40. Small Scale Catalytic Syngas Production with Plasma

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The production of syngas has been desired for nearly a century as a starting point towards an effort to achieve the synthesis of higher-energy liquid fuels. Methods that are utilized for obtaining syngas have undergone profound technological transformations over the years. The formation of plasma is one such concept capable of energizing molecular chains through dielectric manipulation in order to excite electrons and form radicals. Many types of plasma configurations exist under a range of variable parameters such as pressure, temperature, current, power intensity, and physical structure. Nonthermal plasma in conjunction with catalysis is a relatively new concept that takes a more subtle approach that eliminates the intensive energy requirement while maintaining high conversion efficiency. The technology and process presented in this book chapter will encompass a hybrid plasma/catalysis (PRISM) system having the ability to ionize and reform any vapor phase species with a focus on short to long chain hydrocarbons. The apparatus promotes reactions that would otherwise be disadvantageous from either a high activation energy standpoint or from the yield of unfavorable side products. Catalytic partial oxidation (CPOX) using a low-energy, nonthermal plasma is capable of nearly perfect conversion of a carbonaceous starting material into clean, homogeneous, hydrogen-rich syngas.

This chapter documents work done on small- to mid-scale plasma enhanced catalysis for platform-flexible fuel reformers in an effort to improve conventional (i. e., internal combustion) vehicle operation as well as the commercial standard reformation efficiency. Although industry has been focusing on methane, the system performs as a cost-effective method in the production of hydrogen-rich, process-ready syngas from any carbonaceous source/feedstock.

There exist several applications of stationary and onboard hydrogen production:

- Supplementation and augmentation of hydrogen into internal combustion engines (ICEs) for improved operation and pollutant elimination
- Diesel PRISM fuel reformation for after-treatment application
- Onboard hydrogen generation for fuel cell power production
- Clean-burn electrical generation (turbines, gen sets)
- Liquid drop-in fuel production.

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The chapter is organized as follows: First, an introduction of plasma and its different forms and attributes are defined in Sect. 40.1. The primary reaction of interest is partial oxidation (POX) and this, along with the micro- and macrokinetics of the PRISM process in terms of theory, will be described in detail in Sect. 40.2. Section 40.3 details the experimental process from start to finish with a broad overview of operational perspective. In Sect. 40.4, we expound on a discussion of the data including process challenges, areas of improvement, and future development. Some of the synergistic effects of plasma over typical gas-phase processes can be found in Sect. 40.5, which leads to the conclusion of how and why plasma-assisted POX in a catalytic environment is a viable and cost-effective technology.

40.1 Plasma

40.1.1 Introduction

There are many different paths that lead to the production plasma, which is universally known as the fourth state of matter and also the most abundant state present in the universe. Some generally known devices and methods of generating plasma include the plasmatron, plasma jet or torch, spark, corona discharge, electrical or gliding arc, and glow discharge. For our purposes, plasma is regarded as a collection of freely charged particles in random motion that is, on average, electrically neutral [40.1]. Typically generated from a gaseous phase, application through an electrical field induces a temporary condition of a plasma state regardless of bulk medium temperature. Additional ways to accomplish this include, but are not limited to, a radio frequency (RF) treatment or a microwave treatment of the gas in a strong electromagnetic field. When utilized to augment a reaction, plasma adds substantial beneficial factors to the molecular interactions and kinetics of the reaction at hand.

Breakdown and Ionization

The standard gas molecule is stable in an environment when at or near a state of equilibrium with its surroundings. As intensive and extensive properties change, molecules begin to lose their stability. Electron movement rapidly increases and ionization is achieved when electrons gain enough energy to remove themselves from their respective orbitals unbound from their normal position within or around the molecule. Ionization may also be achieved when temperatures rise beyond a distinct threshold level of the molecule. With less difficulty than applying extreme amounts of heat, ionization can be reached inside an electrical field supplied by an adequate voltage source. This approach causes a dielectric *breakdown* of the gas molecule into plasma consisting of charged species (electrons, ions, radicals) and neutral species (atoms, molecules, and excited particles). The plasma thus becomes a highly energetic state of matter characterized by an elevated electrical conductivity [40.2]. Strongly bonded molecules like hydrocarbons such as methane (CH_4) in a plasma-induced state have been documented to disassociate ($C_1H_4 \rightarrow C_1H_{[x<4]} + H + H_2$) then quickly recombine into intermediate compounds such as C_2H_2, C_2H_4, and C_2H_6 [40.3]. This can be achieved and maintained as long as the methane is exposed to the electrical field. The intermediate molecules are a short-lived species and will reform back into methane if not converted while yielding some amount of molecular hydrogen.

Generation of Plasma Field

Multiple methods exist to produce a viable plasma field, the most practical being two electrodes in close enough proximity supplied with a voltage creating an arc of electricity, or plasma, through the air gap between the electrodes. This can be seen in Fig. 40.1b using parallel conductive plates. The power supply drives the current between the conductive electrodes ionizing the gas flowing through it. Pressure plays an important role for the generation of the field. At pressures below

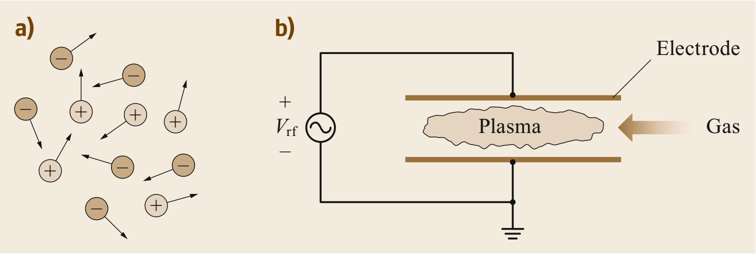

Fig. 40.1 (a) Visual of excited ion motion that makes up plasma. **(b)** Simple plasma discharge apparatus (after [40.1])

atmospheric and above vacuum, the electrical energy required to create a plasma field arc or glow discharge is reduced to a minimum. The augmentation of the dielectric strength of vacuum by matter and pressure is the primary function for sustaining the plasma field.

Another factor in field generation refers to the geometry of the electrodes. Industrially, these can vary from sharp singular points to infinitely long plates to annular arrangements physically similar in appearance to concentric pipe heat exchangers. In the case of processing gas, the annular apparatus is highly efficient and isolates the system from the surrounding environment. It is difficult to classify and analyze the plasma generated from an external electromagnetic field because of the inconsistent nature of the ionized particles. The generated plasma is on a very short time and space scale (10^{-7}–10^{-9} s) as the excitation weakens, dissipating quickly upon departure from the applied electrical source. If not utilized properly, the plasma will return to a stable gaseous ground state.

Stability and Equilibrium

Plasma requires constant treatment via an external energy source in order to maintain its phase stability, making it a short-lived species at ambient conditions. In a continuous process, it's wise to consider the placement of the plasma generating field in order to optimize overall system efficiency. Ionization and dissociation are a requirement for the existence of plasma, but these induced conditions also cause a fluctuation in equilibrium. Plasma density, also defined as electron or ion density (n_i), is the number of free electrons per unit volume. Ion density can be used to determine the degree of fractional ionization (x_iz) of plasma represented by the equation

$$x_\mathrm{iz} = \frac{n_\mathrm{i}}{n_\mathrm{g} + n_\mathrm{i}}$$

where n_g is neutral gas density. If the degree of ionization is ≈ 1 then the plasma can be considered fully ionized and if $x_\mathrm{iz} \ll 1$, the plasma is weakly ionized. No matter how minute the presence of ionization in the gas phase, plasma characteristics still show to some degree [40.3]. Threshold levels for ionization exist during excitation of a gas-phase substance and depending on the amount of energy applied, different charged and neutral molecules will be produced that are of overall equal constituents to the original gas molecule. These excited forms consist of rotational excitation, vibrational excitation, disassociation, and full plasma ionization. Rotational and vibrational excited states are generally considered impractical for most processes due to their low threshold energy (< 2 eV) and short lifetimes (nanoseconds) [40.1]. Electrical field energy is directly proportional to electron energy responsible for greater molecular decomposition from the electron-impact dissociation and ionization reactions. As an example, bonding energy of most hydrocarbons is between 3–6 eV. This range expresses C–H and C–C bond strength varying from molecule to molecule of any hydrocarbon in general. C–H bonds are stronger and closer to 6 eV in strength than that of C–C bonds, which reach the lower interval of 3 eV in strength. An electron-volt (eV) is energetically equivalent to about 1.6×10^{-19} J (Joules). The following electron-impact reactions of methane show the threshold energy barrier necessary to achieve specific levels of plasma excitation [40.3]:

- Vibrational excitation

$$\begin{aligned}&\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_4}(\nu 24) + e^-\\ &\qquad \text{Threshold energy} = 0.162\,\mathrm{eV}\\ &\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_4}(\nu 13) + e^-\\ &\qquad \text{Threshold energy} = 0.361\,\mathrm{eV}\end{aligned}$$

- Dissociation

$$\begin{aligned}&\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_3} + \mathrm{H} + e^-\\ &\qquad \text{Threshold energy} = 9\,\mathrm{eV}\\ &\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_2} + \mathrm{H_2} + e^-\\ &\qquad \text{Threshold energy} = 10\,\mathrm{eV}\\ &\mathrm{CH_4} + e^- \rightarrow \mathrm{CH} + \mathrm{H_2} + \mathrm{H} + e^-\\ &\qquad \text{Threshold energy} = 11\,\mathrm{eV}\end{aligned}$$

- Ionization

$$\begin{aligned}&\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_4}^+ + 2e^-\\ &\qquad \text{Threshold energy} = 12.6\,\mathrm{eV}\\ &\mathrm{CH_4} + e^- \rightarrow \mathrm{CH_3}^+ + \mathrm{H} + 2e^-\\ &\qquad \text{Threshold energy} = 14.3\,\mathrm{eV}\end{aligned}$$

Methane is a highly stable compound and, as a result, requires more energy to break the threshold barrier than most other hydrocarbons. This data can be used as an initial guide for determining the necessary energy requirement for any intended plasma application. Threshold levels affecting plasma stability lead to one possible reason as to why the plasma state is almost never in chemical or physical equilibrium with its surroundings. Since the discharges are electrically driven and weakly ionized, the applied power preferentially heats the mobile electrons while the heavy ions exchange energy through collisions with the background gas [40.1]. At or below ambient pressure, the ion temperature (T_i) representing the overall temperature (T) is typically much less than the electron temperature (T_e). An immense amount of energy is required for neutral species and charged species to be in thermal equilibrium with each other ($T_\mathrm{e} = T_\mathrm{i} = T$). This is known as hot plasma and the requirement differs from element to element where, for example, a temperature of 20 000 K must be reached for complete thermal ionization of helium while around 4000 K is needed for cesium [40.1]. When not in thermal equilibrium ($T_\mathrm{e} \gg T_\mathrm{i}$), the phase state is considered cold plasma meaning that the overall temperature (T) of the plasma is at least equal to the ambient system process temperature.

