Part One Introduction

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Synopsis

Some of the fundamental and most frequently used terms are explained. Fischer– Tropsch (FT) technology involves the conversion of syngas (a mixture of CO and H_2) into liquid hydrocarbons. It is a key element in the industrial conversion processes X-To-Liquids (XTL), where X = C, coal; G, natural gas; B, biomass; or W, organic waste. For example, a gas-to-liquids (GTL) process converts natural gas into syncrude, a mixture mainly of long-chain hydrocarbons. The conversion reactions are usually catalyzed by metals (iron, cobalt, and sometimes ruthenium) often carried on oxide supports such as silica or alumina. The liquid hydrocarbons are important sources of transportation fuels and of specialty chemicals. Syngas is now mainly obtained from coal, oil, or natural gas, but will in future be increasingly made from renewable sources such as biomass or organic waste. Since the available reserves of fossil fuels are diminishing, the renewables should provide more sustainable feedstocks in the long term.

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1.1 Feedstocks for Fuel and for Chemicals Manufacture

Syngas, the name given to a mixture of carbon monoxide and hydrogen, is the lifeblood of the chemicals industry and helps to provide a lot of our energy. It can be made from many sources, including coal, natural gas, organic waste, or biomass. The Fischer–Tropsch (FT) process converts syngas catalytically into organic chemicals, mainly linear alkenes and alkanes, which are used as both liquid fuels and feedstocks for making further useful chemicals. Some oxygenates can also be formed (chiefly methanol and ethanol) (see Chapters 4 and 6).

Alkene and alkane formation in the FT-Hydrocarbon Synthesis can be summarized as follows:

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{1.1}$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$
 (1.2)

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Box 1.1 What its all about: some definitions

To avoid ambiguity, we will use the following terms with reference to the metalcatalyzed conversion of syngas into organic compounds.

Fischer–Tropsch process (FTP) will refer to the overall industrial process wherein the syngas is catalytically converted in a reactor into a mixture of primary (largely but not exclusively linear aliphatic hydrocarbons) and secondary products. Water is also a major primary product. Secondary products that are believed to be formed in the reactor from the primary products include internal alkenes, branched chain and cyclic aliphatics, some aromatics, and some oxygenates such as alcohols.

Fischer–Tropsch hydrocarbon synthesis (or FT-HS) will refer to the hydrocarbons (1-*n*-alkenes and *n*-alkanes) that are generally considered to be the primary products of the metal-catalyzed syngas conversion when the reaction is carried out under mild conditions where further secondary reactions are minimized. A subset of the FT-HS, the formation of methane, is sometimes treated separately as **methanation**.

We will use the term **Fischer–Tropsch reaction** (or FT reaction) largely in the discussions on the mode(s) by which the primary products are formed, for example, the kinetics and reaction mechanisms of the FT-HS.

We also introduce two terms. **Sustainable development** is the use of natural resources that "meet present (world) needs without compromising the ability of future generations to meet their own needs" and was coined by the Brundtland Commission. **Renewable energy** is energy that is renewed naturally. It includes traditional biomass (biofuels), hydroelectricity, wind, tidal, solar, and geothermal sources. It excludes raw materials that are depleted in use such as fossil fuels and nuclear power.

Energy has been said to be "the single most important scientific and technological challenge facing humanity in the twenty first century" [1], and we agree. There is the global requirement for more energy, especially as transportation fuels, as populations increase in number and sophistication. In addition, there is also a more specific need for new feedstocks for chemicals manufacture. As we will see, these two needs have features in common. And above all, we recognize the imperative now demanded by Society to produce both fuel and feedstocks in an environmentally acceptable and preferably sustainable manner. We also aim to correct some of the erroneous beliefs and myths present in the energy and chemicals sectors in order that our students, who will be tomorrow's academic and industrial leaders, have reliable foundations on which to build.

Mankind literally lives off energy. Most of it comes from the sun, indirectly via plants that use carbon dioxide and water to grow. Eventually they die and decay and, very slowly, over geological timescales, are turned into the fossil fuels (coal, oil, natural gas) that we extract and combust to provide heat, light, and other forms of power [2].

