3.1 Introduction

Hydrogen is not readily available in nature in the unbound molecular form. Thus, hydrogen is not a primary energy source but, like electricity, is an energy carrier and must be converted from other sources of energy. While hydrogen as an energy carrier has low environmental impact at the point of use, there may be significant impacts from the production and distribution of hydrogen. There are many hydrogen production methods ranging from well-developed industrial processes to emerging pathways in both biological and thermochemical pathways. The most commonly used process to generate hydrogen is reforming of fossil fuels. This chapter will discuss the basic principles and state of the art of steam and autothermal reformation (ATR) processes.

Figure 3.1 shows the energy density of some fuels on both mass and volumetric bases. Note that for Figure 3.1, these values include only the fuel itself and not the tank required to hold such a fuel. The low volumetric energy content of hydrogen and the lack of infrastructure for hydrogen refueling present a significant obstacle for enabling hydrogen-fueled systems for power generation. Producing hydrogen via reforming of a liquid fuel for onboard mobile hydrogen applications shows the potential of using hydrogen technologies while avoiding storage difficulties by allowing the storage and transport of a higher-energy-density liquid. While significant progress has been made recently in hydrogen storage issues, reforming high-energy-density liquid hydrocarbons allows for fast refueling, ambient pressure storage, and potentially higher total energy storage capacity in a given volume. For stationary

![Figure 3.1](image-url)

A comparison of various fuels. Hydrogen has the highest energy per unit weight but the lowest energy per unit volume. Currently, diesel, gasoline, and LPG are common fuel for transportation application.
applications, catalytic reforming of a hydrocarbon feedstock can potentially be combined with carbon dioxide capture and sequestration systems to reduce greenhouse gas emissions.

For about a century, stationary large-scale hydrogen production plants have been providing hydrogen for industrial processes such as refinery hydrogenation, ammonia production, and gas-to-liquid (GTL) plants, that is, converting methane to methanol.

While large-scale hydrogen production plants are well established, small-scale fuel processors are not as established and are found in the research and development field or in niche markets [1–6]. These potential hydrogen applications include standby and auxiliary power systems, mobile power generation (i.e., auxiliary power units, forklift applications), and stationary distributed power generation.

### 3.2 What Is Reformation?

Reformation is a chemical process that breaks hydrocarbon molecules into hydrogen from a compounded element to its elemental form. Equation 3.1 represents the typical overall reaction in steam reformation (SR) of a hydrocarbon. In a pure definition, reformation is when the characteristics of a certain fuel

\[ C_nH_m + nH_2O \rightarrow nCO + \frac{n+m}{2}H_2 \quad \Delta H (298 \text{ K}) > 0 \]  

are reformed into a desirable trait. The SR process shown in Equation 3.1 and other processes like it can be used to change the characteristics of fuels.

Reformation is typically an endothermic reaction due to the hydrogen product having a higher energy state than the hydrocarbon fuel or fuel–water mixture. Thus, energy is needed to volatilize the hydrocarbons and break the C–C and H–C bonds. A heat source, such as an external burner, is used to provide the energy in a typical system. Internal heat sources can also be used by introducing an oxidizer into the fuel–water stream, but this typically will dilute the output stream purity with nitrogen when air is used. A variety of hydrocarbon fuels have been used in reformation studies and have been successfully used in some prototypes and commercial applications: gasoline [7,8], ethanol [4,9], methanol [10–12], dimethyl ether, propane, butane, methane (natural gas), diesel [1,13,14], isoctane, and jet fuel such as JP-8 [15] are some of the examples [5–7,12,16–18]. The reassembly of the elemental hydrocarbon constituents with oxygen, either supplied with the fuel–water mixture or externally added in small amounts, is thermodynamically favored as being exothermic. Thus, with typical reformation of hydrocarbon feedstocks, one has a highly endothermic and rate-limiting fuel steam breakdown followed by a moderately exothermic reassembly through the water–gas shift reaction with the total reaction being endothermic.

Although reformation can proceed unaided by using solely thermal processes at high temperature, the typical reformation system uses a catalyst bed or a series of catalyst beds to shift selectivity toward the desired products (H\(_2\) and CO\(_2\)). Inside the fuel processor, the catalyst aids the reformation of the hydrocarbon fuel into a hydrogen-rich gas mixture. The main reformer can be followed by numerous catalytic water–gas shift reactors that bring the H\(_2\) concentrations up and minimize problematic compounds. The conversion,
efficiencies, cost, and usable life of the catalysts are strongly dependent on the temperature at which the catalyst is operated; thus, temperature is an important aspect of the control of the fuel processor.

For complex hydrocarbons, dry reforming (or partial oxidation [POX]) is used in prereformers to break apart long-chain hydrocarbons prior to SR. If water or steam is added to the process, then part of the water will be consumed to produce additional hydrogen via the water–gas shift reaction. POX and ATR can use either oxygen or air to produce heat in the overall process. This improves the heat and mass transfer of the catalyst bed by trading off reformate stream purity and results in product dilution when using air as the oxidizer.

3.3 History of Reformation

Historically speaking, reformation is as old as flame itself and is not independent of combustion especially regarding solid or liquid fuel combustion. It is well known that a typical solid or liquid fuel does not burn directly but only in gaseous phase. Thus, the endothermic heating and vaporization as seen with most diffusion flames lead to a local gasification or reformation of the fuel. This gaseous fuel then diffuses until it reaches the oxidizer and then burns to the end products.

Reformation is then an effective short-circuiting of the combustion process and is usually classified in the combustion field as gasification. While it can be argued that reformation has always occurred with combustion and it is not an independent field, reformation as known in literature as a deliberate action had its roots in the late 1700s in solving England’s early street lighting problems.

Table 3.1 shows early milestones in the uses of reformation or gasification. In the late 1700s, coal and biomass fuels were not readily applicable to distributed lighting systems because of their traits regarding solid transportability. With the price of whale oil skyrocketing with resource depletion, a crisis in the lighting systems of London was developing. William Murdoch is attributed with devising ways of changing solid fuels such as wood and coal into distributable gaseous fuels by POX or gasification of the solid fuel. One of the early commercial uses of reformation was deriving town gas or syngas from coal in the early 1800s. This was used for lighting and cooking before natural gas and electricity became more available in the mid-1900s.

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1792–1794</td>
<td>Scottish scientist William Murdoch produced gas from heating coal for lighting.</td>
</tr>
<tr>
<td>1804</td>
<td>Coal gas first patented for lighting.</td>
</tr>
<tr>
<td>1813</td>
<td>London and Westminster Gas Light and Coke Company, Great Peter Street, illuminates Westminster Bridge with town gas lights on New Year’s Eve using wooden pipes.</td>
</tr>
<tr>
<td>1816</td>
<td>Baltimore, Maryland, becomes the first US city to light streets with town gas.</td>
</tr>
<tr>
<td>1959</td>
<td>British Gas Council started to replace coal gas with liquid natural gas.</td>
</tr>
</tbody>
</table>

3.4 Modern Reformation: State of the Art and Technological Barriers

The use of town gas was essentially that of converting a fuel from a solid form to a form that had desirable transport characteristics. Modern reformation also converts liquid, solid, or gaseous fuels into hydrogen that has desirable environmental point-of-use characteristics or allows hydrogen to be used in chemical processing. Reformation can also be used to convert marginally usable low-energy fuels as is found with some biomass sources into a hydrogen gas with benefits in transportability and energy intensity.

The dominant use of hydrogen is in the chemical industry [20]. The primary use of hydrogen is for the production of ammonia and methanol, for hydrotreatment in refineries, and for hydrogenation of unsaturated hydrocarbons. Approximately 90% of the hydrogen used is produced by SR of natural gas and other light refinery hydrocarbons. Other production methods used include gasification and reforming of heavier hydrocarbon fuels, electrolysis, and biological methods.

In a modern reformation facility, natural gas is joined with steam and fed across a catalyst bed. Product gas is collected and fed into various purification steps. The product gas typically carries more chemical energy than the input fuel and steam; thus, the reformation is endothermic, and heat is supplied externally from a combusted fuel.

In a typical methane steam reformer, the reforming process typically requires a temperature from 500°C to 950°C. The reformate, or the product of hydrocarbon reformation, is usually fed into high-temperature and low-temperature water–gas shift reactors to increase the hydrogen concentration and decrease the CO content. The output stream of the water–gas shift reactors is fed into a pressure swing adsorption (PSA) system for purification that gives 99.9% or higher purity. While large-scale hydrogen production has been commercialized for many decades, the current gap to make hydrogen readily available for distributed power generation and transportation applications is dependent on decentralized hydrogen production [21]. Smaller fuel processors for point-of-use application are now actively studied.