40.1.2 Types of Plasmas

As stated before, there exist many different types of plasma, both natural and conventional (Fig. 40.2). The focus of this chapter is on one form of conventional plasma used in a reformation process; it is still worthwhile, however, to note other types. For instance, most plasma is naturally occurring in the universe from stars and interstellar matter. An example of hot plasma, also known as thermal plasma, is the Sun's surface or a bolt of lightning. A neon light can be considered nonthermal plasma or cold plasma. This classification depends on temperature, electronic density, and level of energy of the medium [40.2].

Conventional plasma is synthetic and every synthesized type carries different micro- and macroscopic benefits for process use. Plasma is also categorized by pressure in response to the method of ionization and the structure of the electrical field. For instance, in very low pressure environments plasma may always be considered nonthermal. The following is a list of conventional plasmas with descriptions grouped by pressure.

Low Field Pressure (0 atm $< P_\mathrm{Plasma} <$ 1 atm)

Capacitive coupled plasma (CCP) and inductive coupled plasma (ICP) (Fig. 40.3a–d) are produced by high frequency RF electric fields where positive ion collisions are the dominant factor leading to electron dissociation. The bombarding ions are directly affected by the magnitude of frequency, typically at the MHz level, capable of causing an electron or Townsend avalanche cascading the electrons into a plasma state. CCP is generally used in material processing to enhance surface properties like that of integrated circuitry via etching or film deposition. A substrate is present upon one of the two interacting electrodes that are aided by a positive sheath material maintaining excess negative charges and directing them appropriately. ICP utilizes a coiled electrode (Fig. 40.3c,d) placed outside of the reactive zone instilling an electromagnetic field that negates the direct current (DC) requirement necessary to reach efficient power in CCP. For analytical methods such as spectrometry, ICP provides a reliable detection limit over a wide range of sample elements. The RF power source can also be directed into the plasma gap itself as opposed to through the electrodes for both ICP and CCP.

Cascaded Arc

High-density, low-temperature cascaded arc is plasma in a relatively homogeneous thermal equilibrium. This creates an exception to the hot-thermal plasma classification since the gas, ions, and electrons are all thermally equal ($\approx$ 1 eV) at ambient conditions. The field is stabilized by cascaded plates with a floating voltage potential and is typically structured cylindrically. Operated under a DC supply, the power requirement is in the lower kW range (1–10 kW). This form of plasma and device is used in material deposition and surface treatment as well.

Electron Cyclotron Resonance (ECR) and Helicon Discharge

Electron cyclotron resonance (Fig. 40.3a) and helicon discharge (Fig. 40.3b) are produced by an axial varying DC magnetic field sustained by electromagnetic coils. The coils surround a cylindrical chamber in which microwaves are injected through a dielectric window propagating a rotating polarized wave. This generates the source plasma where it can be directed into the processing chamber. Electron cyclotron resonance (ECR) is operated with a strong magnetic field versus helicon discharge, which is much weaker by comparison. Helicon discharge uses an RF-driven antenna coupled with the weaker magnetic field to create a resonant helicon wave at the plasma source where it is believed that the particle-wave interaction is the cause of the wave energy transfer into the plasma. Conventional areas of interest for these plasma devices include semiconductor manufacturing, electric propulsion devices, or in advanced medical treatment.

Glow Discharge

Glow discharge is produced by a low frequency electrical field induced by DC or RF in the open area between interacting electrodes. Once adequate voltage is met, ionization occurs releasing a vibrant light based on the ionized gas. The system is usually enclosed in a nonconducting transparent tube. Known for its usage in fluorescent lamps and neon lights as well as plasma-screen television devices, glow discharge plasma also has applications in analytical chemistry via spectroscopy and mass spectrometry and in material surface treatment via a method known as sputtering.

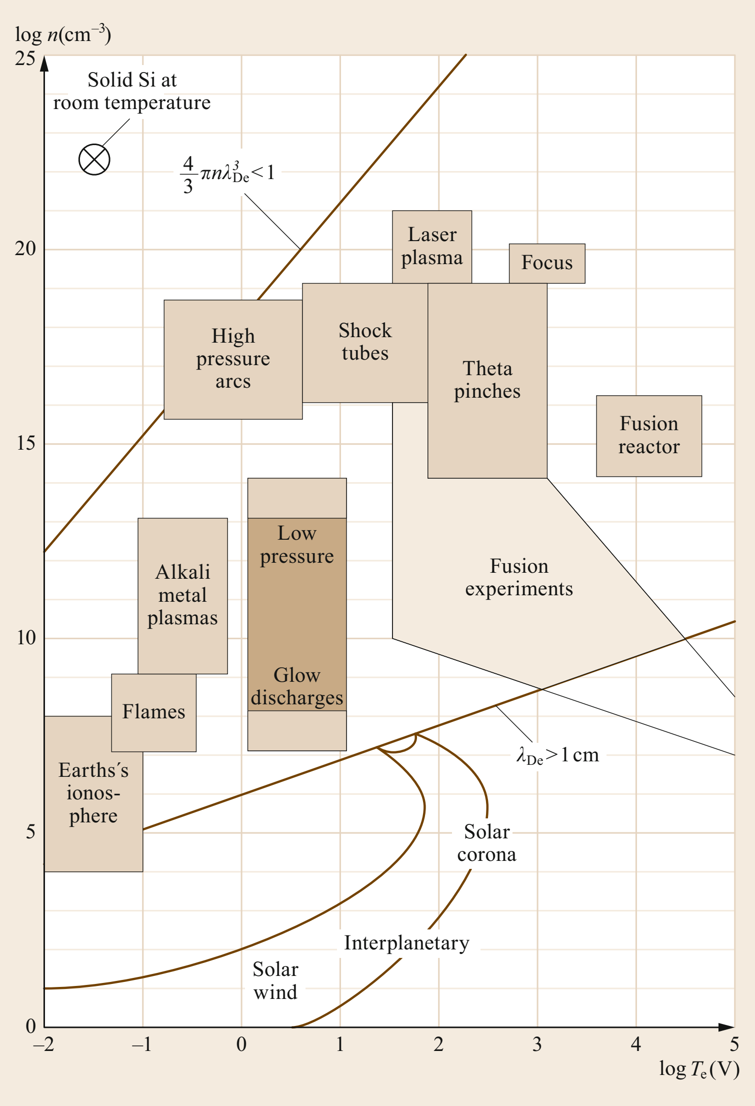

Fig. 40.2 Synthetic and universal plasma on energy (logarithmic temperature voltage equivalent) versus density plot. λ_{De} = Debye length – the distance scale over which charge densities can exist spontaneously or more simply, how far the electrostatic effects travel. As an example, low-voltage and undriven plasmas are generally a few Debye lengths wide (*middle portion* of figure) (after [40.1])

High Field Pressure ($P_{\text{Plasma}} > 1$ atm) Plasma Torch and Thermal Plasmatron

Plasmatron is a high-powered DC thermal plasma generated by electric resistive heating of a turbulent flow of gas molecules. The plasmatron provides highly controllable electrical heating, but requires resilient electrodes to withstand corrosion from the strong arcs and extreme heat. A relatively large amount of energy is required to harness a homogeneous field in thermal equilibrium due in part to the elastic collisions of the propagating energized electrons. Utilizing an annular configuration, the input gas is injected tangentially to produce a vortex that extends the plasma arc field inside of the ionization zone. Water is used as a heat sink to cool and control electrode temperature preventing thermal damage to the components. The high power requirement pitfall limits widespread use of the thermal plasmatron in industry, but the plasma torch finds a niche in plasma cutting, pollution control and hydrocarbon reformation.

Corona Discharge

This form of nonthermal plasma is generated through finely pointed electrode tips at a voltage high enough to initiate a conductive field, but not so high to cause an electrical arc discharge to the grounded path. Although the corona charge can be positive or negative, the positive corona is undesirable due to the extremely high energy requirement to excite positive ions. This is not the case for a negative corona, in which electrons are much lighter and more easily ionized in a non-

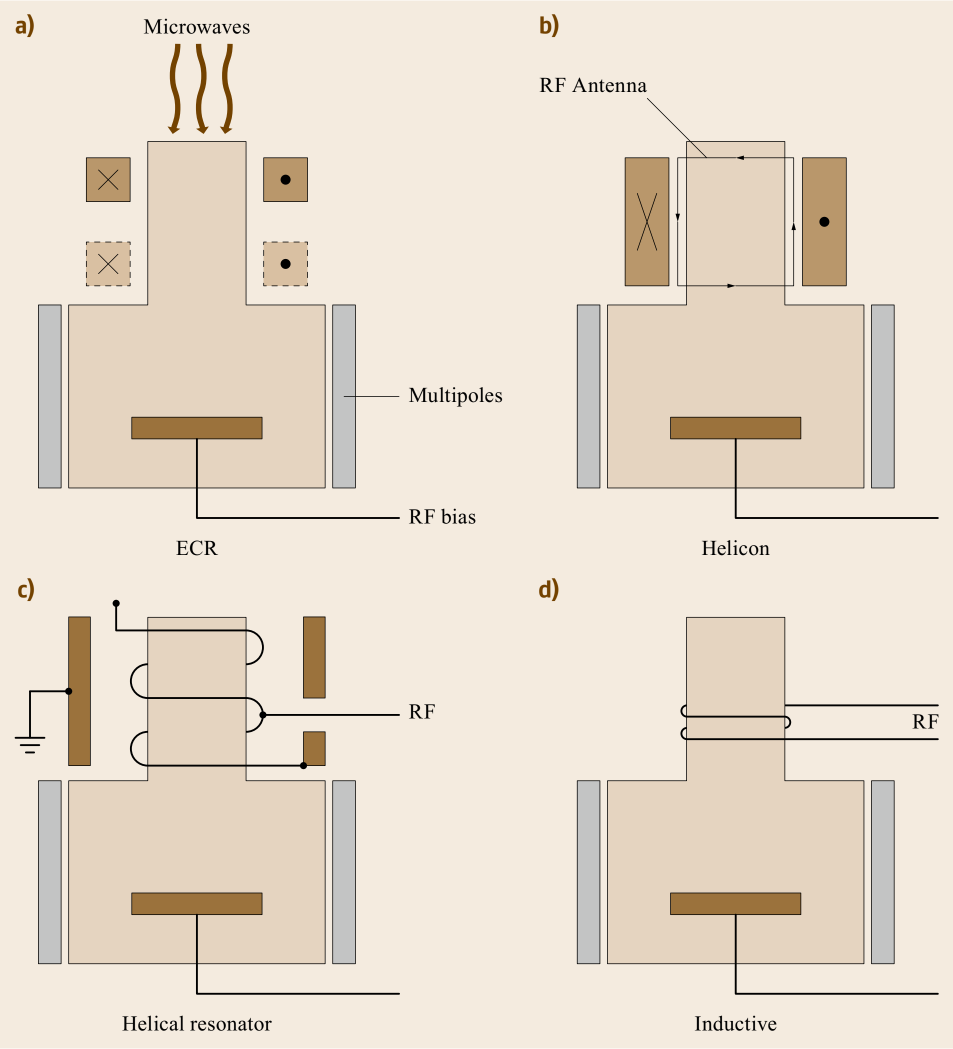

Fig. 40.3a–d Example sources of low-pressure, high-density plasma in basic configurations (after [40.1])

thermal low-pressure setting. The Townsend avalanche causes the highly energized and separated electrons to move radially in all directions creating a plasma cloud. As the electrons move further and further away from the voltage point, they lose energy and eventually are no longer able to force ionization as they begin to approach the grounded electrode. The field, or cloud of electrons, maintains ionization for as long as a voltage is supplied. Corona discharge is a method for ozone production, volatile organics (VOCs) removal, air clean-up, and water sanitization as well as for analytical techniques.