Box 1.2 Fossil fuel resources

In 2000, global oil reserves were estimated at about 1105 billion barrels; by the end of 2010, new discoveries had increased the proven reserves to 1383 billion or 1476 billion barrels ($\sim 200 \times 10^9$ tons) if Canadian oil sands and shale oil and gas are included. Similarly, gas reserves were estimated at 109 trillion cubic meters (Tcm) in 1990, 154.3 Tcm in 2000, and 187.5 Tcm in 2010 [3]. Based on the data for current and previous years, the US Department of Energy makes forecasts of the use and the production of energy. Currently, it projects that world consumption of marketed energy will increase from 495 QUAD (quadrillion, 10^{15} British Thermal Units or 1.055×10^{20} J) in 2007 to 590 QUAD in 2020 and then to 739 QUAD ($\sim 780 \times 10^{20}$ J) in 2035, an overall increase of 49%. Liquids (i.e., largely hydrocarbons) supply a large proportion of world energy consumption, and although their share is predicted to fall somewhat, it will still be around 32% in 2030 [4].

"Unconventional" resources (including oil sands, shale oil and shale gas, extraheavy oil, biofuels, coal-to-liquids, and gas-to-liquids) are expected to become increasingly competitive; world production, which totaled 3.4 million barrels per day in 2007, is forecast to increase to 12.9 million barrels per day and to account for 12% of total world liquids supply in 2035. The proportion of biofuels, largely ethanol and biodiesel, from the United States and Brazil, is forecast to grow slowly.

1.2 The Problems

There are two main problems with fossil fuels: the reserves are finite and slowly running out and, since all fossil fuels contain combined carbon, their combustion (oxidation) produces carbon dioxide, which accumulates in the atmosphere and which is likely to have serious consequences for the climate of our planet. Combustion also generates other materials that can harm mankind and the environment, such as CO, oxides of sulfur and nitrogen, and metallic oxide ashes, arising from incomplete oxidation and from impurities in the fuel.

For some end-uses there are many alternatives to fossil fuels, such as hydroelectric and nuclear power and others that are being developed commercially, including solar, wind, tidal, and geothermal power. The latter technologies will play their very important role mainly by providing electric power via large fixed installations. However, they will not have a direct part in providing more liquid transportation fuels or new feedstocks for the chemicals industry.

Why should Fischer–Tropsch be the approach to replace or supplement crude oil as a source of transportation fuels, gasoline (in the United States), or petrol and diesel (in the United Kingdom)? Today transportation fuels from crude oil must undergo extensive cleaning to remove materials containing heteroatoms (N, S, metals, etc.) from the raw feedstocks; if these materials are not removed,

the impurities will quickly spoil and deactivate the catalyst. The amounts of hydrogen and energy needed for this cleaning have steadily increased as the crude oils have become heavier (i.e., more impure) over the years. Today, about 15–20% of the energy in the oil is required to produce environmentally acceptable transportation fuels, and the percentage can only increase as the crude becomes heavier. Thus, the energy advantage of crude oil over other fossil fuels is becoming narrower as time passes. Even today (2012), one is able to convert coal (a very "dirty" material) into transportation fuels in a Fischer–Tropsch process at a cost that is competitive with crude oil.

The environmental properties of the FT-synthesized transportation fuels meet or usually exceed those of crude oil-derived fuels. There are of course a number of other approaches that can be used for converting coal into transportation fuels. For example, the Exxon-Mobil methanol to gasoline process is able to convert coal first into syngas, then methanol, and then gasoline; however, the gasoline obtained by this process is high in aromatics and essentially no diesel range fuels are produced. Another variation converts the coal to low molecular weight alkenes and then further to gasoline and diesel range fuels; however, the diesel that is produced will be multiple branched and have a lower cetane number than the FT diesel.

Environmental concerns today cause governments to provide subsidies to allow renewable fuels to be utilized, as, for example, ethanol in the United States. Even without this subsidy, FT fuels are competitive with the subsidized renewables in some areas. In addition, improvements in gasification procedures are allowing fuels to be obtained from a mixture of renewables and coal so that the FT oil will have the environmental advantage over crude oil.

