Oriental Renaissance: Innovative, educational, natural and social sciences
Research BIB / Index Copernicus
(E)ISSN: 2181-1784
4(8), Sep., 2024
www.oriens.uz

OIL AND GAS PETROCHEMICAL AND FISCHER-TROPSCH TECHNOLOGY

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ABSTRACT

In this article Chemicals derived from petroleum or natural gas – petrochemicals – are an essential part of today's chemical industry. Petrochemical plants produce thousands of chemical compounds. The main feedstock is natural gas, condensates (NGL) and other refinery byproducts such as naphtha, gasoil, and benzene. Petrochemical plants are divided into three main primary product groups according to their feedstock and primary petrochemical product:

Keywords: *Olefins, Aromatics, Synthesis gas (syngas), Chemical, petroleum, Fischer-Tropsch, oil.*

НЕФТЬ И ГАЗ НЕФТЕХИМИЯ И ТЕХНОЛОГИЯ ФИШЕРА-ТРОПША

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АННОТАЦИЯ

В этой статье химикаты, полученные из нефти или природного газа – нефтехимия – являются неотъемлемой частью современной химической промышленности. Нефтехимические заводы производят тысячи химических соединений. Основным сырьем является природный газ, конденсаты (ШФЛУ) и другие побочные продукты нефтепереработки, такие как нафта, газойль и бензол. Нефтехимические предприятия делятся на три основные группы первичной продукции в зависимости от используемого сырья и первичной нефтехимической продукции:

Ключевые слова: *олефины, ароматизаторы, синтетический газ (сингаз), химия, нефть, Фишер-Тропш, нефть.*

Natural gas, which is comprised primarily of methane, is one of our most abundant natural resources, both domestic and abroad. Unfortunately, many of the natural gas reservoirs are located in relatively remote areas, or offshore, and high transportation costs tend to prohibit extensive use of this potentially valuable resource. To overcome this limitation, the Department of Energy=s Federal Energy Technology Center (FETC) has developed a highly diversified research program to evaluate, promote and develop processes that convert natural gas, methane, into higher value products (*i.e.*, liquid fuels) which will offset the high transportation costs and allow use of this untapped, environmentally friendly resource.

By advancing technologies to convert unmarketable gas resources into valuable products, cooperative efforts between DOE and industry could yield the following benefits by 2010.

(1) Our domestic production of oil will be increased through the supply of 200,000 to 500,000 barrels per day of high quality liquid transportation fuel made from Alaska=s North Slope gas resources; (2) Advanced gas-to-liquids conversion technology that yields ultra clean burning diesel fuels that meet the most stringent emissions requirements, at costs below those of comparable fuels made from crude oils, will be utilized; and (3) Small-scale gas-to-liquids technology for both natural gas liquefaction and chemical conversion to higher hydrocarbon liquids will enable economic and environmentally sound usage of remote offshore oil reservoirs with associated gas, and also onshore gas reservoirs without pipeline access.

Three potential routes for the conversion of natural gas have emerged: direct, indirect and physical conversion. Direct conversion focuses on the chemical transformation of natural gas to ethane, ethylene, acetylene or methanol. Indirect conversion methods concentrate on the production of syngas (CO and H2), which is subsequently converted to liquid fuels. Physical conversion techniques center on the conversion of natural gas to liquefied natural gas (LNG). All three approaches are currently under investigation under the gas-to-liquids conversion program at FETC. In addition, the economics of gas to-liquids conversion is continually evaluated.

Fischer-Tropsch Technology

Chemistry

What is "Fischer-Tropsch" technology? Simply stated, it is a process that rearranges carbon (and hydrogen[1]) molecules. Without giving a chemistry lesson, it is important to understand something about the chemical make up of hydrocarbons in order to have a basic understanding of Fischer-Tropsch. It should come as no surprise that "hydrocarbons"-crude oil and natural gas-contain carbon (and hydrogen) and simply stated, the number of carbon atoms in each molecule determines whether or

[1] While hydrocarbons generally consist of both carbon and hydrogen atoms, the short-hand for referring to hydrocarbons is to refer to just the number of carbon atoms (C) so we will adopt that approach herein as well.

not, at room temperature, the hydrocarbon is generally in a gaseous state-natural gas-or in a liquid state-crude oil[2]. Generally, at room temperature, if there are 1 to 4 carbon atoms per molecule (C_1 to C_4), the hydrocarbon is gaseous-natural gas; if there are more carbon atoms than 4, the hydrocarbon exists in a liquid state-oil; and above 20 carbon atoms per molecule, typically the hydrocarbon exists in a solid state.

To be completely accurate, both oil, and to a much lesser extent, natural gas, have lots of other "things in them"; sulfur, heavy metals, etc. Moreover, crude oil is not a liquid with a uniform number of carbon molecules. In other words, oil is not just say C_6 or C_{10}. It is a gumbo or jumble of various molecules with different numbers of carbon (and other) atoms[3].

