GASOLINE:

From Unwanted By-product to Essential Fuel for the Twentieth Century

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MONOGRAPH SERIES
OF THE
NEW LIBERAL ARTS PROGRAM

The New Liberal Arts (NLA) Program of the Alfred P. Sloan Foundation has the goal of assisting in the introduction of quantitative reasoning and concepts of modern technology within liberal education. The Program is based on the conviction that college graduates should have been introduced to both areas if they are to live in the social mainstream and participate in the resolution of policy issues.

The New Liberal Arts Program has led to significant, new courses and course changes in many colleges and universities. MIT Press and McGraw-Hill are jointly publishing an NLA series of books. These monographs are planned to provide teaching/learning materials for other educational developments. A complete list of the monographs can be found on the last page of this book.

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NLA Monograph Series

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Preface

TO THE STUDENT: Both the history and the technology of gasoline are interwoven within the fabric of industrialized society in the twentieth century. As a student of the liberal arts, you need to understand the significant engineering accomplishments and to appreciate the impact of these technological achievements on our modern, global society.

At Davidson College in 1986, I first told the story of gasoline when I offered a course entitled, "From Petroleum to Penicillin", which presents petroleum, polymers/plastics, nuclear power and pharmaceuticals as significant examples of modern chemical technology. Gasoline: From Unwanted By-Product to Essential Fuel for the Twentieth Century grew out of some of the lectures given in that course. These liberal arts students had a strong interest in the technology surrounding them, and they were able to understand many scientific, social and symbolic elements of chemical technology, including gasoline, without any science or mathematics courses as prerequisites.

As a typical student of the liberal arts, you can comprehend the science, engineering, and mathematics presented in Gasoline. If you are a student of the sciences and engineering, the historical context for these advances in engineering will enrich your technological expertise. Gasoline should give to all students of technological studies new perspectives on chemical technology in our society.

TO THE PROFESSOR: Gasoline is divided into three parts: historical studies, technological discussions, and questions for students. The narrative surveys the chronological development of gasoline, beginning with the discovery of crude oil and ending with the modern catalytic cracking of petroleum to produce gasoline for the automobile. Eleven units in a series, called ChemTech, are interspersed throughout the historical story to help the student understand the technological achievements presented in the historical case studies. Students should be able to comprehend the historical and technological topics without any prior college level science and engineering courses.
You may wish to ask students to answer the questions and problems in Appendix III. Some of these questions and problems simply review topics discussed in the narrative, but others require additional study and library research to prepare satisfactory answers. Many of the references listed in Appendix I may be good beginning points for further study and for preparation of short research papers on various topics, such as those suggested in the problem set. Appendix V contains answers to the problems in Chapter 6 and Appendix III.

From my efforts to teach liberal arts students about technology, I have found that the use of visual materials is absolutely essential if you are to attract and hold their interest. Once they focus their attention on these technological topics, liberal arts students can readily learn and even surprise themselves with their degree of understanding. Appendix IV lists visual resources for use in the classroom. From the reference books and commercially available sets, I have assembled a photographic slide collection to illustrate my discussions of the people and places, the chemical processes and plants. Some of the videos are good substitutes for plant tours; others illustrate chemical reactions and properties of chemicals. The computer programs allow the student to be involved. The simple technique of "show and tell" returns many benefits to both students and professors.

TO MY BENEFACTORS: Since the Alfred P. Sloan Foundation created the New Liberal Arts Program in 1982, I have had the privilege to meet, to study with, and to learn from many colleagues in some of the finest liberal arts colleges and universities across America. To all of them, I express my appreciation for helping me to learn about the history of modern chemical technology.

To Professor David P. Billington in the Department of Civil Engineering at Princeton University, I owe a very special debt of gratitude. Because of his initial suggestions in 1982, his continuous encouragement, and his steadfast friendship, I undertook the study of the history of chemical technology, the development of the course, "From Petroleum to Penicillin," and the writing of Gasoline. His guidance and influence, as well as his special gift for presenting engineering to all students of the liberal arts, underlie all that is worthwhile in Gasoline.
Also, I wish to acknowledge with gratitude the photographic assistance of Mr. J. Wayman Williams and the financial assistance of the Alfred P. Sloan Foundation through grants made to the New Liberal Arts Programs at Davidson College and Princeton University.

Although many colleagues gave generously to assist me, I alone remain responsible for all errors and shortcomings which you may find in the following pages.

