CHAPTER 7

Gas-To-Liquids (GTL)

7.1 Introduction

Natural gas is likely to capture a larger market share of the world’s energy mix, and its transportation, using pipelines, CNG, and LNG, has been covered in Chapters 5 and 6. However, inroads of natural gas as a fuel into the motor vehicle sector are not easy, and the two methods that often come to mind are through the use of CNG, or indirectly, through the production of electricity, and ultimately, electric vehicles. Some of the latter issues will be covered in Chapter 9.

Because liquid fuels will be required for decades and for certain applications, such as aircrafts, there is nothing realistic in the horizon, even for the longest possible term. Gas-to-liquids (GTL) allows the conversion of natural gas into liquid hydrocarbons and oxygenates through chemical reactions. These hydrocarbons are compatible with fuels and chemicals produced in the gasoline and middle distillate range of an oil refinery. They include naphtha, diesel, kerosene, lubricants, and waxes. GTL products may include other chemicals such as ammonia, methanol, or methyl tert-butyl ether (MTBE), a major motor gasoline additive.

While interest in GTL was driven by political (e.g., South Africa during apartheid) rather than economic factors for decades, recent technical advances have made GTL more competitive. In 2009 there were still relatively few facilities in commercial operation (e.g., by Sasol in South Africa and Shell in Malaysia); however, a number of commercial scale facilities were seriously considered, and GTL activity may grow in the future as a result of both private business initiatives and strategic investments by governments of nations with significant natural gas reserves.
This chapter outlines potential benefits from GTL conversion, basic GTL methods and their history, scientific and engineering principles of GTL, and the most important technologies and implementations.

7.2 Why GTL?

The chemical conversion of natural gas to liquids allows an alternative source of liquids to the traditional refinery products deriving from crude oil. There are obvious benefits to this activity, such as energy security for nations that have little or difficult access to oil but better access to natural gas. In addition, GTL facilitates the transportation of natural gas from remote production sources to consumption destinations if alternative methods, such as pipeline or LNG, are not economically or technically attractive. Since liquid fuels are easier to transport and distribute by ship, rail, or car, and to store at the destination, natural gas conversion to GTL offers superior flexibility in comparison to pipeline and LNG. GTL is not an alternative for places where CNG is attractive because the capital investment for GTL and the operating costs would not be suitable for the size of resources that would fit CNG applications.

A number of additional benefits, all subjected to both local and international economics, may result from the use of GTL technologies. The following list illustrates these benefits:

- *Stranded natural gas monetization from large but difficult places.* Even though global reserves of natural gas are abundant and are expected to last longer than oil, most of these reserves (1/2 to 2/3 in the Former Soviet Union and Middle East) are not just separated by bodies of water, but may be significantly inland and in very hostile environments, such as the Arctic. This is a very difficult form of “stranded” gas. In the absence of pipelines, for efficient gas transportation from sources to destinations, GTL may provide a technically and economically viable transportation alternative. While GTL products may not always be competitive economically against conventional oil products, they may be the only alternative for monetizing stranded natural gas of low opportunity value.

Key factors affecting GTL competitiveness are the cost of capital, operating costs, plant scale, and degree of facilities utilization. Thus, on many occasions, GTL could bring natural gas to markets that might otherwise be inaccessible, and make
producing significant quantities of natural gas that would not ordinarily be extracted from the ground.

- **Exploitation of associated gas.** Historically, natural gas associated with petroleum production in offshore or remote fields has been a nuisance. In the past, associated gas was usually flared or reinjected into the reservoir in the absence of means for gas transportation to markets. It is now environmentally unacceptable or economically wasteful to follow these practices. GTL may convert associated gas into "synthetic" crude (syncrude) and then use the existing liquid pipelines or liquid transport vessels. GTL plants for associated gas conversion have a small environmental footprint, are safe, and are well integrated with production sites, particularly offshore.

- **Synthesis of environmentally friendly fuels.** The main products of GTL are fuels, such as diesel, and because of the way these fuels are produced they can offer higher performance and lower pollution. For example, GTL diesel fuel has a higher cetane number (greater than 70 versus 45–50 for conventional diesel) ensuring better thermodynamic efficiency of combustion, and practically no particulates, such as sulfur (less than 1 ppm versus more than 50 ppm) or aromatics (0.45% volume versus 1.4%). GTL fuels can be easily blended with conventional fuels to meet environmental specifications. The recent use of GTL diesel fuel to power sports cars in endurance racing highlighted the high performance of these fuels.

- **Life extension of pipelines.** Pipelines built for oil transportation are of little value if there is no more oil for them to transport from fields that have been depleted. A typical case is the Trans-Alaska pipeline, built in 1977 to transport oil from Prudhoe Bay to Valdez. It is estimated that liquids from GTL conversion of natural gas available in the North Slope area could be transported through the same pipeline, thus extending its useful life by at least 20 years (Khataniar et al., 1997).

### 7.3 GTL Processes

Conversion of pipeline quality natural gas (essentially methane) to liquids is a polymerization process. Hydrogen is removed and methane

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1. Some of the information in this chapter is derived from lectures by Prof. James Richardson, University of Houston.
molecules are polymerized to longer chain hydrocarbon or related molecules, similar to molecules found in crude oil fractions. Such fractions include diesel fuel, naphtha, wax, and other liquid petroleum or specialty products.

There are two basic GTL technologies: direct conversion of natural gas to liquid fuels and indirect conversion via synthesis gas (syngas). The direct conversion avoids the production of synthesis gas, but is difficult to control, has low selectivity (<20%), and low conversion (<40%). Several direct conversion processes have been developed, but none has been economically viable so far.

By contrast, indirect conversion relies on three basic steps:

1. Reforming (catalytic conversion) of natural gas to synthesis gas (mainly a mixture of carbon monoxide and hydrogen at varying proportions).

2. Fischer-Tropsch synthesis (named after Franz Fischer and Hans Tropsch who pioneered the process in Germany in the early 1920s) for catalytic conversion of synthesis gas to liquid hydrocarbons or oxygenates.

3. Upgrading of products via a number of standard refinery processes, such as hydrocracking, isomerization, or catalytic reforming (Figure 7–1).

![Figure 7–1](image-url) Basic flowchart of indirect conversion of natural gas to liquids through syngas and Fischer-Tropsch synthesis
Although complicated, the indirect synthesis approach has a long history of development, and forms the foundation for production by the petrochemical industry for a variety of chemicals using natural gas as the main feedstock. It should also be mentioned that Fischer-Tropsch synthesis may be used to produce liquids from syngas coming from other sources, such as coal or biomass.

The fundamentals of both direct and indirect GTL methods are discussed below. Since the indirect conversion method is commercially more important, it will occupy most of the following discussion.

### 7.4 GTL Based on Direct Conversion of Natural Gas

Direct conversion of methane to higher hydrocarbons may result from a number of reactions: (Note: In this chapter both equations and reactions are numbered sequentially.)

**Dehydrogenative self interaction**

\[
2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}_2, \quad \Delta G^\circ(500^\circ\text{C}) = +35.6 \text{ kJ/mol. \tag{7.1}}
\]

**Oxidative coupling**

\[
2\text{CH}_4 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}, \quad \Delta G^\circ(500^\circ\text{C}) = -374.2 \text{ kJ/mol. \tag{7.2}}
\]

\[
2\text{CH}_4 + 0.5\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}_2\text{O}, \quad \Delta G^\circ(500^\circ\text{C}) = -169.3 \text{ kJ/mol. \tag{7.3}}
\]

**Partial oxidation**

\[
\text{CH}_4 + 0.5\text{O}_2 \rightleftharpoons \text{CH}_3\text{OH}, \quad \Delta G^\circ(500^\circ\text{C}) = -86.1 \text{ kJ/mol. \tag{7.4}}
\]

\[
\text{CH}_4 + 0.5\text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2, \quad \Delta G^\circ(500^\circ\text{C}) = -83.7 \text{ kJ/mol. \tag{7.5}}
\]

**Oxydehydrochlorination**

\[
\text{CH}_4 + 0.5\text{O}_2 + \text{HCl} \rightleftharpoons \text{CH}_3\text{Cl} + \text{H}_2\text{O}, \quad \Delta G^\circ(500^\circ\text{C}) = -119.9 \text{ kJ/mol. \tag{7.6}}
\]

**Complete oxidation**

\[
\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}, \quad \Delta G^\circ(500^\circ\text{C}) = -792.9 \text{ kJ/mol. \tag{7.7}}
\]
In Reaction (7.1), hydrogen is removed from two molecules of methane that are assembled to produce ethane thermally. It is the most direct reaction, but unfortunately its free energy is so positive, that the reaction is not feasible at reasonable temperatures. The use of oxygen makes the removal of hydrogen from methane and successive coupling of C–C bonds easier, as in Reactions (7.2) through (7.6).