Dielectric Barrier Discharge (DBD)

An insulating dielectric barrier is used to separate, including the space gap, the field producing electrodes that uses low-RF or microwave frequency from a high voltage alternating current (AC) (1–10 kV) power source. The material used for the dielectric barrier ranges from polymers to glass or ceramics, all nonconductive in nature. Planar or axial configurations may be utilized depending on flow applications and can be seen in Fig. 40.4. DBD is another form of nonthermal plasma that can be generated at ambient pressure and low temperature that is not in total particle equilibrium. Microdischarges occur at the dielectric surfaces and propagate like a glow discharge while maintaining homogeneity, but within a more pressurized environment. Originally designed for ozone generation, DBDs find use in catalysis enhancement, surface modification of materials, emissions control, excimer lamps, and silent-discharge CO_2 lasers.

Gliding arc

Gliding arcs are arc discharges that initiate from the point of shortest distance between parallel, but diverg-

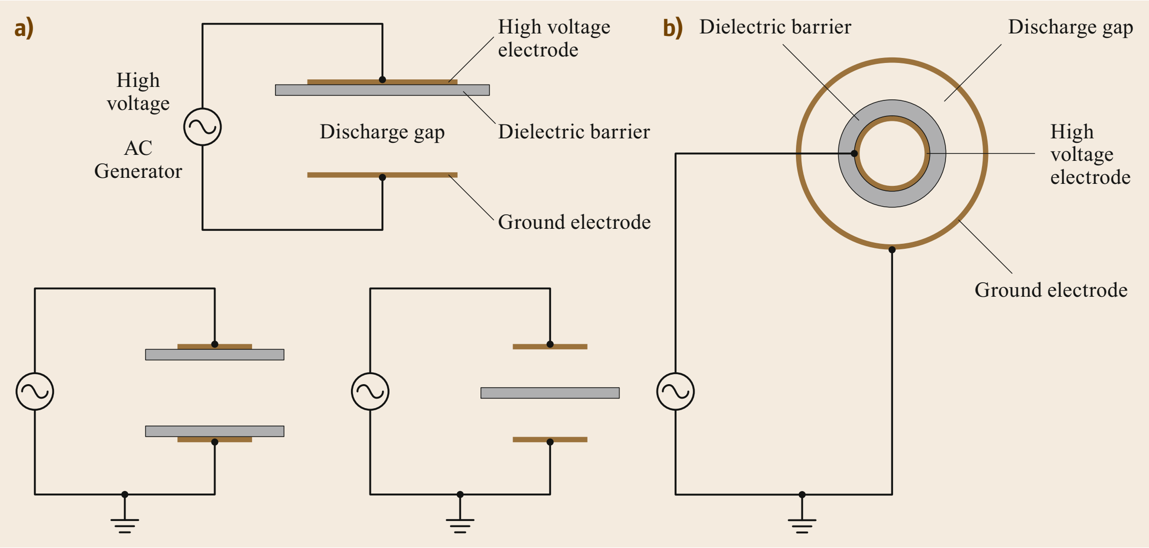

Fig. 40.4a,b Configurations of different DBD plasma devices (apparatus similar to other plasma devices minus the dielectric barrier) (after [40.4])

ing electrodes. The arcs travel along the length of the electrodes until complete breakdown of the arc occurs near the endpoints of the divergent electrodes [40.5]. As the gliding arc dissipates, the encompassing turbulent gas maintains a glow discharge plasma state. This continuous cycle is determined by the system parameters, which include characteristics of the electrical power source (AC or DC), range of current and voltage capacity, gas type, gas velocity, electrode geometry, and field pressure. Associated with a high level of current ($\approx 50\,\mathrm{A/arc}$ discharge), this thermal plasma reaches extreme temperatures ($T > 10\,000\,\mathrm{K}$) energizing all the chemically active species (CAS) present in the medium. The power requirement varies from 1–10 kW based on the parameter conditions. Gliding arc can be considered a hybrid form of thermal and nonthermal plasma reaching only temporary equilibrium with traits similar to the plasmatron and glow discharge. Some of the many applications of gliding arc plasma include metallurgy, chemical reformation, reformation of flue gas, dissociation of CO_2, and decontamination.

40.2 Partial Oxidation Reformation Using Cold Plasma

40.2.1 Methane Reformation

Industrial practices often vary in regards to reformation techniques as the end goal is unique to each process. Hydrocarbon reformation can be utilized as a supplement to larger-scale processes by making use of utility streams and side products that would otherwise be a detriment to overall system efficiency. For instance, when a surplus amount of steam is generated after primary and secondary cooling, it can be in the engineer's interest to make use of it. If a steady supply of natural gas is also available, then steam methane reforming (SMR) could be a source of additional revenue for a wide range of production applications, the most common and basic of these being the synthesis of hydrogen or methanol. Below are the ideal reactions that accompany the SMR process:

- Steam methane reformation (SMR)

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \qquad \Delta H_r{}^{\circ}{}_{298\,\mathrm{K}} = 206\,\mathrm{kJ/mol}$$

- Water gas shift (WGS)

$$H_2O + CO \rightleftarrows H_2 + CO_2 \qquad \Delta H_r{}^{\circ}{}_{298\,\mathrm{K}} = -41\,\mathrm{kJ/mol}$$

- Methanol synthesis

$$2H_2 + CO \leftrightarrows CH_3OH \qquad \Delta H_r{}^{\circ}{}_{298\,\mathrm{K}} = -91\,\mathrm{kJ/mol}$$

Being diverse in its usage and easily storable, methanol typically equates into a positive revenue source. It is possible to deploy SMR as a primary process, but would require large-capacity equipment and a high rate of production to compensate for the high cost of generating steam given SMR's low conversion efficiency. The SMR process is well documented and currently used at the commercial level, but is only one method of methane reformation and the focus of this chapter is on partial oxidation reformation techniques.

Reformation with the goal of hydrogen production has seen real promise for small-scale and on-hand applications like fuel cell technology or enhancement of internal combustion engines (ICEs). The advantages of hydrogen include fast flame speed and high octane (which enables high-pressure operation), allowing either high compression ratios or strong turbocharging with associated downsizing. The use of hydrogen-rich gas addition to spark-ignited (SI) engines allows for highly diluted operation. It is possible to extend the dilute-operation burn limits where nitrogen oxides are reduced to near nonexistent levels, eliminating the need for NO_x after-treatment (thus removal of the three-way catalyst). Dilution also allows for improved efficiency, from either reduced pumping losses at light load or lower in-cylinder temperature, thus reducing heat transfer to the cylinder walls. Running with hot hydrogen-rich gas further improves the flame speed as well as extends the dilution limit. Faster flame speed is another contributor to increased engine efficiency by enabling a more isochoric combustion zone.

Hydrogen is unfortunately a difficult molecule to store for extended periods of time. Aside from a high mass heating value, 120 kJ/g compared to methane (50 kJ/g), methanol (20 kJ/g), and gasoline (42.8 kJ/g), hydrogen is characterized by a low volumetric heating value due to its low density (2.016 g/mol): 11 kJ/l versus 16 MJ/l for methanol at standard temperature and pressure [40.2]. Volatility, flammability, and small molecule size all add to the storage difficulties of hydrogen. Some presented solutions to these issues are cryogenic and high-pressure containment, which have some validity but are not ideal due to further increase in efficiency losses and explosion hazards that are deemed high risk for mobile applications. Methanol has been used on occasion as a storage medium for utilities like fuel cells that are typically designed to operate on a source of hydrogen.

The integral step of methane reformation is the production of synthesis gas or syngas, a mixture of hydrogen and carbon monoxide. Often, realities of operation interfere, producing a syngas with adulterants such as carbon dioxide, methane, water, oxygen and nitrogen. Generally, these side constituents are unfavorable and limit overall efficiency in downstream processing requiring minimization when possible throughout operation. The methane POX reaction and other macroreactions of concern that are associated with methane POX (which include the SMR reactions above) are listed below. The following reactions can be considered competitive as well as reversible in nature:

- Methane partial oxidation

$$CH_4 + \left(\frac{1}{2}\right) O_2 \leftrightarrows 2H_2 + CO$$
$$\Delta H_r{}^\circ{}_{298\,K} = -36\,kJ/mol$$

- Combustion reactions

$$CH_4 + 2O_2 \leftrightarrows 2H_2O + CO_2$$
$$\Delta H_r{}^\circ{}_{298\,K} = -891\,kJ/mol$$
$$H_2 + \left(\frac{1}{2}\right) O_2 \leftrightarrows H_2O + heat$$
$$CO + \left(\frac{1}{2}\right) O_2 \leftrightarrows CO_2 + heat$$

Other Possible Side Reactions

- Thermal decomposition

$$CH_4 \leftrightarrows C + 2H_2$$
$$\Delta H_r{}^\circ{}_{298\,K} = 122\,kJ/mol$$

- Dry methane reformation

$$CH_4 + CO_2 \leftrightarrows 2H_2 + 2CO$$
$$\Delta H_r{}^\circ{}_{298\,K} = 247\,kJ/mol$$

- CO reduction (undesired)

$$CO + H_2 \leftrightarrows C + H_2O$$
$$\Delta H_r{}^\circ{}_{298\,K} = -84\,kJ/mol$$

- Boudouard reaction (undesired)

$$2CO \leftrightarrows C + CO_2$$
$$\Delta H_r{}^\circ{}_{298\,K} = -172\,kJ/mol$$

- Methanation (undesired)

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O$$
$$\Delta H_r{}^\circ{}_{298\,K} = -206\,kJ/mol$$
$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$$
$$\Delta H_r{}^\circ{}_{298\,K} = 42\,kJ/mol$$
$$2CO + 2H_2 \leftrightarrows CH_4 + CO_2 + heat$$

Partial oxidation is an exothermic reaction capable of producing an ideal syngas product of a 2 : 1 ratio of hydrogen to carbon monoxide. The reaction is able to reach temperatures in excess of 1300 °C that need to be levied and maintained through use of a catalyst in order to avoid nitrogen-based reactions. Nitrogen oxides (NO_x) are considered an emission that have, by orders of magnitude, a much greater environmental impact than unburned hydrocarbons and carbon oxides. Not only does NO_x cause the formation of ground-level ozone, but it also has negative effects upon the human respiratory system. The rate of formation of NO_x increases exponentially as temperatures rise in a lean and oxygen-rich flame zone during partial or total oxidation with air. Nitrogen, if not removed before reformation, must remain inert throughout the process. This factor is taken into consideration along with reactant conversion and hydrogen yield, all of which are influenced by thermal conditions.

Thermal Equilibrium

Not including plasma interaction, the factors that affect syngas production are reactor size, space velocity, flow dynamics, catalyst type, reactor and catalyst geometry, feed material and feed ratio, system pressure, and thermal equilibrium. Exothermic processes are controlled not only for safety reasons, but also for system efficiency and minimization of side products. Thermal equilibrium helps justify why the SMR reaction is inefficient and energy intensive while also explaining POX efficiency and NO_x formation.