Finally, as you read Gasoline: From Unwanted By-Product to Essential Fuel for the Twentieth Century, I hope that you will find as much excitement in your studies as I have found in mine. Also, I hope that you will want to learn more about the chemical technology which permeates modern society and to discover how it can serve us and future generations in even better ways.

John Nicholas Burnett

Davidson, North Carolina
May, 1991
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INTRODUCTION

Why Is Gasoline an Important Fuel in the Twentieth Century?

GASOLINE IS BIG BUSINESS. Each day 25 million Americans spend over $300 million to pump 242 million gallons of gasoline into their cars. Each year since 1978, American automobiles and trucks have consumed between 103 and 117 billion gallons of gasoline to travel over one trillion miles at a cost in excess of $130 billion. The energy consumed by these American vehicles was 50 times greater than the combined energy output of all the electric power companies in the United States.¹

The average American uses the equivalent of over 450 gallons of gasoline per year or twice as much gasoline as the average Australian, four times as much as the average European, and ten times as much as the typical Asian.² American autos travel about half of the over two trillion miles traveled by all autos worldwide. About three of every four Americans commute to work in their private automobiles and trucks.³

During the OPEC crisis of 1973, Americans lined up at the pumps, willing to wait hours and to pay almost any price to fill their tanks with gasoline. In 1985, the average American household spent $16.73 per week on gasoline. In the summer of 1989, car drivers in Atlanta, Georgia paid $1.24 per gallon for gasoline but drivers in Caracas, Venezuela paid 14 cents a gallon; in Abidjan, Ivory Coast regular gasoline sold for $4.16 per gallon, but in Lagos, Nigeria super sold for 30 cents a gallon. In Europe, prices ranged from $3.80 in Milan, Italy to $3.03 in Lisbon, Portugal. The difference is due in part to taxes. But, with an oversupply of oil in the marketplace in 1989 and predictions of shortages in the near future, it is not easy to say what a tankful of gasoline is actually worth.⁴

Almost all items in an American’s daily life — food, clothes, shelter, etc. — were at some point moved by trucks in the process of converting natural resources into manufactured products and deliv-
ering those products to the consumer. Although trucks account for about one-fifth of the motor vehicles on the road, they travel over 330 billion miles per year (ca. 65% more miles per truck than the average auto).\textsuperscript{5}

The modern refining of crude oil into valuable products, such as gasoline, is a very complicated technological process. It employs sophisticated chemical reactors on a large scale for efficient operations and uses computers extensively to control the processes and to achieve maximum profits. These chemical processes must be operated within strict laws and regulations which are designed to protect the environment. Such was not always the case. As recently as the beginning of this century, an oil refinery was a very simple operation. It would have received little praise for its processes, equipment, and concern for the environment. A typical refinery used a few pieces of simple equipment to carry out relatively crude distillations and reactions, often under very hazardous conditions.

Refinery operations were improved because of two major events: (1) large quantities of crude oil were discovered around the world to provide a steady supply of oil to sustain large-scale refinery operations; and (2) the automobile, followed by the airplane, revolutionized transportation. These events stimulated the design of the most important process in the refining of petroleum to produce gasoline: cracking. In the cracking process, heat, pressure and catalysts are used in creative combinations to break large molecules into smaller ones having high octane ratings suitable for the synthesis of various blends of gasoline. The history of petroleum in this century is essentially the story of innovations in the methods of cracking oil.

During the nineteenth century, there was essentially no market for the gasoline produced in these early refineries. This straight-run, or naturally occurring gasoline, was distilled as a by-product in the refining of crude petroleum to produce the two major desired products: kerosene as a fuel for lamps, and lubricants for machinery. Early refiners, such as John D. Rockefeller, faced a major disposal problem in connection with this non-marketable product. The gasoline fraction from their petroleum distillation was a low boiling, volatile, flammable hydrocarbon mixture, and therefore a serious fire hazard at these first petroleum refineries. The typical solution for this problem was to dump the gasoline into adjacent
rivers and to hope that the gasoline would evaporate before it set the river on fire.