1.3

Fuels for Transportation

1.3.1

Internal Combustion Engines

The form in which the energy is available is important. Although it has been done (e.g., in wartime), it is unrealistic to try and run cars, trucks, or planes on coal, wood, or natural gas. Wikipedia has estimated that there were over 1 billion cars and light trucks on the road in 2010. As motor vehicles are now manufactured in many countries, developed as well as developing, the total must exceed 1.1 billion (10^9) quite soon. Almost all of them run on liquid hydrocarbons and it has been estimated that they burn well over 1 billion cubic meters (1 Bcm, 260 billion US gallons, or 8.5×10^8 tons) of fuel each year. The engineering has been well worked out so that the internal combustion engines are now extremely efficient for the appropriate fuel. The optimum gasoline has a high proportion of branched chain alkanes (giving a high octane number), while the best diesel has a high component of linear alkanes (with a high cetane number). It should be remembered that it will

be necessary to continue to provide fuel for all the (older) vehicles at present on our roads, as well as those currently being built and planned.

1.3.2 Electric Cars

There is considerable interest in using electricity for transportation and most manufacturers are making electric cars, as they are perceived to cause less pollution in their immediate neighborhoods. However, there are some serious disadvantages. Some of the problems as well as the benefits of the electric car have been amusingly illustrated by Jeremy Clarkson, the presenter of the BBC TV's very popular car show "Top Gear," when he reviewed the projected Mini E being built by BMW [5]. This car works well but requires 5088 lithium ion batteries (weighing 260 kg) and even then has a range of only 104 miles, after which it requires charging for 4.5 h. Eventually, the batteries will need replacing, the cost of which does not bear thinking about. The wide acceptance of electric cars depends on the availability of inexpensive and high-power batteries and also on the availability of national networks of fast-charging stations, which are at present hardly on the drawing board. To get round the problems, many manufacturers add on a liquid hydrocarbon fuel motor to extend both the range and the convenience of electric cars. There are many now available or coming on to the market, for example, the hybrid (electricgasoline) Toyota Prius or the Chevrolet Volt or Ampera.

There are several serious snags on the way to commercially viable electric cars. Not only are the batteries costly and heavy, but also the lithium they require is difficult to source. The provenance of the electricity for recharging them must also be considered. Thus, the US Energy Information Agency estimates that two-thirds of world electricity is generated from fossil fuels (coal 42%, natural gas 21%, and oil 4%), 14% from nuclear and only 19% from renewables. Furthermore, it has been estimated that the average CO_2 output for electric cars is 128 g/km compared to an average of 105 g/km for hybrids such as the Toyota Prius, when the emissions from coal- and oil-fired electricity-generating stations are included [6]. If we want to minimize CO_2 production by diminishing the use of fossil fuels, given the technology available at present (2012), the nuclear option currently seems the choice for generating sustainable electricity. But that also has serious problems as the disasters at the Chernobyl, Fukushima, and Three Mile Island nuclear plants showed.

1.3.3 Hydrogen-Powered Vehicles

Hydrogen is a very attractive source of power as the only product of combustion is water; unfortunately, large-scale commercial applications are further in the future, even though the science is well known and hydrogen is easily made by splitting water, for example, by electrolysis or solar heating. However, the cost of doing so, in terms of the energy required, makes it very expensive.

Currently, hydrogen is produced mainly by gasification/reforming; thus, hydrogen should be considered a by-product of the petrochemicals industry in the formation of carbon monoxide, for example, from hydrocarbons:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \tag{1.3}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
 (1.4)

The water-gas shift reaction (WGSR) is then employed to increase the proportion of hydrogen, but this in turn produces carbon dioxide:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 (1.5)

Thus, the conventional production of hydrogen today is always associated with the production of CO_2 .

Perhaps the development of hydrogen-powered fuel cells for cars is a promising direction [7].

One requirement for viable electric or hydrogen-powered transportation systems is the availability of widespread national grids for recharging, the setting up of which will be a mammoth and vastly expensive task. And if the electricity for the grid comes from burning fossil fuels, we have not addressed the sustainability problem – merely moved it sideways to another area.

1.4

Feedstocks for the Chemical Industry

The raw materials for the organic chemicals industry are largely carbon based; in the eighteenth century, the pyrolysis of wood provided useful chemicals. In the nineteenth century, coal tar was exploited as the source of many materials, especially aromatics; while in the twentieth and twenty-first centuries, the feedstocks for many organic chemicals have been derived from oil. To that extent therefore, the supply of feedstocks for chemicals and of fuel for transportation currently run parallel and both depend on nonrenewable resources.