The tubular reactor is commonly employed in industry and most often utilized for homogeneous gas-phase reactions. It is assumed that the reactants are consumed over the length of the reactor while experiencing some concentration variance both radially and in the direction of flow. This forces the rate of reaction to adjust accordingly as reactants are consumed and products are formed that become intermediate reactants themselves. In a POX reactor, the plug flow apparatus is selected to maximize production rate. The reactor can be used with, or without, a form of packed catalyst; when under a turbulent flow regime, equilibrium is maintained in a quasisteady state of operation creating a relatively stable, predictable thermal profile. As the process approaches completion under this configuration, different zones of the reactor experience a rise and fall in temperature due to the multitude of occurring reactions. This effect is more apparent in a shorter amount of reactor length using a packed-bed catalyst design and even more so if the reactor diameter is reduced. The thermal profile and reactions that take place are directly proportional to the ratio of fuel and oxidizer. More specifically, a carbon-to-oxygen atomic ratio of 1 correlates to stoichiometric POX while a ratio of 0.25 gives way to stoichiometric and complete combustion. Oxygen, within these stoichiometric bounds, is depleted quickly after injection due to its fast reaction rate and will not be present in the product stream. Oxygen can only be present postreactor if the system is not functioning properly or if lean operation is being conducted. Any ratio < 0.25 is considered lean (or fuel deficient) combustion and a ratio > 1.0 inactivates the reaction by extending the gas mixture past its flammability and reactive limits.

In order to lower reaction temperature, eliminate NO_x formation, and increase methane conversion, a catalyst is typically present inside the reactor. Currently, catalytic reformation is commonplace in the industry and as so, it is the most economically well-developed technique for hydrogen production. Typical POX catalysts include Pt, Rh, Ni, Co, Ir, Pd, or Ru metals that are supported on metal oxides, which include Al_2O_3, CeO_2, MgO, and TiO_2 in different proportions, mixtures, and geometric configurations [40.3, 6]. Though difficult to fully model theoretically, the experimental reaction pathways using catalysis are consistent and repeatable. Initially, exothermic reactions of POX and combustion are activated together to provide heat to the reactor. This spike in temperature allows the intermediate products of H_2O, CO, and CO_2 to then immediately react via the SMR and WGS reactions with unconverted hydrocarbon as well as the hydrogen product. Due to the continuous nature of the plug flow reactor and high gas space velocity, the residence time of the reactive species is short ($< 1.0\,s$). The short residence time in relation to the competing exothermic and endothermic reactions forces the process to reach completion that is not necessarily preferential to the best possible results.

Thermal equilibrium tends to develop in localized spots of the POX reactor and is contributed mostly from gas flow convection, downstream or upstream radiation, catalytic reaction, and heat conduction of the reactor and catalyst wall [40.7]. Even through well-controlled operation, the active species are always in a constant state of reactive flux. The bed temperatures along the length of the reactor help justify these claims, which have been seen thorough experimentation and are well documented in literature.

Maximization of hydrogen yield and selectivity can be achieved through manipulation of reactor temperature. Figure 40.5 shows this relationship and provides an example of thermal equilibrium influencing the product composition [40.7]. It is easy to see the asymptotic increase in conversion and the perfect selectivity that is achieved as temperatures rises in the reactor.

The syngas yield of purely two hydrogen molecules to each CO molecule from a 1.0 ratio of C/O would the-

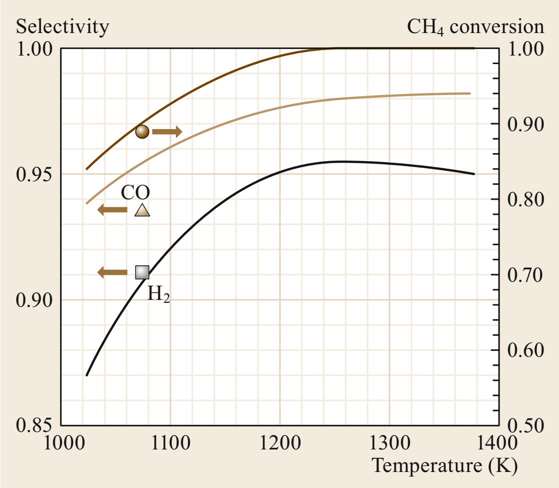

Fig. 40.5 Experimental POX using Rh-coated foam monolith catalyst. CH$_4$ conversion with H$_2$ and CO selectivity versus temperature (after [40.7])

oretically be perfect for downstream applications like methanol production, but combustion is unavoidable during POX making this idealization next to impossible. It should be noted, that some CO$_2$ is necessary for methanol production as well, and though mostly viewed as a negative aspect to the process, combustion can be controlled to assist in reformation. As more oxygen is introduced to the feed, hydrogen yield tends to increase until a peak is reached (C/O ratio ≈ 0.85) where further addition of oxygen begins to lower hydrogen yield. Peak ratio is unique to each process with high dependency on reactor structure and plasma or catalysis assistance. The stability of feed ratio also contributes greatly to thermal equilibrium and, from a mechanical standpoint, reactor temperature provides a quick indication of syngas quality and possible system deficiencies. If the reaction is controlled solely by thermal activation then product selectivity is predictable, but will limit maximum product potential. When plasma becomes a dominant presence in the system, thermal equilibrium is overcome and the achievement of an even greater efficiency is then possible [40.8].

Chemical Kinetics

The reformation process can be summarized by the enthalpy changes exhibited throughout the system. Each reaction either imparts or removes heat in an effort to approach completion. The POX reaction itself has relatively slow kinetics and cannot initiate without the assistance of energy from an external source or an internal source such as combustion. Overall, the process of POX is still exothermic even with the multitude of associated competitive endothermic reactions. In the event that the total net enthalpy change to the system is approximately zero ($\Delta H_\mathrm{r}{}^\circ \approx 0\,\mathrm{kJ/mol}$), the process can then be considered autothermal. In order to compensate, some form of direct injection is required using water, CO$_2$, a process recycle stream, or simply the exhaust from an internal combustion engine:

- Partial oxidation

$$\mathrm{C}_n\mathrm{H}_m + \left(\frac{n}{2}\right)\mathrm{O}_2 \leftrightarrows n\mathrm{CO} + \left(\frac{m}{2}\right)\mathrm{H}_2$$
$$\Delta H_\mathrm{r}{}^\circ < 0$$

- Steam reformation

$$\mathrm{C}_n\mathrm{H}_m + n\mathrm{H}_2\mathrm{O} \leftrightarrows n\mathrm{CO} + \left[\left(\frac{m}{2}\right) + n\right]\mathrm{H}_2$$
$$\Delta H_\mathrm{r}{}^\circ > 0$$

- Combustion

$$\mathrm{C}_n\mathrm{H}_m + \left(\frac{(2n+m)}{4}\right)\mathrm{O}_2$$
$$\leftrightarrows n\mathrm{CO}_2 + \left(\frac{m}{2}\right)\mathrm{H}_2\mathrm{O} \quad \Delta H_\mathrm{r}{}^\circ \ll 0$$

- Autothermal reformation (ATR)

$$\mathrm{C}_n\mathrm{H}_m + \left(\frac{n}{2}\right)\mathrm{O}_2 + n\mathrm{H}_2\mathrm{O}$$
$$\leftrightarrows n\mathrm{CO}_2 + \left[\left(\frac{m}{2}\right) + n\right]\mathrm{H}_2 \quad \Delta H_\mathrm{r}{}^\circ \approx 0$$

The above global reactions give a straightforward overview and are the initial basis for modeling any reformation process. Reaction kinetics can then be utilized to help more thoroughly map the intrinsic system properties for determination of syngas product composition and yield. Temperature, pressure, and phase all play a role in the mechanism determining the pathway for reactions to follow. The homogenous gas phase reactions of POX do not inherently promote the formation of a high-quality syngas; this problem is partly resolved with the insertion of a durable and appropriate supported catalyst placed within the reactive zone [40.6]. The heterogeneous catalytic environment enhances the normal molecular pathway via active sites on the catalyst that reduce the energy barrier required for stoichiometric POX and lower the amount of combustion heat necessary for reaction stability. In a prior study, the CPOX of methane on a rhodium-coated catalyst has been indirectly modeled based on combustion, steam reformation, water gas shift, and dry methane reformation (DMR) kinetics. These equations, which are listed below, follow the Arrhenius model and have been determined using empirical methods [40.9, 10].

$$R_{\text{Combustion}} = 2.119 \times 10^{10} \exp\left(\frac{-80}{RT}\right) p_{\text{CH}_4}^{0.2} p_{\text{O}_2}^{1.3}$$

$$R_{\text{SMR}} = 1.0 \times 10^{-9} T^5 \exp\left(\frac{-47.3}{RT}\right) \times \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - K_{\text{eq,SMR}}^{-1} p_{\text{H}_2}^3 p_{\text{CO}}\right)$$

$$R_{\text{DMR}} = 7.0 \times 10^{-7} T^4 \exp\left(\frac{-32}{RT}\right) \times \left(p_{\text{CH}_4} p_{\text{CO}_2} - K_{\text{eq,DMR}}^{-1} p_{\text{H}_2}^2 p_{\text{CO}}^2\right)$$

For the WGS reaction ($r =$ steam/CO ratio)

$$R_{\text{WGS}} = k\left(p_{\text{CO}} p_{\text{H}_2\text{O}} - K_{\text{eq}}^{-1} p_{\text{CO}_2} p_{\text{H}_2}\right)$$

$$k_{\text{HTSR}} = 1.78 \times 10^{22} (1 + 0.0097r - 1.1364r^2) T^{-8} \times \exp\left(\frac{-70}{RT}\right)$$

$$k_{\text{LTSR}} = 1.74 \times 10^{17} (1 + 0.154r + 0.008r^2) T^{-8.5} \times \exp\left(\frac{-35}{RT}\right)$$

Overall thermodynamic equilibrium constant (K_{eq})

$$K_{\text{eq}} = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right) (P_{\text{atm}})^{\sum_{j=1}^{N} \upsilon_j'' - \upsilon_j'} .$$

The equilibrium constant (K_{eq}) takes into account the reversibility of each of the process reactions. This must be addressed due to the variability of conditions during operation. As an example, the WGS reaction approaches completion at two different temperature ranges. The high-temperature shift (HTSR) and low-temperature shift (LTSR) are performed in the ranges of 300–500 and 200–300 °C respectively. Lower temperatures support better CO conversion, but the kinetics favor an increased reaction rate at higher temperatures. The WGS reaction is always present, shifting the product composition towards thermodynamic equilibrium between CO, CO_2, H_2, and water. The subsequent production of hydrogen-rich syngas with minimal CO content, in particular to polymer electrolyte membrane (PEM) fuel cell application, is also based on WGS kinetics [40.11]. Industrial-scale applications looking to maximize hydrogen production tend to operate both HTSR and LTSR in separate reactors in series downstream of the reformation reactor. The use of both shift reactors as ancillary units downstream from the reformer allows for near-total conversion of CO into CO_2 and provides additional hydrogen from steam with further intent to isolate the product hydrogen. This happens through the most economical form of separation possible and can be accomplished using one of the several following techniques: pressure-swing adsorption (PSA) to separate hydrogen, PSA to separate the CO_2 followed by condensation of the remainder of water, and membrane or sieve separation of the hydrogen [40.12]. With regards to the overall POX process, WGS is unavoidable and can be seen as neither beneficial nor detrimental to downstream application. This is especially true when engine combustion or electrical generation directly follows syngas production, as CO is also a suitable, burnable energy source.