In commercial large-scale hydrogen production systems, the steam reformer operates with the catalyst bed temperature typically at 450°C–800°C at 30–45 bar using a Ni-based catalyst held on a ceramic pellet substrate. Cobalt and other noble metals can also be used as catalysts but are generally more expensive. The selection of the catalyst is typically a trade-off in the costs associated with operational life and avoidance of solid carbon (coke) formation, which is also affected by the steam-to-carbon (S/C) ratio. Along with the S/C ratio, other cost factors include flow throughput and pressure drop that reflect operational costs. The catalyst is loaded into high-strength alloy tubes with an outer diameter that ranges from 100 to 150 mm and the length ranges from 10 to 13 m. These tubes must have long creep life and high creep rupture strength due to the high-temperature and high-pressure operation inside the reformer. Central external burners operating at slightly negative gauge pressure provide heat to arrays of steam reformer tubes that can have over 1000°C external wall temperatures. Furnaces holding hundreds of reformer tubes are not unheard of and even small plants might have a 72-tube array in a single furnace. The standard reformer tube is mechanically simple with a header and an orifice at each tube entrance to ensure similar flows in each tube. Temperature for the entire reformate stream is typically monitored by a single temperature sensor at the merged reformate exit. Some operators will monitor tube temperature down the center line of each tube with a multijunction device. Areas of high heat flux can also be noted by observing the dark or cooler regions of the tube from observation points within the furnace. Lifetimes on the
order of years with continuous use are expected with the commercial system catalysts and reformer apparatus. Other than methane, various heavy hydrocarbon feedstocks can be used with additional prereforming and suitable catalysts as longer-chain molecules as fuels have the tendency to form carbon at hot spots on the Ni-based catalyst. Ammonia formation and other minor species can also be problematic.

For small-scale hydrogen production, adopting technology from well-understood industrial processes and scale down shows unique challenges [22–24], such as optimizing catalyst operation life and reformer design. In recent years, detailed studies of small-scale reformers for hydrogen production have been published [15,25–27]. Unlike large-scale reformers, small-scale reformers are expected to experience significant transients in normal operation. Frequent start-up and shutdown of reformers can degrade the catalyst and apparatus reducing the life and performance of the system. Reformation systems have been adapted to mobile applications including several iterations of the Georgetown fuel cell buses (1994–2000). The earliest system (1994) is shown in Figure 3.2. Reformation was also used by early fuel cell vehicles including those demonstrated by Daimler (NECAR 3), Toyota (fuel cell electric vehicle [FCEV]), General Motors, and Hyundai motors. An excellent review of small-scale fuel processing for fuel cells and fuel cell vehicles is given in Gunther Kolbs’ recent book [28].

3.5 Quantifying Reactor Performance and Parameters

A somewhat standard set of terms and language is used in the reformation industry. Typical parlance includes flow rate in terms of space velocity, stoichiometric terms such as oxygen-to-carbon (O₂/C) ratio and S/C ratio, and output and analysis terms such as conversion, selectivity, and yield.
3.5.1 Flow Rate

Flow rate is typically normalized to an inverse residence time parameter known as space velocity, which can be further distinguished to indicate gaseous species or equivalent liquid species if applicable. Space velocity (sv) is a quasi-nondimensional term that is defined as the reactor volumetric flow rate divided by the reactor volume. This is shown in the following:

\[ SV = \frac{\dot{V}}{V} \]  

where

- \( \dot{V} \) is the volumetric flow rate
- \( V \) is the reactor volume

The units are inverse time so as flow rate increases so does space velocity. The units can be done in any time unit but hourly space velocity is commonly used. For gas space velocity, the species temperature and pressure can change the volumetric flow rate at any location in the reactor; thus, nonreacted reactor inlet conditions are often used. Standard temperature and pressure can also be used for normalization. S/C ratio can often change, but as the fuel stream is often the only reactant supplying energy, the space velocity can remove the steam-to-carbon dependence by stating just the volumetric flow rate of the fuel and not the water or steam flow. For fuels that are liquids under standard temperature and pressure, liquid space velocities can be used although the reactants are vaporized and are certainly not reacting in liquid phase. A denotation of LHSV-M would represent a liquid hourly space velocity of methanol, whereas liquid hourly space velocity (LHSV) might be methanol or a premix of methanol and water. GHSV could also be used to represent this flow as gas hourly space velocity at specified inlet conditions and S/C. GHSV-MSTP would mean gas hourly space velocity of methane at standard temperature and pressure, whereas GHSV could mean any or all reactants at standard or another given inlet condition. Another issue with all space velocity terms is the definition of the reactor volume. Those in industry generally prefer to indicate the entire tube including empty locations as it indicates the true length and volume required by the reactor, while those in academic studies typically will only include the volume displaced by the catalyst because the typical research reactor housing is not filled to its full capacity with the catalyst. Those reporting flow values in space velocity should be careful to include a full description of their values to avoid ambiguity or mistranslation of the values.

3.5.2 Stoichiometry

\( \text{O}_2/\text{C} \) ratio and S/C ratio are parameters used to describe the stoichiometry in reformation processes. Those reporting values should clearly define \( \text{O}_2/\text{C} \) ratio nomenclature especially when using air as the oxidizer and/or using fuels with oxygen contained therein (i.e., alcohols). S/C ratio and stoichiometry can also be potentially confused in the \( \text{O}_2/\text{C} \) ratio. Typically, oxygen bound up in compounds will not be counted in the \( \text{O}_2/\text{C} \) ratio, and oxygen is counted in its bound \( \text{O}_2 \) form and not as an oxygen radical. When using alcohols, it is helpful to note the oxygen–alcohol ratio (i.e., oxygen to methanol [\( \text{O}_2: \text{CH}_3\text{OH} \)]) rather than just \( \text{O}_2/\text{C} \) to avoid mistranslation.
3.5.3 Output and Analysis

Outputs of reformation reactors can be equally ambiguous and many output metrics can include all or selected species. Typical output nomenclature includes conversion, selectivity, and yield. These outputs should also be defined carefully for a system as some outputs can be defined by the user and most are specific to a certain reactant or a certain product.

Conversion is defined as the reactant consumed divided by the reactant fed as shown in the following:

\[ \text{Conversion} = \frac{\text{Reactant consumed}}{\text{Reactant fed}} \] (3.3)

Conversion is typically given in percent and only indicates how much reactant was consumed. For a single pathway system, this does give insight of the fuel consumption and reactant progression. It does not however give any indication of the product produced. This is an important distinction because in reformation systems, the hydrogen product is typically what is desired. Thus, even though conversion may be high, the hydrogen output could be nonexistent especially with POX reforming or ATR systems that employ an oxidation step. For example, complete combustion implies complete conversion but no hydrogen production.

The selectivity has at least two potential definitions. These are shown in the following:

\[ \text{Selectivity} = \frac{\text{Desired product produced}}{\text{Undesired product produced}} \] (3.4)

and

\[ \text{Selectivity} = \frac{\text{Desired product produced}}{\text{Reactant consumed}} \times \text{SF} \] (3.5)

where the stoichiometric factor (SF) is used to normalize the selectivity to 100%.

For example, in methanol reformation, the stoichiometric equation is shown in the following:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \] (3.6)

In this case, if the desired product is hydrogen and the reactant is methanol (CH$_3$OH), the SF would be 1/3 as 3 mol of hydrogen H$_2$ is produced per 1 mol CH$_3$OH reactant. This factor allows normalization to 100%.

The yield shown in the following also uses a similar SF:

\[ \text{Yield} = \frac{\text{Desired product produced}}{\text{Reactant fed}} \times \text{SF} \] (3.7)

3.5.4 Reformer Characterization

Space velocity describes the fuel-processing capacity and the volume of the reactor but is insufficient to quantify the properties of the reactor. However inadequate, reactors are often compared using space velocity as a metric. Many researchers speak of a break point in space velocity where the reactor begins to break away from the 100% or previously
Reformation of Hydrocarbon Fuels

defined percent conversion or yield. While this is useful to know the limits of performance, the first-order behavior of the reactor is not captured by such characterization. As seen in Figure 3.3 [29], performance can vary greatly for reactors that have the same space velocity. In this figure, the catalyst, flow rate, reactor set point temperature, control scheme, and reactor volumes are identical. The only difference between these data is that the reactor radius of configuration (i) is 0.635 cm (¼ in.) less than that of configuration (iii). This clearly shows that reactor performance cannot be described by space velocity alone.