However, Reaction (7.7) inadvertently dominates when oxygen is used, producing undesirable products. Selective acceleration of Reactions (7.2) through (7.6) has been achieved using various catalysts (e.g. 1 wt% Sr/La₂O₃, Mn/Na₂WO₃/SiO₂, and 2 mol% Ba/MgO) at high temperatures. These are compounds and are known as such, e.g., Barium/Magnesium Oxide (Ba/MgO). The others are Strontium (Sr), Lanthanum (La), Manganese (Mn), Tungsten (W), etc. As a result, selectivity (i.e., percentage of useful products in the product mix) up to 20% has been achieved at 40% conversion. While this is an improvement over past selectivities, it is still not industrially viable. Future development of better (more selective) catalysts might make direct conversion more attractive given its relative simplicity.

**Example 7–1** Methanol production via direct conversion GTL

Calculate the mass of methanol (in lb) that can be produced from 4 Bcf of natural gas. Assume that it is all methane. How many pounds of oxygen would be required?

**Solution**

The stoichiometric relationship is given by Reaction (7.4). The standard molar volume of natural gas, calculated from ideal gas law with

\[ p_{sc} = 14.7 \text{ psi}, \ T_{sc} = 60^\circ F = 520 \text{ R}, \text{ and } Z_{sc} = 1, \text{ is } 10.73 \times 520/14.7 = 380 \text{ scf/lbmole.} \]

Thus, 4 Bcf correspond to \[ 4 \times 10^9/380 = 1.05 \times 10^7 \text{ lb mole.} \] Based on Reaction (7.4), this would require \[ 5.3 \times 10^6 \text{ lb-mole of oxygen and produce } 1.06 \times 10^7 \text{ lb-mole of methanol.} \]

Therefore, the mass of methanol produced is

\[ (32) \times (1.06 \times 10^7) = 3.4 \times 10^8 \text{ lb}, \]

and the mass of oxygen required is

\[ (32) \times (5.3 \times 10^6) = 1.7 \times 10^8 \text{ lb.} \]
7.5 GTL Based on Indirect Conversion of Natural Gas

7.5.1 Basics

As shown in Figure 7–1, the indirect conversion of natural gas to liquid fuels goes through two main steps (reforming and Fischer-Tropsch) and may be followed by a third step (upgrading).

The first step is natural gas reforming. The main reaction in the reforming step can be loosely described as

\[ \text{CH}_4 + \text{oxygen source} \rightleftharpoons \text{CO} + \text{H}_2, \]

where the oxygen source can be steam, CO\(_2\), or air. Depending on the source of oxygen, different technologies have been developed, and are discussed below. The product resulting from reforming is composed predominantly of CO and H\(_2\). It is called synthesis gas (syngas) because it is used to synthesize products without the need for additional reactants.

The next step is Fischer-Tropsch synthesis. The main reactions in this step can be summarized as

\[ a\text{CO} + b\text{H}_2 \rightleftharpoons \{\text{C}_x\text{H}_y\} + \{\text{H}_2\text{O and/or CO}_2\}, \]

where \(\{\text{C}_x\text{H}_y\}\) refers to a mixture of liquid straight-chain hydrocarbons that include alkanes (paraffins) and alkenes (olefins) with \(x\) ranging from 1 to more than 40, depending on process conditions, catalyst, and syngas composition (ratio \(a:b\)). These hydrocarbons result from polymerization of \(=\text{CH}_2\) groups. The ratio \(a:b\) determines whether \(\text{H}_2\text{O}\) (hydrogen in excess) or \(\text{CO}_2\) will be formed.

The final step is product upgrading, and usually involves operations such as hydrocracking, isomerization, catalytic reforming, or alkylation. Standard refinery technology can be used in this step. For example, waxes (\(\text{C}_{18+}\)) are converted into naphtha (\(\text{C}_5–\text{C}_{11}\)) and diesel (\(\text{C}_{12–\text{C}_{18}}\)) in a hydrocracker.

Of the above steps, generation of synthesis gas is the most capital intensive, accounting for more than half of the fixed cost of an entire GTL process. However, the performance of Fischer-Tropsch synthesis is the most critical for the overall performance of GTL, because it is in this step that the composition of GTL liquids is determined. Critical for Fischer-Tropsch synthesis is the development of catalysts that selectively accelerate reactions resulting in desirable products, as well as the design of corresponding reactors.

Natural gas reforming and Fischer-Tropsch synthesis play a central role in GTL, and are discussed in more detail below.
Example 7–2 Volume reduction resulting from GTL

What volume reduction does GTL accomplish for natural gas? How is that compared to volume reductions achieved by LNG or CNG?

Assume the final product of GTL is a mixture of hydrocarbons of the form \( C_x H_y \). A typical composition may be 75% diesel \((C_{12–C_{18}})\) and 25% gasoline \((C_5–C_{11})\).

The density of \( \text{CH}_4 \) is 0.68 kg/m\(^3\) at 15°C (59°F) and atmospheric pressure. The density of gasoline is about 750 kg/m\(^3\) and the density of diesel fuel is about 850 kg/m\(^3\) at normal conditions.

Solution

The density of typical GTL fuel is

\[
0.75 \times 850 + 0.25 \times 750 = 825 \text{ kg/m}^3. \quad (7.10)
\]

To find the volume reduction ratio, a carbon balance is needed to find the mass of GTL fuel produced from a corresponding amount of natural gas. Carbon balance across Figure 7–1 (further detailed by the simplified reactions of reforming, Reaction (7.8), Fischer-Tropsch synthesis, Reaction (7.9), and product upgrading, presented in Sections 7.5.2, 7.5.3, and 7.5.4, respectively) yields that \( x \) moles of \( \text{CH}_4 \) are required for one mole of the long-chain hydrocarbon. The average chemical formulas for diesel fuel and gasoline are \( C_{12}H_{23} \) and \( C_8H_{18} \), respectively. The stoichiometry of carbon for producing a mixture of 75% diesel and 25% gasoline is

\[
44 \text{CH}_4 + \ldots \rightarrow 3C_{12}H_{23} + C_8H_{18} + \ldots. \quad (7.11)
\]

Therefore the mass of GTL fuel produced per unit mass of methane is

\[
\frac{3 \times (12 \times 12 + 23) + (8 \times 12 + 18)}{44 \times (12 + 4)} = 0.874 \text{ kg GTL fuel/kg methane.} \quad (7.12)
\]

It follows that the volume reduction ratio is

\[
\frac{1}{0.68} / \frac{0.874}{825} = 1,400. \quad (7.13)
\]
The result for the part of the methane that actually gets converted compares quite favorably with LNG and CNG, for which typical volume reduction ratios are about 600 and 200, respectively. The penalty, however, for this volume reduction is the high fixed and operating cost (in capital and energy) of GTL conversion.

7.5.2 Natural Gas Reforming and Synthesis Gas

Syngas was first commercialized in the second half of the nineteenth century, as a result of the coal gasification process; even though the main reaction (passing steam over incandescent carbon) was known in the eighteenth century. In fact, it was in part the importance of liquid fuels produced from coal derived syngas that prompted the development of the Fischer-Tropsch process in Germany and its intensive use during World War II. The production of syngas from natural gas became important in the twentieth century, as inexpensive natural gas became widely available. In addition to forming the basis for liquid fuels, syngas provides hydrogen for use in the chemical industry (mainly for ammonia synthesis) or as a fuel. It could also serve as feed to fuel cells in the future.

Syngas can be produced from natural gas using steam, dry (CO₂), or oxy reforming. An important difference between these approaches is the composition (proportion of H₂ to CO) of the syngas produced, as summarized in Table 7–1. This composition is important for the subsequent steps in GTL, namely Fischer-Tropsch synthesis.

Steam Reforming

Steam reforming is the dominant gas reforming technology. It has a long history of development and has served as a source of syngas and hydrogen for years. In addition to its refinery use, steam reforming is now the preferred method of producing hydrogen for ammonia synthesis.