40.2.2 Plasma Catalysis

Low-input energy capable of producing highly active species has become the focal point of potential for development of more efficient plasma reactors. In plasma catalysis, there exist a number of different configurations that rely upon location of the plasma field and catalyst zone. If the placement of the catalyst zone is prior to or much further downstream of the plasma field, then the process is a two-stage system (Fig. 40.7). Hot thermal plasma imparts extreme amounts of heat energy that cannot be used in conjunction with catalysis due to the structural limitations of catalytic material. The coating and the substrate are unable to withstand the high temperatures of the plasma field resulting in immediate thermal degradation as well as sintering of the coating material. In the immediate area surrounding the thermal plasma field, the cost of processing equipment and piping material would also rise in an effort to resist the high temperatures using higher durability equipment. This leads to applications in which thermal plasma has very limited appeal because of the inefficiency from the high energy demand and the inability to integrate into established chemical processes. For thermal plasma to have a role in catalysis, ample distance between the catalyst and plasma field is required, eliminating most of the potential synergy of the combined systems.

When the catalyst zone is located inside the plasma field or in close proximity postplasma generation, the process is known as a single-stage system (Fig. 40.6). In a single-stage plasma catalysis system, the effects of plasma and catalysis that contribute to the process become dependent on each other. This differs greatly from conventional catalysis due to the introduction of highly active species and the creation of a voltage potential and current flow by result of plasma discharge across the catalytic surface. The active species alter the status of the gas-phase reactions and associated reaction kinetics, which no longer ensues from the ground state. Elec-

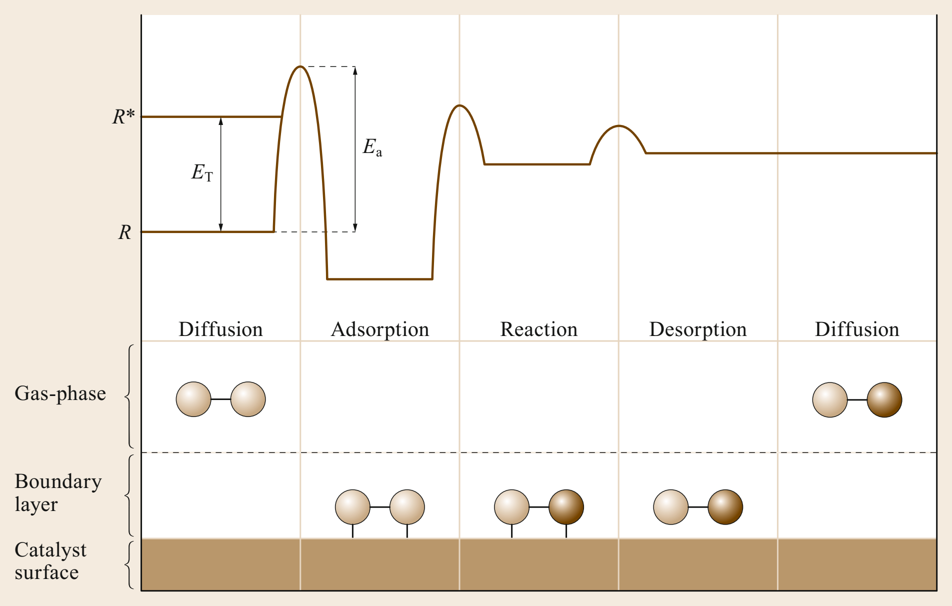

Fig. 40.6 Illustration of vibrationally excited species from a plasma-induced state accelerating a catalytic reaction. R represents the gas-phase molecule at ground state (uncharged) and R^* stands for the reactant in a vibrational state (charged). E_a is the activation barrier of chemisorption for R and E_T is the threshold energy for the formation of R^* through a plasma-induced electron-impact reaction (after [40.3]). The thermal energy required to initiate the catalytic process is now much less than the standard catalytic reaction and even further so than the reaction without catalyst

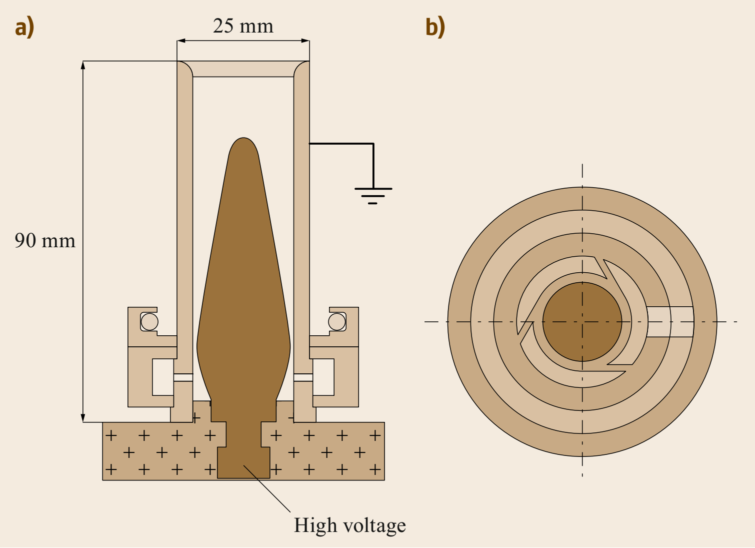

Fig. 40.7a,b Schematic drawing of rotating arc reactor used in a prior study conducted by Dae Hoon Lee et al. Side view **(a)** and overhead view **(b)** (after [40.13])

trical field enhancement depends on curvature, contact angle, and the dielectric constant of the packing pellets. Higher electric field leads to higher electron density promoting the electron-impact reactions responsible for hydrocarbon reforming. The decomposition of hydrocarbons is attributed to ionization and electron-impact dissociation of the excited molecules. Simply through vibrational excitation it has been noted that activation energy is reduced in gas-phase reactions.

Physical adsorption and chemisorption are the methods where gas-phase molecules or ionized particles attach to the surface of the catalyst (Fig. 40.8). Physical adsorption is slightly exothermic and is mainly attributed to the weak Van der Waals attractive forces

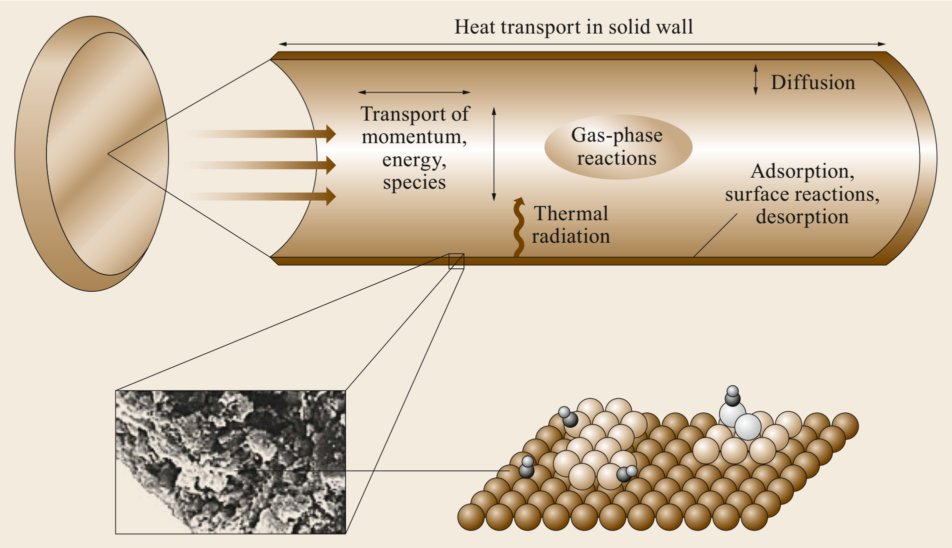

Fig. 40.8 Reaction effects flowing through a catalytic monolith, which include transport processes and a microscopic view at the nanoscale level (after [40.11], reproduced with permission of The Royal Society of Chemistry)

between the interactive surfaces. As the temperature profile surrounding the catalyst rises, the adsorption of particles steadily declines until critical temperatures are obtained in which physical adsorption no longer occurs. At this point, physical adsorption gives way to the sole influence of chemisorption. In the rate-influencing step of chemisorption, valence forces create highly reactive instances via bond stretching of the exposed and absorbed chemical species on the surface of the catalyst. Chemisorption produces heat comparable to the exotherm of the chemical reactions being performed. Atom and metastable compound formation along with electron multiplication cascade into the catalyst bed manipulating the normal conditions in which the catalyst performs. These effects are apparent and usually happen under very short electrical contact times. The heightened interaction between the surface and adsorbate then create new bonds, forming molecules that are specific to the catalyst and operating conditions.

40.2.3 Reactor Apparatus

In a lab setting, a reactor that imparts all of the above-listed chemical and physical effects has been constructed. The proprietary unit, known simply as PRISM and shown in Fig. 40.9, has demonstrated successfully the ability to reform methane gas into syngas at high efficiency and near perfect conversion using very little energy input. The process incorporates a three-step approach coinciding with intermediate stages that contribute to the final composition of the produced syngas.

At ambient or elevated temperatures, a stream of dry air or pure oxygen is introduced to a stream of natural gas and is well mixed prior to exposure of the plasma-generating field within the plasma head. The plasma head is a precision-designed, stainless steel structure consisting of a tapered rod that acts as the anode, which is housed inside a cylindrical wall of like material (the cathode). The point of largest diameter along the length of the anode rod is where the plasma field initiates and can also be considered the choke point of the flowing element. The axial design makes use of the annular gap to hold steady the electrical field. This closely resembles that of a dielectric barrier discharge (DBD) apparatus, but without direct internal insulation while incorporating more of a coronal discharge approach to the plasma type utilized. In place of a fine-tipped point that is typically seen in a coronal design, the annular region is used to grant a larger volume coverage that increases the duration of electrical exposure to the gas molecules ensuring sufficient ionization. The plasma chamber of the PRISM mimics the flow patterns of the schematic shown in Fig. 40.9 for the rotating arc reactor, but differs in dimensionality and in orientation. The radial injection points allow for a toroidal arc that further increases residence time within the plasma head apparatus. As concentrated charges dissipate from the added rotational turbulence, both metal erosion and degradation upon the electrodes are reduced, extending their overall lifetime. An observation of the anode after long-term operation reveals minor impressions of spiral-type markings across its metal surface indicating the tangential path taken by the flowing gases.

The annular chamber provides uniform exposure to the incoming gas assisted by the well-mixed effect of the turbulent flow regime promoting molecular interactions and ion collisions, while the toroidal flow lengthens the space and time of the overall exposure.

These factors all contribute to the formation of the highly energized cold plasma state necessary for the reformation stage of the process.