A better metric is to use the characteristic time constant, which factors additional information such as geometric conditions, heat and mass transfer characteristics, and flow condition and describes the performance directly from the residence time. In addition, the chemical kinetic properties are indirectly captured by the reaction rate coefficient in the residence time distribution (RTD). This is especially important in describing steam reformers as their performances are dependent on the heat transfer characteristic. Since the characteristic time embodies the geometric effect and chemical kinetics, it is more descriptive than using space velocity (SV) [30].

The characteristic time is a modification of the RTD. The overall reformation process based on fuel conversion can be simplified to a first-order reaction. Taking methanol SR as example, using the Arrhenius mechanism, the reaction rate coefficient can be expressed as shown in the following:

\[ k(T) = A e^{E_a/RT} \]  

(3.8)

Following Fogler’s formulation of a segregation model for packed-bed reactors [31], by knowing the reactor’s RTD function, \( E(t) \), and the reaction rate coefficient from Equation 3.8, the theoretical conversion is shown in the following:

\[ \bar{X} = 1 - \int_0^\infty e^{-k(T)E(t)} dt \]  

(3.9)
By assuming an ideal plug flow reactor (PFR) RTD function as a Dirac function, \( E(t) = \delta(t - t_r) \), with an identical residence time \( t_r \) for every molecule in the reactor, and substituted into Equation 3.9 yields the following:

\[
\bar{X} = 1 - e^{-k(t - t_r)/\tau} = 1 - e^{-t/t_r}
\]  

(3.10)

The first-order characteristic time, \( \tau \), represents the time needed to convert 63.2% of the fuel or produce 63.2% of the possible desired product in a particular reactor. Like all first-order systems after five time constants, the reactor should produce near 100% conversion or yield and this characterization captures this behavior. Unlike SV, LHSV-M, or GHSV, characteristic time is descriptive of the actual performance and takes into account catalyst particle size, flow conditions, and other passive enhancements such as baffles and acoustic waves. As characteristic time is based on conversion or yield performance, reactors with the same characteristic time will have the same performance, regardless of temperature, geometry, catalyst, pressure, etc. In other words, given the required characteristic time, there are multiple ways to optimize the reactor design.

### 3.6 Catalyst Selection

By introducing a catalyst into the reaction, new pathways and acceleration of the reaction occur. An ideal catalyst would not be consumed, but in practice, catalysts do undergo physical and chemical changes. There are three modes of action of catalyst [32]: activity, selectivity, and stability (or degradation behavior).

Activity is a measure of how fast the reaction(s) proceeds in the presence of the catalyst. It is influenced by temperature, concentration of the chemical species, pressure, residence time, and other factors. In reformation, the limiting mechanisms are mass and heat transfer and chemical kinetics and are discussed in a later section. They are fully coupled with one another, and improving the control of the catalyst temperature helps to improve catalyst activity and the overall performance.

The selectivity of the catalyst is the measure of desirable product to the reacted quantity of the feedstock. The realistic selectivity is often less than ideal because of a secondary reaction creating an undesirable by-product that reduces efficiencies. Additional cleanup or removal steps are needed to ensure purity of the output stream. In reformation, CO is undesirable because it can poison the electrode of a proton exchange membrane fuel cell (PEMFC). Carbon formation or coke can also degrade the catalyst, which is the third mode of action of catalysts.

Catalysts help introduce new pathways to reduce the activation energy required to reform a hydrocarbon, provided that the catalyst is active by having sufficient temperature. The reformation is typically an endothermic process; thus, the limiting mechanisms are heat and mass transfer. When a hydrocarbon finds an active site on a catalyst, it breaks down the chemical bonds and reassembles, and it consumes heat and reduces the catalyst and fuel temperature in the process. Heat is added to the system to ensure high catalyst activity to sustain the operation. If the catalyst is highly active, the reformation continues to go forward as long as fuel can find an active site on the catalyst. The porous structure of the catalyst allows fuel to diffuse into the catalyst. After the
reactants diffuse into the catalyst and reform, products need to diffuse out from the catalyst to allow the active site to reform the next reactant.

Catalyst degradation is an important issue in catalytic reformation. The chemical, thermal, and mechanical stability of the catalyst determine the operation life of the reactor [32]. Desulfurization is often necessary with most fossil-fuel-based liquids. Care must be taken in controlling the temperature because of the poor heat transfer property of the catalyst or the catalyst bed. A Ni-based catalyst is often used in the high-temperature reformers because it is cheap, active at elevated temperature, and stable. On the other hand, Cu-based catalysts cannot operate at high temperature but have high selectivity toward hydrogen. Care is taken when using a Cu-based catalyst with an exothermic reaction to ensure the integrity of the catalyst. Additionally, other operating conditions such as S:C and O₂:C, where appropriate, should be controlled to minimize carbon formation. The two general types of catalyst substrates are pellets and monolith structures shown in Figure 3.4.

The choice of catalyst depends on the feedstock used. There are wide selections of catalyst formulations for reforming hydrocarbon fuels, and many more are in development. In general, monolith catalysts produce less pressure drop than do pellets. A small amount of catalyst material is washcoated onto a monolith substrate to form the monolithic catalyst. Pellets are usually porous alumina structures with open sites for the catalyst. The advantage of pelletized catalyst over the monolith catalyst is their resistance to poisoning and high amounts of internal surface area.

The reforming catalyst is usually based on nickel/nickel oxide or cobalt composite. They require high temperature to become active and are generally suitable for higher-order hydrocarbon reformation. Lighter hydrocarbons, such as methanol, can be reformed using copper-based medium temperature shift (MTS) [20] catalysts. Many of these formulations used for methanol and ethanol reformation have been used as water–gas shift catalysts for the natural gas reforming industry because of their high selectivity toward hydrogen and CO₂. The catalyst system of copper (Cu) in the presence of zinc oxide (ZnO) supported by alumina (Al₂O₃), derived from industrial catalysts, is the most popular. There have been other catalysts proposed [33–42], but Cu/ZnO/Al₂O₃ remains the primary interest [10,34,43–46]. The low-temperature catalyst allows a less complex heat exchanger and is potentially compatible with phosphoric acid fuel cell (PAFC) or PEMFC applications. Another advantage for reforming at low temperature is the low level of CO formation. The high temperature allows the reverse water–gas shift reaction to consume hydrogen.

FIGURE 3.4
Variations of catalysts for steam and ATR. On the left are examples of monolith catalysts. On the right are examples of pelletized catalyst. (Courtesy University of California, Davis, CA.)
even if the catalyst has high selectivity for $\text{CO}_2$ over CO. Other expensive precious metal catalysts are used in high-temperature steam reformers. Rh, Ru, Pt, Pd, and Re supported by porous alumina or magnesium alumina spinel structures are highly active at elevated temperature [47,48]. Current catalyst development is targeting ways to improve selectivity and resistance to degradation by incorporating various oxides and compounds [49], as well as micromachining techniques in fabrication [50–53].

3.7 Types of Reformation

There are currently three major methods for reforming hydrocarbon fuels into hydrogen-rich gas. These are SR, POX reforming, and ATR. Figure 3.5 shows a graphical representation of each process. Today, in large-scale plants, SR is the most common method to obtain hydrogen from a hydrocarbon fuel.

3.8 Steam Reformation

SR is the most widely used method to reform hydrocarbons in large-scale hydrogen production plants. A typical reformer schematic is given in Figure 3.6. This system would be coupled with significantly complex water–gas shift and cleanup devices as well as heat exchangers and preheaters. Specific catalysts are used depending on the hydrocarbon feedstock. The general SR steps are described as fuel breakdown and the water–gas shift reaction and are sometimes followed by methanation as shown in Equations 3.11 through 3.13. All of these reactions can happen at the same physical location, or these may be separated into individual reactors with different catalysts to promote one reaction or another. Higher temperature typically speeds up the rate-limiting steps of fuel breakdown.
but higher temperature typically promotes CO and CH\textsubscript{4} production. It is thus typical to have multiple reactors in series each operating at a different temperature with increasing hydrogen purity as the gas progresses through the plant. With heavy hydrocarbons, intermediate species and radicals often are produced and these potentially have carbon or coke formation difficulties:

\[
\text{CH}_2\text{H}_m + n \text{ H}_2\text{O} \rightarrow n \text{ CO} + \frac{n+m}{2} \text{H}_2 \quad \Delta H (298 \text{ K}) > 0
\]

(3.11)

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H (298 \text{ K}) = -41 \text{ kJ/mol}
\]

(3.12)

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H (298 \text{ K}) = -206.2 \text{ kJ/mol}
\]

(3.13)

