same energy amount as the produced hydrogen [20]. For the thermal cracking method to gain popularity as a commercially viable system, the processing costs must be reduced and secondary value-added products should also be produced.

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 [21–24]. 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. The amount of hydrogen that can be produced from hydrocarbons can be equivalent to the amount produced from water, but the amount of energy consumed is much lower [25]. Moreover, carbon components can be simultaneously solidified using the in-liquid plasma method. Therefore, the in-liquid plasma technology solves the problems associated with both electrolysis and steam reforming.

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 [25, 26].This technology can also be applied for the collection of hydrogen from methane hydrides in sea beds [27–29]. In this research, it is proposed that a continuous flow, microwave-based in-liquid plasma device could be used as a method for continuously

producing hydrogen through the decomposition of waste oil. The effects of the pressure inside the device and the shape of the electrode on the hydrogen production rate were investigated.

1.2 The outline of the study

The dissertation comprises six chapters including two journal publications. The outlines of the chapter are as follows:

Chapter 1: It discusses the research background and also it describes shortly the influence of the fossil fuel for the green house effect.

Chapter 2: It gives a technical background and discuss the technologies available for synthesis gas production, specifically from reactor aspects. Further various plasma technologies are discussed.

Chapter 3: It is hydrogen production literature review. The purpose of this paper is to provide a brief summary of significant current and developing hydrogen production technologies. The areas to be examined include: hydrogen production using fuel processing technologies and, hydrogen from alternative resources such as waste oil.

Chapter 4: It provides information for the first journal publication. The in-liquid plasma method is a technology in which plasma of several thousand degrees Kelvin is generated within bubbles in a liquid. The purpose of this study is to enhance the hydrogen production rate from waste oils by using in-liquid plasma. Two types of microwave in-liquid plasma apparatus are adopted for hydrogen production. One is a conventional microwave (MW) oven, the other is a microwave generator with a waveguide to apply the in-liquid plasma steam reforming method in *n*-dodecane.

Chapter 5: It provides information for the second journal publication. The aim of this study is to analyze the effect of steam reforming on the hydrogen production rate from *n*-dodecane using microwave in-liquid plasma method. A steam feeding system was introduced into an in-liquid plasma reactor, and steam reforming of *n*-dodecane was carried out within the reactor vessel. The liquid medium used for plasma generation, was *n*-dodecane, a type of commercial reagent oil. The tip of a single electrode was positioned in the bottom center of the reactor vessel. The produced gas was trapped in a water filled container, and the gas production rate was measured. The gas was collected and analyzed using a gas chromatograph. The gas production rate by plasma with steam feeding was 1.4 times greater than that by plasma without steam feeding. The maximum hydrogen production efficiency indicated by the ratio of the enthalpy difference of the chemical reactions to the input energy was approximately 12%. At the optimal efficiency of hydrogen generation using 2.45 GHz of microwave plasma, the product gas is approximately 73% to 82% hydrogen, which means that the hydrogen production efficiency with this method is improved approximately 59% over that by alkaline water electrolysis for the same power consumption. The energy payback ratio （EPR_{H2}）of hydrogen production was also calculated in order to determine the hydrogen production efficiency.

Chapter 6: The general summary of all chapters is concluded and future works for the research is added.

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Chapter 2: Synthesis Gas

2.1 Introduction

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 [1]. Syngas with the desired composition ranging from the 3:1 mixture of hydrogen and nitrogen used for production of ammonia to the 1:1 mixture of hydrogen and carbon monoxide is preferred for production of DME, acetic acid or methyl formate [2]. Syngas can be produced from NG, petroleum coke, naptha, residual oil, coal and biomass, and even from organic wastes. Though significant quantities of syngas are being made from coal [3], NG is the largest source of syngas at present and its use for this purpose is growing because of its lowest cost routes and good environment performance [4]. In the recent years, the interest in the conversion of biomass derived resources to syngas and bio-oils has been increasing. These resources are currently being recognized as attractive options due to their renewable, reliable and CO2-neutral features.

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.

2.2 Steam reforming

Steam reforming is the conversion of hydrocarbons (HCs) with steam into a mixture of carbon monoxides, hydrogen, methane and unconverted steam. Steam reforming is carried out in several different types of reactors. Each of these may be optimized for specific applications [2]. The reactions taking place for the steam reforming process are given in **Table 2.1** along with the enthalpy of reaction. Reaction 1 (R1) and 3 (R3) in **Table 2.1** are the steam and CO2-reforming reactions, respectively, for methane and reaction 2 (R2) is the water gas shift (WGS) reaction, which takes place simultaneously. Reaction 4 (R4) is the steam reforming reaction of higher HCs. The enthalpy is given for steam reforming of *n*-heptane [2].

Table 2.1. Key reaction in steam reforming [2]

Reactions	Reaction description	Standard enthalpy of reaction $(\Delta_R H^o_{298}, kJmol^{-1})$	
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	Steam reforming	206	R1
$CO + H_2O \rightleftharpoons CO_2 + H_2$	WGS	-41	R2
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	CO_2 reforming	247	R3
$C_nH_m + nH_2O \rightleftharpoons nCO + (n + m/2)H_2$	Higher HCs steam reforming	1175^a	R4

^{a}For n-C_7H_{16}.

The overall steam reforming is highly endothermic and it is carried out at high temperature (1173 K) and at pressure between 15 and 30 bar [5] over a Ni/Al2O3 catalyst [6]. However, higher H2/CO ratio comes at the expense of high temperature requirements; methane is the most stable HC and requires energy input to react with steam. Methane steam reforming is thermodynamically favored at high temperatures and at high molar steam-to-carbon (S/C) ratios in the feed. Thermodynamic

predictions estimate 90% methane conversion at ca. 923 K, 1 bar and at a S/C ratio of 3, and complete conversions are estimated at temperatures in excess of 1073 K [7]. Steam can be partially substituted by carbon dioxide to perform CO2- reforming reaction (R3). This reduces the H2/CO ratio in the product gas, which in cases may be more economical, especially if a source of low-cost carbon dioxide is available. Steam (and CO2) reforming is always accompanied by the WGS reaction (R2) which is generally fast and may be considered in equilibrium at most conditions [8]. However, low S/C ratios lead to high methane concentration in the outlet. To compensate this, a higher temperature can be used [9]. In addition, carbon formation is a challenge in steam reforming processes. The potential for carbon formation is highest when S/C ratio is lower or under CO2-reforming. In steam reforming processes carbon formation is avoided through proper design of the catalyst and specific process conditions [2].

Steam reforming can be described by a first-order reaction, irrespective of pressure. At high temperatures the overall rate can be limited by pore diffusion, but at lower temperatures the molecular diffusion rate is much higher than the reaction rate so that the catalyst activity can be fully used [10]. The overall rate in steam reforming is typically limited by the rate of heat transfer through the tubes, the rate of heat transfer through the gas film surrounding the catalyst pellets and mass transport restrictions including film and pore diffusional effects. The commercial Ni-catalysts are often in the form of thick walled Raschig rings, with 16 mm in diameter and height, and a 6-8 mm hole in the middle. If the heat load per unit area is too high, the limits of such catalyst will be reached, and hence small particles will be necessary in

order to make use of more of the catalyst. Smaller particle will however lead to increase pressure drop [10].

2.3 Catalytic partial oxidation

The production of syngas based on heterogeneous catalytic reactions is normally referred to as CPO. The principle of CPO is illustrated in **Fig. 2.1**. The HC feed and the oxidant are mixed in an inlet zone upstream the catalyst bed. Syngas production via the CPO route proceeds through coupled exothermic oxidative reactions and endothermic reforming reactions in the same catalyst bed. This simultaneous occurrence of exothermic and endothermic reactions makes this process attractive since it offers the advantage of vastly reduced energy requirements. Possible reactions for methane CPO are summarized in **Table 2.2.**
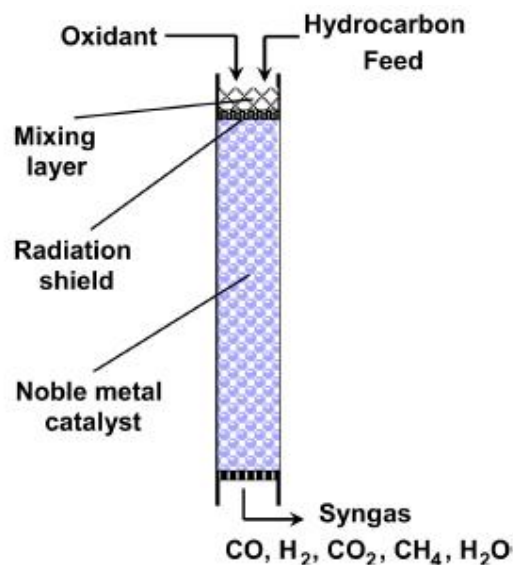
Fig. 2.1 CPO principle [2]

Table 2.2 Reactions in the HC partial oxidation system [11]

Reactions	Reaction description	Standard enthalpy of reaction $(\Delta_R H^o_{298}, kJmol^{-1})$	
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Combustion	-802.6	R5
$2CH_4 + O_2 \rightarrow 2CO + 4H_2$	Partial oxidation	-71.4	R6
$CH_4 + O_2 \rightarrow CO_2 + 2H_2$		-318.6	R7
$CO + H_2O \rightleftharpoons CO_2 + H_2$	WGS	-41	R2
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	Steam reforming	206	R1
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	CO_2 reforming	247	R3
$CO + H_2 \rightleftharpoons C + H_2O$		-131.3	R8
$CH_4 \rightleftharpoons C + 2H_2$	Methane decomposition	74.9	R9
$2CO \rightleftharpoons CO_2 + C$	Boudouard	-172.4	R10
$2CO + O_2 \rightleftharpoons 2CO_2$	Oxidation of CO	-566	R11
$2H_2 + O_2 \rightleftharpoons 2H_2O$	Oxidation of H_2	-483.6	R12

Partial oxidation reaction (R6) in **Table 2.2** can be seen as an example of direct route to syngas, and the question of whether it is possible to catalyze only R6 has been a keynote in the research on methane partial oxidation. Considering only R6, it is theoretically possible to produce pure syngas at all temperatures where methane and oxygen are activated. It is, however, typically observed that the remaining 10 overall reactions (R1-R3, R5, R8-R12) in **Table 2.2** play important roles in the CPO of methane and the product composition is therefore governed by or limited by the global thermodynamic equilibrium of all possible species [11]. In the indirect mechanism, at the top of the bed, all oxygen is consumed by the exothermic reaction with a portion of the methane in the feed. This region can be on the order of 10% of the total bed and is controlled by the O/C ratio and temperature. A temperature spike as well as localized hot spots promotes the formation of combustion products. The remaining methane is converted in the bottom portion of the catalyst bed through endothermic secondary reforming reactions with the unreacted methane and water

produced in the first region [12]. Gas compositions indicating higher conversions than thermodynamic equilibrium most likely reflects the temperature of the catalyst.

CPO has been investigated extensively for many years. Before 1992, most studies were carried out at moderate or low-space velocities at a residence time of 1s or above [13]. However, during the later years CPO has been carried out at least in the laboratory at very short contact times between 0.1 and 10 ms in some cases without preheating the feedstock and with no steam addition. Additional information regarding research, mainly of fundamental nature, can be found for example in a series of paper by Nogare et.al., [14, 15]. Both air and oxygen may in principle be used as oxidant in a CPO reactor. Experiments with CPO and air as oxidant have been conducted at the Topsoe pilot plant in Huston, Texas. In all cases, the methane conversion corresponds closely to the equilibrium of the methane steam reforming reaction [2].

2.4 Autothermal reforming

ATR has received a considerable attention. Lower capital cost, relative compactness, greater potential for economies of scale and its flexibility with respect to the product composition made ATR a very good alternative to steam reforming. From last decades, hydrogen-rich and carbon monoxide-rich syngas has been produced using ATR. Autothermal reformers were used to produce synthesis gas for ammonia production and methanol in 1950s and 1960s [2]. Low S/C ratio is beneficial for the production of carbon monoxide-rich syngas as feed for e.g., methanol or FT synthesis. S/C operation with a ratio of 0.6 has been demonstrated on pilot and industrial scale [2]. ATR is an adiabatic reactor where combined

combustion and catalytic process is carried out as illustrated in **Fig. 2.2**. The ATR reactor consists of a burner, a combustion chamber and a catalyst bed, all of which are contained in a refractory lined pressure shell. NG and steam mixture is partially converted by pressurized combustion in the combustion chamber under fuel-rich conditions. The temperature is about 1100- 1300 °C in the combustion chamber near the catalyst bed and more than 2500 °C in the flame core depending upon the process conditions [2]. Due to high temperature, steam reforming and WGS reactions also take place non-catalytically in the combustion chamber including radicals and combustion reactions. General reaction which are often used to represent the combustion chamber are shown in **Table 2.3**.
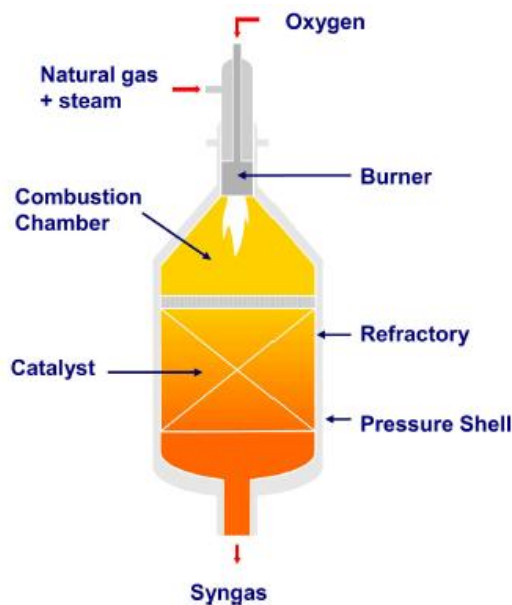
Fig. 2.2 Illustration of ATR reactor [16]

Table 2.3 Simplified reactions in the combustion chamber of ATR [2]

Reactions	Reaction description	Standard enthalpy of reaction $(\Delta_R H^o_{298}, kJmol^{-1})$	
$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$	Combustion	-519	R13
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	Steam reforming	206	R1
$CO + H_2O \rightleftharpoons CO_2 + H_2$	WGS	-41	R2

Combustion reactions quantitatively consume the oxygen. However, the methane conversion is incomplete in the combustion chamber and final conversion takes place in the catalyst bed according to described reactions (R1) and (R2) in **Table 2.3**. The syngas is at chemical equilibrium and leave the ATR reactor typically around 850-1100 ^oC [2]. There are three zones in the reactor: (a) combustion zone, (b) thermal zone and (c) catalytic zone. Mixing and burning of the feed streams take place in a turbulent diffusion flame in combustion zone. "Mixed is burnt" principal is valid, since the combustion reactions are exothermic and very fast. Combustion is sub-stoichiometric with overall oxygen to HC ratio of 0.55-0.6 in ATR but presented as a one-step model in a simplified way. Single reaction of CH_4 to CO and H2O with an O_2/CH_4 ratio of 1.5 (reaction (R13) in **Table 2.3**) take place in the flame zone. The local stoichiometry will vary from very fuel-lean to very fuel-rich in the flame zone [2]. The conversion of HCs takes place via homogeneous gas-phase reactions in thermal zone. Homogeneous gas-phase steam methane reforming and shift reaction (R1 and R2 in Table 2.3) are the main overall reactions taking place in the thermal zone. The methane steam reforming reaction (R1) does not proceed to equilibrium in the thermal zone [2]. HCs are finally converted via heterogeneous catalytic reactions in fixed-bed catalytic zone. Gas mixture will be in equilibrium with respect to steam

methane reforming (R1) and shift reaction (R2) at the exit temperature and pressure of the catalytic zone. ATR operation is soot-free under normal circumstances. The fuel rich combustion takes place in a turbulent diffusion flame and intensive mixing is required to prevent soot formation. The exit gas contains only methane as HC. Soot formation is avoided which would reduce the carbon efficiency of the process whereas soot particles would need to be removed from the syngas [2].

2.5 Gasification

Gasification is one of the most promising technologies for converting coal and biomass into an easily transportable and usable fuel. Transformation of biomass fuels into high quality energy carriers and other commercial products can be efficiently achieved via either biological or thermochemical processes [17]. Among various biomass conversion technologies within thermochemical and biochemical platforms, biomass gasification has received the highest interest since it offers high conversion efficiency and significant environmental benefits. In addition, it also increases options for combination with various high efficiency power generation systems using gas engines, gas turbines and fuel cells. Gasification is the formation of syngas from carbonaceous materials like coal and biomass by reaction with a gasifying agent like H_2O, H_2 or CO_2 [5, 18]. 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 (so-called autothermic gasification) [5]. In the known processes converting solid, carbonaceous feedstocks into fuel chemicals, the production and conditioning of the syngas does in fact constitute the dominant part of the plant cost. For the production of synthetic diesel fuel from coal in the fischer

tropsch (FT) process, the systems for syngas production entering the reactor compose

70% of the plant investment cost [8]. **Tables 2.4** and **2.5** summarize, respectively, the

dominant heterogeneous and homogeneous reactions taking place in the gasifiers.

For the reactions in **Table 2.4** the carbonaceous material is simply represented

as "C". In addition to the reactions in **Tables 2.4** and **2.5,** thermal gas phase cracking

of tar (larger HCs) and small HCs will also occur in the reactor [18]. These cracking

reactions will to some extent be facilitated by the gasification agent [18]. 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.

Table 2.4 Major heterogeneous reactions taking place in the gasifiers [5, 18]

Reactions	Reaction description	Standard enthalpy of reaction $(\Delta_R H^o_{298}, kJmol^{-1})$	
$C + CO_2 \rightleftharpoons 2CO$	Reverse boudouard	172.4	R14
$C + H_2O \rightleftharpoons CO + H_2$		131.3	R15
$C + 2H_2 \rightleftharpoons CH_4$	Methane formation	-74.9	R16
$2C + O_2 \rightleftharpoons 2CO$	Oxidation of CO	-221	R17
$C + O_2 \rightleftharpoons CO_2$	Coke gasification/oxidation of CO	-393.6	R18

Table 2.5 Major homogeneous reactions taking place in the gasifiers [5, 18, 19]

Reactions	Reaction description	Standard enthalpy of reaction $(\Delta_R H^o_{298}, kJmol^{-1})$	
$2CO + O_2 \rightleftharpoons CO_2$	Oxidation of CO	-566	R11
$2H_2 + O_2 \rightleftharpoons 2H_2O$	Oxidation of H_2	-483.6	R12
$CO + H_2O \rightleftharpoons CO_2 + H_2$	WGS	-41	R2
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	Methanation/hydrogenation	-206	R19
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Combustion	-802.6	R5

The reactors used for biomass gasification are quite diverse of which the design ultimately determines other parameters such as gasification temperature and the properties of the biomass used [20]. The most important gasifier types are: (a) fixed-bed (updraft or downdraft fixed-beds), (b) fluidized bed and (c) entrained flow gasifiers.

Fixed-bed gasifiers have been in use since the beginning of the gasification industry. Somewhat confusingly, these gasifiers are sometime also referred to as moving bed gasifiers. The solid feed moves downward through gasifiers but the various zones within the gasifiers are "fixed" in locations. These gasifiers have maintained a strong position in the broad range of reactor types used for coal gasification [8]. They are suitable for small scale applications and generally operated at temperature around 1000 °C [21]. The size of the fixed-bed reactors are below 1 MW in most designs. Increasing the reactor diameter might cause problems in establishing the required high temperature zones to crack the tar content in the product gas [22]. These reactors are further classified according to the flow direction of the gasification agent into updraft, downdraft and crossdraft gasifiers.

The entrained flow type of gasifiers is the most widely used design [8]. The gasifiers are co-current, plug flow reactors. Finely ground feed, in the case of solids, or liquid feed is introduced into the gasifiers along with the oxidant and steam or liquid water as moderator. Coal or biomass and gasses flow co-currently at high speed. As a result, very short gas residence times are experienced, and the gasification yields high temperatures in the gasifiers (1600 to 2200 K). The coal or biomass has to pulverized at high temperatures to ensure high carbon conversion. In addition, the fuel feeding allows for high pressure gasification and large capacities (>

100 MW). All entrained flow gasifiers are of the ash slagging type [8]. Typical

operating parameters of these gasifiers are provided in **Table 2. 6**.

Table 2.6 Comparison of typical operating for the three types of gasifiers, used for coal gasification [8]

Type	Pressure (bars)	Reactor temp. (K)	Exit temp. (K)	O_2 addition (kg/kg coal)	Particle diameter (mm)	Ash condition
Moving bed^a	25-30	1250-1350	700	0.5	20-50	Dry/slagging
Entrained flow	20-40	1600-2200	1300	0.9	<0.1	Slagging
Fluidized bed	10-30	1250-1400	1150	0.7	<.5−6	Dry/ agglomerating

^{a}Counter current operation.