An external power source is placed above the reactor providing voltage directly to the electrodes that are held inside a barrier of ceramic/quartz in order to maintain the uniform three-dimensional electric field throughout the annular gap. The power supply operates at high voltage ($\approx 3\,\mathrm{kV}$) and very low current expending no more than 100 W of combined processing power at maximum feed flow rate. Voltage to the plasma head is variable based on the fluid properties, which are primarily defined by gas density and velocity. The PRISM system operates with a 12+ kV compact transformer that allows for additional reserve voltage when fluid properties drastically change, and will adjust automatically without manual input control to sustain the plasma arc field.

Thermal expansion follows quickly after the gas stream is ionized by the plasma field. From there, the flow path continues by entering the main portion of the reactor that houses the proprietary catalyst crafted specifically for promoting the POX reaction. Catalyst composition is a mostly nickel-based coating prepared upon an alumina substrate. These monolithic, cylindrically sculpted blocks of catalyst remain stationary in a tightly packed fashion; these extend to the inner reactor wall.

In this chamber, the core of the partial oxidation reaction takes place. This is monitored through temperature readouts using multiple thermocouples drilled to the center of each catalyst. The external body of the reactor is 22″ in length and roughly 8.5″ in diameter. The inner wall of the reactor is lined by a nonconductive refractory material of high alpha alumina roughly 1″ in thickness. This refractory participates as an insulator, but more importantly ensures containment of the electrical properties that were imparted to the incoming ionized gas stream. Figure 40.9 is an example schematic of an older generation model of the PRISM reactor.

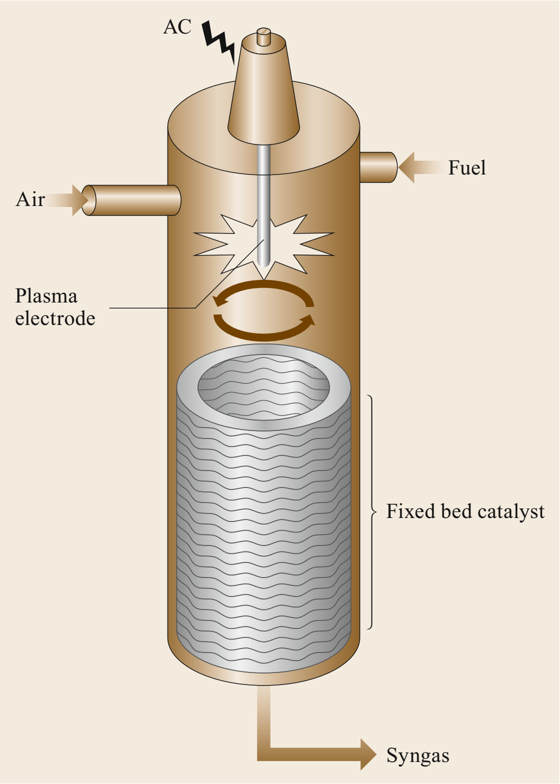

Fig. 40.9 PRISM reactor body and internals

Zonal Reactions

As listed in the section of methane modeling reactions that occur throughout the process (Sect. 40.2.1), each zone of the reactor and catalyst bed itself experience a fluctuation in primary reactions when favorable conditions arise during each reaction. This, however, can be manipulated through a well-controlled system. Initially, the plasma zone operates as an ignition source for the controlled combustion heating to the catalyst bed. When optimal bed temperature is achieved, the plasma field then takes responsibility for molecular breakdown by ionization and electron dissociation of the exposed compounds. Oxygen ionization into its atomic state and the formation of ozone molecules are the first reactions to occur. Not only is ozone formed, but decomposition is also apparent in the complementing stream of hydrocarbons. These feed streams are well mixed and in a preferential syngas yielding ratio prior to introduction into the plasma zone. Hydrogen atoms released from C−H bond breakage and excited electrons that are initially released contribute to the reactions downstream as well as to the final syngas product. The remaining intermediate hydrocarbon compounds also react more readily in their hydrogen-depleted configurations. This first step helps drive the reaction rate of POX up to a level sufficient for effective overall system operation.

In the subsequent portion of the reactor, the diameter is increased to allow expansion of the gases granting longer exposure to the high surface area of the catalyst. Even distribution from turbulent flow of the particles onto the active sites of the catalyst is observed through stability of the temperature profile. Given a consistent feed composition at a specific ratio during steady-state operation, the specific zonal temperatures fluctuate at a ΔT near $\pm 1.0\,^{\circ}\mathrm{C}$. This suggests all the participating reactions are held constant along the length of the reactor in their corresponding zones. As stated prior, oxygen atoms are the first particles to be consumed and do not appear downstream of the reactor. If the oxygen atoms are not reduced with the carbon source into CO, then the atoms along with some CO will be fully oxidized into CO_2 before leaving the catalyst zone. The POX reaction not only produces the syngas mixture, but also releases sufficient enough heat to stabilize the reactor and perpetuate the overall reactionary process. Due to the fuel-rich environment and high process temperature, the unconverted methane tends to react with the steam side product via the SMR reaction also enhancing the syngas ratio [40.14]. The final stage falls to the WGS reaction and the reverse WGS reaction, which augment the CO_2 component forming either more hydrogen or more CO. The WGS reaction is not optimized in this configuration and purely participates as an indirectly controlled and closely monitored side reaction. Should the syngas ratio require more CO than hydrogen or vice versa, then a downstream WGS reactor can be implemented at a low additional capital cost to the system. The combination of reactions resulting in a net exothermic process leaves the product stream hot (> 600 °C) requiring heat exchange, if desired, to cool the syngas as well as condense any residual water.

Thermal Profile

With the operation of the plasma head being under a cold plasma configuration, there is not a significant enough generation of heat to give cause for thermal readings of this zone. Temperature measurement for a predictable profile is thus only conducted in the main body of the reactor housing the fixed bed catalyst, which is monitored via eight equally spaced thermocouples. The thermocouples are placed in predrilled holes of appropriate dimensions and sealed tightly at the protruding ends that are connected to the wiring relay. The temperature of the catalyst bed is directly linked to the exo- or endothermicity of the reactions, and also to the conditions of the catalyst, plasma head activity, system pressure, and gas flow rate. As a comparative example that provides an accurate visual of catalyst temperature distribution, this noninduced flow in a laminar to transitional regime produces the temperature profile shown in Fig. 40.10.

The effect of modifying the flowrate through the catalyst suggests that at higher flows, the reaction encompasses a larger volume and initiates further downstream within the catalyst itself. The PRISM differs only slightly in flow path due to its transitional-to-turbulent regime reducing the radial variability of key parameters.

The thermal profile shown in Fig. 40.11 represents the consistency in occurring POX reactions down the length of the catalyst. In actual operation where flow rate and ratio are unaltered set points, the bed temperature and product composition do not deviate by more than the error present in the sensors-measurement equipment. The overall temperature drop within the

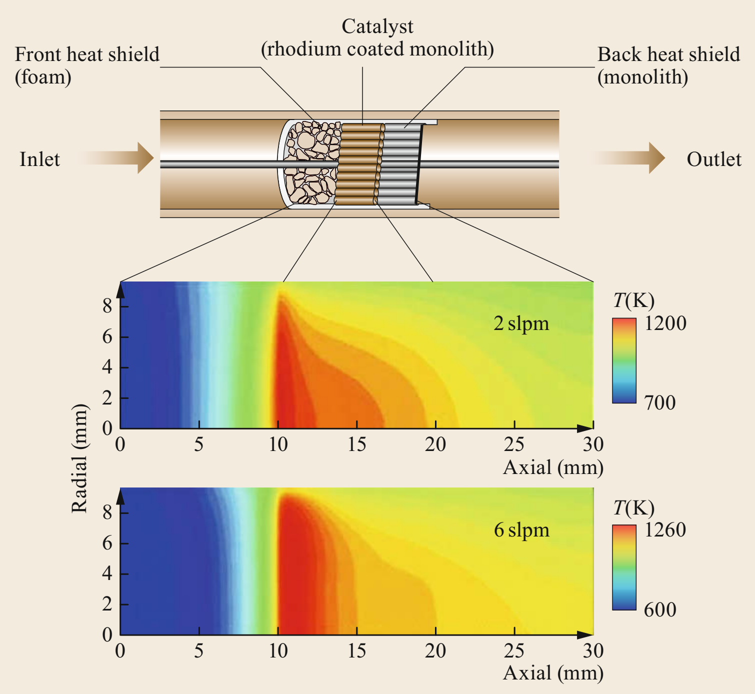

Fig. 40.10 Example POX catalyst temperature profile in laminar setting at differing flowrates. The catalyst coating is rhodium and the hydrocarbon is *iso*-octane (after [40.11], reproduced with permission of The Royal Society of Chemistry)

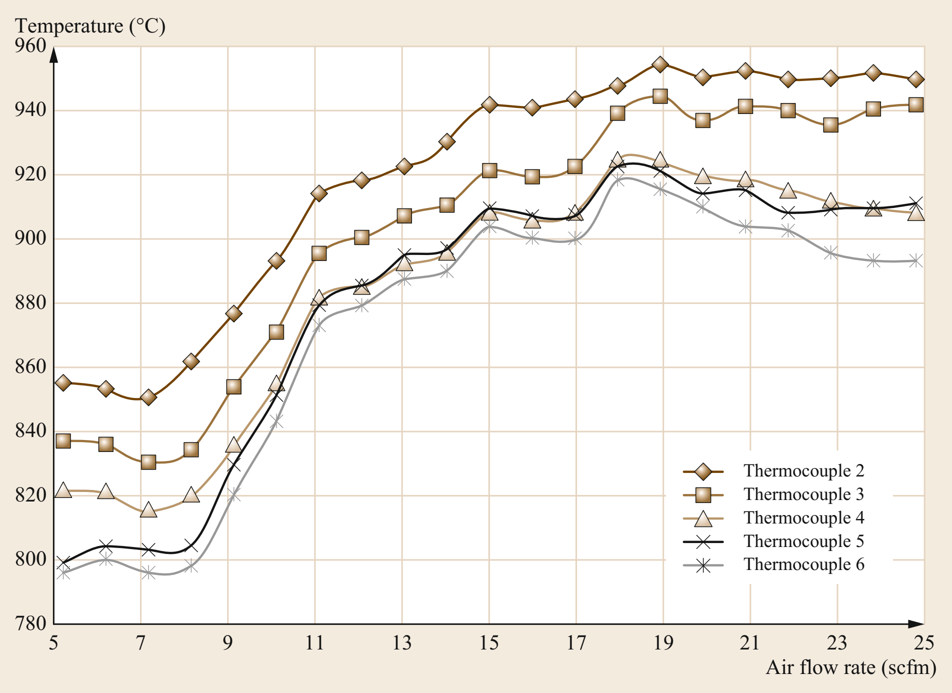

Fig. 40.11 Experimental operation of a PRISM reactor displaying average temperature readings for each catalyst zone over increasing rates of flow. The operational ratio was adjusted only to the automatic feedback control for the temperature rise in the system. The initial set point of the C/O atomic ratio was 0.55, which increased to 0.57 at the completion of the experiment

catalyst bed between thermocouples 2 and 6 is no more than 60 °C translating to good thermal stability throughout reactor operation. The rise and fall of zonal temperatures correspond directly to each other and are dependent on the prior zone's temperature, and even more so the active zone temperature (thermocouple 2). At each discrete flow set point, an accurate representation of the PRISM's temperature profile can be observed if no manipulation of flow rate had been done. It should be noted that the PRISM under this experimental scheme was operated closer to a combustion-oriented ratio at 0.55 of C/O species. As expressed previously in Sect. 40.2.1, *Thermal Equilibrium*, it was stated that peak hydrogen yield is achieved at ≈ 0.85 C/O ratio. While this holds true, results were more than adequate citing consistent results of over 99% methane conversion and a ≈ 1.8 H_2/CO product ratio. It stands to show that improvements can still be made on this already highly effective process, but are not necessary for viability of the technology in the field.