In 1876 Nicolaus Otto built the first practical internal combustion engine. Gasoline proved to be a good fuel for this new engine. Motor vehicles using these internal combustion engines appeared first in the late 1880s. At the beginning of the twentieth century, Henry Ford and Rockefeller won the competition between the gasoline-powered internal combustion engines and the electric battery-powered engines as the standard of choice for the emerging automobile. By 1910 it was clear to refinery operators such as William M. Burton at Standard Oil of Indiana that the demand for gasoline to power these new automobiles would quickly exceed the gasoline available from the simple distillation of crude oil, that the demand for kerosene would continue to drop dramatically as the illumination of cities by Thomas Edison's electric light bulbs continued to spread, and that huge profits could be made by refineries that developed processes to take advantage of this shift in the market.

Beginning with Burton's pressurized thermal cracking process, significant changes in the processing of crude oil occurred over the next fifty years and the yield of gasoline manufactured from a barrel of crude oil increased from 10 to as much as 50%. Today, depending on the seasonal variations in the demand for gasoline, between 40 and 50% of each barrel of crude oil is converted into gasoline. The balance is converted into other products, such as heating oil and petrochemicals. In 1930, 18.5 billion gallons of this "unwanted by-product" were sold. Gasoline production in the United States increased to over 70 billion gallons in 1960, to over 90 billion gallons in 1970, and production stabilized in the range of 103 to 117 billion gallons during the 1980s.

Obviously, gasoline is one of the most important chemical mixtures produced today. It is the fuel, the driving force, and the power of our modern society. In a relatively brief history, it has had pronounced, irreversible effects on the economics and politics of every country, and it has changed the way we live and interact with one another on this globe. *Gasoline* gives an historical summary of petroleum refinery operations in America: the people, their process innovations (separating mixtures by *distillation*; cracking crude oil with *heat*, *pressure*, and *catalysts*; and converting from *batch* to
continuous chemical processes), and their impacts on society at large. It includes an explanation of the modern technology of gasoline: its chemical composition, its source, its manufacture, and its use. Finally, it presents to students some questions and problems for further study as well as bibliographies of literature, video, and computer resources which might facilitate such additional study.

ENDNOTES

3. See Endnote 1.
5. See Endnote 1.
CHAPTER 1

Crude Oil:
Its Formation, Discovery, and Production

Origins of Oil

Scientists believe that the creation of the earth began more than 4.5 billion years ago as a large body of hot, gaseous matter whirled through space. During several million years, this body of matter slowly condensed and cooled.¹ A crust formed around the molten interior mass. This crust consists of a number of sections, called continental plates, which continue to drift slowly over the interior mass. When these plates collide, one plate moves up and over the other, creating immense heat and pressure. Along the edges of some plates, earthquakes occur (e.g., California’s San Andreas fault). Along other plate edges, deposits of crude oil and gas accumulate (e.g., Persian Gulf).

Over long periods of time, erosion from wind and water gradually wore down mountain ranges. Silt was carried from the mountains onto the plains and into the sea where it then began to form sedimentary beds of rock. A record of these sedimentary rocks is revealed, for example, in the Grand Canyon of Arizona. During the last eight million or so years, the Colorado River cut a canyon about one mile deep into the earth’s crust, revealing much of the earth’s history.²

Life on earth probably began during this early period of the planet’s formation. Prehistoric marine animals and plants inhabited the great inland seas covering the continents. When these animals and plants died, their remains were mixed with the silt produced by this erosion process and were deposited on the bottom of the oceans. Some beds of sediment were compacted into dense shale rocks and others became trapped in limestone and sandstone deposits. The organic matter from the marine life was transformed into complex mixtures of organic compounds which we call petroleum or crude oil. These chemical conversions were accomplished through the
action of heat, bacteria, radiation, and other processes. The terms crude oil and petroleum are frequently used interchangeably to mean both crude liquid oil and natural gas since both are almost always found together in these naturally occurring deposits.

Oil in Reservoirs

Geologists believe that oil was squeezed out of the shale beds into the more porous sandstone and limestone. Then, as the crust of the earth was warped due to the movements of these plates, the oil migrated along the rock beds until it became trapped in certain regions of the rock formations. These geological structures are called reservoirs. The oil is not in pools in the reservoirs, as water might stand in a lake on the surface of the earth. Rather, the oil fills the pores of the rock beds, as water fills the pores of a sponge. Because the oil is less dense than water, it is in the upper portion of the reservoir. Sometimes, oil reservoirs may be found very near the surface of the earth’s crust or frequently at depths from a few thousand feet to several miles below the surface.