2. 6 Plasma reforming

The above-mentioned well-established process were investigated under different

operating conditions in the presence of various catalysts, and it would appear that

almost all of the combinations have been evaluated and most of the strategies

examined [23]. The shortcomings of the conventional reformers concern size, large

investments, limitations on rapid response, the extreme operating conditions that

limit the lifetime of a reactor, heat management (during the front end of the catalyst

bed as the methane undergoes total oxidation), as well as safety and operability [24].

The alternative novel plasma reforming option could provide original responses to

these drawbacks in terms of reactivity, compactness, and efficiency. Recently,

plasmas 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. Some evidence has been found for the plasma

catalysis effect in lowering the required ignition temperatures for combustion

systems; however, more work is needed to elucidate the catalytic effects in fuel-rich syngas production systems [25].

Plasma is often described as the fourth state of matter and this refers to the chemical, thermal or electrical breakdown of a gas, often forming a luminous ionized state comprised of a mix of particles: positive and negative ions, electrons, radicals and neutral gas atoms and molecules [25]. Plasma reforming is electrically assisted reforming of fuel in which electrical energy is dissipated directly in the process gas through a specific high-voltage discharge [25]. Depending on the energy, temperature and ionic density, plasma reactors are classified as thermal or non-thermal (cold). A thermal plasma in a local thermodynamic equilibrium has an electron temperature (>10,000 K) in each small volume of plasma that is equal to the gas temperature, excluding the radiation temperature. In a non-thermal plasma, the electron temperature is not in the local thermodynamic equilibrium, and the electrons can reach a temperature of 104 to 105 K, while the temperature of the gas can be as low as room temperature (300 to 3000 K) [25].

Different paths have been investigated for the last two decades using various plasma technologies such as gliding arc [26–28], dielectric barrier discharge (DBD) [29], corona [25] and microwave (MW) [30–32] to reform HCs such as methane [24], [33], diesel [34] and bio fuels [35].

2.6.1 Dielectric barrier discharge

The DBD is a well known type of non-thermal plasma discharge. It is commonly used to generate the low-temperature plasma at atmospheric pressure, which has been successfully used to many industrial process related to the surface treatments of

materials such as polymers and textiles [36], ozone generation [37] and air sterilization in heating, ventilation and air conditioning (HVAC) systems [38]. In addition, some recent publications discuss the influence of DBD on pure methane [39] and mixtures of methane with air, oxygen and carbon dioxide [40], and aim mainly on the production of syngas, methanol or higher HCs. Furthermore, some basic studies dealing with methane steam reforming using DBD have been performed.

DBD plasmas have a layered electrode structure in which two metal electrodes are separated by a thin layer of dielectric material, often made from ceramic, quartz, or glass (**Fig. 2.3**). The dielectric barrier acts to limit current flow once the plasma discharge is ignited and prevents the discharge from transitioning into a plasma spark, which can result in much higher gas temperatures, shock waves and noise. 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. DBD plasmas are often used in basic research studies because they are weakly ionized, yet strongly non-equilibrium, and are relatively easy to construct [41].

The conversion of reactants was reported low and also the selectivity of the main products such as carbon monoxide and hydrogen was low compared to the conventional catalysis method [40, 42]. This mainly because of their low power density due to their limited current and low gas temperature. Since CPO and steam reforming reactions require an elevated initial temperature to proceed (800 to 1100 K), non-thermal DBD systems usually require additional energy to be spent for
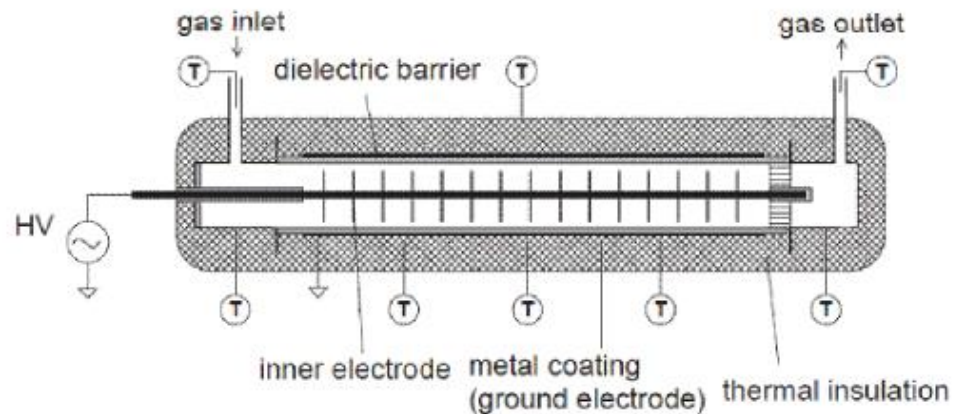
Fig. 2.3 Dielectric barrier discharge plasma [29]

reactant preheating in order to be effective. In addition, the irregular structure of DBD plasmas is not ideal for uniform gas treatment within fuel conversion systems [41]. However, many reports showed that the discharge can effectively lower the temperature range of the optimum catalyst performance [43].

2.6.2 Corona discharge

The corona discharge is another type of strongly non-equilibrium, yet weakly ionized plasma that can be found in nature during electrical storms near sharp edges, points, or thin wires (i.e., near regions of high electric field strength) [41]. They are actively studied in connection with their possible use for various plasma chemical applications such as ozone generation from air and oxygen, removal of toxic agents from flue gases and polluted air [44].

Corona discharge as shown in **Fig 2.4** is inhomogeneous discharge with low current density [45]. It could be generated at atmospheric pressure and has high electric field intensity for ionizing or decomposing feed gas particles. Corona
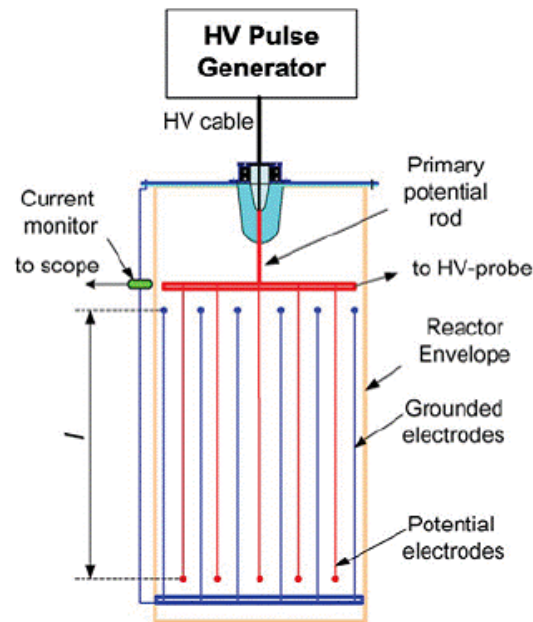
Fig. 2.4 Schematic diagram of corona discharge reactor [46]

discharge usually involves two asymmetric electrodes; one high curvature, such as a plate or a cylinder. When a voltage applied exceeds a certain value, the electric breakdown is caused near the high curvature electrode locally, and the corona discharge is brought on. 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} [45]. However, high electron density mainly occupies the region around the high curvature electrode. The corona discharge can become unstable if additional voltage or current is applied causing breakdown between electrodes and forming a strong plasma channel, known as a spark. Spark formation should be avoided because it causes local overheating of the gas as well as non-uniformity of treatment, which is undesirable for many applications [41].

2.6.3 Microwave discharge

MW discharges offer significant advantages as plasma sources. When properly designed, they are very stable and efficiency of MW power transfer to plasma can achieve almost 100%. They allow obtaining plasma of high purity. As a rule, MW plasmas are characterized by high density of electrons and active species, such as ions and free radicals [47]. Due to these features MW plasmas find applications in spectroscopy, technological process like surface treatment, carbon nano tubes synthesis and sterilization [48]. Special interest find MW discharges in different kind of gas processing, such as purification of gases, abatement of gases containing fluorinated compounds, decontamination of chemical warfare agents [49].

Fig. 2.5 shows the configuration of MW plasma reactor. These reactors have the unique advantage that the plasma does not need to be in direct contact with the electrodes. Electrode-less operation is often preferred for extremely high temperature reforming applications because it can eliminate the need for complicated electrode cooling. Initiating high-frequency plasma is more challenging than DC plasma because they require complex and somewhat more expensive power supplies that include a high frequency generator. More importantly, the plasma must be coupled and matched as a load in the power circuit [41]. In MW plasmas, the wavelengths are very small, on the order of centimeters and approach the dimensions of the reactor itself. Often, waveguides are used to collect and concentrate the electromagnetic waves in within the reactor. Not all of the wave power is dissipated in the discharge; however, typical about half is absorbed, a quarter of it is transmitted through the discharge and another quarter is reflected. The benefit of using complex discharges such as MW plasmas, is that the high degree of coupling between the,
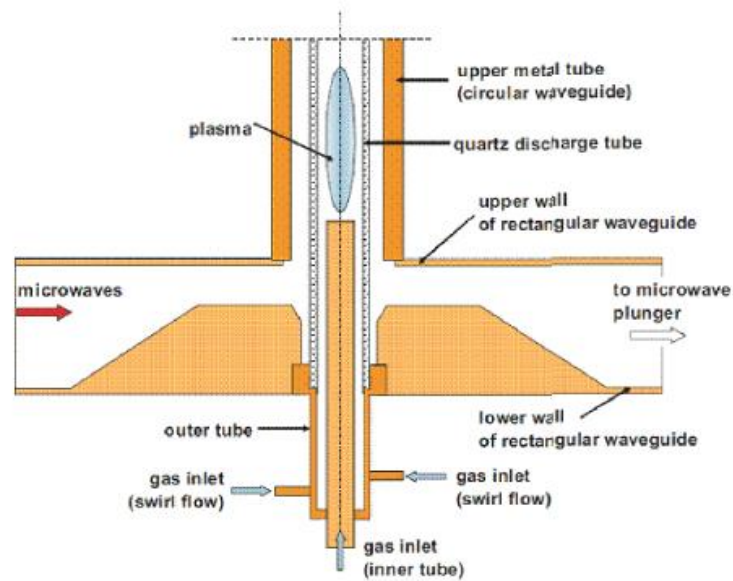
Fig. 2.5 Schematic diagram of microwave plasma reactor [49]

electromagnetic field and discharge creates conditions that are strongly non-equilibrium with a high degree of ionization. This is much better than the other non-thermal plasmas, where energy density is low and ionization is weak, with only a small fraction of high energy electrons created. MW 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 [41].

2.6.4 Gliding arc discharges

The principal of the GlidArc discharge was developed by Czernichowski [23]. **Fig. 2.6** shows the consists of two or more diverging metallic electrodes. The electrical are form between the two knives is powered by a single-phase transformer; the discharges are formed at the closest points of the electrodes, has a very short contact time and are spread by gliding along the edges of electrodes. The arc
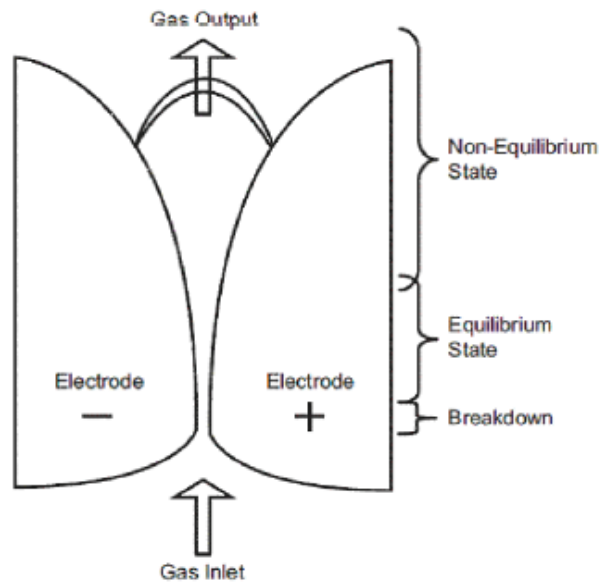
Fig. 2.6 Schematic of the planar gliding arc showing how the discharge is pushed and elongated by the gas flow, causing a transition from equilibrium to non-equilibrium state [41]

disappears at the end of the knives and a new discharge immediately re-formed at the initial locations. The high-voltage, self-maintained discharges struck directly across the gas flow. The electrodes are not cooled, so all of the electrical energy is directly and completely transferred to the process gas.

2.7 Conclusion

Steam reforming is the conversion of hydrocarbons (HCs) with steam into a mixture of carbon monoxides, hydrogen, methane and unconverted steam. Steam reforming is carried out in several different types of reactors. Steam reforming can be described by a first-order reaction, irrespective of pressure. At high temperatures the overall rate can be limited by pore diffusion, but at lower temperatures the molecular diffusion rate is much higher than the reaction rate so that the catalyst activity can be fully used. The production of syngas based on heterogeneous catalytic reactions is

normally referred to as CPO. The HC feed and the oxidant are mixed in an inlet zone upstream the catalyst bed. ATR has received a considerable attention. Lower capital cost, relative compactness, greater potential for economies of scale and its flexibility with respect to the product composition made ATR a very good alternative to steam reforming.

Gasification is one of the most promising technologies for converting coal and biomass into an easily transportable and usable fuel. Transformation of biomass fuels into high quality energy carriers and other commercial products can be efficiently achieved via either biological or thermochemical processes. Plasma reforming is electrically assisted reforming of fuel in which electrical energy is dissipated directly in the process gas through a specific high-voltage discharge. A thermal plasma in a local thermodynamic equilibrium has an electron temperature (>10,000 K) in each small volume of plasma that is equal to the gas temperature, excluding the radiation temperature. 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.

Corona discharge is inhomogeneous discharge with low current density. It could be generated at atmospheric pressure and has high electric field intensity for ionizing or decomposing feed gas particles. Corona discharge usually involves two asymmetric electrodes; one high curvature, such as a plate or a cylinder MW discharges offer significant advantages as plasma sources. Electrode-less operation is often preferred for extremely high temperature reforming applications because it can eliminate the need for complicated electrode cooling. Initiating high-frequency plasma is more challenging than DC plasma because they require complex and

somewhat more expensive power supplies that include a high frequency generator. In GlidArc, the arc disappears at the end of the knives and a new discharge immediately re-formed at the initial locations. The high-voltage, self-maintained discharges struck directly across the gas flow.

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Chapter 3: Background of Hydrogen Production

3.1 Introduction

Light vehicles are responsible for a significant amount of carbon dioxide and volatile organic compound (VOC) emissions, and a majority of carbon monoxide and nitrogen oxide (NOX) emissions produced in the U.S [1]. To deal with these issues, there has been an effort to diversify our energy supply particularly for the transportation sector and to find cleaner fuels. But alternative fuels are not available everywhere—one location may prefer ethanol, another may be dominated by biodiesel, or gasoline, or methane. Most of these fuels require a different engine technology for efficient operation. However, hydrogen can be produced from all of these feedstock as well as many others making it a universal fuel. Recently there has been international attention on the development of new hydrogen technologies as a potential solution to the current fears and to increase energy and economic security. The targeted hydrogen cost is $2–4 kg.l (energy equivalent of 1 gallon of gasoline) delivered [2]. In addition to using the hydrogen from these processes as energy directly in fuel cells, the hydrogen rich streams can be used for the production of gasoline, methanol, ethanol, and other high value chemicals. **Fig. 3.1** shows the conceptual flow sheet of hydrogen production technologies.

The purpose of this paper is to provide a brief summary of significant current and developing hydrogen production technologies. The areas to be examined include: hydrogen production using fuel processing technologies and, hydrogen from alternative resources such as waste oil.
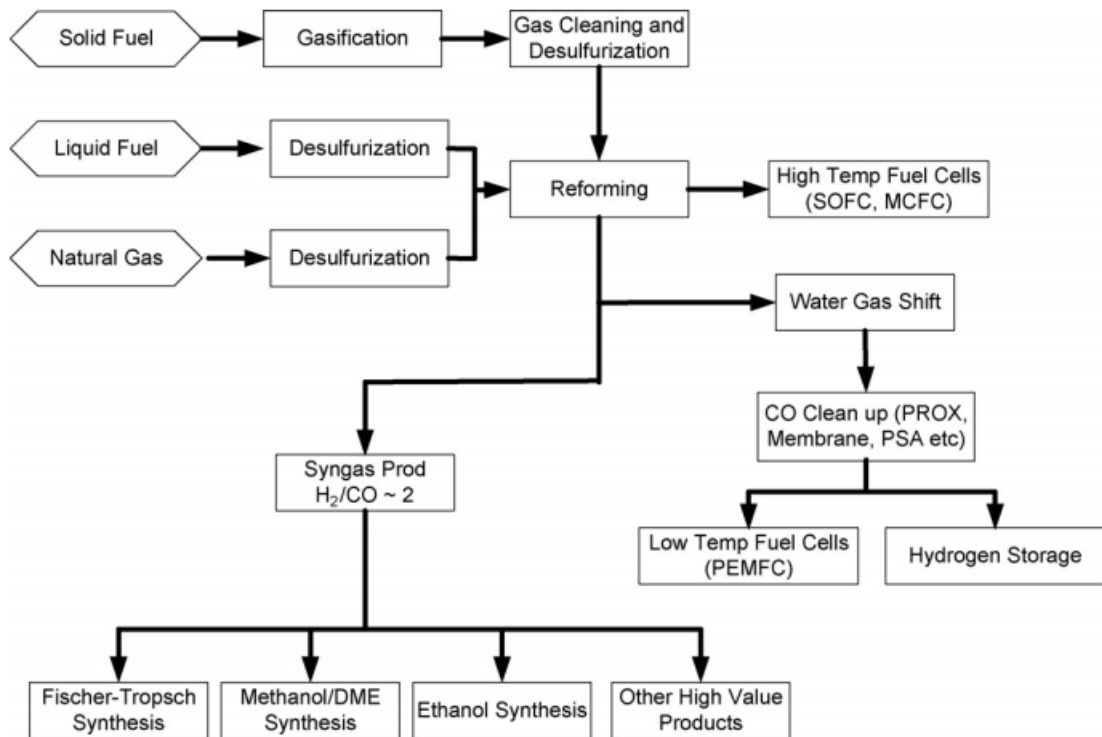
Fig. 3.1 Fuel processing of gaseous, liquid, and solid fuels for hydrogen production [2]

3.2 Fuel processing

Fuel processing technologies convert a hydrogen containing material such as gasoline, ammonia, or methanol into a hydrogen rich stream. Fuel processing of methane is the most common hydrogen production method in commercial use today. Most hydrocarbon fuels contain at least some amount of sulfur which poisons the fuel processing catalyst. This presents perhaps the biggest challenge to reforming. As a result, desulfurization will also be discussed. In addition, hydrocarbon reforming, plasma reforming, aqueous reforming, and pyrolysis will also be presented.