40.3 Cold-Plasma-Assisted Experimentation

40.3.1 Steady State Operation

Many experiments have been conducted at a facility in Brooksville, FL through research as well as trial and error. The PRISM system in a standalone configuration is ready for early-stage commercialization for stable, continuous production of usable clean syngas. Another experimental-phase application has been performed for syngas-hydrogen enhanced combustion in spark-ignited (SI) engines. The benefits of hydrogen fuel addition during combustion are well known to the scientific community, and the difficulties of its implementation have been discussed. A skid that consists of a General Motors 8.1 l overhead valve/eight-cylinder V configuration (OHV/V8) natural gas, turbocharged engine and a 100 kWe corresponding alternator have been integrated with a single PRISM unit for successful continuous slipstream engine operation.

The PRISM is a relatively simple system requiring a fuel valve, air valve, power source, and control system along with some corresponding instrumentation. In continuous operation, the system is stable under a well-controlled apparatus of a quick response ratio feedback loop based on system temperature. Attached are mass flow controllers that dictate the feed input based on ratio control and oxidizer flow rate. Adjustments can be allocated to either set point resulting in an automatic change in fuel flow. The feedback control loop is responsive to changes in catalyst bed temperature, but focused on the main zone of operation, which is also the highest temperature zone of the process. This keeps reactor conditions favorable for higher hydrogen production and safe during long term operation. The control mapping has been optimized through many phases of testing on the PRISM unit. Manual control input is unnecessary when consistent homogeneous fuels are being used as the system will respond accordingly. This follows suit for the power supply, which operates within its voltage limits to always provide the electrically induced plasma field within the plasma head. The simplicity of the system and stability of the reactor make it possible for the need of only one operator overseeing the process. As syngas is being produced, it is then guided through heat exchange removing the formed water and lowering gas temperature to ambient levels. After a final water knockout point, the syngas is led to a low-tolerance oxygen sensor confirming the absence of oxygen before compression and then to storage of the syngas product. Excess syngas is sent to flare during experimentation.

When added to the 8.1 l engine skid, the PRISM functionality remains the same; filtered air is either actively fed to the reactor or naturally pulled through the reactor via the engine requirement. The controls in place respond accordingly to either arrangement. In this case, the gen-set engine is brought to steady operation first, followed by the PRISM reactor, which is fully introduced to the engine fuel inlet. The natural gas valve is then slowly closed until the engine is no longer being fed with fuel other than freshly produced syngas. From this point, system operation will continue until shutdown. It must be noted that there is a drop in engine power return when fully supplied with only syngas, which is mainly due to the excess dilution of nitrogen from air being processed twice during the same system loop. Syngas can also be introduced hot or cold, eliminating the need for heat exchange if deemed unrequired. The main focus of this system is to eliminate NO_x production and the need for exhaust gas after-treatment. Using a five-gas analyzer, NO_x levels have been routinely recorded at less than 10 ppm prior to after-treatment while using slipstream syngas operation.

40.3.2 Transients: Startup/Shutdown

The startup sequence for operation of the PRISM begins with simply turning on the power supply and opening system flow. The plasma field is on at all times and initiates the process acting as a spark to ignite a very lean mixture of air to fuel. These gases are well mixed before introduction to the plasma head chamber. As temperatures rise, the fuel mapping for the controls approaches a fuel-to-air ratio that is richer in operation. Above 900 °C the methane will flood the system and be too rich for any oxidation, thus cooling the catalyst bed and stabilizing the reactor conditions. At this point, the temperature of the system reaches its peak moment $\approx 1000\,°\mathrm{C}$ and will no longer approach this temperature range again under steady operation. The system is now self-sustained and very stable. Any adjustments to the fuel mapping at this point will only induce minor changes in temperature. If flow is increased, then the main reaction moves toward the next catalyst zone followed by the controls. Given added backpressure, a gas chromatograph (GC) analysis can be processed at any point during this time. In order to shut the system down, simply turn off the power supply and close the fuel valve. A slight air peak may cause a minor combustion instance with any remaining fuel in the system, but quickly subsides as shown by the drop in measured temperature. The reactor retains heat well and may require roughly 3 h to return to ambient levels.

In engine operation, many more transient situations must be considered. Startup ensues in the same manner, with normal engine startup first followed by PRISM startup. Once the temperature change in zone 1 approaches zero, syngas is being produced and can now give way to reduced fuel consumption on the engine's main line. Discontinuities from the piston's compression strokes do not affect the stability of the reactor even when air is being pulled through. This setup requires minimal manipulation to operate steadily, but additional instrumentation would be necessary in a real-life application using a motor vehicle where stops are frequent. A few ideas are in place to alleviate these potential transient issues. The most logical approach would be to implement the lowest possible flow through the reactor during engine idle. The system, though it retains heat well, would fluctuate more than desired since the unit is designed for continuous flow and not for on–off applications. If added to current motor vehicles, the benefit of the hydrogen-rich syngas can be used in a cursory manner; this makes the PRISM advantageous in highway situations. To shut the system down, fully open the engine fuel valve while shutting off the reactor fuel valve and power to the unit. After this, total shutdown is as simple as turning the ignition key.

40.3.3 Conversion and Efficiency

In order to achieve high conversion and efficiency, optimization on a working system is vital. True optimization requires experimentation, analysis of experiments, and adjustment thereafter from theory. This is a repeatable, stepwise process that demonstrates the versatility of the technology and potential for performance im-

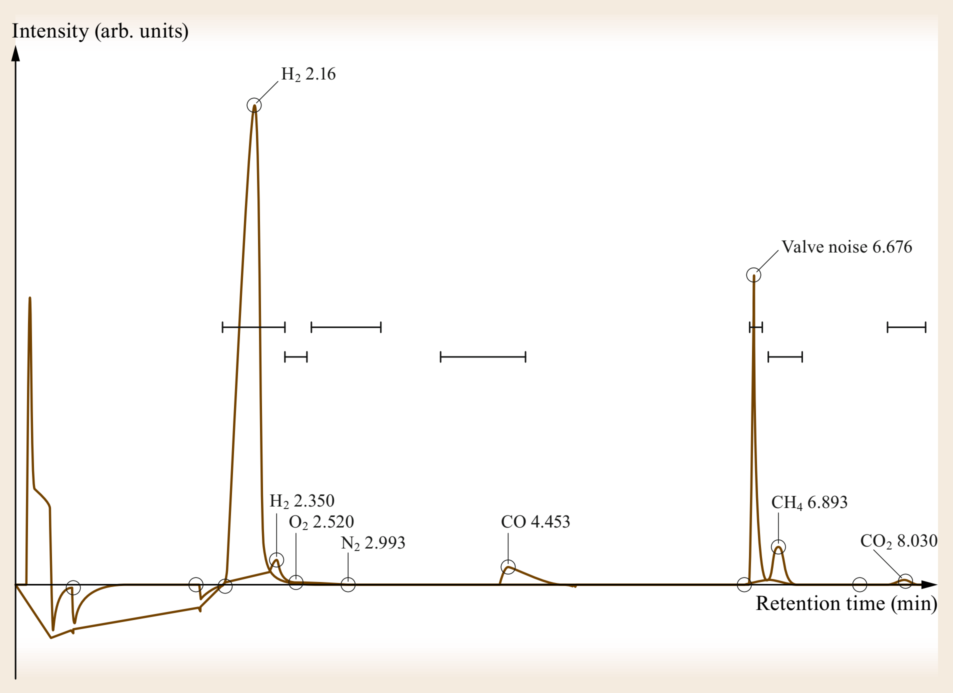

Fig. 40.12 GC results of PRISM operation with pure oxygen

provement. For instance, nonthermal plasma on its own does not provide enough energy or the environment to achieve any significant selectivity of hydrogen and carbon monoxide production. On the other hand, thermal plasma is capable of converting methane into hydrogen unassisted, but the high amount of energy required for thermal plasma generation coupled with the low methane conversion and low hydrogen selectivity is not an economically feasible path to any commercial application. There exists a point, between nonthermal and thermal plasma, which instills the necessary amount of energy required to fully convert the feed stream when coupled with other processes. Plasma does not simply exist in one form; it is affected by intensive properties just as any other phase of matter would by a change in its density or viscosity. The difference with plasma is the constant fluctuation of every property over short time intervals. Methane conversion into hydrogen using only a pure methane feed and nonthermal plasma is close to 6.0%, while thermal plasma with pure methane is near a 12.0% conversion. In an environment supportive of POX using air and methane, thermal and nonthermal plasma systems are capable of achieving a 99.0% conversion of starting material.

Conversion weighed against the energy input to the system is at its peak when nonthermal plasma is used in conjunction with catalysis. The active field of the system provides an ideal environment for the chemical species to react. Deviation from stoichiometry of POX by decreasing the C/O ratio enhances the selectivity and yield of hydrogen (peaked curve) approximately around $C/O \approx 0.85$ and $T \approx 800\,°C$. Efficiency is also increased at higher temperatures. The leaner partial oxidation ratios suggest that a little combustion initially assists in producing greater amounts of hydrogen through the side reactions (mainly steam reformation) immediately downstream in the reactor.

A number of reactions occur simultaneously along the length of the reactor while carrying the electrical properties of the plasma field throughout the process. The participating reactions are combustion, partial oxidation, steam methane reforming, and water gas shift. All of these reactions are reversible in nature, making it difficult to surmise and predict the product outcome from so many variables. The goal is to influence the outcome to the end user's needs, and this can be accomplished through manipulation of the necessary parameters. With a feedback control loop based on internal catalyst temperature and reactant ratio, stable reactor conditions are maintainable and adjustable. Through experimentation and analysis of these parameters at varied set points, a database is established for specific product yield. A production database also allows for early problem detection and error analysis.