When one refines crude oil, what one is doing is breaking up that jumble of molecules. Of course, one must extract the "bad stuff"; the sulfur and heavy metals, but after that, the process basically consists of • separating the molecules into homogeneous batches. You can think of it as a kind of collating process where one puts all of the C_5 molecules together, all of the C_{10}s, etc. That "batching" process produces petroleum products such as naphtha and diesel. (In fact, the batches are not limited to single categories of carbon content, but rather, a range. Typically, naphtha is C_5 through C_9, Diesel is C_{10} through C_{20}. These ranges are also called "fractions" or "cuts.")

The batching is accomplished through a variety of means, the simplest of which is the application of heat, as many of the different fractions will separate at different temperatures. (It should also be noted that often, natural gas is in effect commingled with crude oil—so-called "solution gas"—and must be separated out from the oil before the oil is further refined.[4] It should also be noted that this simplest form of heating crude oil in order to cause the fractions to separate is called "distilling" and the fractions or cuts are sometimes referred to as "distillates.")

It is interesting to note that in the early days of the oil industry, simple distilling was the only known refining technique and refiners used it to "get at" the kerosene fraction in the oil which was used to replace whale oil in lamps. The remainder (of

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[2] Like many of the technical descriptions in this report, this explanation is somewhat of an oversimplification for it is not only the number of carbon atoms but, the arrangement of those, and other atoms in the hydrocarbon molecule that determine if the hydrocarbon exists in a gaseous, liquid, or solid state.

[3] Likewise, natural gas contains several distinct and different gases with distinct chemical structures such as: methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). Further, natural gas often contains sulfur, trace amounts of metals and even a light form of crude oil referred to as condensate.

[4] At this point you may be confused as we have said that natural gas can contain oil and we call that oil "condensate" and we have said that oil can contain natural gas and we call that natural gas "solution gas." What gives? The answer is the natural state of things is far more complex then we can describe in simple terms. But, both of our statements are accurate. The high-pressure stream of natural gas that comes flowing out of a well into a gathering system may contain some condensate and that condensate will get separated out merely by allowing the gas to stand still for a period of time (though more robust approaches are often used). Likewise, some amount of natural gas is found in most oil.

the fractions), they just threw away, often by burying the material. In a way, that old story encapsulates the entire technological history of the refining industry. Refiners have been on a quest, from day one, to improve technology so that they can use more and more of each barrel of oil—and throw away or sell for low prices, less and less. As we shall see later in this report, one important application of Fischer-Tropsch is nothing more than a continuation of that quest.

At this point it may also be helpful to introduce some nomenclature we will be using throughout the remainder of this report. Refiners often refer to the refined fractions as "light" or "heavy." The light fractions have less carbon atoms per molecules and are literally lighter in weight by volume such as naphtha from which gasoline is made.

Diesel is often referred to as a "middle distillate" because its number of carbons is in the middle range relative to the overall type of fractions produced in the refining process. It is also important to point out that in the "collating" or "batching" process we referred to earlier, in some cases, the fractions or cuts are viable, usable end products with no requirement for further processing or upgrading (as in the case of diesel fuel) but, most fractions do require further refining and processing steps to get to the end product (like gasoline).

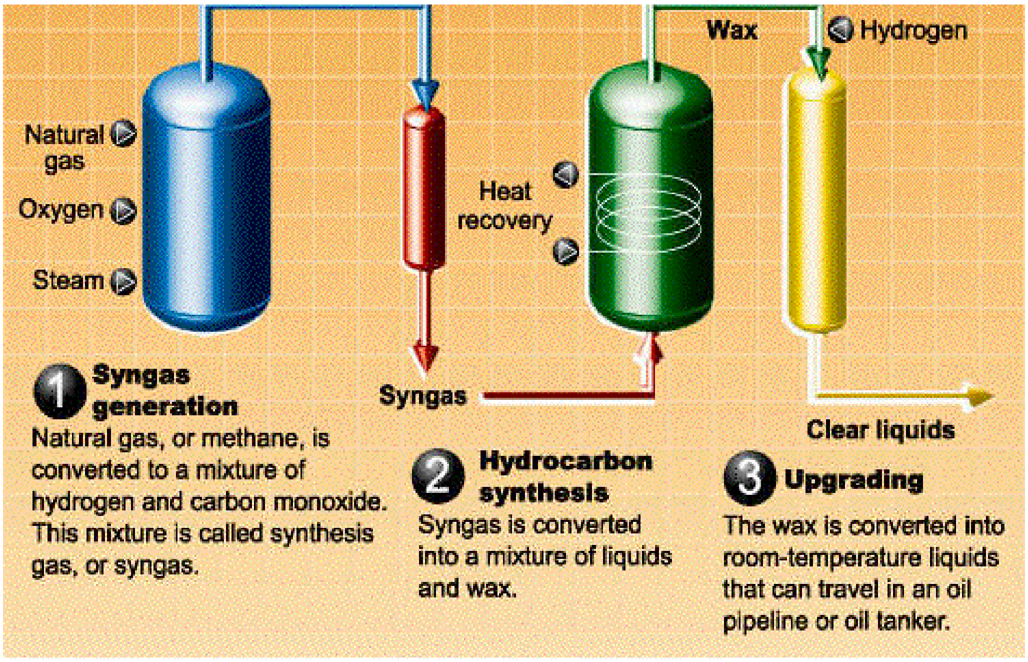
Olefins include ethylene, propylene, and butadiene. These are the main sources of plastics polyethylene, polyester, PVC), industrial chemicals and synthetic rubber.