<table>
<thead>
<tr>
<th>Steam Reforming</th>
<th>Dry Reforming</th>
<th>Partial Oxidation</th>
<th>Autothermal Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>&gt;2</td>
<td>2</td>
</tr>
</tbody>
</table>
The main reaction in steam reforming is syngas production as

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2, \quad \Delta H^\circ (1,000^\circ \text{C}) = +226.1 \text{ kJ/mol.} \quad (7.14) \]

Additional hydrogen is generated by the water-gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H^\circ (1,000^\circ \text{C}) = -41 \text{ kJ/mol.} \quad (7.15) \]

Since Reaction (7.14) is reversible and highly endothermic, high temperatures (e.g., 1,000°C) are necessary to achieve significant conversions. Reaction (7.15) is slightly exothermic, and therefore favored at low temperatures. Combined, Reactions (7.14) and (7.15) yield thermodynamic equilibrium compositions that depend on temperature, pressure, and relative amounts of methane and steam. The equilibrium moves toward product formation at higher temperatures and lower pressures. Excess steam results in higher production of hydrogen as shown in Figure 7–3.

The equilibrium constants of the above two reactions depend on temperature as

\[ K_{\text{syngas}} = \exp\left[30.53 - \frac{4.85 \times 10^4}{T} + \frac{2.42 \times 10^6}{T^2} + \frac{2.49 \times 10^9}{T^3}\right], \quad (7.16) \]

\[ K_{\text{WaterGasShift}} = \exp\left[-2.93 + \frac{3.61 \times 10^3}{T} + \frac{5.04 \times 10^6}{T^2} + \frac{1.82 \times 10^9}{T^3}\right], \quad (7.17) \]

where the temperature \( T \) is expressed in degrees F (Rase, 1977). Plotting the relative values of these equilibrium constants (Figure 7–2) quantifies that the synthesis gas in Reaction (7.14) becomes practically not feasible as temperature is lowered from 1,000°C to 700°C. However, the opposite is true for the water gas shift in Reaction (7.15).

**Example 7–3** Steam reforming equilibrium as a function of feed composition

A steam reformer feed of 85% mole steam and 15% mole methane achieves 95% methane conversion through the syngas and shift (Reactions (7.14) and (7.15)). The hydrogen produced is 75% mole pure when dry (i.e., with all water removed). Both reactions are
assumed to reach thermodynamic equilibrium: (a) What is the resulting ratio $H_2/CO$? (b) What should be the feed composition to make the $H_2/CO$ ratio equal to 3.2 at the same temperature and pressure? (c) What range of values is expected for $H_2/CO$ when the molar ratio of steam to methane spans the range 1 to 9?

**Figure 7–2**  *Relative values of equilibrium constants for steam reforming and water gas shift Reactions (7.14) and (7.15), respectively*

**Figure 7–3**  *Equilibrium compositions for steam reforming at 20 atm and stoichiometry $H_2O/CH_4 = 3$. Methane conversion is complete at about 1,000°C. The production of CO$_2$ from the water gas shift reaction is maximum around 700°C*
Solution

(a) Assume a feed of 100 moles, of which 85 are steam and 15 are methane. Then denote the number of moles of steam reacting in Reactions (7.14) and (7.15) by \( x \) and \( y \), respectively. The corresponding equilibrium compositions of all species are shown in Table 7–2.

Since methane undergoes 95% conversion, then
\[
\begin{align*}
\frac{x}{100} &= 0.95 \\
x &= 0.95 \times 15 \\
x &= 14.25 \text{ mol}.
\end{align*}
\]

The concentration of hydrogen in the products is
\[
\frac{3x + y}{15 - x + 3x + y + x - y + y} = 0.75,
\]
from which \( y = 2.25 \). Therefore, equilibrium composition per 128.5 mole is
\[
(H_2O, CH_4, H_2, CO, CO_2) = (68.5, 0.75, 45, 12, 2.25), \quad (7.18)
\]
and the ratio \( H_2/CO \) is \( 45/12 = 3.75 \).

(b) To select the feed composition that will result in \( H_2/CO = 3.2 \), consider again 100 moles, of which \( w \) are steam and \( 100 - w \) are methane. Then the equilibrium compositions are as shown in Table 7–3, where \( x', y' \) have new values that have to be calculated along with \( w \). The calculation will be based on the desired ratio \( H_2/CO \) and the two equilibrium conditions.

Table 7–2 Feed and Equilibrium Compositions for Steam Reformer, Example 7–3

<table>
<thead>
<tr>
<th>Species</th>
<th>% mole in feed</th>
<th>% mole at equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>85</td>
<td>85 - x - y</td>
</tr>
<tr>
<td>CH4</td>
<td>15</td>
<td>15 - x</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>3x + y</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>x - y</td>
</tr>
<tr>
<td>CO2</td>
<td>0</td>
<td>y</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100 + 2x</td>
</tr>
</tbody>
</table>
The equilibrium constants for both Reactions (7.14) and (7.15) can be computed from the results of part (a):

\[
K_1 = \frac{c_{CO}^3 c_{H_2}}{c_{CH_4} c_{H_2O}} = \frac{H_2}{Total} \left(\frac{CO}{CO \text{ Total}}\right)^3 = 1.29 , \tag{7.19}
\]

\[
K_2 = \frac{c_{CO_2} c_{H_2}}{c_{CO} c_{H_2O}} = \frac{CO_2}{Total} \left(\frac{H_2}{H_2 \text{ Total}}\right) = 0.123 . \tag{7.20}
\]

The equilibrium equations must also be satisfied for the new feed composition:

\[
\frac{H_2}{Total} \left(\frac{CO}{CO \text{ Total}}\right) = \frac{(3x' + y')^3}{100 + 2x'} \left(\frac{x' - y'}{100 + 2x'}\right) = 1.29 , \tag{7.21}
\]

\[
\frac{CO_2}{Total} \left(\frac{H_2}{H_2 \text{ Total}}\right) = \frac{y'}{100 + 2x'} \left(\frac{3x' + y'}{100 + 2x'}\right) = 0.123 . \tag{7.22}
\]
In addition, the H$_2$/CO ratio must be

\[
\frac{H_2}{CO} = \frac{3x' + y'}{x' - y'} = 3.2 . \tag{7.23}
\]

Eliminating denominators from Eqs. (7.21, 7.22, and 7.23) and solving

\[
\{w, x', y'\} = \{60.3, 26.4, 1.26\} . \tag{7.24}
\]

For a H$_2$/CO product ratio equal to 3.2 at the same temperature and pressure, the feed composition should be

\[
\text{CH}_4 : \frac{100 - w}{100} \times 100\% = 39.7\% \text{ and H}_2\text{O: } \frac{w}{100} = 60.3\% . \tag{7.25}
\]

(c) If the molar ratio of steam to methane spans the range 1 to 9, then

\[
1 < \frac{w}{100 - w} < 9 ,
\]

or 50 < w < 90.

The corresponding values of the ratio H$_2$/CO are calculated as

\[
\frac{H_2}{CO} = \frac{3x' + y'}{x' - y'} , \tag{7.26}
\]

where x’, y’ are the solutions of Eqs. (7.21 and 7.22) for w ranging from 50 to 90. The results of numerical solution of the above equations are shown graphically in Figure 7–4.

Catalysts (Appendix) are commonly used to accelerate Reaction (7.14) preferentially to Reaction (7.15) in order to improve selectivity. The most commonly used catalyst is Ni because of low cost; although higher steam reforming and lower gas shift activity can be achieved with Rh or Ru catalysts, but at a higher cost. Commercial steam
reforming catalysts typically contain 15–25 wt% Ni on $\alpha$-Al$_2$O$_3$, CaAl$_2$O$_4$, MgO, or CaAl$_2$O$_4$ supports. Figure 7–5 provides the relative activity of various commonly used catalysts for steam reforming.

A significant problem with steam reforming is carbon formation (coking). Carbon can be deposited on the reactor walls, creating heat

\[ \text{Figure 7–4 } The \ ratio \ of \ H_2/CO \ as \ a \ function \ of \ the \ ratio \ of \ steam/methane \ for \ Example \ 7–3 \]

\[ \text{Figure 7–5 } Relative \ activity \ of \ transition \ metal \ catalysts \ for \ steam \ reforming \]
transfer problems, or on the catalyst, resulting in its deactivation. Carbon can be formed as a result of the following reactions:

Methane cracking

\[ \text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2. \tag{7.27} \]

Boudouard reaction

\[ 2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2. \tag{7.28} \]

Methane cracking, Reaction (7.27), is endothermic and consequently creates coking problems at higher temperatures. The Boudouard Reaction (7.28) is exothermic, and therefore favored at lower temperatures. As a result, it does not create problems at ordinary steam reforming temperatures (700–1,000°C) except for cases where temperature is locally lower due to poor heat transfer. Coking in steam reformers using Ni catalysts results in carbon deposition on the surface of the catalyst, and subsequent polymerization until a significant part of the catalyst surface is covered and its activity decreases. Carbon atoms may also diffuse through the Ni bulk to the catalyst/support interface, where they form carbon “whiskers” with detrimental effects (rupturing of catalyst pellets and plugging of the reactor).