Many hydrocarbons have been used as feedstock for SR. To illustrate some of the key parameters in SR, methanol and ethanol will be described here as examples. The SR kinetics of methanol on a Cu-based catalyst are available in the literature [10,36,54,55]. The exact mechanism of SR is still debated [10,56,57]. As commonly understood, different catalyst formulations promote the reaction in favor of certain pathways that is manifested as selectivity. However complex in application, a simplified reformation process can be expressed for methanol as the overall reaction consisting of methanol decomposition and the water–gas shift reaction. These are shown in Equations 3.4 through 3.6:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad \Delta H (298 \text{ K}) = +49 \text{ kJ/mol}
\]

(3.14)

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H (298 \text{ K}) = +90.1 \text{ kJ/mol}
\]

(3.15)

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H (298 \text{ K}) = -41 \text{ kJ/mol}
\]

(3.16)
While the overall reaction is endothermic, the methanol decomposition reaction is endothermic and the faster water–gas shift reaction is exothermic. For methanol SR, 75% dry hydrogen concentration can be produced based on 100% carbon dioxide selectivity as shown in the following:

\[
\% H_2 \text{ selectivity} = \frac{\text{mole } H_2}{\text{mole of } H_2 + \text{mole of } CO_2} = \frac{3 \text{ mol}}{3 \text{ mol} + 1 \text{ mol}} = 75\% \quad (3.17)
\]

In practice, dry hydrogen concentration is less than 75%. The conversion is strongly dependent on temperature and hence the activity and selectivity of the catalyst used. For a reformer operating at less than \(~250\) PSI, the pressure effect has been found as less significant [30]. Higher-pressure operation typically allows for higher throughput and better integration with either feedstock or end use such as high-pressure hydrocracking. It should be noted that Equation 3.16 also has a significant backward component that can form CO from the desired products. In the reverse water–gas shift reaction, hydrogen may be consumed to produce CO if the reactor temperature is too high. CO is typically an undesirable by-product when considering operation of a fuel cell system. On the other hand, sufficient heat is needed to obtain high fuel conversion and to assist the forward reaction considering fuel breakdown.

Another key parameter in methanol SR is the S/C ratio (\(H_2O/CH_3OH\), in the case of methanol) [54]. This parameter impacts fuel utilization, efficiencies, and life of the reactor. Sufficient steam is required to achieve full conversion and suppress CO and solid carbon formation. Excessive steam will reduce energy efficiencies because it must be vaporized with the fuel without adding to the hydrogen product. High-temperature steam may also sinter Cu-based catalysts. Insufficient steam results in carbon formation and degraded catalyst performance by means of coking. Experimental work by many researchers has found that an S/C ratio between 1.3 and 1.6 for methanol steam reforming results in higher dry hydrogen yield at the reformer outlet.

Ethanol SR can be carried out with a Ni-based catalyst at about 550°C–650°C. Relatively higher temperature is needed to break the carbon–carbon bond in the fuel. The use of ethanol can favor carbon formation inside the reactor that potentially will degrade catalyst performance. Solid carbon fouls the catalyst by blocking fuel from contacting the active site inside the catalyst structure. The effect of fouling is more pronounced at low temperature or low S/C. It has been reported that an S/C ratio > 1.5 reduces carbon formation but added water has a trade-off in the energy needed for fuel vaporization [58]. In this respect, the ethanol process is quite similar to methanol SR. The following equations show the simplified reactions:

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \quad \Delta H (298 \text{ K}) = 347 \text{ kJ/mol} \quad (3.18)
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2 \quad \Delta H (298 \text{ K}) = 298 \text{ kJ/mol} \quad (3.19)
\]

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H (298 \text{ K}) = -41 \text{ kJ/mol} \quad (3.20)
\]
### 3.9 Partial Oxidation

POX is an alternative to SR and is generally employed with higher hydrocarbons or if pure oxygen is available [59]. With a lower product concentration of hydrogen, this process sacrifices some efficiency relative to SR but offers rapid dynamic response and compactness. Unfortunately, this process is susceptible to coke formation and must be carried out at high temperatures. POX can be performed with or without a catalyst, but using a catalyst allows for a lower reaction temperature. The POX of methane is described by the chemical reaction shown in the following:

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad (\Delta H = -36 \text{ kJ/mol})
\]  

(3.21)

If the oxygen-to-fuel ratio is increased, then the reaction becomes even more exothermic as shown in the following:

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2 \quad (\Delta H = -319 \text{ kJ/mol})
\]  

(3.22)

These equations illustrate how the amount of heat generated from the POX of methane can be quickly increased from −36 to −319 kJ/mol by simply increasing the amount of oxygen in the reaction, that is, increasing the air flow rate and combusting additional fuel. Therefore, it is possible to reduce reformer start-up times by increasing the temperature rapidly; that is achieved by increasing the air (or oxidant)-to-fuel ratio.

The fast response time of the POX reformer is typically inhibited by the low hydrogen concentration and high CO levels that result. This implies a lagging hydrogen response time because of the potentially necessary water–gas shift and other cleanup systems put in place to clean up the high levels of CO that result from the POX reformer.

POX and catalytic partial oxidation (CPO or CPOX) is similar to a combustion process. With catalyst, CPOX can be carried out at lower temperature. Without catalyst, POX is typically carried out at 1300°C–1500°C to ensure complete conversion. As compared to SR, CPOX has the advantage of short start-up time because of the fast exothermic nature of the reaction. On the other hand, the exothermic nature of the reaction and the heat transfer limitation within the catalyst make it difficult to control the catalyst temperature and reformate composition. Localized hot spots can overheat and sinter the catalyst if present. The product stream is influenced by the process conditions. Temperature, pressure, and \(O_2/C\) ratio are some of the process variables. For example, increasing reformer pressure will reduce the hydrogen yield in POX. A POX or CPOX reformer is comparatively compact because it doesn't require external heating to sustain the reaction and lowers the energy required to vaporize the fuel, but it is relatively less efficient than SR and ATR. Experiments on CPOX of various liquid hydrocarbon fuels have been reported by Cheekatamarla [60].

A general equation for POX is shown in the following:

\[
C_nH_m + nO_2 \rightarrow n\text{CO} + \frac{m}{2}\text{H}_2 \quad \Delta H (298 \text{ K}) < 0 \text{ kJ/mol}
\]  

(3.23)
POX and CPOX have complex reaction systems. The reaction produces various intermediate species and radicals that decrease the purity of the output stream. They are also potentially coke precursors that cause catalyst deactivation for both precious and nonprecious metal catalysts. Pure oxygen and air have been used as oxidizer in these systems. However, the effect of inert gases such as nitrogen in the POX process can reduce the efficiency of the reformer by lowering the output stream hydrogen concentration. In general, other than O₂/C ratio, there is no control over the chemical species in POX or CPOX. Equations 3.24 and 3.25 show the POX of ethanol, and Equation 3.26 shows the complete oxidation:

\[
\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2 \quad \Delta H (298 \text{ K}) = 57 \text{ kJ/mol} \tag{3.24}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CO} + 3\text{H}_2 \quad \Delta H (298 \text{ K}) = -226 \text{ kJ/mol} \tag{3.25}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + 1.5\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2 \quad \Delta H (298 \text{ K}) = -509 \text{ kJ/mol} \tag{3.26}
\]

In POX or CPOX, CO is one of the products in the reformate stream. This is especially problematic for low-temperature fuel cell applications because the high concentration of CO will poison the electrode. An additional CO oxidation reactor, water–gas shift reactor, or preferential oxidation (PROX) reactor can be used for CO removal. On the other hand, with high-temperature fuel cells, solid oxide fuel cell (SOFC) can utilize CO as a fuel source and it is less sensitive to impurities. Moreover, SOFC operation temperature is near 800°C, which is the typical POX reformate stream temperature. This makes POX and SOFC a good combination for fuel cell power system integration. It should be noted that it is not typically economical to use pure oxygen as oxidizer; thus, air is used.

### 3.10 Autothermal Reforming

ATR is essentially a combination between SR and CPOX. This is done by bringing the two reforming reactions into close thermal contact or by placing them into a single catalytic reactor. The single catalytic reactor is the most efficient means of heat transfer. ATR has advantages of both SR and POX in that it has potentially high hydrogen product concentration and adequate response to dynamic loads. Ideally, the heat generated from the exothermic POX reaction is used for rapid start-up and supplying the heat needed for the endothermic SR reaction during operation. Once the reactor is at operating temperature, the fuel, steam, and air are all fed into the reactor in the same step. The reactants ignite and form the ideal products of hydrogen and carbon dioxide. It has been found that on noble metal–based catalysts, ATR generally follows equilibrium concentrations in the output gas based on reaction temperature.