3.2.1 Hydrocarbon reforming

There are three primary techniques used to produce hydrogen from hydrocarbon fuels: steam reforming, partial oxidation (POX), and auto thermal reforming (ATR). **Table 3.1** summarizes the advantages and challenges of each of these processes. The reforming process produces a gas stream composed primarily of hydrogen, carbon monoxide and carbon dioxide. Endothermic steam reforming of hydrocarbons requires an external heat source. Steam reforming does not require oxygen, has a lower operating temperature than POX and ATR, and produces the reformate with a high H_2/CO ratio (3:1) which is beneficial for hydrogen production. However, it does have the highest emissions of the three processes. Partial oxidation converts hydrocarbons to hydrogen by partially oxidizing (combusting) the hydrocarbon with oxygen. The heat is provided by the ''controlled'' combustion. It does not require a catalyst for operation, has minimal methane slip, and is more sulfur tolerant than the other processes. The process occurs at high temperatures with some soot formation and the H_2/CO ratio (1:1 to 2:1) is favored for the feeds to hydrocarbon synthesis reactors such as Fischer-Tropsch. Auto thermal reforming uses the partial oxidation to provide the heat and steam reforming to increase the hydrogen production resulting in a thermally neutral process. Auto thermal reforming is typically conducted at a lower pressure than POX reforming and has a low methane slip. Since POX is exothermic and ATR incorporates POX, these processes do not need an external heat source for the reactor. However, they require either an expensive and complex oxygen separation unit in order to feed pure oxygen to the reactor or the product gas is diluted with nitrogen. Steam reforming is typically the preferred process for hydrogen production in industry [3]. Since all three processes produce

large amounts of carbon monoxide, one or more water-gas-shift (WGS) reactors – typically a high temperature reactor and low temperature reactor – are used. The high temperature (larger than 350°C) reactor has fast kinetics, but is limited by thermodynamics to the amount of carbon monoxide that can be shifted. Therefore, a lower temperature reactor (210–330°C) is used to convert the carbon monoxide to a lower level. High temperature WGS reactors commonly use an iron catalyst, and lower temperature reactors often use a copper catalyst [3].

a. Hydrocarbon reforming reactions

The reforming, WGS, and oxidation reactions can be generalized as follows for hydrocarbon and methanol fuels [4]:

Steam reforming

$$C_mH_n + mH_2O = mCO + (m + \tfrac{1}{2}n)H_2$$
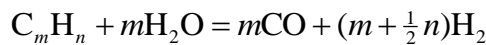
ΔH = hydrocarbon dependent, endothermic (2)

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad \Delta H = +49 \text{ kJ/mol} \qquad (3)$$

Partial oxidation

$$C_mH_n + \tfrac{1}{2}mO_2 = mCO2 + \tfrac{1}{2}nH_2$$
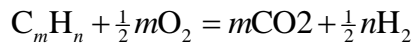
ΔH = hydrocarbon dependent, exothermic (4)

$$CH_3OH + \tfrac{1}{2}O_2 = CO_2 + 2H_2 \qquad \Delta H = -193.2 \text{ kJ/mol} \qquad (5)$$

Autothermal reforming

$$C_mH_n + \tfrac{1}{2}mH_2O + \tfrac{1}{4}mO_2 = mCO + (\tfrac{1}{2}m + \tfrac{1}{2}n)H_2$$
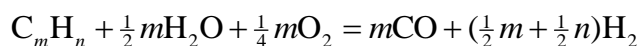
ΔH = hydrocarbon dependent, thermally neutral (6)

$$4CH_3OH + 3H_2O + \tfrac{1}{2}O_2 = 4CO_2 + 11H_2 \qquad \Delta H = 0 \qquad (7)$$

Carbon (coke) formation

$$C_mH_n = xC + C_{m-x}H_{n-2x} + xH_2$$

ΔH = hydrocarbon dependent $\hspace{8cm}$ (8)

$$2CO = C + CO_2 \hspace{4cm} \Delta H = +172.4 \text{ kj/mol} \hspace{1cm} (9)$$

$$CO + H_2 = C + H_2O \hspace{7cm} (10)$$

Water-gas-shift

$$CO + H_2O = CO_2 + H_2 \hspace{3cm} \Delta H = \text{-41.1 kj/mol} \hspace{1cm} (11)$$

$$CO_2 + H_2 = CO + H_2O \,(RWGS) \hspace{5cm} (12)$$

CO oxidation

$$CO + O_2 = CO_2 \hspace{4cm} \Delta H = +283 \text{ kj/mol} \hspace{1cm} (13)$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O \hspace{4cm} \Delta H = \text{-242 kj/mol} \hspace{1cm} (14)$$
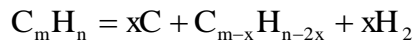
The enthalpies are reported at ambient temperature and pressure with reactants and products in the gas phase. **Table 3.1** shows the comparison of reforming technology using steam reforming, autothermal reforming and oxidation.

Fuel processing reactors are designed to maximize hydrogen production (Eqs. (2)–(7) and (11)–(13)) and minimize carbon formation (Eq. (8)–(10)) using appropriate operating conditions (temperature, pressure residence time, etc.) and catalysts [7, 13]. **Table 3.2** lists the minimum reaction temperatures required for minimizing carbon formation, using iso-octane reforming as an example.

Table 3.1 Comparison of reforming technologies [9, 10]

Technology	Advantages	Disadvantages
Steam reforming	Most extensive industrial experience Oxygen not required Lowest process temperature Optimal H_2/CO ratio for H_2 production	Highest air emissions
Autothermal reforming	Lower process temperature than POX	Limited commercial experience
Partial oxidation	Low methane slip Decreased desulfurization requirement No catalyst required Low methane slip	Requires air or oxygen Low H2/CO ratio Very high processing temperatures Soot formation/handling adds process complexity

Table 3.2 Minimum reaction temperatures required for avoiding coke formation during iso-octane reforming at thermodynamic equilibrium [7, 11, 12]

Reactants	Technology	Oxygen/carbon ratio	Minimum temperature to avoid coke formation (°C)
$C_8H_{18}+4(O_2+3.76N_2)$	POX	1	1180
$C_8H_{18}+2(O_2+3.76N_2)+4H_2O$	ATR	1	1030
$C_8H_{18}+8H_2O$	SR	1	950
$C_8H_{18}+4(O_2+3.76N_2)+8H_2O$	ATR	2	575
$C_8H_{18}+8H_2O$	SR	2	225

❖ **Steam reforming.**

Fuel processing requires modest temperatures (180°C for methanol, DME, and other oxygenated hydrocarbons that can be readily activated, and 500°C for most conventional hydrocarbons) [7, 13]. The catalysts can be divided into two types: non-precious metal (typically nickel) and precious metals from Group VIII elements (typically platinum or rhodium based). Due to severe mass and heat transfer limitations, conventional steam reformers are limited to an effectiveness factor for the catalyst which is typically less than 5%. Therefore, kinetics and thus the activity of the catalyst are rarely the limiting factors with conventional steam reformer

reactors, so less expensive nickel catalysts are used almost universally in industry. The mass and heat transfer limitations have been shown to be overcome by employing micro channel-based reactors, enabling intrinsic kinetics of steam reforming to be exploited [10]. In these systems, the noble Group VIII metals, particularly Rh [11], are preferred since they exhibit much higher specific activities than nickel catalysts [13, 16]. However, the high cost of Rh is driving some researchers to develop alternative catalysts such as Co-based catalysts [17, 18]. Intermediate and high temperatures required for steam reforming may promote carbon formation, and steam to carbon ratios (2.5 or higher) higher than stoichiometry are required to gasify coke when a nickel-based catalyst is used. Coke formation is much less over the noble Group VIII metals. Promoters, such as magnesia or potassium or other alkaline components, are added to the catalyst support to minimize the coke formation. Steam reforming is commonly used in industry for the production of hydrogen from methane where high thermal efficiencies of up to approximately 85%, based on the higher heating values, have been achieved.

❖ **Partial oxidation**

Partial oxidation (POX) of hydrocarbons and catalytic partial oxidation (CPOX) of hydrocarbons have been proposed for use in hydrogen production for automobile fuel cells and some commercial applications [19–21]. The non-catalytic partial oxidation of hydrocarbons in the presence of oxygen typically occurs with flame temperatures of 1300–1500 °C to ensure complete conversion and to reduce carbon or, in this case, soot formation [12]. Catalysts can be added to the partial oxidation

system to lower the operating temperatures. However, it is proving hard to control temperature because of coke and hot spot formation due to the exothermic nature of the reactions [19, 20, 22, 23]. For natural gas conversion, the catalysts are typically based on Ni or Rh; however, nickel has a strong tendency to coke and Rh cost has increased significantly. Krummenacher et al. [16] have had success using catalytic partial oxidation for dodecane, hexadecane, and diesel fuel. The high operating temperatures (800°C - 1000°C) [16] and safety concerns may make their use for practical, compact, portable devices difficult due to thermal management [20]. Typically the thermal efficiencies of POX reactors with methane fuel are 60–75%, based on the higher heating values [20].

❖ **Autothermal reforming.**

Autothermal reforming adds steam to catalytic partial oxidation. It consists of a thermal zone where POX or CPOX is used to generate the heat needed to drive the downstream steam reforming reactions in a catalytic zone [11, 12]. Therefore the temperature profile in the reactor is characterized by a sharp rise in the thermal zone, and then the temperature steadily decreases in the catalytic zone due to the endothermic reactions. The heat from the POX negates the need for an external heat source, simplifying the system and decreasing the start-up time. A significant advantage for this process over SR is that it can be stopped and started very rapidly while producing a larger amount of hydrogen than POX alone. For ATR to operate properly both the oxygen to fuel ratio and the steam to carbon ratio must be properly controlled at all times in order to control the reaction temperature and product gas composition while preventing coke formation [11, 12]. There is some expectation

that this process will gain favorability with the gas–liquids industry due to favorable gas composition for the Fischer-Tropsch synthesis, ATR's relative compactness, lower capital cost, and potential for economies of scale [6]. For methane reforming the thermal efficiency is comparable to that of POX reactors 60–75%, based on the higher heating values, and slightly less than that of steam reformers [21].

❖ **Preferential oxidation and water-gas-shift**

The reforming process produces a product gas mixture with significant amounts of carbon monoxide, often 5% or more [18]. To increase the amount of hydrogen, the product gas is passed through a water-gas-shift reactor to decrease the carbon monoxide content while increasing the hydrogen content. Typically, a high temperature is desired in order to achieve fast kinetics, but results in high equilibrium carbon monoxide selectivity and decreased hydrogen production. Therefore, the high temperature WGS reactor is often followed by a low temperature reactor to decrease CO content to 1% or less. TeGrotenhuis et al. [22] have demonstrated the potential of using micro reactors to build a gradient temperature WGS reactor that contains the high temperature WGS and low temperature WGS in a single unit. The most common catalyst for WGS is Cu based [18], although some interesting work is currently being done with molybdenum carbide [23], platinum-based catalysts [24], and Fe–Pd alloy catalysts [25]. To further reduce the carbon monoxide, a preferential oxidation reactor or a carbon monoxide selective methanation reactor can be used [18]. Sometimes the term selective oxidation is used in place of preferential oxidation, but this is misleading. Selective oxidation refers to carbon monoxide reduction within a fuel cell, typically a PEMFC; whereas preferential oxidation

occurs in a reactor external to the fuel cell. The POX and methanation reactors each have their advantages and challenges. The preferential oxidation reactor increases the system complexity because carefully measured concentrations of air must be added to the system [18]. However these reactors are compact and if excessive air is introduced, some hydrogen is burned. Methanation reactors are simpler in that no air is required; however, for every carbon monoxide reacted, three hydrogen molecules are consumed. Also, the carbon dioxide reacts with the hydrogen, so **Table 3.2** Minimum reaction temperatures required for avoiding coke formation during isooctane reforming at thermodynamic equilibrium [7, 12, 13, 22] Reactants Technology Oxygen/ carbon ratio Minimum temperature to avoid coke formation (8C) C8H18 + 4(O2 + 3.76N2) POX 1 1180 C8H18 + 2(O2 + 3.76N2) + 4H2O ATR 1 1030 C8H18 + 8H2O SR 1 950 C8H18 + 4(O2 + 3.76N2) + 8H2O ATR 2 575 C8H18 + 8H2O SR 2 225 J.D. Holladay et al. / Catalysis Today 139 (2009) 244–260 247 careful control of the reactor conditions need to be maintained in order to minimize unnecessary consumption of hydrogen. Currently, preferential oxidation is the primary technique being developed. The catalysts for both these systems are typically noble metals such as platinum, ruthenium, or rhodium supported on Al_2O_3 [18]. Alternatively, a membrane (ceramic or more commonly a palladium alloy) or pressure swing adsorption can be used to produce high purity (99.999%) hydrogen.

3.2.2 Desulfurization

Current hydrogen production comes primarily from processing natural gas, although with the substantial advances in fuel cells there is increased attention to other fuels such as methanol, propane, gasoline, and logistic fuels such as jet-A,

diesel, and JP8 fuels. With the exception of methanol, all of these fuels contain some amount of sulfur, with the specific sulfur species dependent on the fuel type and source. The typical approaches to organo-sulfur removal can be categorized as chemical reaction technologies and adsorptive technologies. Chemical reaction approaches include hydrodesulfurization (HDS) and alkylation. Most commercial large-scale applications use HDS; therefore, substantial process and catalyst optimization has occurred. In this process, HDS catalysts partially or completely hydrogenate the sulfur-bearing molecules, resulting in a release of sulfur as H_2S [30–32]. The second chemical reaction approach, selective alkylation of organo-sulfur molecules, has been demonstrated at the pilot scale, but to date it has not been implemented on a large commercial scale. This technology increases the molecular weight of the sulfur bearing molecules which increases their boiling point. This enables distillation approaches to remove the sulfur. This approach does not require high-pressure hydrogen, which is a potential advantage over HDS. However, the olefin content in the fuel will vary, and it may be necessary to intentionally add olefins (or alcohols) to the fuel to convert all the sulfur-bearing molecules and to achieve the desired physical and chemical characteristics of the fuel. There is some evidence that alkylation process may occur on a limited basis in the course of HDS operation [31, 32]. As the name implies, adsorptive approaches employ adsorbents for sulfur removal from the fuel. Most often this is achieved by (1) adsorption of the entire sulfur containing molecule in activated carbon, modified zeolites or other materials or (2) adsorption onto metal surfaces such as nickel, wherein nickel sulfide is formed, and the remainder of the hydrocarbon is recovered [30–32]. The former approach is conceptually quite simple to operate, as it can in principle be carried out

at ambient temperature and pressure using conventional fixed-bed equipment. The other approach is more complicated, requiring a fluid bed operating at elevated temperatures and pressures. Adsorptive approaches suffer from limited capacity of the material. Adsorbent implementation to hydrocarbon fuels with high levels of sulfur such as JP-8 and diesel would require significant quantities of adsorbent, dual beds (to allow simultaneous adsorption and regeneration) with switching between beds, as well as significant logistical issues associated with disposal of spent adsorbents. For low sulfur fuels (50 ppm sulfur) such as natural gas, adsorbent technologies can make sense depending on the adsorbent capacity and the reactor's capacity. For gas phase sulfur, such as contained in natural gas, activated carbon is the absorbent of choice [26]. Finally, the sorbent materials tend to be very selective to the types of sulfur containing molecules they adsorb. Therefore, a cocktail approach may be necessary to ensure that all the sulfur is removed.

3.2.3 Pyrolysis

Pyrolysis is another hydrogen-producing technology where the hydrocarbon is decomposed (without water or oxygen present) into hydrogen and carbon [29]. Pyrolysis can be done with any organic material [30] and is used for the production of hydrocarbons and carbon nano tubes and spheres [31]. Since no water or air is present, no carbon oxides (e.g., CO or CO_2) are formed, eliminating the need for secondary reactors (WGS, POX, etc.). Consequently, this process offers significant emissions reduction. However, if air or water is present, for example the materials have not been dried, and then significant CO_2 and CO emissions will be produced. Among the advantages of this process are fuel flexibility, relative simplicity and

compactness, clean carbon by-product, and reduction in CO_2 and CO emissions [33, 34, 36–38]. The reactions can be written in the following form [29]:

$$C_n H_m \rightarrow nC + \tfrac{1}{2} m H_2 \tag{15}$$

One of the challenges with this approach is the potential for fouling by the carbon formed, but proponents claim this can be minimized by appropriate design. Since it has the potential for lower CO and CO_2 emissions and it can be operated in such a way as to recover a significant amount of the solid carbon which is easily sequestered [33, 37, 38], pyrolysis may play a significant role in the future.

3.2.4. Plasma reforming

In plasma reforming the overall reforming reactions are the same as conventional reforming; however, energy and free radicals used for the reforming reaction are provided by a plasma typically generated with electricity or heat [39–44]. When water or steam is injected with the fuel, H, OH, and O radicals in addition to electrons are formed, thus creating conditions for both reductive and oxidative reactions to occur [41]. Proponents maintain that plasma reforming overcomes many limitations of conventional techniques such as cost and deterioration of the catalysts, size and weight requirements, sluggish response, and limitations on hydrogen production from heavy hydrocarbons [40, 44]. In addition, they can also be configured to operate at lower temperatures than traditional reforming [40, 44, 46]. In the cases where no catalysts are used to assist the reforming, the process is highly sulfur tolerant [40, 44, 46]. The main reported disadvantages include the electrical

requirements and high electrode erosion at elevated pressures [40]. Plasma reforming technologies have been developed to facilitate POX, ATR and steam reforming, with the majority of the reactors being POX and ATR [38]. There are essentially two main categories of plasma reforming: thermal and non-thermal [38]. In thermal plasma reforming a high electric discharge is used. A great deal of power is consumed in raising both the electrons and the neutral species to a very high temperature (5000–10,000 °C). Even more power is required to cool the electrodes to stop the metals from vaporizing at these high temperatures [42, 44]. Fig. 2 shows methane conversion as a function of power input for a thermal plasma reactor [40]. This technology has been demonstrated in pyrolysis processes, and (with and without catalysts) in steam reforming, ATR and POX processes [40]. Conventional reforming catalysts (nickel-based with alumina support) have been explored [40]. Reduction in power consumption is a significant challenge for this technology [38].

In non-thermal plasmas, only the electron temperatures are increased to high temperatures (5000°C), while the bulk species temperature does not increase significantly [39, 40, 42, 44, 47]. Since only the electrons are directly excited, only a few hundred watts of power are required [38]. Four types of non-thermal plasma reformers have been described in the literature: gliding arc plasma, dielectric barrier discharge (DBD), microwave plasma, and corona discharge [39, 40, 42, 47].

The first three use dynamic discharge to create the plasma (**Fig. 3.2** of sliding arc discharge example), while the corona discharge generates the plasma with a static discharge [38]. The chief differences between these technologies is how the current and discharge power are controlled via the power supply, flow rate and design. In the
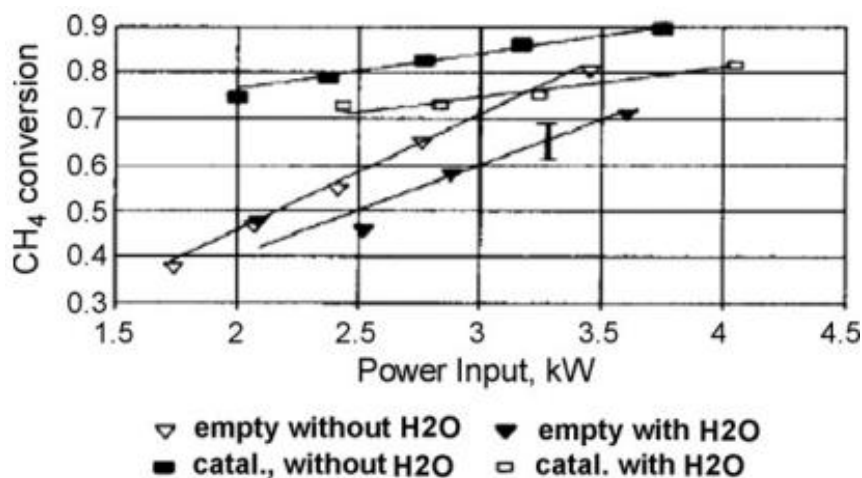
Fig. 3.2 Methane conversion as a function of power input. Empty reactor: plasmatron air = 0.4 g/s, fuel = 0.27 g/s, additional air = 0.7 g/s. In the case of water addition, 0.2-0.5 g/s H_2O added. Catalytic case: plasmatron air = 0.35 g/s, fuel = 0.25-0.5 g/s, additional air = 0.5-1 g/s. In the case of water addition, 0.5-0.8 g/s water. [40]

gliding arc plasma the reactor has two diverging electrodes down the length of the reactor [42, 44]. An arc is formed where the gas enters by applying a high voltage. The gas pushes the arc down the length of the reactor. As the gas reaches the end of the reactor the arc is turned off, and another arc is formed at the gas entrance [38]. The advocates of this reactor claim that it is a flexible technology able to operate over a wide range of gas flow rates, the discharge power can be controlled by acting on the electrode or the voltage, it operates with AC or DC currents, and has a simpler power supply compared to the corona and microwave plasma reactors [38]. The DBD reactor is typically an annular configuration. The gases flow in a millimeter gap between the high voltage electrode encased in a non-conductive material such as quartz, with the outer shell being the ground electrode [39, 48]. This process has been used to create hydrogen and in hydrocarbon synthesis (C2, C3, and C4) using methane as the feed gas. It was found that when a pure methane feed was used, carbon black and a plasma polymerized carbon film were produced [39, 48].