In addition to lowering yield, catalyst deactivation creates overheating problems, because the lower rate of the endothermic reforming reaction results in lower absorption of the heat provided to the reactor (via hot gases or any other mechanism). This may lead to hot spots in the reactor wall that may eventually rupture with potentially catastrophic consequences. To prevent catalyst deactivation by coking, most commercial Ni catalysts contain promoters, such as alkalis or alkaline earth oxides (Appendix), that accelerate the removal of carbon via the reaction

\[ \text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2. \tag{7.29} \]

To promote this reaction, a large surplus of steam is usually required in the feed.

The design of reactors for steam reforming is guided by the need for effective (high rate and uniform) heat transfer to the endothermic Reaction (7.14), while keeping reactor footprint low, and maintaining reactor and catalyst integrity at high reaction temperatures. Typical designs rely on bundles of long, narrow tubes with thick walls (up to 2 cm) made from high alloy steel, as shown in Figure 7–6. The tubes
are packed with catalyst. Such designs enhance heat transfer and can withstand the high temperatures of the reaction. Various configurations of such reactors have appeared over the years. In older designs, heat was provided by radiation from natural gas flames between the tubes, and such reactors are quite bulky. Since they use only 50–60% of the energy in the fuel for the reaction (the rest exiting with the still hot flame gases), they require heat integration to avoid waste through feed effluent heat exchange. Newer designs are more compact and accomplish efficient heat transfer.

Several new designs rely on convective heating with hot gas. The hot gas is usually provided by a smaller partial unit that combusts part of the methane feed (increasing its temperature), then passes over the tubes, and enters the primary reformer as the feed at about 500°C. The gas exits the reactor at the other end with the equilibrium composition corresponding to the exit temperature and pressure.
The catalyst can be shaped in a number of forms, usually as large pellets. Pellet designs aim to keep pressure drop low, increase heat transfer, and increase the surface-to-volume ratio, to provide as much area for catalytic reaction as possible (i.e., increase the effectiveness factor). Since the diffusion rate of the reactants into such pellets is low compared to the reaction rate, only a small fraction of the catalyst mass (about 5%) is actually used in the reaction.

**CO₂ or “Dry” Reforming**

Dry reforming relies on the reaction

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2, \quad \Delta H^\circ(1,000{\degree}\text{C}) = +258.9 \text{ kJ/mol}. \quad (7.30)
\]

Dry reforming is less common than steam reforming, and its main use is for processes that require high proportion of CO in the synthesis gas. The thermodynamics of dry reforming is similar to steam reforming. The main operational difference of dry reforming from steam reforming is its tendency for coking, made more severe by the lack of steam to remove carbon according to Reaction (7.29). In some applications, such as in mixed reforming (combination of steam and dry reforming), steam is added for effective containment of coking problems. Since coking quickly deactivates Ni catalysts, Rh and Ru catalysts are used in most dry reforming applications.

**Oxy Reforming or Partial Oxidation and Autothermal Reforming**

Partial oxidation (POX) is another proven method for production of syngas. In partial oxidation, natural gas reacts with pure oxygen at a temperature above 1,000{\degree}\text{C}. The overall reaction is noncatalytic and slightly exothermic

\[
\text{CH}_4 + 0.5\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2, \quad \Delta H^\circ (1,000{\degree}\text{C}) = -35.67 \text{ kJ/mol}. \quad (7.31)
\]

As Reaction (7.31) suggests, the resulting ratio of H₂/CO for POX is ideally equal to 2, which is in the middle of the desired range for Fischer-Tropsch synthesis (1.8–2.3). However, this ratio is difficult to achieve due to the reverse water gas shift Reaction (7.15), which consumes H₂ to produce CO, thus lowering the ratio of H₂/CO below 2. To avoid the consumption of H₂ and formation of CO via the reverse Reaction (7.15), steam is added to the feed, in a process known as autothermal reforming.
As Figure 7–7 shows, in autothermal reforming, a mixture of methane and oxygen (or air) enters the burner, where part of the methane is combusted, according to the exothermic reaction:

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}. \quad (7.32)$$

The hot mixture of combustion gases and unburned methane passes through a packed catalyst bed (usually Ni), where it undergoes mixed reforming, namely steam (endothermic Reaction (7.14)) and dry reforming (endothermic Reaction (7.30)). Combining Reactions (7.14) and (7.30) with Reaction (7.32) yields the overall Reaction (7.31).

Autothermal reactors are adiabatic. Since heat is provided by partial combustion of methane, no external source of heating is needed, which simplifies reactor design and operation. Combustion consumes about 1/4 of the feed methane, and is either homogeneous in the burner (as shown in Figure 7–7) or catalytic at the top of the bed. The temperature of the combustion gases rises to about 1,000–1,500°C, and subsequently drop as the gases undergo the endothermic mixed reforming reactions in the catalyst bed, to exit as syngas at a lower temperature. If the \( \text{H}_2/\text{CO} \) ratio of the syngas is not as desired, steam may be added to the feed.

Autothermal reformers face the same carbon forming challenges as other reforming reactors. Advantages of autothermal reformers include simple design (no heat transfer concerns), small size, and easy
control of $H_2/CO$ ratios. Their main disadvantage is the need for an oxygen plant, justified economically only for fairly large units.

To avoid the disadvantage of requiring an expensive oxygen plant, a new reactor design (Figure 7–8) based on ceramic membranes has been proposed for small reforming plants. Ceramic membrane reactors perform both air separation and reaction in a single unit and do not require external energy to support the oxidation reaction. The critical component for these reactors is a dense ceramic membrane that can separate oxygen from air, thus making oxygen available for reaction with methane. The thin membrane (about 50–100 $\mu$m thick) sits on the outside of a porous ceramic and is composed of a dense ionic conducting mixed oxide, such as $La_{1-x}Sr_xCo_{1-y}O_3-z$.

The mechanism of separation of oxygen from air relies on the dissociation of oxygen molecules as they pass through the inner tube to form $O^{2-}$ ions. These ions, in turn, diffuse through the thin outer layer and meet $CH_4$ in the annulus, where they recombine to form $O_2$ and react to form syngas according to Reactions (7.32) and (7.30). Features of membrane reactors that need to be addressed include low oxygen permeation rates, membrane stability, and fabrication and sealing of ceramic tubes.

**Prereforming**

Even though natural gas contains mostly methane, in some instances it may contain large amounts of higher hydrocarbons (e.g., 10% $C_2$–$C_4$). This would require large reforming reactors and would exacerbate carbon problems. In such instances, a prereforming process step may be added to a gas reforming process. The main reaction in prereforming is

$$2C_xH_y + 2zH_2O \rightleftharpoons 2(x - z)CH_4 + 2zCO + (6z + y - 4x)H_2,$$  

(7.33)

where $y, x \geq 2$. Prereforming units are adiabatic with the feed entering around 300°C and subsequently reacting on a catalyst comprised of 70 wt% Ni on $\gamma$–$Al_2O_3$ substrate, to produce gas at 550°C. Methane in this gas is then converted to syngas in a downstream reforming unit that is smaller than would be required if the prereformed gas was fed directly at 550°C.

**7.5.3 Fischer-Tropsch synthesis**

The terms “Fischer-Tropsch synthesis” or “Fischer-Tropsch chemistry” refer to a wide variety of similar processes relying on catalytic chem-
ical reactions that produce liquid hydrocarbons from syngas. It was Franz Fischer and Hans Tropsch who made (and patented) significant advances associated with both the chemistry and engineering of corresponding processes, to deserve lending their names to the process. The timeline of Fischer-Tropsch synthesis is summarized in Figure 7–9.

Resulting from R&D at the Kaiser Wilhelm-Institut für Kohlenforschung (Coal Research) in the 1920s, the Fischer-Tropsch process allowed Germany to produce liquid fuels domestically from its abundant coal reserves and address its lack of petroleum resources. With major petroleum resources around the world controlled by the Allies, Fischer-Tropsch technology was used extensively by Germany and Japan to produce ersatz (substitute) fuels during World War II. Germany's industrial capacity was decimated towards the end of the war, as a result of Allied bombing. After World War II, US and British companies started using the Fischer-Tropsch process to produce synthetic...
fuels. However, high capital and operating costs, environmental concerns, and most importantly, widely available cheap oil prompted all such efforts to falter.