With a higher temperature due to the oxidation step, ATR is also capable of reforming multiple fuels, a necessary characteristic if alternative hydrocarbon feedstocks are reformed. Liquid fuels like methanol produced from coal or biomass may contain higher hydrocarbons. For example, at a pulp mill under investigation for hydrogen production from waste, it was found that small amounts of pinenes existed in the methanol fuel used.
In SR systems, the pinenes and other compounds tend to overwhelm any catalyst site until they are reacted. The higher temperatures and oxidation found in ATR may allow faster treatment of the trace levels of higher hydrocarbons. Although the pinenes are relatively small in quantity (about one-tenth of a percent volumetrically for this fuel), their effect on the catalyst can be significant. Similar studies found that trace amounts of heavier oils as found with methanol derived from coal had similar effects in SR [61,62] but could be acceptably dealt with in ATR [63].

ATR is similar to SR with an additional CPOX step. These exothermic steps are fast, and the resulting heat can be used to sustain the SR steps; thus, ATR is termed \textit{autothermal} or thermal neutral. The typical ATR equation of a hydrocarbon is shown in the following:

\begin{equation}
C_nH_m + 0.5mO_2 + 0.5mH_2O \rightarrow mCO + (0.5m + 0.5n)H_2 \quad \Delta H (298 \text{ K}) = 0 \text{ kJ/mol} \quad (3.27)
\end{equation}

The steps in an ATR process of using methanol as feedstock are shown in Equations 3.28 through 3.33. Equation 3.28 shows the CPOX steps, and combined with the carbon monoxide oxidation step in Equation 3.29, much of the CO will be consumed in these steps:

\begin{equation}
\text{CH}_3\text{OH} + 0.5O_2 \rightarrow \text{CO} + 2H_2 \quad \Delta H (298 \text{ K}) = -192 \text{ kJ/mol} \quad (3.28)
\end{equation}

\begin{equation}
\text{CO} + 0.5O_2 \rightarrow \text{CO}_2 \quad \Delta H (298 \text{ K}) = -283 \text{ kJ/mol} \quad (3.29)
\end{equation}

Another CPOX formulation is by substituting combustion/methanol oxidation steps shown in Equation 3.30. The remaining steps in Equations 3.31 through 3.33 are identical SR steps from the previous section:

\begin{equation}
\text{CH}_3\text{OH} + 1.5O_2 \rightarrow \text{CO}_2 + 2H_2O^+ \quad \Delta H(298 \text{ K}) = -675.4 \text{ kJ/mol} \quad (3.30)
\end{equation}

\begin{equation}
\text{CH}_3\text{OH} + H_2O \rightarrow \text{CO}_2 + 3H_2 \quad \Delta H (298 \text{ K}) = 50 \text{ kJ/mol} \quad (3.31)
\end{equation}

\begin{equation}
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2H_2 \quad \Delta H (298 \text{ K}) = 90.1 \text{ kJ/mol} \quad (3.32)
\end{equation}

\begin{equation}
\text{CO} + H_2O \leftrightarrow \text{CO}_2 + H_2 \quad \Delta H (298 \text{ K}) = -41 \text{ kJ/mol} \quad (3.33)
\end{equation}

The amount of heat generated in the reaction is directly related to the available oxygen in the fuel. If the proper stoichiometry fuel mixture is used, it will result in a thermoneutral condition: a self-sustaining operation as shown in the following:

\begin{equation}
\text{CH}_3\text{OH} + 0.1O_2 + 0.8H_2O \rightarrow \text{CO}_2 + 2.8H_2 \quad \Delta H (298 \text{ K}) = 0 \text{ kJ/mol} \quad (3.34)
\end{equation}

However, in a typical reactor, heat lost due to conduction is unavoidable. It is necessary to allow additional oxygen to account for this heat lost, as shown in the following:

\begin{equation}
\text{CH}_3\text{OH} + 0.27O_2 + 1.5H_2O \rightarrow \text{CO}_2 + 2.46H_2 + 1.04H_2O \quad \Delta H (298 \text{ K}) = -81 \text{ kJ/mol} \quad (3.35)
\end{equation}

The \text{O}_2/\text{C} ratio, or \text{O}_2/\text{C}, is an important parameter in ATR. Researchers have found \text{O}_2/\text{C} = 0.2–0.3 to be optimum using a Cu-based catalyst [54,64]. Higher \text{O}_2/\text{C} ratios will
reduce the amount of hydrogen in the output stream and increase the temperature inside the reactor, while lower O₂/C ratios will result in low conversion due to insufficient heat.

The steps in an ATR process of using ethanol as feedstock are described by Equations 3.18 through 3.20, 3.24, and 3.25. The case of complete oxidation of ethanol is described in the following:

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad \Delta H (298 \text{ K}) = -1368 \text{ kJ/mol}
\] (3.36)

In a small fuel processor design, an ATR reactor is compact and has higher heat and power efficiencies when compared to a steam reformer reactor. A typical schematic of the ATR reactor is found in Figure 3.7. The exothermic reactions take place on the surface of the catalyst; thus, they help shorten the warm-up time of the reactor. However, air is typically used to feed into the autothermal reformer; thus, nitrogen dilution will reduce the thermal efficiency and concentration of hydrogen in the reformate output stream. The fast start-up feature has been studied [65,66] for the potential use on fuel cell vehicle [67].

ATR also suffers from mass and heat transfer limitations as in SR but in a different manner. The rate of the exothermic reaction occurring on the catalyst surface is dependent on the rate of reactants mass transfer to and away from active catalyst sites [68,69]. In the case of reforming methanol on Cu-based catalyst, the rate of exothermic reaction is at least two orders of magnitude faster than the endothermic reaction [66,70–72], the heat generated is localized, and a hot spot is created by the heat transfer limitations of the catalyst. This is common in catalytic combustion and often degrades the catalyst by means of sintering. However, a well-designed ATR can take advantage of the exothermic reaction to overcome the heat transfer limitation of the SR step. This reduces the size of the overall reformer while maintaining high H₂ concentration. In addition, the nonlinear relationship between the reaction rate and catalyst temperature has a sharp transition known as the light-off

![FIGURE 3.7](image-url)

Schematic of a typical autothermal reformer.
Reformation of Hydrocarbon Fuels

41

temperature. Operating below the light-off temperature will result in extinction in the combustion process because it is unable to sustain the reaction [31].

The light-off temperature has the following implications. First, selection of a proper \(O_2/C\) ratio is based on both stoichiometry and reactor design. Not only sufficient oxygen is needed to sustain the reaction, but it must have excess oxidizer to account for heat lost by the reactor design. Balancing between \(S/C\) and \(O_2/C\) ratios for a specific catalyst selection can be difficult [65]. Second, if heat lost is significant, excessive oxygen required to sustain the reaction will potentially sinter the catalyst by overheating away from the heat sink. Poor heat transfer of the catalyst will create large temperature gradients, thus degrading (and possibly destroying) the catalyst. Various autothermal methanol reforming reactors have been studied [73,74].

### 3.11 ATR of Different Fuels

Gasoline and heavy hydrocarbons are typically considered for ATR to produce hydrogen for fuel cells. The advantages of gasoline are its existing fuel infrastructure and high energy density (32.3 MJ/L, based on LHV). However, using gasoline or other fossil petroleum products will not solve the long-term problem of fossil fuel dependence. For theoretical calculations, the optimal temperature to reform gasoline into hydrogen is around 400°C [75]. However, in other studies of gasoline and diesel ATR, temperatures of 600°C–800°C have been used [76,77]. From Sandakane, Saitoh, and Oyama’s research [78], a fuel conversion of greater than 97% can be obtained at temperatures in excess of 800°C. High temperatures require expensive materials and longer start-up times for automotive scale reformer systems. The high temperatures required for ATR of gasoline and other higher hydrocarbons make them less than optimal for automotive applications.

Although most work is done on ATR with higher hydrocarbons, focusing on renewably produced alcohols provides a basic understanding of the process. The general form of the ATR reaction of an alcohol fuel using air as the oxidizer, assuming complete conversion of the reactants, is shown in the following:

\[
C_nH_{2n}O_p + (2n - 2x - p)H_2O + x (O_2 + 3.76N_2) \rightarrow (2n - 2x - p + m/2)H_2 + nCO_2 + 3.76xN_2
\]

(3.37)

where \((2n - 2x - p)\) represents the minimum amount of water required in the reaction, and \(x\) represents the air-to-fuel ratio. The air-to-fuel ratio and \(O_2/C\) are related by a factor of \(n\), the number of carbon atoms in the fuel. The heat of reaction is dependent on the \(O_2/C\) and \(S/C\). Note that \((2n - 2x - p)\) is the minimum amount of water required for the reaction and the \(S/C\) ratio in practical applications is typically much higher in order to inhibit coke formation.