1.5

Sustainability and Renewables: Alternatives to Fossil Fuels

It has been estimated that more solar energy strikes the Earth in 1 h (4.3×10^{20} J) than is currently consumed by all mankind in a year (4.1×10^{20} J). That even allows a great expansion of use as there would be more than enough. Thus, there is a continuing search for usable sources of energy that are either from renewable "biofuels," and thus will not deplete our reserves, or that utilize sunlight more directly and do not involve organic intermediates, for example, some form of hydrogen generation by splitting water. The main biorenewables are fast-growing plants, trees, or algae, for example, that can be harvested and burned, directly or indirectly, with the carbon dioxide produced going back to feed more plants.

1.5.1 Biofuels

The best-known commercial example of biofuel manufacture is in Brazil where sugarcane grown on a very large scale is harvested and thereby sugar is extracted and fermented into alcohol that is distilled to be sold in filling stations (as *bioethanol*) to power motor vehicles. Brazil, with a population close to 200 million, has plentiful sunlight, cheap labor, and some government assistance. Prior to the discovery of large offshore oil and gas deposits, it also had the additional stimulus of a lack of home-produced oil fuel. It therefore turned to ethanol to power internal combustion engines, and most Brazilian cars are now able to run on either gasoline or alcohol. Currently, the home-produced ethanol takes care of some 13% of the country's motor fuel needs; the comparable figure is about 4% for the United States [8].

Large amounts of bioethanol, made from maize (corn), are produced in the United States, and ethanol commonly makes up 10% of the fuel at the pump (designated E10). However, it is now recognized that there are major problems with such agriculturally produced fuels. One is that the acreage of arable land needed to grow plants to power transport can seriously hinder the growing of food. This in turn impinges on the cost of food. The energy balance is also more complex than it may appear at first sight since, in addition to sunlight, considerable energy derived from fossil fuels is required to produce the ethanol. Much water is also required, and since water is also a scarce commodity, it must be conserved and recovered, which will also require energy.

It has been calculated that irrespective of crop, one acre of land, pond, or bioreactor can annually yield enough amount of biomass to fuel one motor vehicle or meet the calorific requirement of several people. This amount of biomass therefore makes only a very small contribution to our present road transport requirements and yet can contribute significantly to global food shortages and rising prices [9, 10]. New technology to make ethanol based on lignocellulose, and which does not depend on food crops, is being actively pursued. Thus, while biomass is used as a renewable fuel, it is not yet the cure-all the world is seeking.

Other forms of biofuels are also known, such as biodiesel made from waste fats (long-chain esters); however, this has not been promoted to the extent of bioethanol and is likely to remain a minor source of energy for transportation.

1.5.2

Other Renewable but Nonbio Fuels

The production of energy by such means that do not involve biointermediates is a very active area of science research. There are many ways to harness solar energy: using photovoltaic cells or solar furnaces, it can be turned directly into electricity. Wind and tidal power can also be similarly harnessed; however, all these sources have the disadvantage that the energy is not continuously produced and the electricity must be stored and cabled to the site where it is needed. Although the

technology to mass-produce solar cells has improved and in some countries (Germany, Japan, Spain, and Israel) electricity from such devices is beginning to make a significant contribution to the national grid, the cost of solar power is currently estimated to be between 10 and 20 times that of power from burning coal. Storage on the scale needed to ensure that power is available nationally even during hours of darkness has also lagged behind. Because fossil fuels are still abundant and inexpensive, non-biorenewables are not likely to play a large role in primary power generation until technological or cost breakthroughs are achieved, or environment-driven carbon taxes are brought in.

1.6 The Way Forward

So, where do we go? If the large-scale use of electric and hydrogen-powered cars is only over the horizon and renewable biofuels will supply a small fraction of our needs for transportation, we must make the best of what we have by improving our tools to deal with our present resources. Since major discoveries of oil and gas and coal are still being made, exact numbers are imprecise, but current best estimates indicate that our planet has enough reserves of oil for about 50 years and of natural gas for perhaps 150–200 years at current consumption levels. Coal is more plentiful and some 100–200 years supply may be available. However, the important factor is how difficult (i.e., how expensive) it will become to extract these fuels: cost is very likely to determine the uses to which fossil fuels will be put in future. The other side of the argument is of course the growth in carbon dioxide. The EIA estimates that annual CO_2 emissions will rise from the 2007 level of about 29.7 billion tons to around 42.4 billion tons by 2035. This 43% increase is likely to have a significant effect on many aspects of our lives, in particular through changes in our climate.