Interest in Fischer-Tropsch was rekindled during the energy crisis of the 1970s, but especially in South Africa during its isolation under the Apartheid regime. Years of Fischer-Tropsch development have resulted in better catalysts and better engineering. Although the technology is now fairly well developed, there are currently only a handful of companies that are running commercial installations. Most notable is Sasol in South Africa, which uses syngas from coal and natural gas to produce a variety of synthetic petroleum products,
including most of South Africa’s diesel fuel. However, a number of GTL projects involving Fischer-Tropsch are on the horizon, mainly in the Middle East.

In the following sections the basic Fischer-Tropsch chemistry, catalysts, reactor configurations, and industrial processes are examined.

**Fischer-Tropsch chemistry**

Fischer-Tropsch synthesis of hydrocarbons involves a vast number of reactions that can be summarized in the general form

\[
\text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{CO}_2
\]  

(7.34)

For example, the following general reactions may occur:

\[
\text{nH}_2 \rightarrow \text{C}_n \text{H}_{2n+2} + n\text{H}_2\text{O} \text{ (n-paraffins),}
\]  

(7.35)

\[
\text{nH}_2 \rightarrow \text{C}_n \text{H}_{2n} + n\text{H}_2\text{O} \text{ (olefins),}
\]  

(7.36)

\[
\text{(6 + n)H}_2 \rightarrow \text{C}_6 \text{H}_{6+2n} + (6 + n)\text{H}_2\text{O} \text{ (aromatics).}
\]  

(7.37)

Alcohols or other oxygenates may also be formed, as

\[
\text{nH}_2 \rightarrow \text{C}_n \text{H}_{2n+2} \text{O} + (n - 1)\text{H}_2\text{O} \text{ (alcohols or other oxygenates),}
\]  

(7.38)

but they are in very small amounts and are usually neglected. It is of historical interest that the original Fischer-Tropsch synthesis actually concentrated on oxygenates.

Whether the products of Reaction (7.34) contain alkanes or alkenes (with anywhere from one to 40+ carbon atoms) and H\textsubscript{2}O or CO\textsubscript{2} depends primarily on:

- Ratio H\textsubscript{2}/CO.
- Catalyst.
- Type of reactor.
- Process conditions.
Alkanes formed in Reaction (7.34) are mainly straight-chain and alkenes are mostly tertiary. In general, H₂O is formed if H₂ is in excess, otherwise CO₂ is formed. For syngas generated from natural gas (as part of a GTL process), the ratio H₂/CO is in the range 1.8–2.3 depending on the reforming method (see Section 7.5.2 “Natural Gas Reforming and Synthesis Gas”), and it is this ratio that Fischer-Tropsch is compatible with GTL. The preferred products for GTL are alkanes and H₂O.

Fischer-Tropsch synthesis may be used with syngas from other sources, such as coke, coal, and residue (H₂/CO = 0.6–0.8) and fuel oil or low Btu gas (H₂/CO = 0.9–1.1). Products other than alkanes may be pursued, such as alkenes (desirable for subsequent production of chemicals) or oxygenates (such as alcohols, ketones, and aldehydes) but these products are minimized when Fischer-Tropsch is part of a GTL scheme.

The precise mechanisms of Fischer-Tropsch reactions are quite complicated and details are still debated. Nonetheless, a simplified mechanism in place of thousands of reactions is useful, in that it can be used to explain the formation of observed products in terms of a single parameter, α, as will be explained below.

Fischer-Tropsch starts with the formation of the building block –CH₂– through the reaction

\[
\text{CO} + 2\text{H}_2 \rightarrow [-\text{CH}_2-] + \text{H}_2\text{O}, \quad \Delta H^\circ (25^\circ\text{C}) = -167.4 \text{ kJ/mol (CO), (7.39)}
\]

or

\[
\text{CO} + 2\text{H}_2 \rightarrow [-\text{CH}_2-] + \text{CO}_2. \quad (7.40)
\]

The –CH₂– blocks subsequently polymerize to yield final products. The composition of the final products depends on both the thermodynamics and kinetics of corresponding reactions. In general, the free energy of reaction increases with temperature for a product with a given number of carbon atoms, n, making this product less likely to form as temperature increases (Figure 7–10). At a given temperature, a product becomes thermodynamically less likely to form as n increases. In Figure 7–10 the shaded area represents the thermodynamically feasible area. (At a given temperature, increasing n would increase \(\Delta G^\circ\) and decrease \(\Delta H^\circ\), corresponding to less favorable conversion and more heat released.) In the commercial temperature range of 200–350°C, all desired reactions are thermodynamically favorable. The significantly negative enthalpy of reaction makes it necessary to remove considerable amounts of heat.
Why is Fischer-Tropsch synthesis considered feasible at the range of temperatures shown in Figure 7–10? Because the equilibrium constant, $K$, of a reaction $\alpha A + \beta B \rightarrow \sigma S + \tau T$... is defined as

$$K = \frac{[S]^\sigma [T]^\tau \ldots}{[A]^\alpha [B]^\beta \ldots},$$  

where $[S]$ is the activity of species $S$, a dimensionless quantity that can be thought of as the mole fraction. According to reaction thermodynamics, the equilibrium constant $K$, of a reaction is related to the reaction free energy $\Delta G^\circ$ by

$$K = \exp\left[-\frac{\Delta G^\circ}{RT}\right].$$  

From Eq. (7.42) it is clear that $K < 1$ when $\Delta G^\circ > 0$, generally favoring higher mole fractions for the reactants rather than for the products. Conversely, $K > 1$ when $\Delta G^\circ < 0$, generally favoring higher mole fractions for the products of the reaction. As Figure 7–10 indicates, $\Delta G^\circ < 0$ for the range of products of interest in Fischer-Tropsch synthesis.

How exactly Reaction (7.39) (or (7.40)) occurs on the surface of a metal catalyst and how the subsequent polymerization proceeds can
be represented in terms of the following simplified polymerization scheme that involves three major steps:

1. **Chain initiation**—As shown in Figure 7–11, surface sites M on the catalyst readily chemisorb and dissociate H₂. CO is also chemisorbed initially in a bridged mode (involving two M sites) and equilibrates with a linear mode (only one M site). This is the point at which oxygen is removed, in this case by H₂ as H₂O. Two main paths are possible: (1) adsorbed CO dissociates into surface O (which reacts with H₂ to H₂O) and surface C (which hydrogenates to surface CH₂), and (2) adsorbed CO reacts with surface H to form a surface enol group (which hydrogenates to surface CH₂, liberating H₂O and forms surface CH₂). In either case, the resulting surface CH₂ is the chain carrier that builds the hydrocarbon molecule. There is evidence that option (1) is favored at higher temperatures and leads to excessive CH₄ formation via a parallel reaction. Option (2) prevails at lower temperatures, where the enol group can react further to produce oxygenated products.

2. **Chain growth**—Surface CH₂ (Figure 7–11) is polymerized, leading to adsorbed chains –HC–(CH₂)n–2–CH₃ (Figure 7–12) where n takes a number of values.

3. **Chain termination**—Polymerization terminates when the adsorbed chains –HC–(CH₂)n–2–CH₃ are released from the catalyst surface after combining with surface adsorbed CH₃ or H (yielding alkanes), or with an empty surface site (yielding alkenes (Figure 7–13)).

Secondary reactions, such as dehydrogenation of alkanes to alkenes, isomerization of n-alkanes to iso-alkanes, and hydrogenolysis to lighter alkanes may also occur after a hydrocarbon molecule is released from the catalyst surface, and readsorbed to follow other reaction paths.