Therefore co-feeds such as water, carbon monoxide and carbon dioxide were used as well as catalysts. Carbon dioxide is particularly interesting since the process could be used to eliminate a ''green house'' gas as well as produce useful hydrocarbons [44]. Unlike the gliding arc and DBD plasma, the microwave plasmas does not use an electric arc. It uses, as its name indicates, microwaves [41]. This technique produces electrons with temperatures from 4000 to 6000 °C, while heavier particles have temperatures closer to 2000 K [41]. However, some researchers indicated that this process requires more electric energy than the hydrogen generated can produce with a fuel cell, suggesting that further improvements may be necessary. The corona plasma technique is similar to the gliding arc in set up, but not in operation. In the gliding arc the plasma is pushed down the length of the reactor, but in the corona the plasma is generated between the electrodes through the length of the reactor [45]. The plasma is created using fast rising electric pulses (i.e. 10 ns rise time and 100 ns pulse) [45]. An advantage of this technique is that the length of the electric pulses is shorter than the time between pulses, resulting in relatively low power being consumed compared to other plasma technologies [45]. For example, operating the reactor with a 10 ns rise time and 100 ns pulse duration at 2000 Hz results in electricity only being used approximately 0.02% of the time. This technology has been used to crack hydrocarbon streams prior to them entering traditional reforming reactors, or as the reformer themselves both with and without catalysts [45]. Paulmire et al. [38] compared the efficiency of several plasma reactors. They used the following equation to define efficiency in their case [38]:

54

$$\eta = \frac{(n_{CO} + n_{H_2})\Delta H_{H_2}}{n_{fuel}\Delta H_{fuel} + P_{elec}} \tag{16}$$

where n_{CO} and n_{H2} are the molar flows of carbon monoxide and hydrogen, respectively, which when multiplied by the lower heating value of hydrogen (ΔH_{H2}) is the energy in the outlet stream (assuming all the carbon monoxide is converted to carbon dioxide in WGS reactor). The outlet energy is divided by the input energy (n_{fuel} is the molar flow of the fuel multiplied by the lower heating value of the fuel, ΔH_{fuel}, plus electric power for the plasma generation, P_{elec}) to find the efficiency of the cases investigated, a gliding arc non-thermal plasma appeared to be the most efficient (**Table 3.3**).

Table 3.3 Plasma Reformer Efficiencies [38]

| Technology | Fuel | Experimental Conditions | | | Products (dry vol.%) | | | | Reformate Temperature (K) | η |
		Chem. Reaction	**Air Ratio**	**S/C**	**H₂**	**CO**	**CO₂**	**CH₄**		
Gliding arc non-thermal	Diesel	ATR	0.4	1.8	23	17	6.2	1.2	1000-1300	85
Corona discharge + catalyst	Iso-octane	ATR	0.28	1	46	16	16	-	900-1100	55
Gliding arc thermal	Iso-octane	POX	0.25	-	22	15	2	3	1200	9
Gliding arc thermal	Diesel	POX	0.25	-	23.5	23	0.1	0.03	1200	9
Microwave	Hexane	SR	-	2	66	25	4	-	-	-

3.2.5 Aqueous phase reforming

Aqueous phase reforming (APR) is under development to process oxygenated hydrocarbons or carbohydrates to produce hydrogen [2, 50–52]. These reactors often operate at pressures up to 25–30 MPa and temperatures ranging from 220 to 270 °C. The reforming reactions are rather complex (see the reaction pathways for hydrogen production from oxygenated hydrocarbons in **Fig. 3.3(a)**), but can be summarized to follow the reaction pathways in Eq. (2) for reforming followed by Eq. (12) for the WGS [49]. Most research to date has been focused on supported Group VIII catalysts, with Pt-containing catalysts having the highest activity. Even though they have lower activity, nickel based catalysts have been evaluated due to nickel's low cost [49]. The advantages of APR reactors include elimination of the need to vaporize water and feedstock which eliminates a system component and also enables fuels that cannot be vaporized such as glucose to be processed without first degrading them.

APR occurs at low temperatures which favors WGS to increase the hydrogen yield while suppressing CO. Thus the reforming and WGS occur in a single step eliminating multiple reactors (**Fig. 3.3(b)**) [46]. The advocates of this technology claim that this technology is more amiable to efficiently and selectively converting biomass feedstocks to hydrogen. Aqueous feed concentrations of 10–60% were reported for glucose and glycols. Catalyst selection is important to avoid methanation, which is thermodynamically favorable, along with Fischer Tropsch products such as propane, butane, and hexane [2, 53, 54]. Finally, due to moderate space time yields, these reactors tend to be somewhat large.
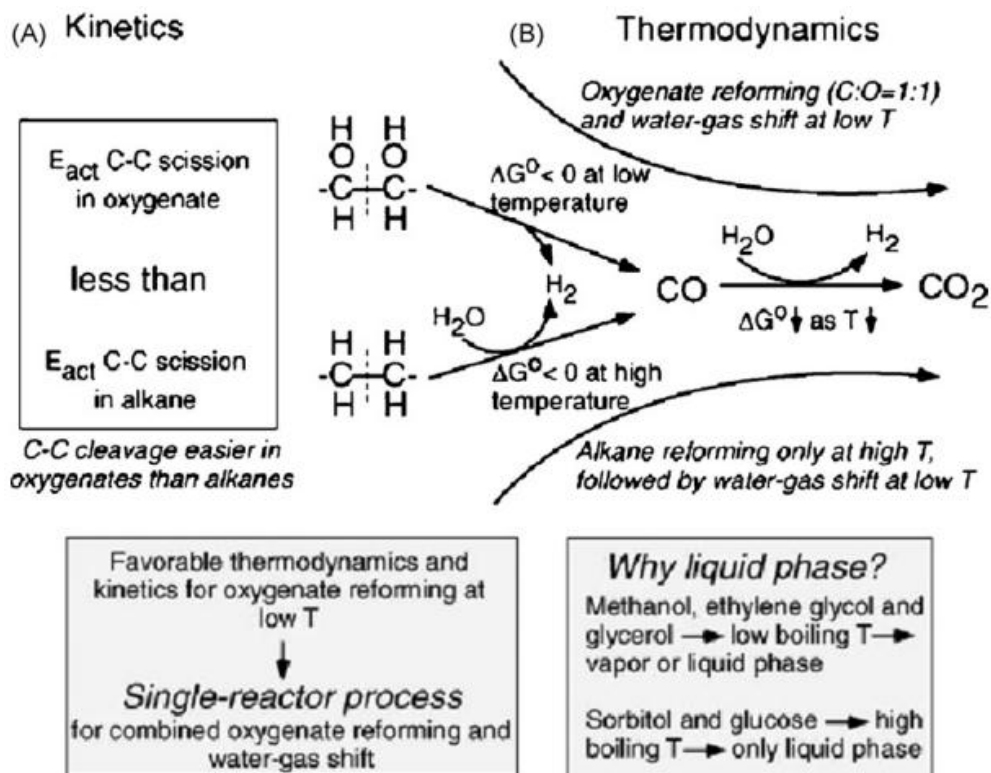
Fig. 3.3 (a) Reaction pathways for aqueous reforming of oxygenated hydrocarbons. **(b)** Summary of thermodynamic and kinetic consideration for aqueous phase reforming [46]

However, this may be improved through the use of micro reactor technology [20]. Improving catalyst activity and durability is an area where significant progress can be made. 2.6. Ammonia reforming Ammonia reforming has been proposed primarily for use with fuel cells for portable power applications [24, 55–58]. It is an inexpensive fuel that, due to its use in fertilizer production, has an extensive distribution system including thousands of miles of pipeline. Pure ammonia has an energy density of 8.9 kWh/kg, which is higher than methanol (6.2 kWh/kg), but less than diesel or JP-8 (13.2 kWh/kg) [55]. Proponents quickly point out that ammonia's strong odor makes leak detection simple, reducing some of the risk [54]. Another challenge is that PEM fuel cells require ammonia levels to be reduced below ppb

levels to ensure long life, since exposure of ammonia to the acidic PEM electrolyte causes severe and irreversible loss in performance. The losses are cumulative since the ammonia will build up in the electrolyte. However, for SOFC, ammonia can be fed directly to the fuel cell without any reforming [57, 58]. Ammonia cracking is endothermic and is regarded as the reverse of the synthesis reaction. In industry, ammonia synthesis occurs at approximately 500°C and 250 atm, and its synthesis is represented by the following reaction [54] :

$$N_2(g) + 3H_2(g) = 2NH_3(g) \qquad\qquad \Delta H = \text{-92.4 kj/mol} \qquad\qquad (17)$$

Typical catalysts used in both ammonia synthesis and cracking include iron oxide, molybdenum, ruthenium, and nickel. Ammonia cracking operates at temperatures around 800 to 900 °C, and unlike ammonia synthesis, low pressures are preferred [54]. The high temperatures can be obtained by either burning some of the hydrogen produced by ammonia cracking or carrying a second fuel such as propane or butane which is combusted.

3.3 Non-reforming hydrogen production

Hydrogen is produced by many methods other than reforming. A brief description of some of the biomass-based approaches, along with production of hydrogen from water, is induced here. Although chemical hydrides are typically considered hydrogen storage materials, a very brief review will also be provided.

3.3.1 Hydrogen from biomass

In the near term, biomass is the most likely renewable organic substitute to petroleum. In the modern. Biomass is available from a wide range of sources such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, municipal solid wastes, crop residues, short rotation herbaceous species (i.e., switch grass), waste paper, corn, and many more [1, 59–63]. For hydrogen generation, the current biomass technologies include: gasification pyrolysis, conversion to liquid fuels by supercritical extraction, liquefaction, hydrolysis, etc. followed in some cases by reformation, and biological hydrogen production. A brief description of gasification and biological hydrogen production will be given here. Conversion to liquid fuels is beyond the scope of this paper.

a. Biomass gasification

Gasification technology, commonly used with biomass and coal, is very mature and commercially used in many processes. It is a variation of pyrolysis and, therefore, is based upon partial oxidation of the materials into a mixture of hydrogen, methane, carbon monoxide, carbon dioxide, and nitrogen known as a producer gas. Since pyrolysis and steam reforming have been described previously, only a brief examination of the salient differences occurs here. The gasification process typically suffers from low thermal efficiency since moisture contained in the biomass must also be vaporized [56]. It can be done with or without a catalyst [60] and in a fixed bed or fluidized bed reactor, with the fluidized bed reactor typically yielding better performance [60]. Addition of steam and or oxygen to the gasification process results in steam reforming and produces a syngas stream (H_2 to CO ratio of 2:1), which can

be used as the feed to a Fischer-Tropsch reactor to make higher hydrocarbons, or to a WGS for hydrogen production [34, 62]. Superheated steam (900 °C) has been used to reform dried biomass to achieve high hydrogen yields as seen in **Fig. 3.4** [56].

Gasification, even at high temperatures of 800–1000 °C, produces a significant amount of tar in the product gas (**Fig. 3.4**). Therefore, a secondary reactor, which utilizes calcined dolomite or nickel catalysts, is used to catalytically clean and upgrade the product gas [60]. Ideally, oxygen should be used in these plants; however, oxygen separation unit operations are cost prohibitive for small-scale plants. This limits the gasifiers to the use of air resulting in significant dilution of the products as well as the production of NOX. Low cost, efficient oxygen separators are needed for this technology. For hydrogen production, a WGS process can be employed to increase the hydrogen concentration, and then a separation process used to produce pure hydrogen [58]. Several processes have been proposed to decrease the amount of tar produced in the gasification reactor. For example, the employment of an $Rh/CeO_2/M$ (M = SiO_2, Al_2O_3, and ZrO_2) catalyst for use in the gasification process has been found to reduce the tar formation [60].

Much cheaper catalysts would be required to make such an approach viable. Typically, gasification reactors are built on a large scale and require massive amounts of material to be continuously fed to them. One of the problems with this technology is that a tremendous amount of resources must be used to gather the large amounts of biomass to the central processing plant. Currently, the high logistics costs typically limit the gasification plants to be located. Development of smaller efficient distributed gasification plants may be required for this technology for cost effective hydrogen production using this technology.
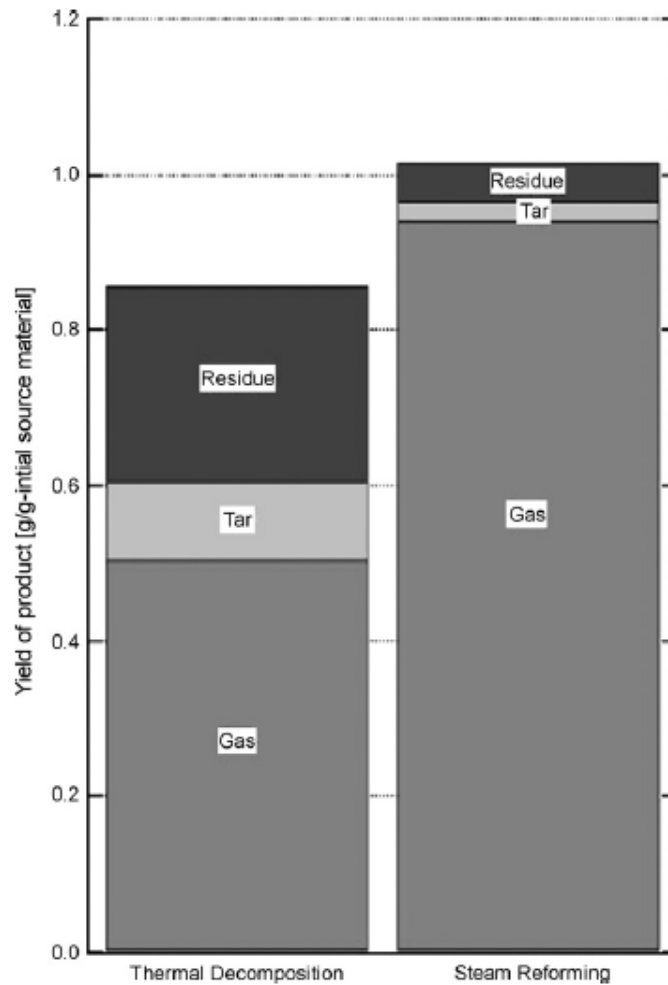
Fig. 3.4 Production yield for thermal decomposition and superheated steam reforming [56]

b. Biological hydrogen

Due to increased attention to sustainable development and waste minimization, research in bio-hydrogen has substantially increased over the last several years [64–67]. The main bioprocess technologies used for bio-hydrogen production include: photolytic hydrogen production from water by green algae or cyano bacteria (also known as direct photolysis), dark-fermentative hydrogen production during the acidogenic phase of anaerobic digestion of organic material, photo-fermentative processes, two stage dark/fermentative, and hydrogen production by water-gas shift

61

[66, 68, 69]. It should be noted that only a small fraction of naturally occurring microorganisms have been discovered and functionally characterized. In addition, the known organisms are being modified to improve their characteristics. The feeds for biological hydrogen are water for photolysis processes and biomass for fermentative processes. Brief descriptions with their advantages and limitations will be presented here. There are several recent **Fig. 3.4**. Production yield for thermal decomposition and superheated steam reforming [56]. J.D. Holladay et al. / Catalysis Today 139 (2009) 244–260 251 review articles that provide in-depth descriptions of the reaction pathways and types of enzymes being used in bio-hydrogen production and the interested reader is referred to them for more details [66, 68, 70].

❖ **Direct photolysis**

Photosynthesis user solar energy to convert carbon dioxide and water to carbohydrates and oxygen. For some organisms, excess solar energy is ''vented'' by production of hydrogen via direct photolysis of water. Researchers are trying to engineer algae and bacteria so the majority of the solar energy is diverted to hydrogen production, with enough diverted to carbohydrate production to solely maintain life. Direct photolysis of water is done in two ways. First it can use green algae's photosynthesis capabilities to generate oxygen and hydrogen ions. The process occurs along the thylakoid membrane where two photosystems are located (**Fig. 3.5**). The first step is the splitting of water into oxygen using solar radiation. The hydrogen in this reaction is bound in the plastiquinone (pqH_2) molecule. The
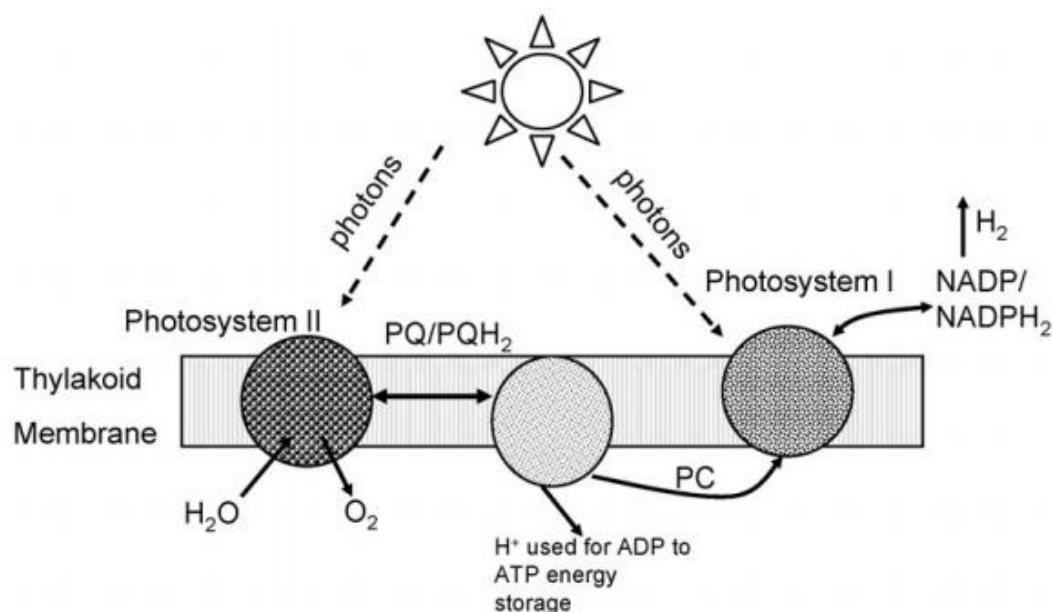
Fig. 3.5 Direct photolysis process [69]

pqH$_2$ is conveyed down the membrane to the cytochrome b6f which transfers the stored energy from pqH$_2$ to plastocyanin (pc). The pq is recycled back to photosystem II. Additional solar radiation is absorbed in photosystem I which is used to transfer the chemical energy in pc to ferredoxin (fd). The fd is used to convert the NADP to NADPH$_2$. The NADPH$_2$ by means of the Benson-Bass Ham-Calvin Cycle converts CO$_2$ to carbohydrates. However, under anaerobic conditions or when too much energy is captured in the process some organisms vent the excess electrons by using a hydrogenase enzyme which converts the hydrogen ions in the fd to hydrogen gas [69]. The advantage of this technology is that the primary feed is water, which is inexpensive and available almost everywhere [67]. Currently, this process requires a significant surface area to collect sufficient light. Unfortunately, these microorganisms in addition to producing hydrogen, produce oxygen, which, when sensed by the organism, causes it to cease hydrogen production [69, 72]. Therefore

work is being done to either, identify or engineer less oxygen sensitive organisms, separate the hydrogen and oxygen cycles, and/or change the ratio of photosynthesis (oxygen production) to respiration (oxygen consumption) in order to prevent oxygen buildup. The addition of sulfate to the solution has been found to depress oxygen production and sensitivity; however, the hydrogen production mechanisms are also suppressed [69]. Since oxygen and hydrogen are co-produced in a mixed gas, significant safety and separation issues occur. Recent innovative research has resulted in substantially increased light utilization efficiency of up to 15% compared to the previous utilization of 5% [71]. For photosynthetic to biomass, efficiency is as high as 2% on coral reefs, but averages 0.2% globally. This translates into a maximum theoretical efficiency for photosynthetic hydrogen production of about 1% [69]. Proponents of photolytic hydrogen production claim that 10–13% is achievable by engineering the organisms to better utilize the solar power [69]. Another challenge is achieving continuous hydrogen production under aerobic conditions. This technology has significant promise, but also tremendous challenges.

❖ **Dark fermentation.**

Dark fermentation uses primarily anaerobic bacteria, although some algae are also used, on carbohydrate rich substrates grown, as the name indicates, in the dark [66, 69, 72]. For fermentative processes, the biomass used needs to be biodegradable, available in high quantities, inexpensive, and have a high carbohydrate content [59], [67]. Pure, simple sugars, which are easily biodegradable such as glucose and lactose are preferred, but are not readily available in high quantities and/or are relatively expensive [67]. Major biomass wastes which can be readily utilized for bio-hydrogen

are listed in **Table 3.4**. The pathways are dependent on the type of bacteria used. Standard fermentative pathway has a theoretical maximum production of 4 moles of hydrogen per mole of glucose. Currently fermentative processes produce 2.4 to 3.2 mole of hydrogen per mole glucose [70]. However, it may be possible to change the fermentative pathway using molecular engineering with the objective to increase hydrogen production's theoretical maximum to 12 moles hydrogen per mole glucose. The gas produced is a mixture of hydrogen, carbon dioxide, methane, carbon monoxide, and some hydrogen sulfide [64]. Therefore a separation step is required to produce high purity hydrogen. For dark fermentation processes, the partial pressure of hydrogen is a factor; as the hydrogen pressure increases the hydrogen production decreases [64]. The obvious solution to this limitation is to remove the hydrogen as it is generated. The fermentation process produces acetic, butyric and other organic acids, which is a more significant problem. These acids can depress hydrogen yield by diverting the metabolic pathway toward organic chemical production. In addition, their production requires subsequent wastewater treatment which adds cost and complexity to the system. This pathway either needs to be eliminated to maximize

Table 3.4 Biomass waste that is readily utilized for bio-hydrogen production [66, 69]

Biomass material	Comments
Starch agricultural and food industry waste	Must by hydrolyzed to glucose or maltose, followed by conversion to organic acids and finally hydrogen
Cellulose agricultural and food industry waste	Must be finely ground and go through delignification, then is processed as starch
Carbohydrate rich industrial waste	May require pretreatment for removal of undesirables and for nutritional balancing, then it is processed as starch
Waste sludge from waste water treatment plants	May require pretreatment, the converted to organic acids and finally converted to hydrogen

hydrogen production and simplify the process or it needs to be taken advantage of by the integrated multi-step processes described below [21].