For the twin reasons of conserving our fossil fuels and curbing the increase in CO₂ levels, our primary concern should be in using our resources better and more efficiently. One way to do that is to improve the conversions of the raw materials into conveniently usable fuels and/or chemicals. Doing that is not necessarily straightforward or obvious. Taking natural gas (which is largely methane) as an example, while direct approaches such as partial oxidation of methane to methanol or to higher alkanes may become commercially viable in the future, the best way currently is to reform the natural gas into syngas $(CO + H_2)$ and then to build on that. The engineering needed for reforming is well established and there are many well worked out reactions making useful products from syngas. One of these is of course the Fischer-Tropsch hydrocarbon synthesis in which the syngas is converted into linear hydrocarbons that can be used either as fuel (diesel) or as chemical feedstocks. Our thesis therefore is that improvements to Fischer-Tropsch are desirable, possible, and necessary and should be developed as soon as practicable. Some other paths that are being followed are outlined in Section 1.7.

1.7 XTL and the Fischer–Tropsch Process (FTP)

The Fischer–Tropsch Process (FTP) is a key part of the technology that is needed to convert one type of carbon-based fuel into another. This in turn allows industry to choose which feedstock and which technique is most suitable for a given purpose. A number of composite technologies known as XTL have been developed: CTL (coal-to-liquids), GTL (gas-to-liquids), BTL (biomass-to-liquids), and WTL (waste-to-liquids). Thus, for example, GTL reforms natural gas (mainly methane) by partial oxidation into syngas:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \quad \Delta H^{\circ}_{(298 \text{ K})} + 206 \text{ kJ/mol}$$
 (1.6)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, \quad \Delta H^{\circ}_{(298 \text{ K})} + 247 \text{ kJ/mol}$$

$$(1.7)$$

Alternatively, CTL, for example, makes syngas from coal:

$$2C + H_2O + O_2 \rightarrow CO + CO_2 + H_2 \tag{1.8}$$

The CO: H₂ ratio is adjusted by the catalytic Water-Gas Shift Reaction (WGSR):

$$H_2O + 1CO \rightleftharpoons H_2 + CO_2 (WGSR), \quad \Delta H^{\circ}_{(298 \text{ K})} - 41 \text{ kJ/mol}$$
(1.5)

and the gases are then led to another reactor where they are contacted with a different metal catalyst (usually iron or cobalt) in the Fischer–Tropsch reaction. For cobalt and other metals, the catalytically active metal is generally deposited as nanoparticles on an oxide such as silica or alumina that was classically thought to act simply as an inert support. Iron-catalyzed reactions are generally carried out over the unsupported (massive) metal. Details of the various XTL processes are given in Chapters 2 and 5.

The product distribution of hydrocarbons formed during the FT process follows an Anderson–Schulz–Flory distribution, expressed as $W/N = (1 - \alpha)^2 \alpha^{n-1}$ where *W* is the weight fraction of hydrocarbon molecules containing *N* carbon atoms and α is the chain growth probability [11]. This can be visualized by plotting log (*W*/*N*) against *N*, and shows a monotonic decrease from lower to higher molecular mass products, indicative of a step-growth polymerization of a C₁ species (see Figure 12.3).

Methane is always the largest single product; however, by bringing α close to one, the total amount of methane formed can be minimized and the formation of longchain hydrocarbons is increased. Very long-chain hydrocarbons are waxes, which must be cracked in order to produce liquid transportation fuels.

Although the FT process has been applied on a large scale, its universal acceptance has been hampered by high capital costs, high operation and maintenance costs, and environmental concerns. In practice, FT liquid fuels compete with natural gas that can be supplied by conventional gas pipelines and liquefied natural gas (LNG) technology. Thus, FT gas as a feedstock becomes economically viable as a supply of "stranded gas," in other words, a source of natural gas that is impractical to exploit as it is far from major conurbations.

1.7.1 Some History

The history of the FTP is a classical example of the stepwise development so characteristic of science: there was really no single "Eureka" moment. It also illustrates how closely advances in science and technology are coupled to economic and political circumstances.