It is evident from the above discussion that Fischer-Tropsch reactions are not selective towards a single product or an arbitrarily specific range of products; the only exception being methane, which can be produced with very high selectivity. Instead a distribution of products is obtained (Stenger and Askonas, 1986). Remarkably enough, the distribution of products as a function of the number of carbon atoms n in the chain of a product can be approximated in terms of a single parameter, the chain growth probability, α, defined as
7.5 GTL Based on Indirect Conversion of Natural Gas

Figure 7–11  *Initiation step of Fischer-Tropsch reactions*

Figure 7–12  *Chain growth step of Fischer-Tropsch reactions*

Figure 7–13  *Chain termination step of Fischer-Tropsch reactions resulting in alkanes (first two) or alkenes (third)*
where $r_G$ and $r_T$ are the reaction rates of chain growth (Figure 7–12) and termination (Figure 7–13). Application of classical polymerization concepts leads to the celebrated Anderson-Flory-Schultz (AFS) distribution function

$$W_n = n(1 - \alpha)^2 \alpha^{n-1},$$  \hspace{1cm} (7.44)
Figures 7–15 and 7–16 show the theoretical distribution and cumulative distribution of Fischer-Tropsch products according to the AFS Eq. (7.44), for different values of the growth probability, $\alpha$. It is clear that even though no arbitrary product compositions can be achieved, product distributions can be influenced by appropriately selecting the value of $\alpha$, as shown in Figure 7–17. In Figure 7–17 fuel gas is $C_1$ and $C_n$, LPG is $C_3$ and $C_4$, gasoline is $C_5$ to $C_{11}$, diesel is $C_{12}$ to $C_{18}$, and wax is $C_{18+}$. In addition to catalysts used, the main factors affecting $\alpha$ are process conditions, as shown in Table 7–9. For GTL plants, values of $\alpha > 0.95$ are desired to achieve almost complete conversion to liquids.

Note the increasing prevalence of low number hydrocarbons as $\alpha$ decreases. Note also that for $\alpha = 0$ (zero probability of chain growth) methane is the only product theoretically expected by AFS, according to Figure 7–14. In fact, measured values of methane and ethane mass fractions $W_1$ and $W_2$ always appear to deviate from the theoretical values predicted by AFS, as shown in Figure 7–15. The higher experimental selectivity of methane is due to parallel methanation reactions, and the lower selectivity of ethane results from readesorption and incorporation into growing chains. Long chains usually show higher selectivity than predicted by AFS.

![Figure 7–15](image-url)  

**Figure 7–15**  
Theoretical cumulative distribution ($W_{k\leq n} = \sum_{k=1}^{n} W_k$) of Fischer-Tropsch products according to the AFS Eq. (7.44), for different values of growth probability, $\alpha$.
Figure 7–16  Theoretical cumulative distribution of Fischer-Tropsch products according to the AFS Eq. (7.44), for different values of the growth probability, $\alpha$.

Figure 7–17  Theoretical composition of fuel product from Fischer-Tropsch synthesis according to the AFS Eq. (7.44), for different values of the growth probability, $\alpha$. 
### Example 7–4

**Maximum weight fractions of Fischer-Tropsch products**

What is the maximum mass fraction for gas fuel, LPG, gasoline, diesel, and wax as well as the corresponding values of $\alpha$ predicted by the AFS equations?

**Solution**

These numbers can be computed by solving the equation:

$$
\frac{d}{d\alpha} \sum_{n=n_{\text{min}}}^{n_{\text{max}}} n(1-\alpha)^2 \alpha^{n-1} = \sum_{n=n_{\text{min}}}^{n_{\text{max}}} n(1-\alpha)\alpha^{n-2}(n-1-\alpha-n\alpha) = 0 ,
$$

(7.45)

for $\alpha$. The values of $(n_{\text{min}}, n_{\text{max}})$ are (1, 2) for fuel gas, (3, 4) for LPG, (5, 11) for gasoline, (12, 18) for diesel, and (19, $\infty$) for wax. For wax, the probability calculation identity

$$
\sum_{n=1}^{\infty} n(1-\alpha)^2 \alpha^{n-1} = 1 ,
$$

(7.46)

yields

$$
\sum_{n=1}^{\infty} n(1-\alpha)^2 \alpha^{n-1} = 1 - \sum_{n=1}^{18} n(1-\alpha)^2 \alpha^{n-1} ,
$$

which can be used to compute

$$
\frac{d}{d\alpha} \sum_{n=19}^{n_{\text{max}}} n(1-\alpha)^2 \alpha^{n-1} = -\frac{d}{d\alpha} \sum_{n=1}^{18} n(1-\alpha)^2 \alpha^{n-1} .
$$
Numerical solution of Eq. (7.45) yields the results in Table 7–5. The same results can be visualized in Figure 7–18, where the peaks of corresponding weight fraction curves can be observed.

**Example 7–5  Operating envelop for Fischer-Tropsch to produce desired products**

Assume that operating conditions and a catalyst have been selected to result in the value of $\alpha$ required for production of diesel fuel at its maximum mass fraction, as calculated in Example 7–4. What can be expected if the resulting value of $\alpha$ is within ±10% of its optimal value?

**Solution**

According to Table 7–5, the value of $\alpha$ for maximum diesel production is $\alpha_{\text{diesel}} = 0.87$. Fluctuations of that value by ±10% yield $\alpha_{\text{low}} = 0.78$ and $\alpha_{\text{high}} = 0.96$ for which the corresponding diesel fractions

$$W_{\text{diesel}} = \sum_{n=12}^{18} n(1-\alpha)^2 \alpha^{n-1}$$

are 17% and 9.3%, respectively (see Figure 7–18), i.e., quite lower than the optimum value of 25%.

It should also be noted that the mass fraction of wax

$$W_{\text{wax}} = \sum_{n=19}^{\infty} n(1-\alpha)^2 \alpha^{n-1}$$

at $\alpha_{\text{high}} = 0.96$ is 83%. This might create operating problems, given that waxes become solid at lower temperatures.

**Example 7–6  Average mass fraction of Fischer-Tropsch products for varying $\alpha$.**

Assume again that operating conditions and a catalyst have been selected to result in the value of $\alpha$ required for production of diesel fuel at its maximum mass fraction, as calculated in Example 7–4. What is the average mass fraction of diesel if the resulting value of $\alpha$ fluctuates uniformly within ±10% of its optimal value?
The average mass fraction for diesel can be calculated as

$$\frac{1}{0.96 - 0.78} \sum_{n=12}^{18} \int_{0.78}^{0.96} n(1-\alpha)^2 \alpha^{n-1} d\alpha = \alpha^{12} - \frac{11\alpha^{13}}{13} - \alpha^{19} + \frac{9\alpha^{20}}{10} \bigg|_{0.78}^{0.96} = 21\%.$$
Fischer-Tropsch catalysts

Appropriate catalyst selection can influence the reactions outlined in the basic mechanism of Fischer-Tropsch reactions, thus affecting the distribution of products. Table 7–6 outlines basic activities that Fischer-Tropsch catalysts should exhibit, along with the most important candidates. This table explains the catalyst selections made by the pioneers shown in Figure 7–9. Catalyst selection affects the value of the chain growth probability \( a \), thus affecting product distribution. Table 7–7 summarizes the effect on \( a \) of basic variables related to catalyst composition and preparation.

Table 7–6  Effect of Catalyst Metal Selection on Desired Fischer-Tropsch Activity

<table>
<thead>
<tr>
<th>Desired activity</th>
<th>Candidate catalyst (in order of activity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High CO activation rate</td>
<td>Ru &gt; Fe &gt; Ni &gt; Co &gt; Rh &gt; Pd &gt; Pt</td>
</tr>
<tr>
<td>Low hydrogenolysis</td>
<td>Fe &lt; Pd &lt; Pt &lt; Co &lt; Rh &lt; Ni &lt; Ru</td>
</tr>
<tr>
<td>Low shift activity at high H(_2)/CO</td>
<td>Rh &lt; Pd &lt; Co &lt; Pt &lt; Ni &lt; Ru &lt; Fe</td>
</tr>
<tr>
<td>High shift activity at low H(_2)/CO</td>
<td>Fe &gt; Ru &gt; Ni &gt; Pt &gt; Co &gt; Pd &gt; Rh</td>
</tr>
<tr>
<td>High hydrogenation activity (when alkanes are preferred)</td>
<td>Rh &gt; Ru &gt; Pd &gt; Pt &gt; Ni &gt; Co &gt; Fe</td>
</tr>
</tbody>
</table>

Table 7–7  Effect of Catalyst Variables on Chain Growth Probability, \( a \)

<table>
<thead>
<tr>
<th>Catalyst variable</th>
<th>Effect on ( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Co &gt; Ru &gt; Fe</td>
</tr>
<tr>
<td>Support</td>
<td>TiO(_2) &gt; Al(_2)O(_3) &gt; SiO(_2)</td>
</tr>
<tr>
<td>Promoter (K(_2)O, rare earth oxides, V(_2)O(_5), ZrO(_2), TiO(_2), Cr(_2)O(_3))</td>
<td>+</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>+</td>
</tr>
<tr>
<td>Metal concentration</td>
<td>+</td>
</tr>
<tr>
<td>Pellet size</td>
<td>–</td>
</tr>
</tbody>
</table>
Modern technologies focus completely on Fe and Co, with Co preferred for GTL. Ni and Ru may also be used, but they cause excessive hydrogenolysis leading to the formation of methane and are expensive. Due to their industrial importance, basic facts about Fe and Co catalysts are discussed next. In summary, Fe is more flexible, less delicate, and cheaper than Co; whereas Co is more chemically straightforward, and more susceptible to promotion that improves selectivity and lifetime.