Methanol is a very attractive fuel for hydrogen production. Like hydrogen, methanol can be produced from multiple feedstocks. Ideally, methanol would be produced renewably, but it may also be produced from abundant coal resources and natural gas. Because it is an oxygenated fuel, it requires lower operating temperatures for effective reformation [75]. Ethanol and higher alcohols have longer carbon chains (two or more carbon atoms) and therefore require higher temperatures and more energy to be reformed. Methanol can be reformed at relatively low temperatures, around 250°C. According to one ATR study, conversions of greater than 90% are possible at temperatures just above 250°C, [79]. Based on
In thermodynamic equilibrium, the lower the reaction temperature, the lower the CO concentration that can be achieved [80]. This translates into less reformate cleanup and, therefore, a smaller and less complicated fuel-processing system. The lower temperatures also mean that less energy is required to heat the reforming system to operating temperature, so shorter start-up times are possible. It also means that the reformer can be made from a larger variety of materials that potentially reduces manufacturing costs.

In addition to the ease of reformation, methanol can be produced renewably through gasification of biomass or from coal resources. The different feedstocks of methanol result in different methanol purities. For example, coal-derived methanol may include higher hydrocarbons as an impurity [61]. Fortunately, ATR is a proven method of reforming higher hydrocarbons and should be able to cope with varying purities of fuel, depending on the feedstock [62].

The heat of reaction indicates whether a reaction is exothermic (releasing energy) or endothermic (requiring energy) and is defined as the heat of formation of the products minus the heat of formation of the reactants. Since the heat of formation for the oxygen, nitrogen, and hydrogen reactants and products are all zero, the heat of reaction for methanol ATR is simplified as shown in Equation 3.38:

$$\Delta H_r = \Delta H_{f(CO_2)} - (1 - 2x)\Delta H_{f(H_2O(l))} - \Delta H_{f(fuel(l))}$$

(3.38)

By evaluating the heat of reaction as a function of $O_2/C$, $x$, it is possible to find $x_0$, the thermoneutral point that produces a net enthalpy change of zero. Plotting the heat of reaction for methanol as a function of $x$, from $x = 0$ (SR) to $x = 1.5$ (complete combustion), and assuming an ideal reaction, yields Figure 3.8. The stoichiometry of the reaction is simply $O_2/C = x$ and $S/C = 1 - 2x$, until $x > 0.5$. At this point, water is no longer consumed in the reaction but rather produced as a product of combustion. It is easy to pinpoint the thermoneutral point that occurs at $x_0 = 0.230$.

The efficiency of a reforming process is defined as the lower heating value of hydrogen produced divided by the lower heating value of fuel consumed as shown in Equation 3.39:

$$\eta = \frac{LHV_{H_2 output}}{LHV_{fuel input}}$$

(3.39)

FIGURE 3.8
ATR of methanol, heat of reaction vs. $O_2/C$. (From Dorr, J.L., Methanol autothermal reformation: Oxygen-to-carbon ratio and reaction progression, Master thesis, University of California, Davis, CA, 2004.)
Further evaluation of this simple model reveals that the peak efficiency of ATR of methanol occurs at the thermoneutral point, as seen in Figure 3.9. The peak efficiency of ATR of methanol at the thermoneutral point \( x_o = 0.230 \) is 96.3\%, which is one of the highest theoretical efficiencies of ATR of various hydrocarbon fuels [80]. Therefore, it seems most desirable to operate as close to the thermoneutral point as possible if efficiency is a priority.

It is important to note that below the thermoneutral point \((x < x_o)\), the reaction is endothermic and thus requires a heat input. This heat input is assumed to be provided by combusting additional fuel. Also, the amount of energy required to heat the reactants is not included in this efficiency. The amount of excess water in the reaction does play a great role in the amount of heat required to increase the temperature of the reactants. It is also possible to utilize waste heat from the fuel cell, which would effectively increase the efficiency at lower \( \text{O}_2/\text{C} \) ratios, moving the balance toward an SR reaction.

To maximize the overall benefit of hydrogen, renewable energy sources are desired as feedstock. Methanol, although not currently derived from renewable sources but from natural gas, has the potential to be sourced from renewables. Methanol is an attractive choice for many reasons including the basis of carbon-to-hydrogen ratio, fuel processor start-up and operation energies, availability of biorenewable sources, and overall system complexity [62,82–85]. It has been considered as one of the possible feedstocks for hydrogen fuel cells as it can be stored and transported in a liquid form using the existing energy infrastructure and technology with only slight modification [4,9]. Indeed presently, some methanol refueling stations exist for supplying racing fuel across the United States. Methanol can be reformed at relatively low temperatures as compared to other fuels, and the reaction mechanism for carbon formation is less active, which helps to prolong catalyst operation life. An extensive review of methanol SR was done by Palo et al [86]. Ethanol is another promising fuel candidate based on its potential to be carbon neutral [87–90]. Although much debate surrounds the actual carbon neutrality of the fuel, ethanol can be produced through the fermentation of biomass or organic waste materials from agroindustries, forestry residue, and municipal solid waste. Bioethanol is recognized by the automobile industries as an alternative fuel with near-established infrastructure. Hydrogen from ethanol is likewise considered potentially beneficial.
3.12 Limiting Mechanisms in the Reformation Processes

The conversion of fuel and yield of hydrogen are limited by the presence of the physical mechanisms. Heat and mass transfer and chemical kinetics are the major limiting mechanisms in reformation. The effect of these mechanisms is discussed individually in the following sections. A conventional steam reformer has temperature and concentration gradients inside the catalyst bed. Efforts to improve the reactors limiting mechanisms can have significant cost and flow through improvements.

3.12.1 Chemical Kinetics

Catalyst temperature impacts the catalyst activity. Arrhenius behavior as shown in Figure 3.10 for a methanol SR catalyst indicates that activity is exponential with temperature. As typical reformation systems are endothermic, the presence of activity limits is an indication of insufficient heat transfer.

Increasing activity through increased temperature can also damage the catalyst; thus, rugged low activity catalysts may be desired. For example, Ni-based catalysts are typically most active above 800°C. This high-temperature requirement makes a Ni-based catalyst bed difficult to implement for mobile devices because of the long start-up times required. Cu-based catalysts are attractive because they are active at about 260°C. Since the conventional catalyst effectiveness factor is typically less than 5%, being able to control the catalyst bed temperature can potentially improve the overall performance.

3.12.2 Mass Transfer

SR is typically limited by mass and heat transfer [91]; thus, low-cost catalysts are used. Mass transfer includes both external and internal diffusions. Reactant diffusion through the catalyst bed onto a catalyst is known as the external diffusion. Diffusion inside the catalyst pore onto an active site is known as internal diffusion. To improve diffusion, one can increase the catalyst loading and/or use smaller catalyst pellets. Using crushed catalysts is a common practice although this typically increases limitations in heat transfer and
increases pressure drop. Increased catalyst loading will increase the weight of the reactor, while using smaller catalyst pellets will increase flow resistance.

Typical mass transfer steps are given in Figure 3.11.

3.12.3 Heat Transfer

External heat is required by SR as the overall process is endothermic. Inside the reactor, pelletized or crushed catalyst particles are packed randomly with point-to-point contact with each other. Convection is the dominating mode of heat transfer within the reactor. As a consequence, large temperature gradients exist in the region near the reactor wall. Unreacted fuel can potentially flow past in the center region reducing overall fuel conversion. Unreacted fuel may also deactivate the catalyst by accumulating on the catalyst pores blocking active sites causing fouling. Using a small radius reactor can improve heat transfer to the centerline. However, as reactor radius decreases, the reactor-to-catalyst weight ratio increases, and the pressure drop increases rendering inefficient reactor design. Figure 3.12 shows experimental temperature gradients encountered with SR of methanol [93]. Although conduction errors are evident in this figure, experimentation shows that 100°C/cm temperature gradients are frequently encountered near the wall. This result implies that a catalyst might be degraded by sintering at the wall yet simultaneously experience fouling due to relatively cold condensed species forming at the centerline.
Table 3.2 shows the overall effects of each limitation and the effect of velocity particle size and temperature on the reaction rate.

3.12.4 Degradation Mechanisms

Reformation can also be limited by catalyst degradation. Degradation is typically classified as attrition, poisoning, fouling, and sintering.

Attrition occurs when the catalyst material is broken off of the substrate and is removed from the reactor. Catalyst and substrate attrition can also lead to physical flow restrictions in the reactor system. This phenomenon is common with frequent temperature cycling in metal housings where the thermal coefficient of expansion and resultant displacement of the housing crushes a pelleted catalyst resulting in a large pressure drop over time.