❖ **Photo-fermentative processes.**

Photo-fermentative processes, also called photosynthetic bacterial hydrogen production, capitalize on the nitrogenase functionality of purple non-sulfur bacteria to evolve hydrogen. In this process light harvesting pigments such as chlorophylls, carotenoids, and phycobilins scavenge light energy which is transferred to membrane reaction centers similar to those in photolytic organisms (algae). Sunlight converts water into protons, electrons, and O_2. The nitrogenase catalyst is used to react the protons and electrons with nitrogen and ATP to make ammonia, hydrogen and ADP. Since oxygen inhibits the nitrogenase, cyanobacteria separate nitrogen fixation and oxygen generation either spatially or temporally. In nature the bacteria use the hydrogen by-product to fuel other energy requiring processes via the uptake hydrogenase enzyme. Therefore, researchers are trying to genetically modify the bacteria to suppress this enzyme. The process is done in deficient nitrogen conditions using primarily infrared light energy and, preferably, reduced organic acids although other reduced compounds can be used [66, 69, 72]. The advantages of this process are that oxygen does not inhibit the process, and that these bacteria can be used in a wide variety of conditions (i.e. batch processes, continuous cultures, and immobilized in carrageenan, agar gel, porous glass, activated glass, or polyurethane foam) [66, 69, 72]. The disadvantages are the limited availability of organic acids, the nitrogenase enzyme is slow, the process requires a relatively high amount of energy, and hydrogen re-oxidation [69, 72]. To increase the nitrogenase activity and

decrease the energy requirements, the proper ratio of carbon to nitrogen nutrients must be maintained. Enzyme engineering approaches are under development to decrease the nitrogenase sensitivity to high levels of nitrogen nutrients. In addition, hydrogen re-oxidation is being addressed by micro engineering to deactivate hydrogenase enzymes in the bacteria. The hydrogenase enzymes recycle the hydrogen produced by the nitrogenase to support cell growth.

❖ **Microbial electrolysis cells**

Microbial aided electrolysis cells (MEC), also called bio electrochemically assisted microbial reactor (BEAMR), use electro hydrogenesis to directly convert biodegradable material into hydrogen [74–76]. The MEC is a modified microbial fuel cell. In a microbial fuel cell, exoelectrogens (special microorganisms), decompose (oxidize) organic material and transfer electrons to the anode. The electrons combine at the cathode, after traveling through an external load, with protons and oxygen forming water. A MEC operates in anaerobic state (no oxygen at the cathode) and an external voltage is applied to the cell rather than generated by it. The added energy is required since acetate substrate decomposition is not spontaneous under standard conditions [74–76]. Hydrogen production occurs at the cathode via Eq. (18).

$$2H^+ + 2e^- \longrightarrow H_2 \qquad\qquad\qquad (18)$$

The theoretical potential for hydrogen production in neutral pH (pH 7) is 0.61 V, VCat vs. Ag/AgCl [74]. Exoelectrogens generate an anode potential of approximately Van = 0.5 V. Therefore the minimum applied potential (Vapp = Van

VCat) is 0.11 V [74]. For acetate, the actual applied voltage is larger than 0.3 V due to electrode over potentials and ohmic resistance [74].

The design of MEC systems initially used similar components as used in PEM fuel cells [74]. However, flat electrode designs limited the surface area for the exoelectrogens and the membranes increased the ohmic resistances so alternative designs were developed. The most recent design uses a graphite brush for the exoelectrogen substrate (anode) and no membrane separator [72]. This design succeeded to decrease the applied voltage from 1.0 V using a gas diffusion membrane and 0.5 V with a Nafion membrane to 0.4 V in the membrane less design. The efficiency is a function of the lower heating value of the hydrogen divided by the lower heating value of the organic material plus the electrical energy provided [72].

$$\eta = \frac{n_{\text{Hydrogen}} \Delta H_{c,\text{Hydrogen}}}{\sum_{1}^{n} (IE_{\text{ap}} \Delta t - I^2 R_{\text{ex}} \Delta t) + n_{\text{substrate}} \Delta H_{c,\text{substrate}}} \tag{19}$$

where I is the current, E_{ap} the applied voltage, Δt(s) the time increment for n data points measured during the batch cycle, and R_{ex} is an external resistance which was 10 V by Call and Logan [72]. Using Eq. (19), the efficiency was raised from 23% with a gas diffusion membrane and 53% with a Nafion membrane to 76% in the membrane less reactor [72]. Under these conditions a hydrogen production rate of 3.12 m^3 H$_2$/(m^3 reactor day) [72]. However, the methane production rates also increased to an average of 3.5% methane in the production gas [72]. To control the methanogensis in these reactors, strategies involving intermittent draining and air exposure or in situ air-sparging have been proposed [72]. However, these strategies

will result in more complex systems with significantly increased operations and maintenance requirements, translating into more expensive systems. In addition to methane suppression, continuous operation, decreasing the pH, operating under carbon limited conditions, increasing the microorganisms tolerance to impurities, and examining other feedstocks are all issues to be addressed.

❖ **Multi-stage integrated process**

Multi-stage hydrogen production has been implemented to maximize the hydrogen production from the feed [67]. Initially, the process consisted of two stages, dark fermentation followed by photo fermentation [67]. but three or even four stages have since been proposed in different configurations (**Fig. 3.6**) [21]. In this process, the biomass material is first fed to a dark fermentation reactor where the bacteria decompose the feedstock to hydrogen and an organic acid rich effluent. Since the effluent has organic acids in it, this eliminates the challenge of developing a supply of organic acids for the photo-fermentative process. Since the photo-fermentative process uses primarily infrared light, the sunlight is first filtered through a direct photolysis reactor where the visible light is utilized, but the infrared light is not [21]. The fourth stage is the use of a microbial electrolysis cells which produces hydrogen, not electricity [21]. This cell utilizes the same organic acids, but does not require light. Therefore, it can operate during the night or other times of low light [21]. The effluent from the first stage contains ammonia, which inhibits the second stage, so some dilution and neutralization to adjust the pH to 7 is required prior to feeding it to the second stage [67]. Integration of multiple processes produces significant challenges for the reactor engineering, system design, process control, and operation
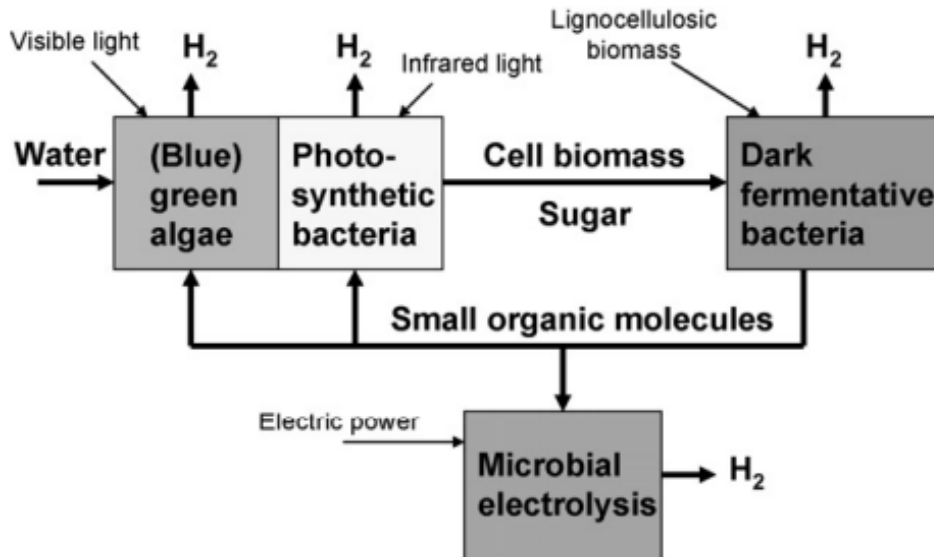
Fig. 3.6 Multi-stage integrated biohydrogen system [21]

and maintenance. The challenges with the coproduction of hydrogen and oxygen from photolytic hydrogen production include:

- Photosynthetic and respiration capacity ratio. Green algae and cyanobacteria become anaerobic when their photosynthesis/ respiration (P/R) capacity ratio is 1 or less. Under such anaerobic conditions, photosynthetic water oxidation produces H_2 instead of starch, and the oxygen evolved by photosynthesis is consumed by respiration, to produce CO_2. Currently, this process is achieved by nutrient deprivation, with the drawback that the resulting P/ R $\leq$ 1 ratio is achieved by partially decreasing the quantum yield of photosynthesis. Alternative mechanisms to bring the P/R ratio to 1 need to be investigated, particularly those methods that focus on achieving a P/R ratio of 1 without changing the quantum yield of photosynthesis. Two further issues will need to

be investigated under these conditions: (1) rate limitations due to the non-dissipation of the proton gradient and (2) the ability of the culture to take up a variety of exogenous carbon sources under the resulting anaerobic conditions [21].

- Co-culture balance. To extend the adsorption spectrum of the H_2- photo producing cultures to the infrared (700 to 900 nm), the possibility of co-cultivating oxygenic photosynthetic organisms with anoxygenic photosynthetic bacteria that absorb light in the visible (400 to 600 nm), thus potentially competing with green algae for these latter wavelengths. Strategies need to be devised to either maintain the appropriate biomass ratio of the two organisms as suspensions in the same cultures. The competition for organic carbon substrates between two organisms in the same medium also needs to be investigated [21].

- Concentration and processing of cell biomass. In an integrated system, cell biomass from either green agae/cyanobacteria or photosynthetic bacteria can serve as the substrate for dark fermentation. The green algal and cyanobacterial cell walls are made mostly of glycoproteins (sugar-containing proteins), which are rich in sugars like arabinose, mannose, galactose, and glucose. Purple photosynthetic bacterial cell walls contain peptidoglycans (carbohydrate polymers cross-linked by protein, and other polymers made of carbohydrate protein and lipid). Pretreatment of cell biomass may be necessary to render it more suitable for dark fermentation. Methods for cell concentration and processing will depend on the type of organism used and how the biological system is integrated [21].

❖ **Water-gas shift**

Finally, certain photoheterotrophic bacteria in the family Rhodospirllacae have been found which can grow in the dark by feeding only upon CO [64]. The oxidation of the CO to CO_2 was determined to follow the WGS reaction (Eq. (11)), but uses enzymes rather than metal to catalyze the process. Since it occurs at low temperatures and pressures, thermodynamics favor a high conversion of CO to CO_2 and H_2 [64]. Its conversion rate is actually relatively high compared to other biological processes, but it does require a CO source and darkness [64].

❖ **Production rates comparison**

Although there have been some advances since Levin et al. published their findings in 2004, the table does provide order of magnitude estimates for the approximate size of the reactors for hydrogen production. One of the major challenges to this technology is the slow hydrogen production rate. For example, a 5 kW PEM fuel cell, sufficient to provide residential power, requires approximately 119.5 mol H_2/h (95% H_2 utilization, 50% efficiency). Therefore a bioreactor ranging from 1 to 1700 m^3 would be required to provide the hydrogen [64]. The complete system with controls and balance of plant equipment is not included in the size estimate.

3.3.2 Hydrogen from water

There has been a great deal of research in splitting water to make hydrogen and oxygen; in fact its commercial uses date back to the 1890s [21]. Water splitting can be divided into three categories: electrolysis, thermolysis, and photoelectrolysis.

a. Electrolysis

Water splitting in its simplest form uses an electrical current passing through two electrodes to break water into hydrogen and oxygen. Commercial low temperature electrolyzers have system efficiencies of 56–73% (70.1–53.4 kWh/kg H_2 at 1 atm and 25°C) [69]. It is essentially the conversion of electrical energy to chemical energy in the form of hydrogen, with oxygen as a useful by-product. The most common electrolysis technology is alkaline based, but more proton exchange membrane (PEM) electrolysis and solid oxide electrolysis cells (SOEC) units are developing [77, 78]. SOEC electrolyzers are the most electrically efficient, but are the least developed of the technologies. SOEC technology has challenges with corrosion, seals, thermal cycling, and chrome migration. PEM electrolyzers are more efficient than alkaline, do not have the corrosion and seals issues that SOEC, but cost more than alkaline systems. Alkaline systems are the most developed and lowest in capital cost. They have the lowest efficiency so they have the highest electrical energy costs.

Electrolyzers are not only capable of producing high purity hydrogen, but recently, high-pressure units (pressures larger than 1000 psig) are being developed [77]. The advantage of high-pressure operation is the elimination of expensive hydrogen compressors. Currently, electrolysis is more expensive than using large-scale fuel processing techniques to produce hydrogen. And, if nonrenewable power generation is used to make the electricity for electrolysis, it actually results in higher emissions compared to natural gas reforming. However, it should be noted, that if the hydrogen must be shipped in cylinders or tankers, then on site production via electrolysis may be less expensive. Several different approaches have been proposed

to address these short comings. These include using renewable sources of energy such as solar, wind, and hydro, to produce the electricity [77], or excess power from existing generators to produce hydrogen during off-peak times [78], and high temperature electrolysis. There have been several studies on the cost of using renewable energy for electrolysis, all reaching the conclusion that as the cost of natural gas increases renewable energy will become economically competitive at central production facilities as well as at distributed generation points especially if carbon dioxide and other pollutants are included in the analysis [79].

❖ **Alkaline electrolyzer**

Alkaline electrolyzers are typically composed of electrodes, a microporous separator and an aqueous alkaline electrolyte of approximately 30 wt% KOH or NaOH [25, 71]. In alkaline electrolyzers nickel with a catalytic coating, such as platinum, is the most common cathode material. For the anode, nickel or copper metals coated with metal oxides, such as manganese, tungsten or ruthenium, are used. The liquid electrolyte is not consumed in the reaction, but must be replenished over time because of other system losses primarily during hydrogen recovery. In an alkaline cell the water is introduced in the cathode where it is decomposed into hydrogen and OH [21]. The OH travels through the electrolytic material to the anode where O_2 is formed. The hydrogen is left in the alkaline solution [21]. The hydrogen is then separated from the water in a gas liquid separations unit outside of the electrolyser [21]. The typical current density is 100–300 mA cm^2 and alkaline electrolyzers typically achieve efficiencies 50–60% based on the lower heating value of hydrogen [69]. The overall reactions at the anode and cathode are:

Anode:

$$4OH^- \rightarrow O_2 + 2H_2O \tag{20}$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{21}$$

Overall:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad \Delta H = \text{-288 kj/mol} \tag{22}$$
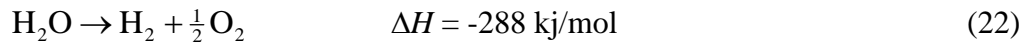
❖ **Proton exchange membrane electrolyzer**

PEM electroyzers build upon the recent advances in PEM fuel cell technology [20]. PEM-based electrolyzers typically use Pt black, iridium, ruthenium, and rhodium for electrode catalysts and a Nafion membrane which not only separates the electrodes, but acts as a gas separator [71, 77]. In PEM electrolyzers water is introduced at the anode where it is split into protons and oxygen [20]. The protons travel through the membrane to the cathode, where they are recombined into hydrogen [20]. The O_2 gas remains behind with the unreacted water. There is no need for a separations unit. Depending on the purity requirements a drier may be used to remove residual water after a gas/liquid separations unit. PEM electrolyzers have low ionic resistances and therefore high currents of 1600 mA cm^2 can be achieved while maintaining high efficiencies of 55 to 70% [69]. The reactions at the anode and cathode are:

Anode:

$$2H2O \rightarrow O2 + 4H^+ + 4e^- \tag{23}$$

Cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad\qquad (24)$$

Overall is the same as for alkaline electrolyzers:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad\qquad \Delta H = \text{-288 kj/mol} \qquad (25)$$
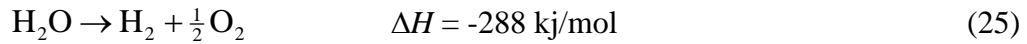
❖ **Solid oxide electrolysis cells**

Solid oxide electrolysis cells (SOEC) are essentially solid oxide fuel cells operating in reverse. These systems replace part of the electrical energy required to split water with thermal energy, as can be seen in **Fig. 3.7** [80]. The higher temperatures increase the electrolyzer efficiency by decreasing the anode and cathode over potentials which cause power loss in electrolysis [81, 82]. For example, an increase in temperature from 375 to 1050 K reduces the combined thermal and electrical energy requirements by close to 35% [81]. A SOEC operates similar to the alkaline system in that an oxygen ion travels through the electrolyte leaving the hydrogen in unreacted steam stream [20]. The reactions are shown in Eqs. (17)–(19). Other advantages for high temperature electrolysis with a solid oxide based electrolyzer include: the use of a solid electrolyte which, unlike KOH for alkaline systems, is non-corrosive and it does not experience any liquid and flow distribution problems [24, 81]. Of course the high temperature operation requires the use of costly materials and fabrication methods in addition to a heat source [20]. The materials are similar to those being developed for solid oxide fuel cells (SOFC), yttria stabilized zirconia (YSZ) electrolyte, nickel containing YSZ anode, and metal doped lanthanum metal oxides [24, 81], and have the same problems with seals
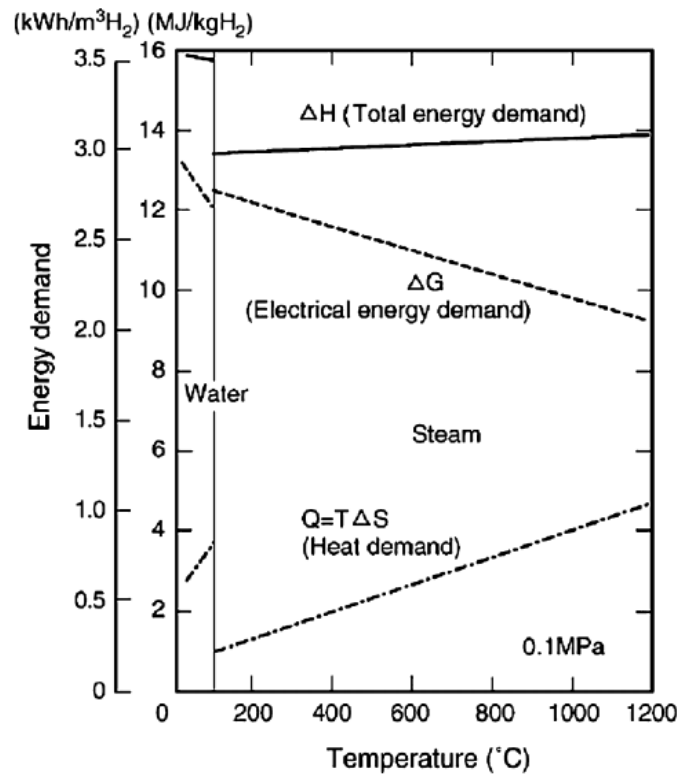
Fig. 3.7 Energy demand for water and steam electrolysis [80]

which are being investigated. High temperature electrolysis efficiency is dependent on the temperature and the thermal source. The efficiency as a function of electrical input alone can be very high with efficiencies 85–90% being reported [20]. However, when the thermal source is included the efficiencies can drop significantly. For example, SOEC operating from advanced high temperature nuclear reactors may be able to achieve up to 60% efficiency. In addition to using conventional combustion or nuclear energy to produce the high temperature source, solar energy is under development and may result in higher efficiencies [81–84]. Combining SOEC with a SOFC for co-generation of hydrogen and electricity has been proposed [84]. In this hybrid system a SOFC and SOEC are manifolded into the same stack and fed the same fuel, such as natural gas. Hydrogen is then produced by the SOEC and

electricity is produced by the SOFC. Proof-of-concept short stacks have been demonstrated with efficiencies of up to 69% [84]. However, the fuel utilization is still relatively low at approximately 40% and coking is a serious issue in addition to the other challenges faced by SOEC [84].