In 1902, Sabatier and Senderens reported that a reaction occurred between carbon monoxide and hydrogen to give methane over a nickel catalyst; then, in 1910 Mittasch, Bosch, and Haber developed promoted iron catalysts for ammonia synthesis from hydrogen and nitrogen. That was shortly followed (in 1913) by patents issued to BASF for the production of hydrocarbons and oxygenates by the high-pressure hydrogenation of CO over oxide catalysts. In the 1920s, Fischer and Tropsch working at the Kaiser Wilhem Institute in Berlin first made Synthol (containing oxygenates) by hydrogenation of CO over alkalized iron, and then in 1925, they announced the synthesis of higher hydrocarbons at atmospheric pressures over Co and Ni. The interest in the process grew rapidly and workers in England, Japan, and the United States, especially at the US Bureau of Mines, devoted much time and effort to improving the methodology. Considerable engineering work and catalyst development continued in Nazi Germany, especially during the 1939-1945 World War when the process was used to make motor fuel from coal. Germany was acutely short of oil, but had copious reserves of low-quality brown coal (lignite) that could be turned into fuel for the war effort. The development of new reactor designs for the FTP continued after the War as there were fears that petroleum would be in short supply. With the discovery of large new oilfields, interest in Fischer-Tropsch waned somewhat until the 1970s brought a large increase in the price of oil and sanctions on the export of oil to South Africa. This encouraged SASOL (Suid Afrikaanse Steenkool en Olie, the South African Coal and Oil company) to expand its CTL plants in order to become more self-sufficient [12]. Although the economic and political pressures have long since changed, SASOL has actively continued to develop its processes in both CTL and GTL. They are based on FT technology using iron or cobalt catalysts, and SASOL continues to play a major role in developing new plants in other countries (including Qatar, Nigeria, Egypt, etc.). Shell has also built major FT plants (in Malaysia and Qatar) using cobalt catalysts (see Chapters 3, 5 and 9). Total world production of FT hydrocarbons has been estimated at about 10 million tons per year.

In parallel with the Fischer–Tropsch hydrocarbon synthesis, work continued on another reaction based on syngas and originally developed in Germany: the synthesis of methanol. That came to fruition in 1966 when ICI in the United Kingdom brought in the low pressure process, using a copper–zinc oxide catalyst, which still dominates the technology (see Chapter 6) and currently enables methanol production of about 30 million tons annually.

1.7.2 FT Technology: An Overview

FT processes are currently used commercially to make hydrocarbons by passing syngas over supported metal catalysts. Fe, Co, Ru, Rh, and even Ni all have FT activity, though in somewhat different ways. The most active catalyst is Ru, but it is not used commercially because of its high cost. The original and most commonly used catalyst is Fe, though Shell uses a Co catalyst to make long-chain alkanes (waxes) that are then broken down to smaller alkanes. The cobalt catalyst generally consists of very fine particles of the metal supported on an oxide surface such as silica or alumina. These nanoparticles have the advantage of high activity due to their large surface areas; however, this also makes it easy for impurities to be adsorbed that can affect the performance of the catalyst. In some cases the activity can be improved, but many substances will diminish the activity and selectivity.

Two main regimes have been used: low-temperature Fischer–Tropsch (LTFT), usually at 200–250 °C, that gives long-chain molecules, and the high-temperature Fischer–Tropsch (HTFT), at 320–375 °C, that gives shorter chain molecules. It is fairly generally agreed that the primary products of the reaction are 1-*n*-alkenes, but under harsher conditions (high pressure of hydrogen, higher temperature, or hydrogenating catalysts such as Co) *n*-alkanes result. The primary alkene products are also further hydrogenated, isomerized, dehydrogenated, cyclized, carbonylated, or even oxidized, under the reaction conditions and thus a wide spectrum of products can be formed.

The best form of the reactors to be used depends on the catalyst, the conditions, and the distribution of products that is desired. HTFT uses iron catalysts in two-phase fluidized bed reactors; LTFT uses either iron or cobalt in three-phase slurry reactors or tubular fixed bed reactors. Much of the skill in running a successful FT plant comes from the use of properly designed reactors [13].

The silica or alumina support was long believed to play little role in the basic FT reaction, though it was significant in the subsequent, secondary reactions. However, studies by surface scientists have shown that the actual FT catalysis usually takes place at the interface between the metal and the oxide, which can be either the support to or a component of the catalyst.

1.7.3 What Goes on?

In progressing from CO that has one carbon atom to an alkene or alkane, quite a complex series of reactions must be occurring. Essentially however, it is a polymerization of C_1 units. The question then arises how this occurs on a metal surface. It is only quite recently that surface scientists have had access to the tools that will allow them to begin to answer this riddle. Thus, there have been many attempts to understand the reactions that occur and many theories, the more important of which are summarized in Chapter 12.