Poisoning occurs in reformation when a species binds to the reaction site blocking the reaction site from the reactants. Poisoning can be either reversible or nonreversible and may have a temperature effect with higher temperatures inhibiting the poisoning of the
Reformation of Hydrocarbon Fuels

catalyst. Sulfur and sulfur-containing compounds are especially problematic for typical reformer catalysts and poisoning agents. Deactivation of the catalyst by poisoning can typically be seen as the endothermic active zone of catalyst progresses through the reformer following the flow pattern. Zinc and related species can be used in a sacrificial manner to slow down the poisoning effect in reformers.

Fouling occurs when the active area of a catalyst is physically blocked by species forming on the external or internal surface of the catalyst. When the entrance and exit pores become blocked by condensed species or coke formation, reformer performance can drop significantly due to the induced mass transfer limitation. Because the internal area can be as high as 1600 m$^2$/g of the catalyst in pelletized catalyst, it is important to keep pore areas clear to avoid mass transfer limitations. Any gas–liquid or gas–solid phase transformations can induce fouling as the liquid or solid blocks the gas reactants from reaching the reaction surface.

Sintering can occur when the catalyst or the substrate changes form. Sintering is typically due to exothermic reactions driving the temperature above the melting point of either the substrate or the catalyst material. In many reformation processes, a ceria substrate is used with a washcoated metal acting as the catalyst material. Typical ceria will melt at 1450°C; thus, high temperatures can lead to pore blocking and absorption of the catalyst through melting of the substrate. It is also important to note that metallic phase transformation and changes can occur far below the melting point of the metal and this phase transformation can change the activity and selectivity of the catalyst. A common rule of thumb is that a certain metal can be used up to 1/3 of its melting point temperature. Structural integrity can also be compromised in extreme sintering cases as shown in Figure 3.13. The need to have fast reactions with heavy complex fuels can be limited by the catalyst’s ability to withstand high temperatures and high heat flux.

3.12.5 Controls

Researchers have modeled the SR process [13,83,95,96] and the reformer [82,97–99] in various literature and have also proposed control algorithms [23,100,101] to better control the

FIGURE 3.13
New monolithic ATR catalyst is shown on the left and a similar cut-away sintered catalyst is shown on the right in this grayscale image.
temperature, but the issue of controlling catalyst temperature has not been fully addressed. A high-level control algorithm sends manipulated inputs to control fuel flow rate and heater power for a given reformer, and the means of getting the heater power to the catalyst is limited by the design of the reformer. It should be noted that these concerns are only dealing with the steady-state control of the reformer temperature and do not address the transients encountered with large flow changes or start-up of the reactor. Slow transient response is a large hurdle for SR. While most current large-scale reformers run continuously for over 12,000 h [20], small-scale reformers will experience frequent fuel rate transients due to changes of demand. Optimizing reactor geometry is one approach to enhance reformer dynamics [102]. However, reformer geometry can impact the characteristic of the heat transfer, thus impacting the control algorithm design. A better approach is to design both the control algorithm and the reformer in parallel.

### 3.13 Comparison of the Reforming Methods

End use of the hydrogen is perhaps the important aspect when considering types of reforming systems. For example, in combustion applications, high concentrations of CO and unconverted fuel are not typically problematic, yet in fuel cell applications, there are significant requirements for fuel purity. Lower operating temperature fuel cell stacks usually have stricter requirements. Impurity in the hydrogen stream will slowly poison the fuel cell anode over time. CO poisoning is an important issue for PEMFC. High-temperature fuel cell stacks such as molten carbonate fuel cell (MCFC) and SOFC have higher impurity tolerance. They are capable of internal reforming and use CO and some volatile organic compounds (VOCs) as fuel. Selecting a proper fuel cell for a specific application can significantly impact the reformer’s technical specifications.

SR has the advantage of a relatively high hydrogen concentration in the product gas, which leads to better utilization by a fuel cell. For example, for SR of methanol, the maximum hydrogen concentration is 75%. The efficiency of the process is also very high, which is desirable for transportation applications. It also has the advantage of a high S/C ratio, which leads to a low instance of coking (solid carbon deposits) without having to raise the reactor temperature. For an onboard steam reformer, the external heat needed for the endothermic reaction is most conveniently provided by simply combusting a portion of the fuel. Therefore, only a fraction of the total fuel used, $Y$, actually enters the reformer. The remaining fuel, $1 - Y$, is fully combusted to provide the energy required for the desired SR reaction.

In an ideal reactor, there would be 100% heat transfer from the combustion reaction to the SR reaction. However, there are limitations to the efficiency of the heat transfer process and this should be considered when selecting a reforming method. SR is endothermic and therefore an inherently slow process. An SR reactor is most commonly heated externally and has slow dynamic responses that may lead to system degradation. If the load is suddenly decreased and the reactant flow rates are decreased, the reformer heats up and can potentially sinter the catalyst. Alternatively, if the load is suddenly increased, the reformer cannot supply the required hydrogen to the fuel cell stack; consequently, the fuel cell extracts protons from the electrolyte membrane causing irreversible damage. This, coupled with a long start-up time, makes SR a less than optimal choice for onboard reforming or small-scale on-site reforming. It is still a good choice for centralized production of hydrogen on a large scale.
A POX reactor can heat up quickly by simply increasing the flow rate of oxygen to increase the combustion of the incoming fuel; this results in a fast start-up. For the same reason, it is extremely well equipped to handle transient loads. The reactor is much smaller and reformers can be made compact. However, POX produces excess CO and must therefore be accompanied by additional cleanup of the product gas. This increases the size and mass of the fuel-processing system. POX reforming is an exothermic reaction that operates at high temperatures usually above 1000°C. Because there is an absence of water (an S/C ratio of zero), reactors must operate at significantly higher temperatures (1180°C for 2,2,4-trimethylpentane) to avoid coking [103]. The system design must also include a heat exchanger that transfers excess heat to the surroundings. Hot spots may develop as a result of nonuniform mixing and can cause catalyst sintering. Most importantly, the major drawback of POX is the low concentration of hydrogen in the product gas. The addition of air into the reaction dilutes the product gases with nitrogen. For example, when POX is used to reform methanol, the highest theoretical concentration of hydrogen is only 41% (when using air as the source of oxygen), compared to 75% for SR [104]. This directly affects the efficiency of the PEM fuel cell and thus decreases the overall system efficiency, an especially undesirable characteristic for automotive applications.

One potential solution to the drawbacks of SR and POX is to combine the two into ATR. ATR operates ideally at a thermoneutral point, neither consuming nor releasing external energy. This gives ATR a higher efficiency and hydrogen concentration than POX and, at the same time, a better dynamic response than SR and the flexibility to accommodate multiple fuels. Rapid start-up is possible because of the ability to produce heat within the catalyst bed rather than transferring heat from the surroundings. Hot spots are reduced because of the addition of steam in the reforming reaction. This thermal integration lowers the temperature rise potential that is caused by the POX of the fuel and thereby reduces the potential for catalyst sintering. ATR has great potential in applications that require a lightweight, compact reactor capable of reforming multiple fuels [103]. These criteria fit into the needs of the automotive industry, whether for onboard or on-site reforming, and therefore ATR should be considered for transportation applications. ATR can provide a rapid response to hydrogen demand with short start-up times, high efficiencies, and fuel flexibility.

It should be noted that reactant mixing is an important consideration for ATR. Possible mixing schemes include the use of bluff bodies, swirling, and acoustic enhancement. Acoustic enhancement has been proven to improve the capabilities of SR, and there is a reason to believe that it may also be beneficial to ATR. These results have yet to be tested. Other reactant mixing schemes may also enhance ATR reactor performance. Should reactant mixing prove to be beneficial to ATR, it will further reduce the size and weight of the reformer. This in turn would decrease start-up time of the reforming system, one of the most critical aspects of a small-scale reformer.

### 3.14 Fuel Selection

Cost and environmental reasons are factors in deciding the choice of fuel. Many researchers have built small fuel processors for various hydrocarbon feedstocks [3,4,7,11]. They have shown competitive advantage in implementation, flexibility, and efficiencies [105–108]. Insulation and heat recirculation are important for these reformers to maintain high...
efficiencies. Coupled with PEMFC, they have demonstrated functional stationary [4,107] and onboard [3,106,109] fuel cell power systems. Although they have presented workable solutions to reform hydrocarbon feedstock, there are a range of issues to be addressed. For example, PEMFCs generally have low CO tolerance at <50 ppm [110–112]; thus, a cleanup system, such as PSA, is necessary to purify the reformed hydrogen stream [3,113–116]. High CO-tolerant electrodes and high-temperature fuel cell operation are also under development to overcome this limitation. Water management [4,105,112] and temperature are also critical to the life and performance of the PEMFC; thus, the temperature and humidity of the hydrogen stream must be regulated [23,24,101,117].