b. Thermochemical water splitting

In thermochemical water splitting, also called thermolysis, heat alone is used to decompose water to hydrogen and oxygen [24, 86]. It is believed that overall efficiencies of close to 50% are achievable using these processes [86]. It is well known that water will decompose at 2500°C, but materials stable at this temperature and also sustainable heat sources are not easily available [20]. All of the processes have significantly reduced the operating temperature from 2500°C, but typically require higher pressures. Three example cycles are:

Ispra Mark-10 [20] :

$$2H_2O + SO_2 + I_2 + 4NH_3 \rightarrow 2NH_4I + (NH_4)2SO_4 \qquad T = 50°C \qquad (26)$$

$$2NH_4 \rightarrow 2NH_3 + H_2 + I_2 \qquad T = 630°C \qquad (27)$$

$$(NH_4)_2SO_4 + Na_2SO_4 \rightarrow Na_2S_2O_7 + H_2O + 2NH_3 \qquad T = 400°C \qquad (28)$$

$$Na_2S_2O_7 \rightarrow SO_3 + Na_2SO_4 \qquad T = 550°C \qquad (29)$$

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 \qquad T = 870°C \qquad (30)$$

Sulfuric acid decomposition [86] :

$$SO_2 + H_2O \rightarrow H_2O + SO_2 + \tfrac{1}{2}O_2 \qquad (31)$$

$$2H_2O + Br_2 + SO_2 \rightarrow H_2SO_4 + 2HBr \tag{32}$$

$$2HBr \rightarrow Br_2 + H_2 \tag{33}$$

$$2H_2O + I_2 + SO_2 \rightarrow I_2 + H_2 \tag{34}$$

ZnO/Zn [20] :

$$ZnO \rightarrow Zn + \tfrac{1}{2}O_2 \qquad\qquad T = 1800°C \tag{35}$$

$$Zn + H_2O \rightarrow ZnO_{(s)} + H_2 \qquad\qquad T = 475°C \tag{36}$$
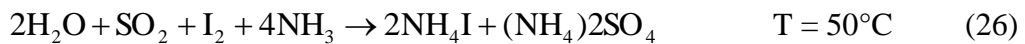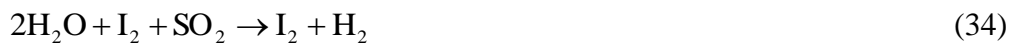
In choosing the process there are five criteria which should be met [20]. (1) Within the temperatures considered, the DG of the individual reactions must approach zero. This is the most important criterion. (2) The number of steps should be minimal. (3) Each individual step must have both fast reaction rates and rates which are similar to the other steps in the process. (4) The reaction products cannot result in chemical-by-products, and any separation of the reaction products must be minimal in terms of cost and energy consumption. (5) Intermediate products must be easily handled [20]. Currently, there are several processes which meet the five criteria, such as the Ispra-Mark 10, 11, 13, 15, UT-3 process, and the sulfuric acid decomposition process; however, they are still not competitive with other hydrogen generation technologies in terms of cost and efficiency which is the major focus of research in those processes [24, 87]. In addition, these processes require large inventories of highly hazardous corrosive materials. The combination of high temperatures, high pressures, and corrosion results in the need for new materials. Finally, several of them such as the hybrid sulfur Ispra-Mark 11 process require inefficient electrochemical steps which need to be improved [24, 87]. It is believed

that scaling up the processes may lead to improved thermal efficiency overcoming one of the principle challenges faced by this technology [86]. In addition, a better understanding of the relationship between capital costs, thermodynamic losses, and process thermal efficiency may lead to decreased hydrogen production costs [86]. The current processes all use four or more reactions, and it is believed that an efficient two reaction process may make this technology viable [86].

c. Photoelectrolysis

Photoelectrolysis uses sunlight to directly decompose water into hydrogen and oxygen, and uses semiconductor materials similar to those used in photovoltaics. In photovoltaics, two doped semiconductor materials, a p-type and an n-type, are brought together forming a p–n junction [20]. At the junction, a permanent electric field is formed when the charges in the p-type and n-type of material rearrange. When a photon with energy greater than the semiconductor material's bandgap is absorbed at the junction, an electron is released and a hole is formed. Since an electric field is present, the hole and electron are forced to move in opposite directions which, if an external load is also connected, will create an electric current [24, 71]. This type of situation occurs in photoelectrolysis when a photocathode, type material with excess holes, or a photo anode, n-type of material with excess electrons, is immersed in an aqueous electrolyte, but instead of generating an electric current, water is split to form hydrogen and oxygen (**Fig. 3.8**) [20, 69, 79]. The process can be summarized for a photoanode-based system as follows: (1) a photon with greater energy than the bandgap strikes the anode creating an electron–hole pair.
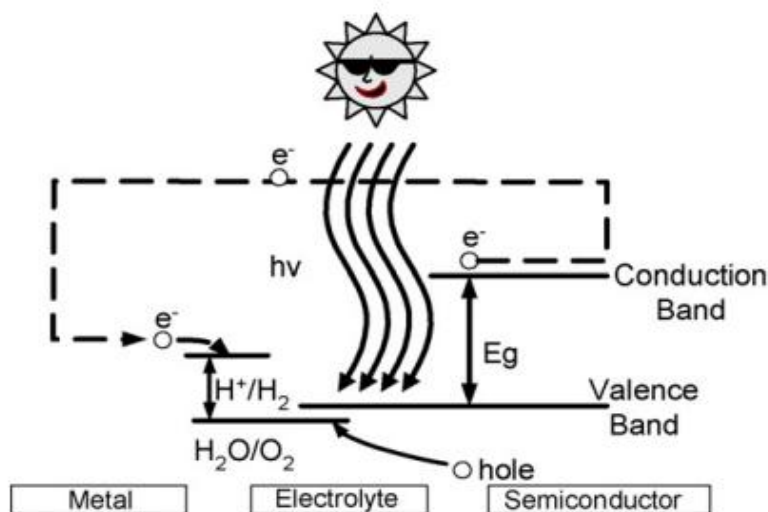
Fig. 3.8 Energetic of n-type semiconductor photoelectrochemical cells [20, 69, 79]

(2) The holes decompose water at the anode's front surface to form hydrogen ions and gaseous oxygen, while the electrons flow through the back of the anode which is electrically connected to the cathode. (3) The hydrogen ions pass through the electrolyte and react with the electrons at the cathode to form hydrogen gas [20, 69, 79]. (4) The oxygen and hydrogen gasses are separated, for example by the use of a semi-permeable membrane, for processing and storage.

Various materials have been investigated for use in photoelectrodes such as thin-film WO3, Fe2O3 and TiO2, as well as nGaAs, n-GaN, CdS, and ZnS for the photoanode; and CIGS/Pt, p-InP/ Pt, and p-SiC/Pt for the photocathodes [180,187–189].

The materials for the photoelectrodes and the semiconductor substrate determine the performance of the system. The hydrogen production efficiency is generally limited by imperfections in the crystalline structure, bulk and surface properties of the photoelectrodes, the material's resistance to corrosion from the aqueous

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electrolytes, and the ability to drive the water decomposition reactions [20, 69, 79]. In order to maximize the efficiency of this process, the energetics of the electrochemical reaction must be harmonized with the solar radiation spectrum, which is a non-trivial problem. A mismatch of the solar radiation and materials can produce photo-generated holes that can cause surface oxidations leading to either a blocking layer on the semiconductor surface or corrosion of the electrode via dissolution [20, 69, 79].

Current photoelectrodes used in PEC that are stable in aqueous solutions have a low efficiency for using photons to split water to produce hydrogen. The target efficiency is larger than 16% solar energy to hydrogen. This encompasses three material system characteristics necessary for efficient conversion: (1) the band gap should fall in the range sufficient to achieve the energetics for electrolysis and yet allow maximum absorption of the solar spectrum. This is 1.6–2.0 eV for single photoelectrode cells, and 1.6–2.0 eV/0.8–1.2 eV for top/bottom cells in stacked tandem configurations; (2) have a high quantum yield (> 80%) across its absorption band to reach the efficiency necessary for a viable device; (3) straddle the redox potentials of the H_2 and O_2 half reactions with its conduction and valence band edges, respectively. The efficiency is directly related to the semiconductor band gap (Eg), i.e., the energy difference between bottom of the conduction band and the top of the valence band, as well as the band edge alignments, since the material or device must have the correct energy to split water. The energetics are determined by the band edges, which must straddle water's redox potential with sufficient margins to account for inherent energy losses. Cost efficient, durable catalysts with appropriate Eg and band edge positions must be developed. To achieve the highest efficiency possible in

a tandem configuration, ''current matching'' of the photoelectrodes must be done. Electron transfer catalysts and other surface enhancements may be used to increase the efficiency of the system. These enhancements can minimize the surface over-potentials in relationship to the water and facilitate the reaction kinetics, decreasing the electric losses in the system. Fundamental research is on-going to understand the mechanisms involved and to discover and/ develop appropriate candidate surface catalysts for these systems [83, 87–92]. In addition to semiconductor devices for photoelectrolysis, it is possible to use suspended metal complexes in solution as the photochemical catalysts.

3.4 Conclusion

There is a tremendous amount of research being pursued in the development of hydrogen generation systems. Currently, the most developed and most used technology is the reforming of hydrocarbon fuels. In order to decrease the dependence on fossil fuels, significant development in other hydrogen generation technologies from renewable resources such as biomass and water is being done. Table 6 summarizes the technologies, along with their feedstocks and efficiencies. How the efficiency is calculated depends on the technology. 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. Development of these technologies may decrease the world's dependence on fuels that come primarily from unstable regions. An often over-looked impact is that by producing and using hydrogen internal to one's country keeps money and jobs from being exported. The ''in house'' hydrogen production may increase both national energy and economic security. The ability of hydrogen to be produced from a wide variety of feedstocks and using a wide variety of processes makes it so that every region of the world may be able to produce much of their own energy. It is clear that as the technologies develop and mature, hydrogen may prove to be the most ubiquitous fuel available.

Table 3.5 Technology summary list [24, 42, 71, 74]

Technology	Feedstock	Efficiency (%)	Maturity
Steam reforming	Hydrocarbons	70-85	Commercial
Partial oxidation	Hydrocarbons	60-75	Commercial
Autothermal reforming	Hydrocarbons	60-75	Near term
Plasma reforming	Hydrocarbons	9-85	Long term
Aqueous phase reforming	Carbohydrates	35-55	Medium term
Ammonia reforming	Ammonia	NA	Near term
Biomass gasification	Biomass	30-50	Commercial
Photolysis	Sunlight + water	0.5	Long term
Dark fermentation	Biomass	60-80	Long term
Photo fermentation	Biomass + sunlight	0.1	Long term
Microbial electrolysis cells	Biomass + electrolysis	78	Long term
Alkaline electrolyzer	H_2O + electricity	50-60	Commercial
PEM electrolyzer	H_2O + electricity	55 – 70	Near term
Solid oxide electrolysis cells	H_2O + electricity + heat	40 – 60	Medium term
Thermochemical water splitting	H_2O + heat	NA	Long term
Photoelectrochemical water splitting	H_2O + sunlight	12.4	Long term

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Chapter 4: A Novel Method for Producing Hydrogen from Hydrocarbon Liquid using Microwave in-Liquid Plasma

4.1. Introduction

In recent years, energy consumption driven by economic growth has increased dramatically, resulting in degradation to the environment. Therefore, sources of clean energy are becoming increasingly important in order to protect the environment while maintaining an ample energy supply. Recycling of waste from organic and non-organic materials such as household garbage, waste oil, or plastics can protect the environment by reducing the amount of waste and mitigating the effects of greenhouse gasses. Processing organic and non-organic materials to produce hydrogen gas is a challenging task and has been studied by several researchers [1–3]. The main reason that hydrogen used as fuel is water could be its source and hydrogen has enormous potential energy per unit mass than any other fuel [4, 5].

However, hydrogen is not a primary energy source like coal, oil, and natural gas, which exist in nature. Rather, it is a secondary energy source that is obtained by processing a primary energy source. Accordingly, a relatively large amount of energy is needed to extract and capture hydrogen [6–8].

Electrolysis of water is the dominant method for manufacturing clean hydrogen. However, since water is an extremely stable material, creating hydrogen from this material would be required tremendous amount of energy. Steam reforming of

natural gas is another method that has been commercially used for generating large amounts of hydrogen [9–11]. However, in the steam reforming method, carbon dioxide is released in the final stage of the reaction, so provisions for capturing and storing the CO_2 are required [12, 13].

One method for extracting and capturing hydrogen from waste materials that has been studied in recent years is the in-liquid plasma process [14–17]. This process can produce hydrogen gas and solidified carbon simultaneously without emitting CO_2 [18–21]. However, this method is only focus on hydrogen production, which is not as productive as other methods.

Based on the previous study [19], a conventional microwave (MW) oven is used to irradiate at 2.45 (GHz) with the ability to circulate the liquid. The power output of the conventional MW oven is 1260 W with the magnetron using 750 W to generate plasma from the total power of MW oven. The microwaves were irradiated and received at the tip of each antennas used to generate plasma inside the bubbles. Six antennas were arranged on a copper plate and placed on a Teflon platform. The device could be applied as a method for continuous production. The configuration includes an effective bubble control plate [19, 22–24] which is selected based on gas production rate.

Additionally, in-liquid plasma steam reforming, which is plasma fed by steam created in hydrocarbon liquid. The power supplied into the vessel reactor for each experiment was varied from 150 to 330 W. The microwaves were irradiated through a waveguide in order to prevent loss of energy to the reactor vessel. This method is investigated to accelerate the in-liquid plasma reaction [25–28]. The chemical

reactions of discharge in water are used for purification of polluted water [29–31]. In general, the process of discharge in a liquid is a more complicated phenomenon than that in a gas, because discharges in a liquid are unstable and involve phase transitions. When discharge occurs in a liquid, in most cases, bubbles appear. There have been many reports which focused on bubbles in relation to the generation of plasma in a liquid by a variety of methods [32–35]. The behavior of bubbles and plasma generated by high frequency waves and microwaves is observed using a high speed camera [36–39]. Microwave plasma is generated when the electrode is heated to the saturation temperature of *n*-dodecane [33, 40] .

The main reason for conducting this study is to compare the hydrogen gas production efficiency of the in-liquid plasma steam reforming method when using a conventional MW oven and microwave generator with a waveguide as the power supply and *n*-dodecane as the source material. It is expected to offer the most efficient hydrogen production rate with a method that is both simple and environmentally friendly.

4.2. Plasma decomposition experiment in conventional MW oven

Fig. 4.1 shows the schematic diagram of a conventional MW oven used in this experiment. Not only can the MW oven easily generate microwaves, but also it becomes commonplace in most households, so there is much anticipation that they will be able to be used as a distributed-type hydrogen generator.

Fig. 4.2(a) shows a curve-shaped antenna unit. By applied the curved antenna, the tips of the electrodes are closer to each other and it appears that the generation of
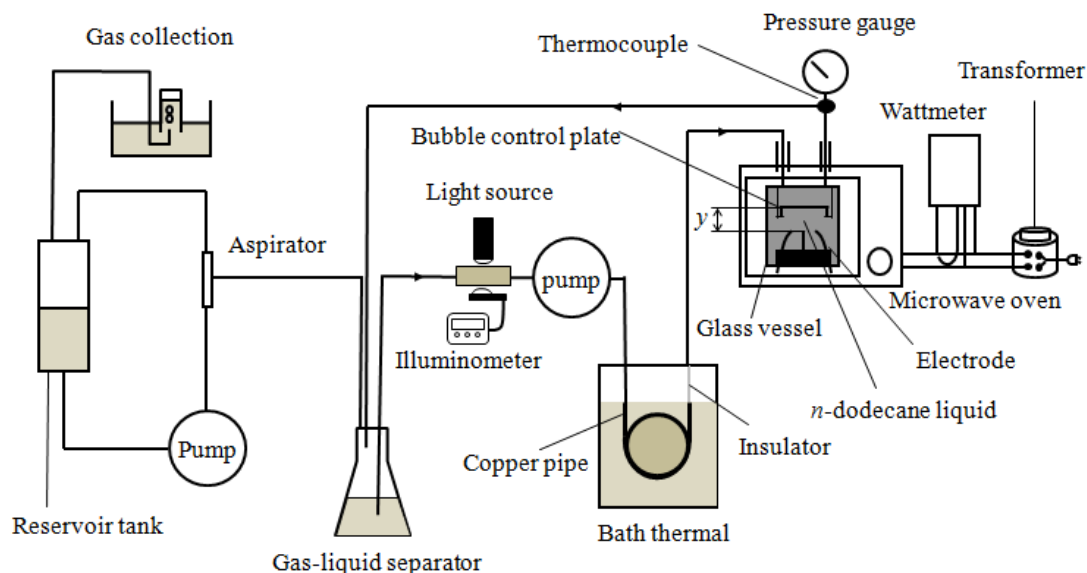
Fig. 4.1 Experimental setup of hydrogen production using a conventional MW oven.

plasma usually occurs near the center of the antenna, which makes the volume of the generated plasma larger. While the reason for this cannot be confirmed at this time, with the curved antenna, since the tips of the electrodes are closer to each other, the electric field breakdown occurs near the center of the antenna, which makes for an increased volume of the generated plasma [38] .

Experiments were conducted to investigate the optimal shape of the curve-shaped antenna unit by changing the length of the antenna *L* and distance between the tips of the electrodes *d* and measuring the decomposition gas rate. The length of the antenna is adjusted according to the type of liquid in order to optimize the generation of gas. The length of the antenna is approximately one-fourth of the microwave wave length (λ) [33, 41]. The optimal value of gas rate was 33 (ml/s) when *d* was 8 to 12 (mm). It was determined that the optimal antenna shape is comprised of *L*=21 (mm) and *d*=10

(mm). In order to generate plasma, a 550 (ml) heat-resistant glass container was placed in a MW oven to be used as a cracking furnace.

Fig. 4.2(b) shows the reactor platform and piping that were made of heat-resistant glass and silicone rubber to avoid energy absorption from any internal energy reaction. The decomposition furnace was connected to an aspirator. A bubble plate is introduced because use of the plate enhances continues generation of the plasma [27, 36].

A pressure gauge was setup from the reactor pipe in order to control the air pressure from the MW oven. Experiments were carried out by depressurizing the reactor using an aspirator. The liquid was circulated by a pump from a reservoir tank. The liquid was heated before being introduced to the reaction field, with the liquid temperature set at 80 °C in heating case, and at 25 °C for that without heating. Prior to generating the plasma and collecting gas, the air inside the device was replaced with argon or helium gas, which was then exchanged by the gas generated by the plasma. A thermal conductivity detector was used as the detector for the gas chromatography for analyzing the generated gas. Helium was used as the carrier gas. For the analysis of the gas composition, a gas chromatograph (GC-8A, Shimadzu) equipped with thermal conductivity detector (TCD) was utilized and Argon gas was used as a carrier. With *n*-dodecane there is ratio of 58% to 90% hydrogen in the gas generated by plasma decomposition. Low-grade flammable hydrocarbon gases, such as C_2H_2, C_2H_4, and CH_4 were also generated. Simultaneously, a large quantity of graphite is synthesized in the vessel.