Iron catalysts for Fischer-Tropsch synthesis generally consist of precipitated or fused Fe and need no support because of its low cost. A number of promoters for higher activity and selectivity (such as K and Cu) and structural stabilizers (such as Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}) may be added (see Table 7–8). The active phase is Fe carbides (Fe $\rightarrow$ Fe\textsubscript{3}C $\rightarrow$ Fe\textsubscript{5}C\textsubscript{2}). The presence of steam in the gases oxidizes the catalyst (Fe\textsubscript{5}C\textsubscript{2} $\rightarrow$ Fe\textsubscript{3}O\textsubscript{4}). Iron catalysts can work in a wide range of conditions, but are sensitive to S in the feed gas. They do not last long (order of weeks), are not worth regenerating, and are easy to dispose of. They can be used with syngas of H\textsubscript{2}/CO ratios 0.7–2, but result in low yields. They tend to lower the value of the chain growth probability $\alpha$, favor the production of light olefins (alkenes) with low selectivity towards CH\textsubscript{4}, lower the production of heavy waxes, and form CO\textsubscript{2} (cf. Reaction (7.34)).

Cobalt catalysts consist of precipitated Co on an inexpensive support, such as TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, C, or MgO acting as promoters, in decreasing order of activity (Table 7–10). The active phase is metallic Co. Steam has practically no effect on Co catalysts. Cobalt catalysts can work in a limited range of conditions (without shift reactions), and are even more sensitive to S in the feed gas than Fe catalysts. They can last for years, can be regenerated, but are difficult to dispose of because of environmental concerns (necessity to reclaim Co as heavy metal). They can be used with syngas of H\textsubscript{2}/CO ratio 2, but result in high yields. They tend to increase the value of the chain growth probability $\alpha$, form mostly paraffinic products (alkanes), and favor the production of heavier hydrocarbons because they can easily readsort and induce further polymerization of intermediate products. The main oxygen containing byproduct is H\textsubscript{2}O (see Reaction (7.34)).

**Fischer-Tropsch reactors**

Reactor design for Fischer-Tropsch synthesis has significant effects on product composition (by influencing the chain growth probability $\alpha$), operability, safety, and economics. Although different designs are provided by various companies, the following three reactor categories can be identified, namely fixed-bed, circulating and entrained fluidized-bed, and slurry reactors (Figure 7–19).
Fixed-bed reactors

Fixed-bed reactors consist of a bundle of a few thousand long narrow tubes sitting vertically inside a vessel. Each tube contains catalyst particles (about 2–3 mm in diameter). The vessel also acts as heat exchanger to remove the Fischer-Tropsch reaction heat by generating steam on the outer side of the tubes.
Fixed-bed reactors are simple, flexible, and easy to scale up. However, they have a number of disadvantages:

- High cost.
- Multiple reactors in parallel are required for larger plants.

Table 7–10  Promoters of Co Catalysts

<table>
<thead>
<tr>
<th>Promoter</th>
<th>Effect</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂O</td>
<td>Increases α</td>
<td>Donates electrons to Fe</td>
</tr>
<tr>
<td></td>
<td>Decreases CH₄</td>
<td>Increases CO adsorption</td>
</tr>
<tr>
<td></td>
<td>Increases olefins</td>
<td>Decreases H₂ dissociation</td>
</tr>
<tr>
<td>ZrO₂, V₂O₅</td>
<td>Increases α</td>
<td>Increases surface concentration of H, CO</td>
</tr>
<tr>
<td>TiO₂, Cr₂O₃, La₂O₃</td>
<td>Increases light paraffins</td>
<td>Increases CO dissociation at metal/interface; lowers reducibility of mixed oxide</td>
</tr>
<tr>
<td>Ru</td>
<td>Increases activity</td>
<td>Decreases carbon poisoning</td>
</tr>
<tr>
<td>Fe, Re, Au</td>
<td>Less attrition</td>
<td>Increases active sites</td>
</tr>
</tbody>
</table>

Figure 7–19  Types of Fischer-Tropsch reactors  (Spath and Dayton, 2003)
• To avoid high pressure drop in the reactor tubes, large catalyst particles are needed resulting in low effectiveness factor (low catalyst activity per unit mass, resulting from difficulty of reactants to diffuse into the core of a catalyst particle).

• Low heat transfer from the catalyst bed and temperature variation in the tubes. This results in (a) difficulty in controlling product composition due to variability of the chain growth probability $\alpha$; (b) hot spots in the catalyst bed that may lead to catalyst sintering and reactor instability; and (c) low conversion (35–40%) necessary to avoid excessive temperatures (in this case, unreacted feed may be recycled).

Packed-bed reactors were originally used by Fischer and Tropsch and by Sasol. They remain an option for relatively small GTL plants.

Circulating and entrained fluidized-bed reactors

Circulating fluidized-bed reactors address the heat removal problems that affect fixed-bed reactors. Heat is removed through internal cooling coils that make steam in the reaction section (in Figure 7–19), where small catalyst particles (100 μm) circulate with the feed. The products of the reaction and the catalyst circulate from the reaction section to the separation section (right) where products are removed.

Fluidized-bed reactors have a number of advantages:

• Better heat removal results in isothermal operation with better product control.

• Smaller catalyst particles result in higher effectiveness factor.

• Small unit size.

• Because of circulation, fresh catalyst can be added and deactivated catalyst removed.

However, fluidized-bed reactors also have a number of disadvantages:

• Complex design and difficult scale-up. More recent designs using an entrained fluidized-bed have resulted in increased capacity, and lower complexity, size, cost, and catalyst consumption.

• Catalyst agglomeration caused by liquid product sticking to the particles. To avoid this, the operating temperature can be maintained above the dew points of the products, which may
inadvertently force the value of $\alpha$ to be low (with products only suitable for gasoline and chemicals markets).

A comparison of fixed-bed and circulating-bed reactors is shown in Table 7–11.

**Slurry reactors**

Another way to alleviate the poor heat transfer problem of packed-bed reactors is the use of slurry reactors. The slurry is a mix of catalyst particles (10–200 $\mu$m) and product oil at about 35% in a reactor (in Figure 7–19). Reaction heat is removed by internal cooling coils that generate steam. Part of the slurry is taken out of the reactor where the oil is removed at a filter, and catalyst particles are separated and recycled.

Slurry reactors have the following advantages:

- They are suitable for large-scale designs.
- Temperature control is effective, resulting in high conversion and high values for $\alpha$ (0.95–0.98).
- Pressure drop is low.
- Catalyst can be replenished after separation at the filter.
- Units are compact, easy to scale up, and less expensive than packed-bed designs.

Slurry reactors have the following disadvantages, which will be likely overcome in the future:

- High viscosity of slurries.
- Catalyst particle settling and attrition.
- Low mass transfer in the liquid.
- Filtration difficulties.

**7.5.4 Product upgrading**

Product upgrading uses standard processes from petroleum refining to make GTL products more desirable.

Since Fischer-Tropsch units are operated at high values of $\alpha$ to avoid gases in the products (Figure 7–17), they produce large percentages of heavy linear waxes. These waxes are converted to more
valuable hydrocarbons in the middle distillate range (diesel and naphtha) through the process of hydrocracking. Hydrocracking is a mature catalytic process developed in petroleum refining, where it serves the same purpose. There are many reactor designs, using different types of catalysts to perform both cracking with acidic sites and hydrogenation with metal sites. Examples are Pt incorporated into zeolites and Co, Ni, Mo, and W supported on SiO₂–Al₂O₃ or zeolites. Since Fischer-Tropsch products contain no sulfur or nitrogen compounds and no aromatics, they are cleaner than petroleum feeds, making GTL streams much easier to hydrocrack than petroleum.

Adiabatic fixed-bed reactors are used with extruded catalysts. Inlet temperatures range from 300 to 350°C and pressures from 30 to 45 atm. The linear alkanes are cracked almost completely in half, so that only the C₂₀⁺ Fischer-Tropsch products are treated. Alkenes are hydrogenated to alkanes and oxygenates converted through hydrogenolysis. An excess of hydrogen of two to three times the amount needed for hydrotreating is used to control coking. Hydrogen is produced by steam reforming of the light ends from the Fischer-Tropsch unit.Typical compositions of products before and after hydrocracking are shown in Figure 7–20.