Table 3.3 is an estimate of the hydrogen yield by reforming various hydrocarbons.

Comparing the weight of hydrogen produced per liter of fuel, methanol and ethanol are clearly not competitive with gasoline and diesel. However, both alcohols can be reformed at relatively low temperature and can be made from renewable fuels. The low-temperature reformation process allows less complex reformer design, lower CO selectivity, and good compatibility with low-temperature fuel cell applications. Typical reformer temperatures and catalysts are shown in Table 3.4.

Other fuels such as diesel, gasoline, propane, and logistic fuels such as kerosene and jet fuel have also been used as feedstock. Typically, heavier hydrocarbons will require higher temperature and additional cleanup prior to or after reforming. Desulfurization and pre-reformers are used to ensure high-purity fuel is fed into the fuel processor. Gasoline and

<table>
<thead>
<tr>
<th>TABLE 3.3</th>
<th>Hydrogen Yield by Reforming Various Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel</strong></td>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>Methane (LNG)</td>
<td>CH₄</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C₈H₁₃</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>C₁₄H₂₅</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>TABLE 3.4</th>
<th>Typical Reforming Temperature of Various Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel</strong></td>
<td><strong>Reformation Temperature (°C)</strong></td>
</tr>
<tr>
<td>Glycerol</td>
<td>650–900</td>
</tr>
<tr>
<td>Isooctane/gasoline</td>
<td>650–800</td>
</tr>
<tr>
<td>Hexadecane/diesel</td>
<td>700–800</td>
</tr>
<tr>
<td>Natural gas</td>
<td>650–800</td>
</tr>
<tr>
<td>Methanol</td>
<td>200–300</td>
</tr>
<tr>
<td>Ethanol</td>
<td>200–300</td>
</tr>
<tr>
<td>Dodecane</td>
<td>450–550</td>
</tr>
<tr>
<td>JP-8</td>
<td>&gt;520</td>
</tr>
<tr>
<td>Propane/n-butane</td>
<td>600–800</td>
</tr>
<tr>
<td>Methane</td>
<td>&gt;500</td>
</tr>
<tr>
<td>Kerosene/n-octane</td>
<td>&gt;500</td>
</tr>
</tbody>
</table>
diesel have a well-established infrastructure and higher energy storage density for hydrogen. A gasoline reformer can be started and deliver 90% rated hydrogen capacity with less than 50 ppm CO in 60 s [7]. Natural gas or methane is abundant in many parts of the world and is used as feedstock for hydrogen production in industrial settings. It can also be converted to methanol and transported using existing infrastructure. Liquefied petroleum gas (LPG), which has been widely used for cars and buses, is also a potential fuel for mobile reformer systems.

3.15 Internal Reforming in High-Temperature Fuel Cells

Internal reforming refers to reformation taking place at or near the anode of the fuel cell. With SOFC and MCFC, the stack temperature is sufficient to reform low–molecular weight hydrocarbons [119]. Internal reforming has the advantage of reducing cost and complexity since a separated reformer and heat exchangers are not necessary. It is also more energy efficient since less steam is required and heat loss is minimized. The anode catalyst must be able to reform the hydrocarbon fuel and catalyze the oxidation reaction in the high-temperature anode of these fuel cells. The internal reforming systems are favored by Le Chatelier’s principle that drives the reaction toward the product side at high temperatures and pressures as the hydrogen produced by reformation is immediately consumed by the fuel cell oxidation reaction.

3.16 Reactor Design

In SR, CPOX, and ATR, maintaining chemical reaction kinetics by activating the catalyst becomes the important aspect in controlling the reformation process. In order to activate the catalyst, sufficient heat must be available for the reaction. Insufficient temperature will deactivate the catalyst, thus reducing efficiencies. It is important to address the need for maintaining proper temperature in reformation processes. For MTS catalysts containing copper, exceeding 300°C generally will make the catalyst unstable and degrade by sintering [35,42,120]. Ni-based catalyst is stable at higher temperatures, but this becomes a trade-off with the material and operating cost of a high-temperature reformer. Maintaining a uniform temperature profile inside the reactor is ideal but is difficult to achieve. Heat distribution is limited by convection; thus, high-temperature gradients exist inside the catalyst bed. Modifying the reactor design to improve the heat and mass transfer limitation is one possible solution [121–123].

Inside the steam reformer catalyst bed, convection is the primary means to transfer heat from the reactor wall to the catalyst; thus, a small diameter tubular configuration is advantageous. Passive flow baffles can be used inside the reactor to enhance heat transfer [124]. Structured catalysts have also been employed [125]. Figure 3.14 shows how passive flow disturbance can be used to enhance the heat distribution.

Inside the autothermal reformer, an exothermic reaction occurs on the surface of the catalyst in the presence of oxygen; thus, controlling the flow of oxygen can control heat generation. Employing a porous membrane within the catalyst bed to distribute air inside the
reactor has been investigated by Lattner [25] and Liu et al. [126]. Other variations of using multiple heating zones [67], dual catalysts [127], and coupling exothermic to endothermic regions of the reactor [128] have also been proposed. These passive methods all intend to optimize energy efficiencies by moving heat from the exothermic reaction region or exhaust to the endothermic reaction region. The various operation conditions can be incorporated into a control algorithm. However, these efforts reduce the flexibility in designing the control algorithm. The best approach is the combination of active control and passive reactor enhancement.

FIGURE 3.14
Simulation of the convective heat transfer inside a large radius cylindrical reactor with and without baffles. The axis of symmetry is on the left side of the domain and heat flux is applied on the right. These two reactors have the same space velocity, but one has dramatically better heat transfer properties. (From Tang, H.-Y., Reactor controller design for steam and autothermal reforming for fuel cell applications, PhD dissertation, University of California, Davis, CA, 2009.)
3.17 Reformer Control Issues

Temperature control of the reformer influences fuel conversion and catalyst degradation. The poor heat transfer properties of the catalyst make transferring heat in and out of the catalyst bed difficult as shown in Figure 3.14. In ATR, if excess heat is produced on the catalyst, it will sinter and melt the catalyst. In SR, if insufficient heat is available, unreacted fuel may poison or foul the catalyst. In implementing feedback control, the feedback or the sensor placement location and control variables are not obvious. In ATR, the exothermic reaction typically takes place near the top of the catalyst bed. To control the catalyst temperature, it is necessary to control the available oxidizer in the fuel stream. In SR, the centerline usually is the region with the lowest temperature because convection is the primary mode of heat transfer from the reactor wall to the center. However, using the centerline as the feedback location can produce oscillations in temperature inside the reformer. The high thermal resistance of the catalyst bed potentially creates a long lag in temperature response. Using strictly temperature control can lead to sintering of the catalyst near the reactor wall by excessive heating from the external burner. The situation is more problematic during transients. By the time the centerline temperature has increased, the reactor wall temperature may reach a much higher temperature creating a large temperature gradient. This could reduce the overall efficiencies as heat is not effectively utilized, and the catalyst can be degraded by multiple high-amplitude thermal cycles. A possible solution is to regulate heat flux in the steam reformer to avoid such problems. This is done by combining the ability to control the fuel feed rate and external burner input. The controller will incorporate the heat transfer properties of the reactor and the chemical kinetics of the reformation process to adjust the fuel feed rate and the external heater temperature. This concept allows maintenance of the catalyst in a certain temperature range during transient ramps [129].

3.18 Summary

Direct transport and storage of hydrogen is costly. Hydrogen production at the point of use may be a viable near-term solution. Reforming liquid hydrocarbon fuels for hydrogen production has several advantages for transportation applications: the existing infrastructure for transporting hydrocarbon fuel is well developed; refueling liquid fuel is faster and much more familiar and intuitive than recharging gaseous fuels; and there are wide ranges of possible hydrocarbon feedstocks. SR is the most widely used method of generating hydrogen and produces the highest-quality reformate. POX can respond quickly to transient demand but is associated with low-quality hydrogen. ATR generally combines a higher output gas purity, similar to though not attaining that of SR, with a fast response time, similar to but not attaining that of POX. All of the methods are presently studied in earnest for the small-scale reformers required in mobile and distributed generation applications. In the known and practiced reformation techniques, the resultant reformate is not a pure hydrogen stream; thus, additional cleanup steps are needed for stringent purity applications. If an inert gas, such as nitrogen, is present, it will lower the hydrogen concentration. End use of the hydrogen may change the reformate requirements and hence the fuel processor.
References

49. De Rogatis, L., Montini, T., Casula, M.F., and Fornasiero, P.: Design of Rh@Ce0.2Zr0.8O2-Al2O3 nanocomposite for ethanol steam reforming, Journal of Alloys and Compounds, 2008, 451(1–2), 516–520.