Fig. 4.3 shows the effect of the concentration of graphite generated by plasma on

the hydrogen yield. The hydrogen concentration in the production gas decreases as
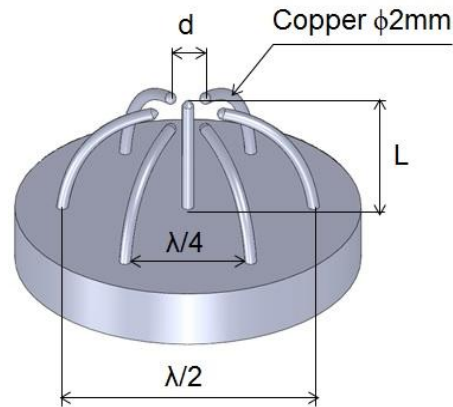
(a) Schematic dimensions of receiving antenna
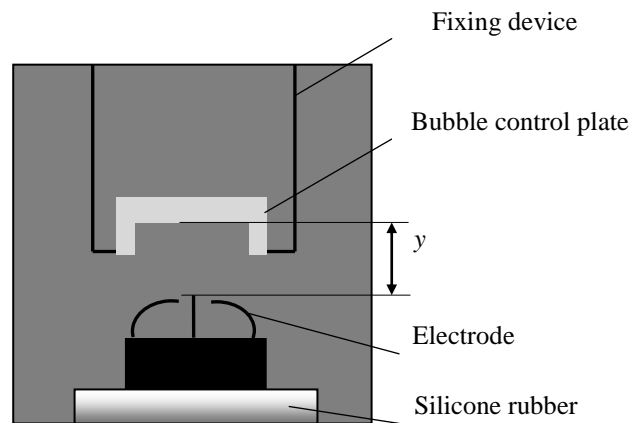
(b) Position of receiving antenna for MW

Fig. 4.2 Position tip of receiving antenna for microwave.
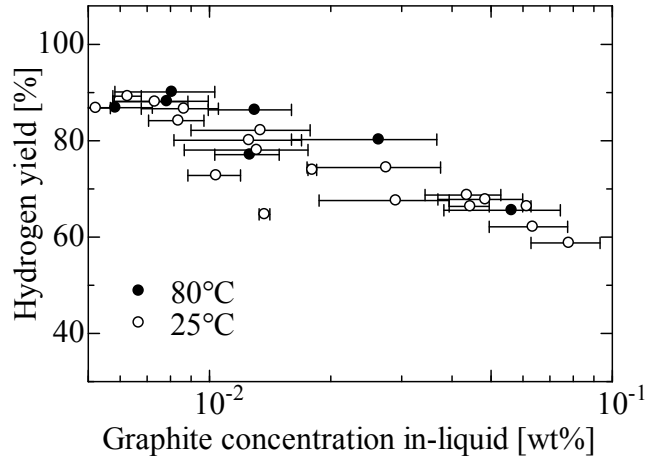
Fig. 4.3 Hydrogen yield of produced gas

the graphite concentration increases in the liquid, with the effect of the liquid temperature becoming negligible. It is highly probable that a reaction of H_2 with the graphite is promoted as graphite density increases leading to the production of the hydrocarbons such as C_2H_2.

Fig. 4.4 shows the experimental results for using a bubble control plate. By using the bubble control plate, the gas production rate can be increased up to 1.3 times. Vapor filled the gap replacing the gas due to the plate, so the gas production rate improves. However, when the gap is increased, the bubble continuously changed in shape in the gap, eventually making the plate ineffective.
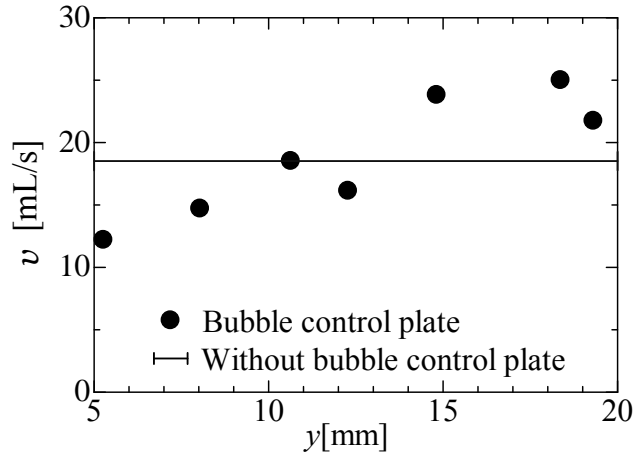
Fig. 4.4 Effect of the bubble control bubble plate

4.3. In-liquid plasma steam reforming

Fig. 4.5 shows the schematic diagram for the steam reforming method, including

the gas flow that would be reacted in the vessel reactor. The experiment was

conducted under predetermined conditions in which the pressure was at 101.3 (kPa).

The water was heated to approximately 60 °C and then the steam was supplied into

the vessel through the control valve. A reaction container made of a glass pipe of

250 (ml) was set up in a wave guide. The microwave irradiation was supplied from a

microwave generator to the antenna in the reaction container, with the plasma then

generated at the antenna tip where the electric field concentrates.

The antenna was made of a copper material with an outside diameter of 3 (mm)

and inside diameter of 2 (mm). After plasma was generated, the valve was opened

and steam began to flow into the reaction container from the water tank through the
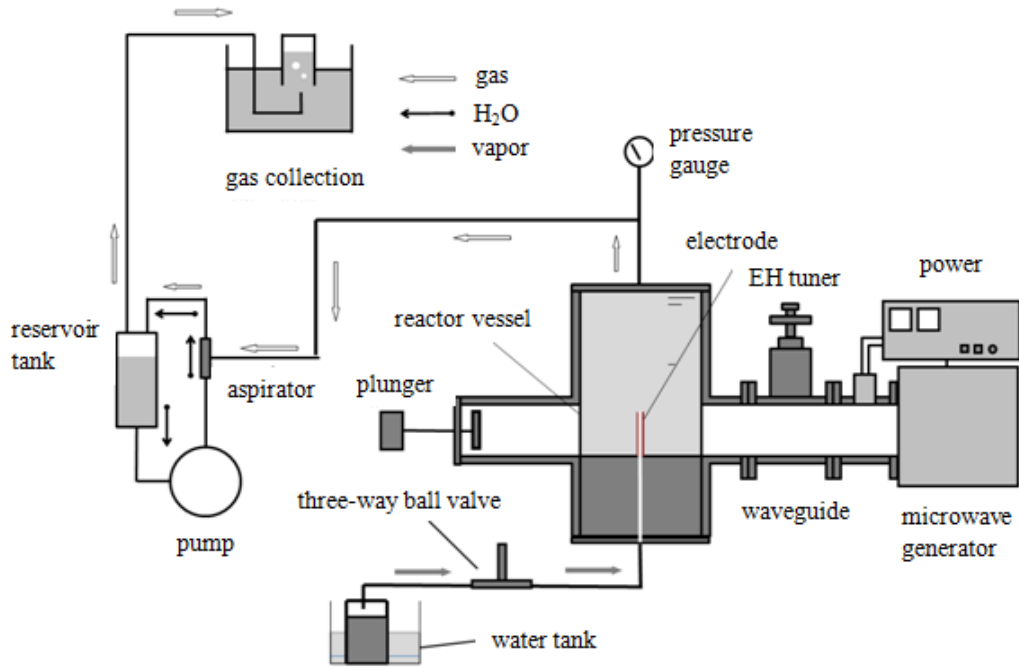
Fig. 4.5 Schematic of hydrogen production in-liquid plasma using the steam reforming method

electrode. The steam temperature was varied by changing the temperature T of the thermostatic bath. The pressure in the reaction container was depressed by an aspirator. The mixture of the gas generated and the water flowing through the aspirator was then separated at a water reservoir tank. Measurement of gas generation rate v and analysis of the compositions of the gas generated was conducted.

Fig. 4.6 shows the rate gas generation for that with steam and without steam using MW. The figure also shows that by using steam, the gas production rate was increased 1.4 times over that without using steam. In steam reforming, the alkaline water temperature was kept constant at 60 °C in order to produce steam while plasma was generated. The input P power was varied between 100 (W) and 325 (W).

The higher the input power supplied, the greater the rate of generated gas. However, in order to avoid the excessive steam pressure in the reactor, the optimal input power was limited to 325 (W).
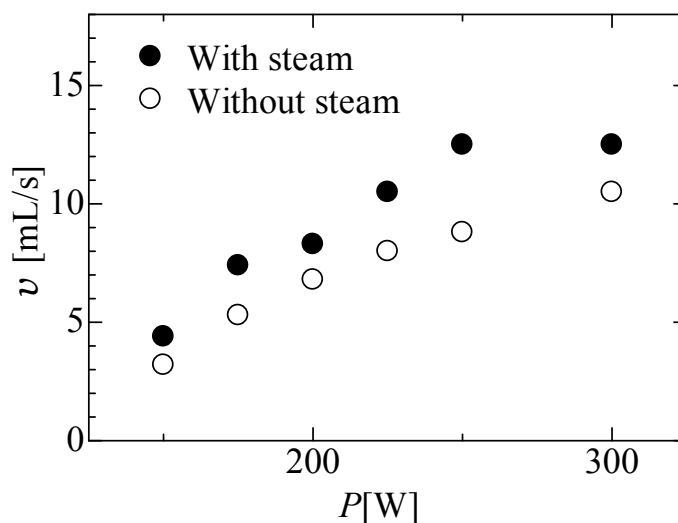
Fig. 4.6 Rate of generated gas between steam and without steam in the MW reforming method

Fig. 4.7 shows the gas yield using steam and without steam. At input power of 300 (W), the gas yield from decomposition of *n*-dodecane with steam reforming was H_2 (82.0%), CO (6.5%), CH_4 (1.5%), C_2H_2 (6.7%) and C_2H_4 (3.2%). On the other hand, the gas yield from decomposition of *n*-dodecane without steam reforming was H_2 (82.5%), CH_4 (3.1%), C_2H_2 (10.5%) and C_2H_4 (3.9%). The obtained results obviously show that the steam supplied into the process caused production of carbon monoxide (CO) and reduced other hydrocarbon gases yields. The reduction of hydrocarbon gases yield was suggested due to the reaction of oxygen atoms from steam with carbon atoms from *n*-dodecane for production of carbon monoxide.
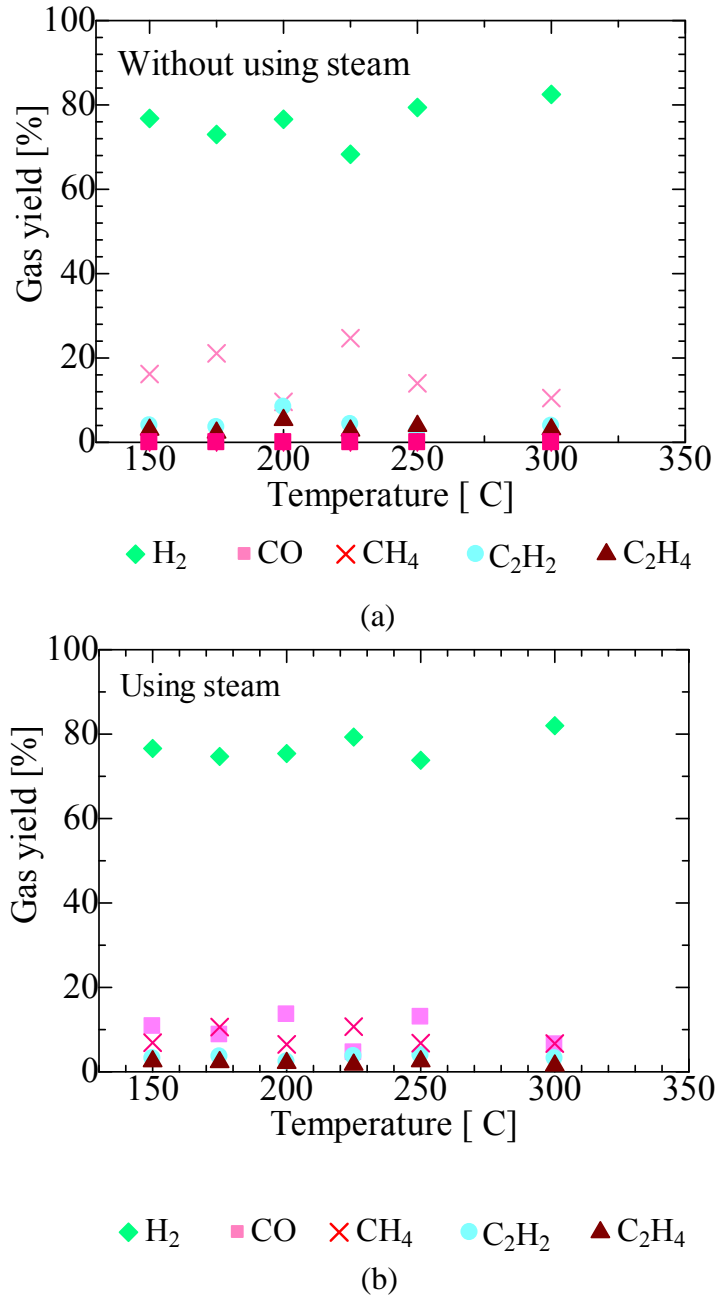
Fig. 4.7 Gas yield for hydrogen production in MW steam reforming: (a) without using steam, (b) using steam reforming method.

4.4. Conclusion

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 58-90% 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.

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Chapter 5: Hydrogen Production from n-dodecane using Steam Reforming in-Liquid Plasma Method

5.1 Introduction

Hydrogen is not a primary energy source like coal, oil or natural gas, which freely exist in nature. Rather, it is a secondary energy that can only be obtained by processing a primary energy source [1–3]. Accordingly, energy is required to extract and capture hydrogen produced from these processes. Electrolysis of water is the dominant method for manufacturing clean hydrogen [4, 5]. However, since water is an extremely stable material, creating hydrogen from it requires a large amount of energy. Water electrolysis can be used to generate hydrogen by using toluene in an exothermic hydrogen reaction to produce methyl cyclohexane [33]. Steam reforming of natural gas is another method for manufacturing large amounts of hydrogen that is seeing commercial application [7–9]. However, the greenhouse gas, carbon dioxide, is released in the final stage of the steam reforming reaction so there is a need for some method to capture and store it [10–12]. If we take into account the energy required for solidifying the carbon, this method may actually be less energy efficient than the electrolysis method [13-15]. In order to make hydrogen energy a viable alternative energy source, the development of a low-cost hydrogen manufacturing method that does not produce carbon dioxide is necessary. While thermal plasma decomposition of methane gas to extract hydrogen is one method that does not release carbon dioxide, this method is not practical because the amount of energy required for thermal cracking is approximately the same as the amount of the resulting hydrogen energy [16].

In previous research, in-liquid plasma was first conducted by Nomura and Toyota for the purpose of depositing diamond-like carbon on to a variety of surface materials. By using the plasma method, the reaction was 9,000 times faster than that of gas-phase plasma[18, 19]. The bubbles created in *n*-dodecane were irradiated simultaneously by microwaves and ultrasonic waves. Recently, hydrogen production using non-thermal plasma technologies have been examined due to their relatively low energy requirements. Also, they have the capability to induce physical and chemical reactions under low temperature conditions because of their non-equilibrium properties [19–21].

In-liquid plasma is created by the application of microwaves or high-frequency waves to a liquid medium. The temperature of plasma within the liquid exceeds 3000 K at atmospheric pressure, enabling decomposition of nearly any waste product and extractions of any existing hydrogen in the processed material (e.g. hydrocarbons) [22–26]. By definition, hydrocarbon liquids contain large amounts of hydrogen. Therefore, lesser energy is required for their decomposition and release of the hydrocarbon. In previous studies, the amount of energy needed to produce hydrogen using several methods, water electrolysis, steam reforming, methane hydrothermal, and in-liquid plasma efficiency ratios for hydrogen production were found to be 286, 41.3, 37.5, 27 kJ/mol in respectively [57]. The required change in enthalpy for creating 1 mole of source material to produce hydrogen from water is ΔH_{H_2} 286 kJ/mol, whereas for hydrocarbon, it is ΔH_{H_2} 351 kJ/mol [19]. An additional benefit of using the in-liquid plasma process is that the carbon components can be solidified simultaneously. Therefore, in-liquid plasma technology solves the problems associated with electrolysis and steam reforming. Previous research has indicated that hydrogen with a purity of 66% to 81% can be produced by using plasma to decompose organic solvents and waste oils

[28, 29]. This technology can also be applied for the collection of hydrogen from methane hydrates in sea beds [16, 17, 30]. In this research, it is proposed that a continuous steam flow, microwave-based in-liquid plasma device could be used as a method for continuously producing hydrogen through the decomposition of *n*-dodecane.

5.2 Experimental Setup

The experiment was conducted on the *n*-dodecane liquid at a pressure of 101.3 kPa as measured by pressure gauge. **Fig. 5.1** shows the experimental setup including the gas flow direction in the vessel. The mass balance was measured by filling 20 cm^3 of *n*-dodecane into the reactor vessel to which microwave input power in range from 150 W to 300 W with 200 V was applied to produce plasma. The temperature of the *n*-dodecane was 21°C at a room temperature. The reaction container consisted of a 25 cm^3 glass pipe and a waveguide was set up consisting of aluminum rectangular tubes to guide electromagnetic waves to propagate a minimal loss of energy. Microwave energy was supplied from a standard power supply to the electrode in the reaction container where plasma was generated by the electric field concentrated at the electrode tip as shown in **Fig. 5.2** .

The electrode was made of copper. The electrode had an outside diameter of 3 mm, an inside diameter of 2 mm and a length of 22 mm. The copper electrode was connected to the bottom of water tank immersed in a thermostatic bath. After plasma generation, a valve was opened to introduce steam with a 1 cm^3/s flow rate at a temperature of under 60 °C into the reaction container through the copper pipe of the electrode from a water tank. The steam temperature can be varied by changing the temperature *T* of the thermostatic bath. The pressure in the reaction container was reduced by an aspirator.

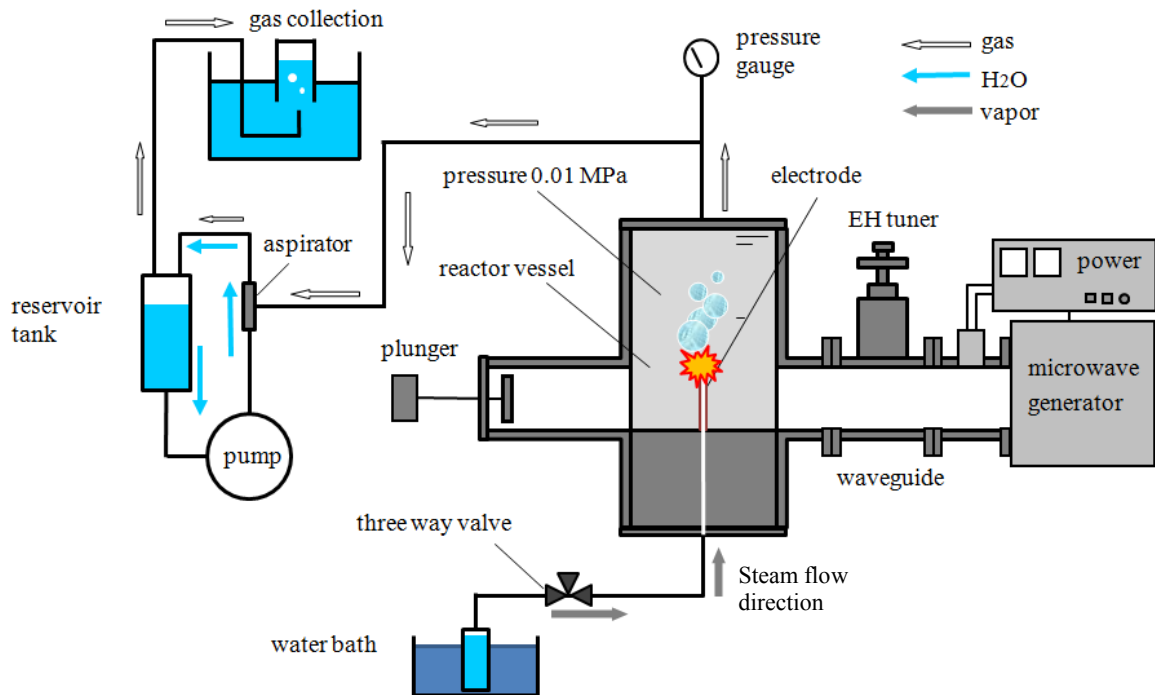**Fig. 5.1** Experimental setup for hydrogen production using the steam reforming method
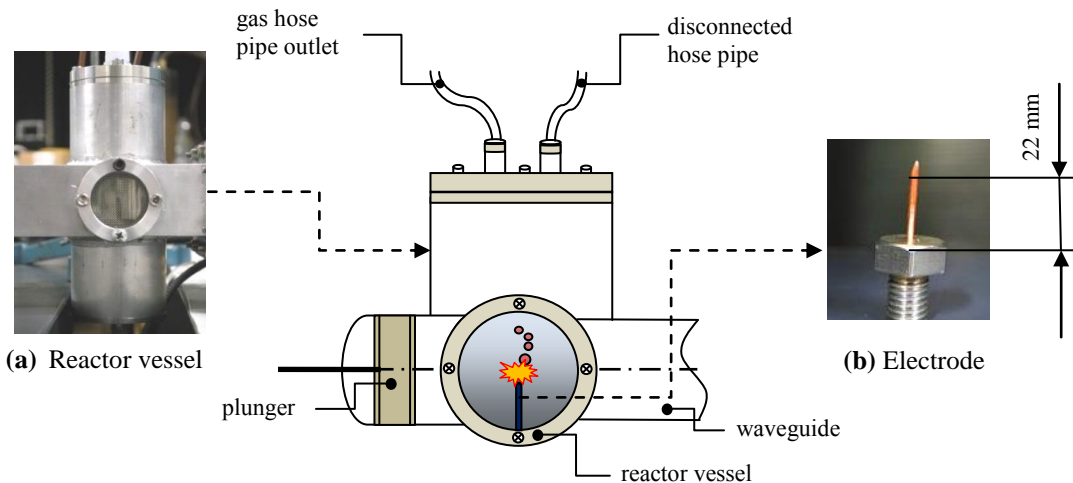

Fig. 5.2 Reactor vessel with a single electrode for creating plasma placed in the bottom center of reactor: **(a)** Actual reactor vessel, **(b)** Single tip electrode

The generated gas was mixed with water streaming from the aspirator and then separated in a water reservoir tank and finally gathered by water substitution.