There are other upgrading processes, such as isomerization and catalytic reforming, which convert Fischer-Tropsch products into gasoline and chemicals. These are the same as practiced in petroleum

<table>
<thead>
<tr>
<th>Table 7–11 Comparison of Fixed and Circulating-Bed Selectivities</th>
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<tbody>
<tr>
<td>Process variable</td>
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<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>α</td>
</tr>
<tr>
<td>Product</td>
</tr>
<tr>
<td>CH₄</td>
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<tr>
<td>C₂–C₄ alkenes</td>
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<tr>
<td>C₂–C₄ alkanes</td>
</tr>
<tr>
<td>Gasoline (naphtha)</td>
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<tr>
<td>Middle distillate (diesel)</td>
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<td>Waxes</td>
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Making an accurate economic feasibility analysis of GTL projects is difficult, given the fluctuation of oil and gas prices, as well as the continuous evolution of GTL technology and cost of GTL plants. Nevertheless, there are cost/benefit drivers that dominate GTL processes (Seddon, 2004). In this section, the most basic drivers of GTL economics are outlined, with a full understanding that these drivers evolve with time.

In general, GTL is expected to cover a small part of the global demand for fuels in the foreseeable future. Rather than producing fuels economically, GTL’s main claim (in addition to facilitating natural gas transportation) is the quality and environmental friendliness of produced fuels. As such, GTL fuels can be blended with refinery fuels, to improve quality. For example, GTL diesel is sold in small quantities as blendstock in a number of locations.

GTL processes are both capital and energy intensive. However, fixed costs have been steadily going down as a result of technological improvements. From a value of about $120,000 of investment per barrel of fuel produced in the 1950s, the cost has decreased to less than $50,000/bbl, and recent claims place that value below $35,000/bbl. The target is to reach below $20,000/bbl. This may become feasible in the future, if scientific (catalysis) and technological advances can improve efficiency of GTL processes. By comparison, the corresponding value for crude oil refining is a little over $10,000/bbl.

The dominant step in a GTL process is the production of syngas through reforming. Reforming accounts for more that half of the capital cost and about 20–30% of the total energy losses of a GTL process.

![Figure 7–20 Typical compositions of Fischer-Tropsch products before and after hydrocracking](image-url)

refining, and are not discussed here since the main objective of GTL is to convert natural gas into transportable liquids.
The fixed and operating costs of Fischer-Tropsch synthesis are roughly half of those of reforming. Product upgrading accounts for the remaining costs.

Several efforts are underway to reduce GTL costs. In general, these efforts strive to balance fixed and operating costs. As an example to contain fixed costs, compact reforming processes have been developed to reduce cost by eliminating the need for large and expensive oxygen plants. Optimization of operating costs is more complicated. Economic optimization is based on efficient conversion of natural gas to high value products, without excessive fixed cost requirements. When producing GTL fuels, the key issue is how to economically maximize the production of liquids, particularly middle distillates (such as diesel) in the Fischer-Tropsch and upgrading steps. As Example 7–4 illustrates, the products of Fischer-Tropsch synthesis cannot contain more than 25% diesel fuel. At that optimum, there will be significant amounts of both light hydrocarbons and waxes, which are not of high value. Upgrading would then be necessary. To avoid having to upgrade both light hydrocarbons and wax, Fischer-Tropsch synthesis conditions are adjusted so that either light hydrocarbons or wax are not produced (see Figure 7–17). If light hydrocarbons are avoided, then significant amounts of wax will be produced. Wax is then upgraded (cracked) to produce liquid fuels. Alternatively, the fraction of light hydrocarbons produced by Fischer-Tropsch synthesis can be increased and the amount of wax minimized. Light hydrocarbons can be made rich in olefins (by dehydrogenation of paraffins produced). The olefins can then be oligomerized, to produce liquids, which can be further hydrogenated to produce diesel fuel. As another example of operating cost optimization, high value chemicals rather than fuels may be produced. However, this approach may introduce operational complexity.

### References


Catalysis is a technique that accelerates (or sometimes decelerates) a chemical reaction towards equilibrium. The acceleration is accomplished by a catalyst, namely a substance that facilitates the reaction, without itself being altered or consumed by the reaction. The degree to which a reaction is accelerated is termed catalyst activity, and can reach several orders of magnitude. Since a catalyst may selectively accelerate a chemical reaction from a set of competing possible reactions, it can steer a system of reactants towards rapid production of desirable products, thus improving the selectivity of the system. Catalysis is both a naturally occurring phenomenon and a human-made technology—with very long history. Life itself relies on catalysis, as thousands of enzymes (biological catalysts) continuously steer biological reactions towards highly specialized directions in living organisms. As a technology, catalysis is ubiquitous in shaping many aspects of modern life. Catalytic converters have made modern cars much less polluting. Fluid catalytic cracking (FCC), a process discovered serendipitously in the 1940s, accounts for more than half of the global production of gasoline. Of course, catalysis is of paramount importance for GTL technologies.

Industrial catalysts are usually solids, catalyzing reactions involving gases or liquids. They are shaped as pellets or powders. An industrial catalyst works by providing a catalytic surface with active sites or centers, on which reactants are chemisorbed and are thus facilitated (by having to overcome lower energy barriers) to react with neighboring molecules that are also adsorbed on the surface. Selectivity results from the catalyst surface steering adsorbed reactants...
towards specific products. For example, synthesis gas (CO and H₂) can be steered to react towards production of mostly methane, methanol, or hydrocarbons if Ni, Cu, or Fe catalysts are used.

Since catalytic activity is available at the surface of the catalyst, solid catalysts, such as metals, oxides, sulfides, or alumino-silicates, are prepared as small crystallites to make as much surface area as possible available to reactants. These classes of main components of catalysts function in different ways. Metals and oxides initiate redox-type reactions, such as hydrogenation, oxidation, and hydrogenolysis. Metals have more activity, but oxides exhibit better selectivity because of their complex structures. Alumino-silicate materials are solid acids and induce carbonium-type reactions, such as cracking, isomerization, and polymerization. An industrially important class of alumino-silicate catalysts is zeolites, which are molecular cages that allow shape selective reactions, in which the size of the openings into zeolite cages restricts reaction of molecules because of their size.

Catalyst activity or selectivity may decrease as a result of sintering or poisoning. Sintering refers to the growth of crystallites with time and it accelerates with time. Poisoning results from chemisorption of feed impurities, such as sulfur, on active sites, which then become deactivated. It is catalytic converter deactivation problems (in addition to public health concerns) that have prompted the elimination of lead based additives for octane number boosting from gasoline. Catalyst deactivation may also result by carbon deposition on active sites as a result of a number of coking reactions (carbon formation from hydrocarbon decomposition at high temperature), all of which are undesirable. Coking may be so severe, that continuous catalyst regeneration may be required, as in the case of fluidized catalytic cracking (FCC) reactors.

In addition to the preparation of the main component, catalytic activity and stability can be optimized by appropriate choice of catalyst support and promoters. The most important function of catalyst support is to ensure that the active component is dispersed enough to provide the largest possible number of active sites on the catalyst surface. To accomplish this, the crystallites of the active material are spread over an inert surface to avoid interactions. The support material is made of materials with high melting points, such as α-Al₂O₃, γ-Al₂O₃, MgO, or ZrO₂, to avoid sintering. Support materials often have acidic activity, which leads to inadvertent carbon deposition. Another important role of catalyst support is to impart desired properties (e.g. size, shape, hardness) to catalyst pellets or powders, suitable for a variety of reactors. The role of a catalyst promoter is to affect the performance of either the active component or the support.
Promoters are added in small amounts to a catalyst. For example, small (<3 wt%) amounts of K₂O added to γ-Al₂O₃ neutralize inherent acid sites and prevent excessive coking. Metals are promoted by alloying with a second metal that changes either the activity or selectivity of the host metal.

The development of catalysts remains a combination of solid science and art. Catalyst designers rely on a vast database of known catalysts, high performance computations that purport to predict the most promising candidates for a certain kind of catalytic activity, and experiments. The performance of a catalyst depends critically on a number of factors besides composition, such as method of preparation and pretreatment before use. Finding the best recipe for making a catalyst is an iterative process, involving trial and error. Elements of this process are carefully guarded industrial secrets.

Catalysis is prevalent in GTL technologies, particularly in Fischer-Tropsch synthesis, where the design of a successful catalyst is often the deciding factor for the success of a proposed process.