Table 1.1 Energetics of CO hydrogenation.

$3H_2 + 1CO = H_2O + CH_4, \Delta G_{(500\;K)}^\circ - 94\;kJ/mol$	(1.9)
$2H_2 + 1CO = H_2O + 1/3(C_2H_6), \Delta G^\circ_{(500\;K)} - 31kJ/mol$	(1.10)
$3H_2 + 1CO = CH_3OH, \ \ \Delta G^\circ_{(500\ K)} + 21\ kJ/mol$	(1.11)
$3H_2+2CO=HOCH_2CH_2OH,\ \ \Delta G^\circ_{(500\ K)}+66\ kJ/mol$	(1.12)
$4H_2 + 2CO = CH_3CH_2OH + H_2O, \ \ \Delta G^\circ_{(500\ K)} - 27\ kJ/mol$	(1.13)
$3H_2 + 1CO_2 = CH_3OH + H_2O, \ \ \Delta G^\circ_{(298\ K)} + 3\ kJ/mol$	(1.14)
$\mathrm{H_2O} + 1\mathrm{CO} \rightleftarrows \mathrm{H_2} + \mathrm{CO_2} \ (\mathrm{WGSR}), \Delta G^\circ_{(298 \ \mathrm{K})} - 28 \ \mathrm{kJ/mol}$	(1.5)

1.7.4 CO Hydrogenation: Basic Thermodynamics and Kinetics

As in all chemical transformations, although the rates are governed by the kinetics of the individual steps, it is important to ensure that the thermodynamics of the steps are favorable or if one step of a sequence is unfavorable, it is coupled to a very favorable one.

As Table 1.1 indicates, the formation of hydrocarbons from CO hydrogenation is generally favored overall, but, as shown in a comparison of the free energies (ΔG°), the reaction can be thought of as driven by formation of water. Thus, making methane also involves making 1 mol of water is more favorable, but higher hydrocarbons are less favored. If free water is not formed, then the thermodynamics are much more difficult as is shown by the positive ΔG° for methanol and glycol; only when some water is also formed, as with ethanol, does the reaction become favored.

1.8

Alternatives to Fischer–Tropsch

Given that at present the best way of using fossil fuels is to reform them into syngas, some of the alternatives to FT are discussed in Chapter 6. In fact, the highest volume use of syngas is the reaction to methanol, which can be used as a fuel additive and which is also a very useful chemical and a C_1 feedstock. Examples include the Mobil process that converts methanol into gasoline over an acid zeolite catalyst (HZSM-5), and the Haldor–Topsoe A/S TIGAS process that uses dimethyl ether for the same transformation. Several processes also exist for converting methanol into olefins. These include the UOP/Norske Hydro process (with a pilot plant in Norway and a demonstration plant in Belgium) and Lurgi has a similar methanol-topropylene (MTP) process. The Institute of Chemical Physics (in Dalian, China) commissioned the first commercial methanol-to-olefin process (DMTO) in the world in 2010. This has a production capacity of 600 000 tons of lower olefins per year (http://english.dicp.cas.cn/ns/es/201008/t20100811_57266.html.).

Other widely practiced alternatives use syngas together with an organic substrate to extend the chain lengths, as, for example, in the hydroformylation of propene to butanal and isobutanal,

$$RCH = CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO + RCH(CHO)CH_3$$
(1.15)

A large number of related reactions of olefins with carbon monoxide, for example, giving acids and esters, are known and some of these are important industrially [14]:

$$CH_2 = CH_2 + CO + H_2O \rightarrow CH_3CH_2CO_2H$$
(1.16)

$$\label{eq:RCH} \begin{split} \text{RCH} = & \text{CH}_2 + \text{CO} + \text{MeOH} \rightarrow \text{RCH}(\text{CO}_2\text{Me})\text{CH}_3 + \text{RCH}_2\text{CH}_2\text{CO}_2\text{Me} \end{split} \tag{1.17}$$

Last but not least, the WGSR is used to greatly increase the proportion of hydrogen in the syngas, which can then be separated and used as a nonpolluting fuel or in a hydrogenation plant. Since the WGSR is an equilibrium, the trouble is that by increasing the amount of hydrogen in syngas, it also increases the amount of the very undesirable CO₂.

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