Measurement of the gas generation rate v and composition analysis of the generated gas was performed. For the analysis of the generated gas, a gas chromatograph (GC-8A, Shimadzu) was used. The detector was a thermal conductivity detector (TCD) and argon gas was used as a carrier.

5.3 Results and Discussion

Experiments were conducted to investigate the effect of steam reforming on *n*-dodecane using microwave in-liquid plasma method. The following formula shows the decomposition reaction of *n*-dodecane with the vapor :

$$a\text{C}_{12}\text{H}_{26} + b\text{H}_2\text{O} \rightarrow n_{\text{H2}}\text{H}_2 + n_{\text{CO}}\text{CO} + n_{\text{CH4}}\text{CH}_4 + n_{\text{C2H2}}\text{C}_2\text{H}_2 + n_{\text{C2H4}}\text{C}_2\text{H}_4 + c\text{C(s)} \quad (1)$$

where

$$a = (2n_{\text{H2}} + 4n_{\text{CH4}} + 2n_{\text{C2H2}} + 4n_{\text{C2H4}} - 2b) / 26 \tag{2}$$

$$b = n_{\text{CO}} \tag{3}$$

$$c = 12a - (n_{\text{CO}} + n_{\text{CH4}} + 2n_{\text{C2H2}} + 2n_{\text{C2H4}}) / 26 \tag{4}$$

The reaction enthalpy formula for the chemical reaction of Eq. (1) using the law of the conservation of energy (Hess's law) is as follows.

$$\Delta H = -a\Delta H_{\text{C12H26}} - b\Delta H_{\text{H2O}} + n_{\text{CO}}\Delta H_{\text{CO}} + n_{\text{CH4}}\Delta H_{\text{CH4}} + n_{\text{C2H2}}\Delta H_{\text{C2H2}} + n_{\text{C2H4}}\Delta H_{\text{C2H4}} \quad (5)$$

This can be used to find the enthalpy change of the reaction per 1 mole of gas in the chemical reaction in Eq. (1). ΔH is shown in **Table 5.1**.

The following formula shows energy efficiency, which is the ratio of the energy consumed in the chemical reaction per unit time in relation to the power P_{net} input.

$$\varepsilon = \frac{\upsilon \varDelta H}{VP} \times 10^{-2} \qquad (6)$$

where, V is the standard mole volume (22.4 L/mol), υ is the gas generation rate generated by plasma breakdown. ε is ranged between 6.8% and 12.2%. For the electrolysis of alkaline water, the required amount of the enthalpy change to produce 1 mol of hydrogen from water is approximately 286 kJ/mol ($H_2O \longrightarrow H_2 + 1/2\ O_2$). In addition, the required amount of energy to create 1 mole of hydrogen is approximately 360 kJ/mol which is around 80% of energy conversion ratio to generate hydrogen using electrolysis method [19]. The amount of hydrogen production efficiency per input energy is a multiple of the hydrogen ratio for gas generated by υ/P. The values for the ratio of hydrogen generation efficiency η as shown in **Table 5.1** using Eq.(7) as follow.

$$\eta = \frac{\upsilon n_{H_2}}{6.27P} \times 10^{-2} \qquad (7)$$

The hydrogen production efficiency Q_{H_2} mm^3/J can be calculated by multiplying the gas generation rate υ with the hydrogen ratio n_{H_2} per input energy as shown in Eq.(8). Therefore, the gas generation rate and hydrogen ratio should be large due to improve hydrogen production efficiency.

$$Q_{H_2} = \frac{\upsilon \times 10^{-6}}{P \times 10^{-3}} n_{H_2} \times 10^{-2} \qquad (8)$$

The required change in enthalpy ΔH_{H_2} to create 1 mol of hydrogen from water is 286 kJ/mol. This is much larger than the changes in enthalpy shown in **Table 5.1**. In order to industrialize the production of hydrogen from *n*-dodecane, the production of microwave in-liquid plasma decomposition process must be considered. Therefore, the energy payback ratio of hydrogen (EPR_{H_2}) which is the ratio of hydrogen production to microwave input power is governed by Eq. (9). The maximum EPR_{H_2} for this experiment is found to be 47% which was when the input power reaches 225 W and 250 W and the gas generation rate reaches 10.5 cm^3/s and 12.5 cm^3/s.

$$EPR_{H_2} = \frac{\upsilon(n_{H_2} \cdot \Delta H_{H_2})}{VP} \times 10^{-2} \qquad (9)$$

The mass balance is calculated to evaluate the performance process. The operating condition for mass balance are determined by measuring the gas composition and the total volume of hydrogen gas produced at each experimental time. The following shows the mass balance equation.

$$V_{H_2,t} = V_{H_2,t-1} + x_{H_2,t}(V_{m,t} - V_{m,t-1}) + V_H(x_{H_2,t} - x_{H_2,t-1}) \qquad (10)$$

Where $V_{H_2,t}$ and $V_{H_2,t-1}$ are the amount of hydrogen gas volume at the current (*t*) and previous (*t-1*) at each experimental time, $V_{m,t}$ and $V_{m,t-1}$ are the total gas production in the current and previous experimental time, $x_{H_2,t}$ and $x_{H_2,t-1}$ are the fractions of hydrogen gas produced in the current and previous experimental time, respectively [3]. The amounts of hydrogen contained in trace by-products such as CO, CH$_4$, C$_2$H$_2$, and C$_2$H$_4$ in the product gas at a reaction time of around 5 to 8 minutes were found to be 82.00, 6.51, 1.54, 6.71,

and 3.19 (%) respectively when input power is 300 W. The carbon balance is found to be

between 40% and 60%.

5.3.1   Optimization of the steam temperature

The temperature was varied from 40°C to 80°C at a constant power supply of 250W. In

order to improve the hydrogen production, steam was injected through the valve into the

reactor vessel. As shown in **Fig. 5.3**, which shows the effect of temperature on the gas

generation rate at 60°C, the gas generation rate became 12.5 cm^3/s. At temperature

higher than 60°C, the steam distributed to the reaction container became excessive

causing some steam to fail to undergo reaction which then condensed and remained as

water at the bottom of the reaction container.

The gas generation rate was decreased because the remaining water absorbed

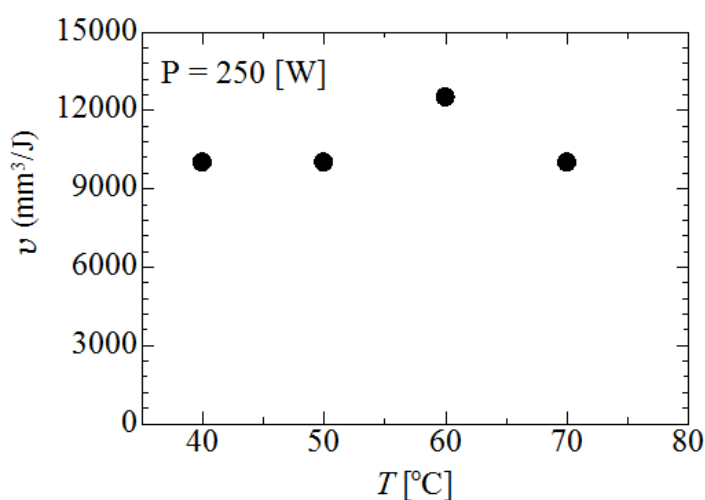microwave energy which impeded the reaction. The rate can be increased by increasing

Fig. 5.3 Effect of temperature on gas generation rate when *P* = 250W

the temperature. However, increased temperatures can cause the electric field breakdown that occurs near the center of the electrode. The *n*-dodecane itself was heated by the microwave energy to temperatures between 40°C and 80°C. Then, the heat of the *n*-dodecane was released into the vessel reactor and to the surrounding atmosphere.

5.3.2 Effect of the steam reforming method

In this experiment the input power P was varied from 150 W to 325 W at 60°C. **Fig. 5.4(a)** shows the hydrogen production efficiency with and without the supply of steam. The steam contains H_2O which decomposed into H and O_2 gases in the reactor vessel. Therefore, the hydrogen production efficiency with using supplied steam is more effective than without one.

The maximum efficiency for the steam reforming method is 37 mm^3/J when 225 W of input power is supplied. The reason for this is because both of the amount and the rate of H_2 gas are relatively large. Due to the steam supply, the rate of the generated gas increased linearly to P when P is from 150 W to 250 W, and then became constant after P exceeded 250 W. When steam was injected at the same power consumption, the gas generation rate increased 1.4 times in comparison to the case without steam supply. **Fig. 5.4 (b)** and **(c)** show the compositions of gas analyzed from the plasma in-liquid using the steam reforming method. The contents of produced gas are shown in **Table (5.1-5.4)** where the steam supply and P were varied. By injecting steam, the contents of hydrogen the in generated gas ranged between 73% and 82% of the total produced gas. Whereas in comparison with no steam supply, it seemed that there was no significant effect on the contents of hydrogen in generated gas. Moreover, when conducting the steam reforming method, carbon monoxide was produced and the ratio of hydrocarbons was decreased.
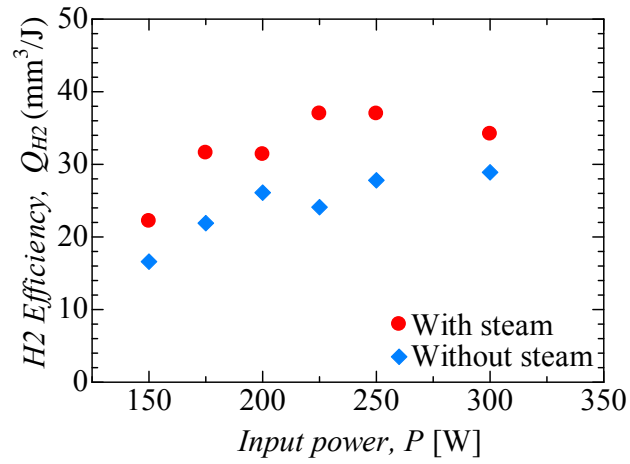
(a) H_2 production efficiency
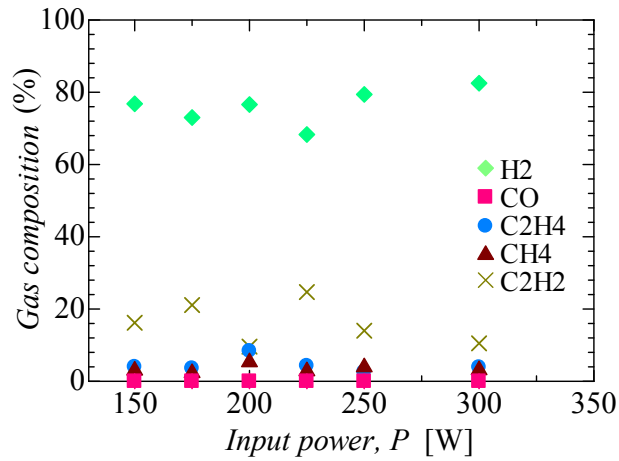
(b) Gas yield without steam
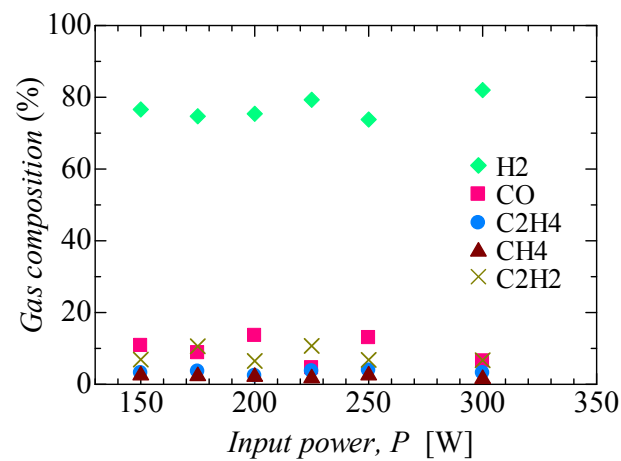
(c) Gas yield with steam

Fig. 5.4 Efficiency and composition of generated gas for hydrogen production
using in-liquid plasma method

Table 5.1 Composition of H_2 gas efficiency in using steam and without steam

Input power, P [W]	Steam	Without Steam
150	22.2	16.6
175	31.6	21.9
200	31.4	26.1
225	37	24.1
250	36.9	27.8
300	34.2	28.9

Table 5.2 Composition gas yield without steam

Input power, P [W]	H_2 (%)	CO (%)	C_2H_4 (%)	CH_4 (%)	C_2H_2 (%)	Total gas composition(%)
150	76.8	0	4	3	16.2	100
175	73	0	3.6	2.3	21.1	100
200	76.6	0	8.4	5.3	9.6	100
225	68.3	0	4.3	2.8	24.7	100
250	79.4	0	2.6	3.9	14	100
300	82.5	0	3.9	3.1	10.5	100

Table 5.3 Composition gas yield with steam

Input power, P [W]	H_2 (%)	CO (%)	C_2H_4 (%)	CH_4 (%)	C_2H_2 (%)	Total gas composition(%)
150	76.6	10.8	3.2	2.5	6.9	100
175	74.7	8.8	3.6	2.3	10.6	100
200	75.4	13.6	2.4	2.1	6.5	100
225	79.3	4.6	3.7	1.7	10.7	100
250	73.8	13	3.9	2.5	6.8	100
300	82	6.5	3.2	1.5	6.7	100

Table 5.4 Composition gas and component reaction for hydrogen generation using microwave with varying input power

Method	P (W)	v (cm³/s)	Contents of produced gas (%)					ΔH (kJ/mol)	ε (%)	η (%)	Q_{H2} (mm³/J)	EPR_{H2} (%)
			H_2	CO	CH_4	C_2H_2	C_2H_4					
Without	150	3.24	76.80	0	3.00	16.20	4.00	65.40	6.30	26.50	16.60	21
steam	175	5.26	73.00	0	2.30	21.10	3.62	76.70	10.30	40.00	21.90	28
reforming	200	6.82	76.60	0	5.30	9.63	8.37	53.10	8.10	41.70	26.10	33
	225	7.95	68.30	0	2.80	24.70	4.26	85.00	13.40	38.50	24.10	31
	250	8.75	79.45	0	3.89	14.03	2.63	30.28	4.73	44.30	27.80	36
	300	10.50	82.50	0	3.10	10.50	3.90	52.50	8.20	46.00	28.90	37
Steam	150	4.35	76.60	10.80	2.50	6.90	3.24	52.30	6.80	35.40	22.20	28
reforming	175	7.41	74.70	8.81	2.30	10.60	3.55	59.60	11.30	50.40	31.60	40
	200	8.33	75.40	13.60	2.10	6.50	2.40	53.20	9.89	50.10	31.40	40
	225	10.50	79.30	4.63	1.70	10.70	3.69	57.00	11.90	59.20	37.00	47
	250	12.50	73.77	12.99	2.46	6.83	3.94	54.50	12.20	58.80	36.90	47
	300	12.50	82.00	6.51	1.54	6.71	3.19	49.00	9.12	54.50	34.20	44

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This decrease in hydrocarbons was due to the oxygen atoms in the steam supplied to the reaction container reacting with carbon atoms in the *n*-dodecane.

5.4 Conclusion

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_{H_2} 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.

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Chapter 6: General Summary

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 [1].

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, CO2 and other greenhouse gases (H2O, O3, CH4, NO, etc [2]) 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 [3].

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 [4–6]. 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 [7, 8]. 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 [9–12]. 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 [13, 14].

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 [15]. 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 (so-called autothermic gasification) [16]. 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 [17–19], 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} [20]. 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 [21]. 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 58-90% 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.

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Appendix

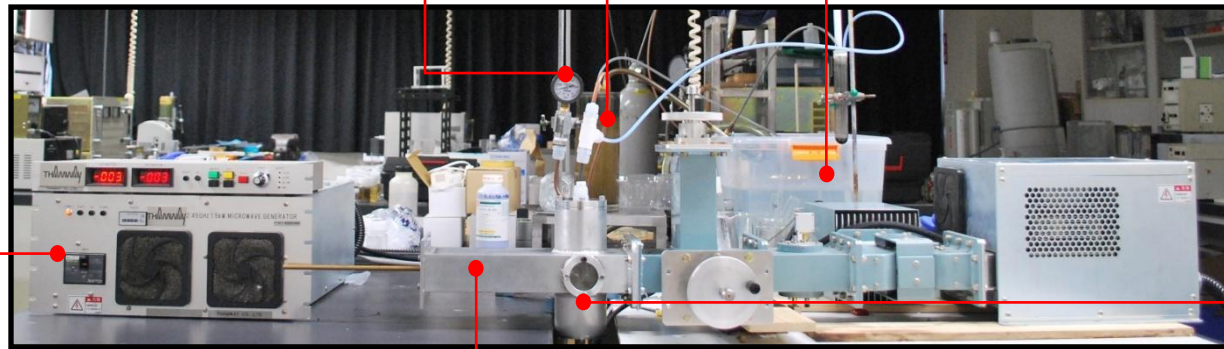- Figures of experimental setup
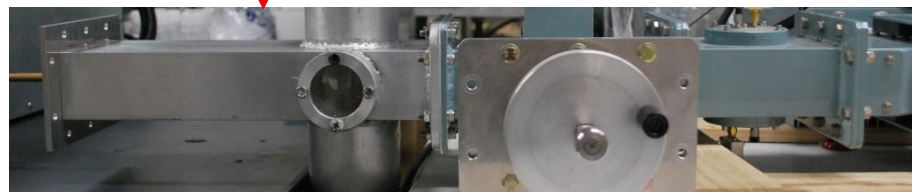- Figures of gas chromatograph unit

Pressure Gauge
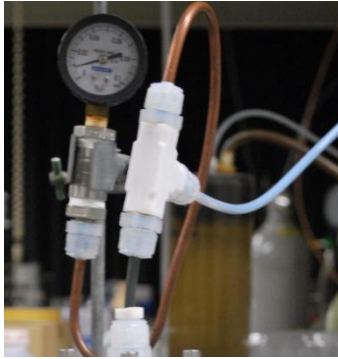
Distilled Water

Water Bath

Experimental setup of hydrogen production using microwave

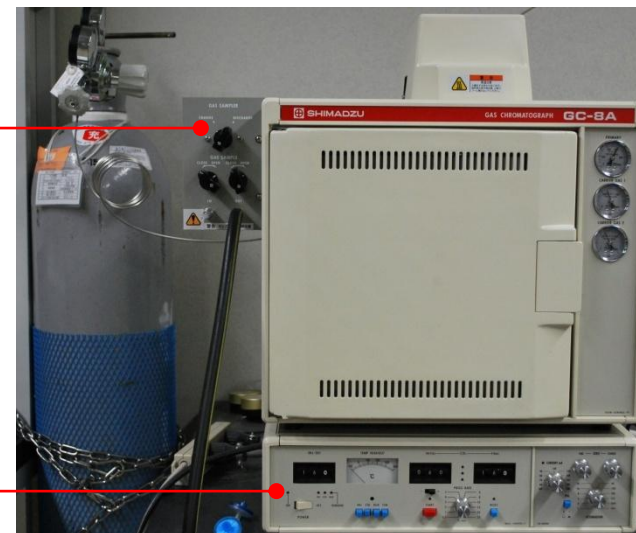2.45GHz 1.5kW Microwave Generator
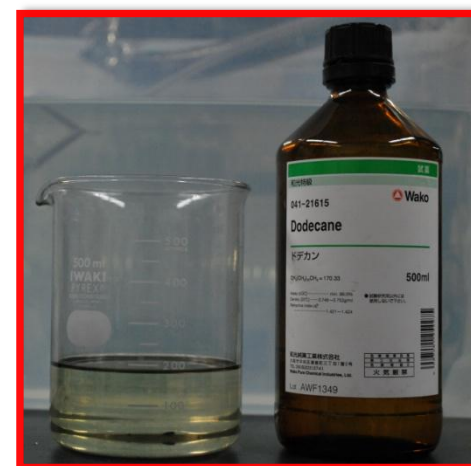(T161-62DD AEM)

Waveguide

Reactor Vessel

Switch on/off for Input Gas

Gas Chromatograph (GC) Unit

Regulator Panel of Gas Chromatograph

The Commercial of *n*-Dodecane Oil