The three principal types of reservoirs are: anticline, fault, and stratigraphic trap. The anticline is simply an underground hill, dome, or ridge line created by an uplift or fold in the rock beds. The oil migrates and becomes trapped in the top of the dome. Sheep Mountain in the Big Horn Basin of Wyoming is an example of an anticline. Rock beds were folded upward, creating a long ridge, and then eroded away to expose this anticline. A fault is a place in the earth’s crust where the rock beds have broken and moved out of position, so that different kinds of rock face each other at the break. The oil migrates through the sandstone until it reaches the break and then is trapped by the impermeable bed of shale. One type of stratigraphic trap is the buried shore line of an old ocean. The permeable bed of rock disappears at the end of the shore line. The large east Texas field is an example of a stratigraphic trap.

The amount of pore space in a reservoir is called the porosity. It ranges from 10 to 30% of the total reservoir volume in most commercial petroleum reservoirs. Part of the pore space volume is occupied by a thin film of water, called connate water, which clings to the surface of the grains of rock. The measurement of the volume of connate water is important in calculating the amount of crude oil in the reservoir. Because the connate water prevents the oil from being
adsorbed on the rock, it is also a very important factor in the physical and chemical processes employed to recover the oil. **Permeability** measures the ease with which a fluid or gas can move through the connected pore spaces in the reservoir rock. **Oil saturation** is the percent of pore space occupied by oil in the sand grains. A fully saturated reservoir yields a high percentage of its oil. If a reservoir is only partially saturated or its saturation level is reduced due to production, the remaining oil becomes increasingly more difficult to recover. So, almost all of the wells which have been abandoned as unproductive still contain over fifty per cent of the oil originally present in the reservoir.

A core, or sample, of the reservoir rock from the Pembina oil field in Canada is an example of very tight sandstone with small sand grains. It has a low porosity, extremely low permeability, and most wells in this field would not produce oil without **artificial lift** or modern **secondary recovery methods** (See ChemTech 2). By contrast, a core from the Ghawar oil field in Saudi Arabia, one of the great fields of the Middle East, is an example of a limestone formation containing large holes and fractures (high porosity) and high saturation. Because many of these holes are connected in limestone deposits, this reservoir also has a very high permeability.

These processes of erosion and sedimentation have occurred over all parts of the earth, so every continent has reservoirs of crude oil formed in the basins of these ancient seas. Maracaibo Basin in Venezuela is surrounded on three sides by ranges of the Andes Mountains, with Lake Maracaibo at its center. It is one of the great oil producing regions of the world, with many billions of barrels of oil beneath the lake. Other examples include: the Middle Magdalena Basin in Colombia; the Texas Gulf coast; Prudhoe Bay, Alaska; and the Persian Gulf of Saudi Arabia. Within a basin, geologists search for oil by looking first at the exposed subsurfaces such as creek beds, railroad cuts, and canyons to get clues about the possibility of oil reservoirs beneath the surface. From seismic recordings of shock waves produced by explosions or dropping heavy weights, contour maps of underground structures such as a round dome or a long ridge can be drawn indicating possible formations which might favor the collections of oil in reservoirs. More modern techniques involve measuring the magnetic and electrical properties of the rock layers and the use of surveys from satellites orbiting the earth.
Col. Edwin Drake began, in 1859, the modern practice of drilling for oil using a rig which is composed of a tall derrick (essential for moving the long strings of pipe in and out of a well) and associated heavy engines, pumps, and gears. The name derrick comes from the last name (no first name) of a famous English hangman of the 1600s.

Today drilling rigs used on land can cost $2–10 million; drilling rigs used at sea can cost over $200 million. Howard R. Hughes developed the cone-shaped roller bit with teeth to cut into hard stone and founded the Hughes Tool Company in Texas. Some modern drill bits combine three of the Hughes-type cones; others are shaped like a fish tail. The exploratory wells are called wildcat wells because in the early days of the Pennsylvania oil exploration the drilling crews heard wildcats howling in the surrounding hills at night.

Drilling mud is circulated through the pipes to carry away the cuttings as the bit drills the well. The mud, a mixture of water and clay, also lubricates the drill bit. When the bit penetrates the reservoir, it may encounter several thousand pounds of pressure, and the weight of the column of drilling mud helps to control this natural pressure of the reservoir. Adding high density minerals to the mud can create a pressure greater than the oil reservoir pressure and prevent a costly blowout. About 85% of the wildcat wells are dry. And this lack of production from such a high percent-
age of the wells drilled drives up the cost of producing oil and gas.