Aromatics include benzene, toluene, and xylenes, which also are a source of plastics (polyurethane, polystyrene, acrylates, nylon), as well as synthetic detergents and dyes.

Synthesis gas (syngas) is formed by steam reforming between methane and steam to create a mixture of carbon monoxide and hydrogen. It is used to make ammonia, e.g., for fertilizer urea, and methanol as a solvent and chemical intermediary. Syngas is also feedstock for other processes such as the Fischer–Tropsch process that produces synthetic diesel.

The first step in the FT process is separating the constituent parts of natural gas (or, as mentioned, coal, or any other carbon bearing or "carbonaceous" feedstocks). These constituent parts are carbon, as previously described, and hydrogen, as previously mentioned. Separation may be accomplished in several different ways, which we will describe in greater detail later (including the various *pros* and *cons* of different approaches). This separation goes under several names including "reforming" or "gasification"[5].

Whatever approach is used, the first step in the process separates or breaks apart the bonded carbon and hydrogen molecules of natural gas (i.e., CH_4) into two separate molecules—hydrogen (H_2) and carbon monoxide (CO). (The ratio of hydrogen to carbon monoxide is a critical factor in the FT process and while not important here, we will have a lot to say about it later in this report). This mixture of H_2 and CO is called "synthesis gas" or simply "syngas."



Without getting into balancing chemical equations, in order to make syngas, we have to add something else into the mix in the syngas generation stage and that something else is oxygen which should make sense because if we start with carbon (C) and hydrogen (H_2) and we want to end up with H_2 and CO, we have to add "O" (the oxygen molecule).

It should be noted that the introduction of oxygen into the process of making syngas is a critical step and a very expensive step. In fact, according to various studies, the cost generally accounts for some 20-30% or so of the combined capital cost of the three steps depicted in the schematic on the previous page. Further, there are several different ways to introduce oxygen into the process—from air, from water (in the form of steam), from CO_2, or from a combination of one or more of these sources. *(It should be noted that Syntroleum, a leading FT technology company, introduces air directly into its syngas step as its oxygen source*[6]*)*. Later in this report, we will have a lot more to say about this introduction of oxygen in some form. It should also be noted that the generation of syngas is not **part** of the Fischer-Tropsch process, but is **essential** to it. Moreover, given the complexity of the syngas step, the many different approaches available, and the high cost, FT technology companies are very focused on this step and generally have their own proprietary, and in some cases, patented, designs. Therefore, when we talk about FT technology, the syngas step is usually considered part of the overall technology. The Fischer-Tropsch process starts when we introduce the syngas into a reactor that contains a catalyst[7]. The design of the **reactor** and the type of **catalyst** are critical to the efficacy of the overall process and again, we will cover both of these topics in depth later in this report but at this point it is important to know that two basic types of catalysts are used in Fischer-Tropsch reactors, cobalt or iron[8]. Once in the reactor, the catalyst accelerates the reaction of the syngas and the H_2 and CO gases are generally chemically altered into longer chain carbon molecules; generally longer than the C_1 to C_4 range described in the previous section. Some of these longer-chain molecules form petroleum waxes and some become middle distillate liquids (from here on in this report, we may refer from time to time to these products as "FT products" or as "synfuels"). The third and final stage in the process is to upgrade the synfuels to the exact specifications for end use[9].

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[7] A "catalyst" is a substance that facilitates or accelerates a chemical reaction without itself being consumed by that reaction.
[8] In reality, there are other catalyst materials that can be used. Moreover, "cobalt" and "iron" catalysts are really short-hand descriptions of the actual composite materials used as catalysts in Fischer-Tropsch reactions. However, for purposes of this report, we will ignore these complications as they are not essential to understanding the basic processes we are describing or the strategic implications of FT as described herein.
[9] It should be noted that in some cases, no upgrade may be necessary. For instance, some end-products may be used as feedstocks to make other products and FT diesel may be directly usable with no further upgrading.