Product Measurement

The product stream is analyzed via a small slipstream of gas into a high-precision SRI 1068C gas chromato-

Table 40.1 Volume/mole percentage display of GC results for air and oxygen

PRISM syngas product – GC analysis (% by volume)		
Compound	**With air**	**With oxygen**
H_2	30.7%	58.5%
CO	15.9%	32.2%
CO_2	3.3%	2.9%
CH_4	1.3%	6.4%
O_2	0.0%	0.0%
N_2	48.8%	0.0%
Total	**100.0%**	**100.0%**

Table 40.2 GC-MS results of producer gas composition directly after PRISM system reformation

Component	Mole percent	Weight percent
Oxygen and argon	1.995	2.787
Nitrogen	53.749	65.723
Methane	10.668	7.471
Hydrogen	17.789	1.565
Carbon monoxide	11.273	13.783
Carbon dioxide	4.488	8.622
Ethylene	ND	ND
Ethane	0.038	0.049
Acetylene	ND	ND
Propylene	ND	ND
Propane	ND	ND
Isobutane	ND	ND
n-Butane	ND	ND
trans-2-Butane	ND	ND
1-Butane	ND	ND
Isobutylene	ND	ND
cis-2-Butene	ND	ND
iso-Pentane	ND	ND
n-Pentane	ND	ND
1,3-Butadiene and methyl acetylene	ND	ND
C_5 Olefins	ND	ND
Hexanes	ND	ND
Heptanes plus	ND	ND

graph (GC) attached with Haysep D and Moleseive 13X columns. The GC uses a thermal conductivity detector (TCD) with the attachments to accurately measure the molecular content of the syngas that the unit is receiving. An algorithm has been implemented to the GC interface based on calibration gas at various compositions pertaining to the compounds of interest being synthesized. Based on the GC configuration, every compound known to be present in the gas product is accounted for and returned to the user in a percent volume composition. Refer to Table 40.1 and Fig. 40.12 for actual experimental GC results. The GC is maintained frequently and recalibrated on a three-month cycle. Third-party analysis of a process-derived fuel (PDF) from municipal solid waste (MSW) reformed into syngas from producer gas has also been performed resulting in high levels of hydrogen yield and a large percentage of tar reduction in the gas stream. Results from this experiment are shown in Table 40.2.

40.4 Analysis and Discussion

40.4.1 Process Challenges

The areas of concern that were encountered during design and operation of the PRISM process are system controls, modeling, catalyst durability, safety precautions, variable feedstock, and overall scale-up. The feedback control loop is responsive to changes in zonal reactor temperature where the fuel-to-air ratio set point adjusts accordingly to balance reaction heat, firstly preventing catalyst damage and secondly for safety in eliminating any potential runaway reaction. Though stable, the system must always be monitored. Plasma-assisted POX with catalysis provides a wide range of variables that are difficult to model at the atomic level. This limits the depth of process understanding to broader generalizations using separate macrolevel modeling techniques and theories that are well established. The catalyst is susceptible to thermal deactivation, coking, carbon deposition, chemical poisoning (typically sulfur), and deactivation after heavy usage over long periods of time. The transient issue is minor and ideas are in place to remedy these negatives, such as timing control to maximize the benefits of hydrogen supplementation.

40.4.2 Design Improvements

Startup requires short-term ignition in the form of a modified fuel-to-air ratio. This is viewed more as an unavoidable hindrance that has a greater affect on an operation with a high-frequency modulation between transient and steady-state operation. It is safe to assume that syngas is in full production from cold startup after approximately one minute; this dead time is lessened if system operation was recently shutdown due to the substantial thermal mass of the system. If possible, a more durable catalyst that has greater resistance to sulfur poisoning and thermal decomposition would be ideal for future experimentation and commercialization. This would loosen the restrictions that decrease the lifespan of the catalyst bed.

The system's flow capacity is high for the small footprint of the apparatus itself providing over 150 scfm of high-quality syngas per unit. Dimensions of each PRISM unit are $15'' \times 18'' \times 50''$, approximately. The limitation thus far is the capacity of the mass flow controllers, which reach maximum allowable flow rate before the reaction is extended beyond the catalyst bed. A safe assumption is that the PRISM is able to produce upwards of 200 scfm of syngas. This coincides with nitrogen displacement that reduces product output and system efficiency. Using pure oxygen from gas cylinders is not a viable avenue for long-term system operation, negating the low cost benefits of the process. Pressure swing adsorption (PSA) or vacuum pressure swing adsorption are both viable methods of producing $> 95\%$ oxygen content from air in a continuous manner at low operating costs. The physical footprint of the systems tend to be large, but even a small separation of oxygen from nitrogen would provide dramatic improvements in production efficiency and power recovery.

40.4.3 Higher Hydrocarbon Reformation

Longevity tests showing system durability are conducted regularly and for months at a time. Under stable operation, process efficiency does not diminish over time and, in fact, results tend to improve slightly. Under a previous control schema, a fluctuation in syngas product yields and conversion is observed in the range of $\pm 2\%$ of the average data acquired over time. For example, average hydrogen percent by volume of syngas was 30% with low-end results being 28% and high-end results being 32% by volume. Some variance could also be attributed to the inconsistent composition of the natural gas pipeline. This range of syngas composition is observed for all components of the product stream during short-term operation as well as month-long continuous experimentation. Data have been logged and thoroughly examined to show stable production of high volume and quality syngas. Reformation efficiency versus stoichiometrically perfect conversion is high in the 80% range for air operation and in the 90% range for oxygen operation. Methane conversion efficiency has been recorded to $> 99\%$ at higher process flows while generally in the $\approx 98\%$ range otherwise.

It has been deemed plausible to reform all chains and types of hydrocarbons using the PRISM reactor. Given a vapor phase of feeds such as heptane or aromatics like benzene in stoichiometric proportions with oxygen for POX, a product that consists of mostly hydrogen and carbon monoxide can be achieved. The plasma field imparts enough energy and the heated catalyst bed allows for activation of the POX reaction that could result in near-perfect conversion comparable to the use of methane. Higher hydrocarbon reformation results in a ratio of H_2 to CO much closer to 1.0 than 2.0, which would inhibit downstream processing, but again could be alleviated by a PSA unit to increase hydrogen content. The reformation of waste has also been successfully observed at the facility.

40.5 Synergistic Benefits of Plasma

40.5.1 Chemical Processes

In gasification, a portion of potential product is lost through tar buildup, which consists of higher carbon chained molecules that are condensable, but only at high temperatures up to 400 °C. Not only is it a loss in production, if not properly removed before downstream processing, the tars will obstruct process flow and cause eventual shutdown. These concerns can be dealt with by a plasma-induced field in a catalytic environment supportive of partial oxidation of the hydrocarbons into syngas (Fig. 40.13).

The production of hydrogen is possible through many processes, as it is such an abundant element. The various methods of obtaining hydrogen are energy intensive and also typically involve the destruction of another compound that could hold value on its own. In processes that create excess side hydrocarbons or hydrogen-containing compounds, there is little to no value in them unless further processing is done. This is true for a side product such as dirty glycerol, which is difficult to handle and costly to remove as well. The PRISM is able to make these side products useful for additional heating to primary processes or for a valuable side product such as methanol. Because of its low operating expense, the PRISM can be utilized in any process looking to maximize its hydrogen potential. PEM and solid oxide fuel cells that run directly on hydrogen are another potential beneficiary of this technology.

40.5.2 Commercial Implementation

This process has the flexibility to create numerous market-worthy products, allowing the user to choose their path of profitability. Syngas, once synthesized, can be taken down any processing path that would use the H_2 and CO molecules as building blocks for the product. Olefins are the raw material for most plastics

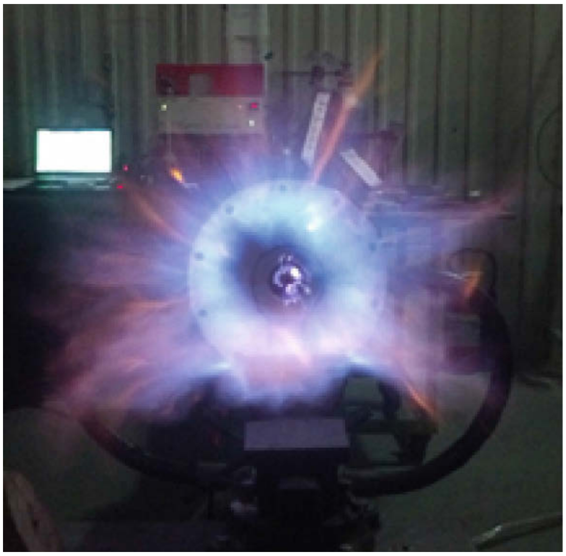

Fig. 40.13 Operation and view of the ionized plasma field exposed to the air (precatalysis)

and can be produced in a high-pressure, temperature-controlled environment when provided with the proper catalyst. Methanol, ammonia, and diesel fuel are just some of the many other products that can be made from feedstock derived of syngas.

Decreasing emissions from motor vehicles and increasing engine efficiency is a necessary step toward improving air quality and decreasing greenhouse gases. Internal combustion engines for transportation constitute as one of the largest consumers of imported oil and are also a major source of ozone-eliminating gases such as NO_x. A variety of potential improvements are presently being investigated: lean-burn engines, engines designed with increased compression ratios, improved catalyst formulations, use of close-coupled catalysts, new types of exhaust treatment, electric and fuel-cell powered vehicles, and alternative fuels.

One outlet for plasma reforming technology, which also presents a solution to the negatives of internal combustion in transportation, is for onboard vehicular implementation. In a fully integrated system, the generation of hydrogen as syngas into an ICE allows for lower combustion temperatures, better flame speed and propagation, increased sparkplug life, and decreased NO_x emissions during engine operation. Onboard production of hydrogen may be attractive for reduction of cold-start emissions and minimizing engine cranking during cold start. This is beneficial for catalyst regeneration and posttreatment as well. The robust, compact design of the PRISM unit can be used with a variety of fuels to provide a rapid response without the necessity of reformed gas storage. Complete integration of the vehicle operating system with the PRISM reactor would call for an intuitive approach to achieve a seamless, well-controlled operation. This would factor in startup, shutdown, ratio control, valve timing, and additional temperature sensors, but would otherwise not require further manipulation of either new or old standard vehicle engine designs.

Upon total oxidation or combustion of fuel with or without syngas, large quantities of water and CO_2 are produced in the exhaust. The hydrogen-rich gas may be useful during cold start, both minimizing the cranking, as well as potentially decreasing the hydrocarbon emissions due to cold-start ignition. In an exhaust gas recycle (EGR) process the dry reforming reaction plays a major role in altering the stoichiometry of the system. The main goal of EGR is to lower peak combustion temperature in the piston chamber. This provides a smoother cycle of operation reducing NO_x and ensuring maximum conversion while boosting thermal-to-mechanical efficiency.

40.6 Conclusion

Very few configurations exist, outside highly specialized areas of use, which allow thermal plasma to be implemented in a profit-worthy system. A low energy, nonthermal plasma creates a better source for utilization of resources, providing efficient production of high quality syngas. Nonthermal plasma also requires assistance from catalysis in the form of a tailored reaction as opposed to simple decomposition. If unassisted, gaseous carbon and hydrogen atoms in a heated environment will preferentially recombine into methane instead of separating into hydrogen and carbon monoxide molecules. Plasma-assisted catalytic POX has great potential to address many environmental concerns while maintaining profitability for the end user. In its present design, PRISM is a viable tool for implementation into small- to middle-scale syngas production plants. Expending roughly 100 W of energy in a robust system configuration built for extended operation, nonthermal single-stage plasma catalysis has proven to be a viable technology for reformation. Full integration of the PRISM reactor into future commercial endeavors is possible with only minor adjustments to the current benchmark operation.

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