When oil is struck, the well must then be "completed" to begin production of oil. Using electrical, sound, and radiation measurements, the well is "logged" by recording and evaluating information about the various layers of rock which have been penetrated. Core analysis also reveals the porosity, permeability, and oil and water saturation of the rock. The productivity of an oil formation can be estimated by replacing the drill bit with a screen device which measures the flow of oil into the end of the drill stem.

If the well is placed in production, the well bore is encased in cement, and an electrical device perforates the cement in the region of the reservoir. Sometimes hydraulic fracturing, using sand or water under very high pressure, will stimulate the flow of oil or gas from the formation.

When the flow begins at a satisfactory rate, the derrick is removed and a system of valves and gauges, called a "Christmas Tree," is installed to regulate the flow and control the pressure. If the well oil does not flow, pumps are installed on the surface and inside the well. In addition, a gas (such as steam, air, or nitrogen) may be circulated through the well to increase the flow rate. This technique is called artificial lift (See ChemTech 2). Nearby, tanks are used to separate the oil from the natural gas and water and to store the oil. The separated crude oil then moves by pipeline to the refineries.
Early Uses of Oil

Some oil has always flowed to the surface of the globe in natural seepages and springs. Lightning probably ignited some of the oil in these ancient springs. In the Middle East, a cult of fire worship developed around these "eternal" flames of oil and gas. People of the early Mediterranean civilizations dug shallow pits around the seepages to let the oil accumulate and then used the sticky pitch as sealing materials for ships and as mortar to bind bricks and stones in buildings. Pharaoh's daughter found Moses floating in a basket made waterproof by rubbing the reeds with pitch. The Book of Genesis tells us that Noah's ark, made of "gopher wood or timber planks," was waterproofed "within and without" with pitch. Nebuchadnezzar paved the roads of Babylon and the terraces of his hanging gardens with crude asphalt. Egyptians, Chinese, and American Indians drank petroleum as a medicine and used it to cover wounds. Although difficult to obtain and very expensive in these early times, it was burned in the lamps of the wealthy and used on the tips of fire arrows shot over the walls of besieged ancient cities.

This ancient oil industry thrived for almost three thousand years, beginning before 3000 B.C. in Hit, Mesopotamia. The Sumerians, Assyrians, and Babylonians used asphaltic bitumen and rock for their industrial arts: road construction, mastic for buildings, paints, and waterproofing ships. When mixed with sulfur, it was used for fumigation and for the treatment of sores on the hands and feet. When mixed with oil, it was prescribed for inflamed eyes and other ailments. The crude oil was mixed into beer and used as magic to keep out evil spirits. In the fine arts, bitumen was a favorite cement for mosaic and inlaid art work.

The early bitumen industry rapidly declined and lost its identity after the Persian conquest of the Neo-Babylonian kingdom about 600 B.C. The Persians used bituminous mastic only for caulking ships. For construction, the Romans used quarried stone and pozzolana, a loosely compacted rock from ancient volcanoes. Because pozzolana formed an excellent mortar and hydraulic cement when mixed with lime and because of the abundance of marble, cedars of Lebanon, and cedar-oil pitch, the Romans did not need the bituminous technology. The Romans, however, did inherit from the Greeks observations on the natural occurrence of petroleum, gas, and asphaltic rocks and also a vague tradition of random uses of bituminous products. The
ancient Greeks failed to transmit the technology of ancient bitumen through the Romans to Western Europe.

As Western Europe neglected the technology of the ancient bitumen industry, Arabs began to build on this ancient technology early in the Christian era. Using the knowledge of chemistry and alchemy accumulated among the Alexandrian Greeks, Persians and Syrians, they turned sharply away from the Babylonian emphasis on asphaltic materials to crude petroleum and the distillation (or separation) of its light fractions (low boiling compounds) into illuminants. These advances in distillation technology inspired searches for new deposits of petroleum and asphalt in seepages and shallow, man-made trenches. Improved distillation techniques contributed to the burning of Cairo in 1077 because about 1,200 barrels of stored naphtha (a kerosene fraction) fueled the fire.

As a result of the Arabic infiltration of Spain, a fairly mature industrial distillation technology was available in Western Europe in the twelfth century. Marco Polo witnessed streams of Russians collecting the oil from springs during his 1272 trip to the Baku region, and returning Crusaders added to Western knowledge of petroleum. In 1300, the retort (a vessel for distilling) was introduced into Western Europe from the East, and Thaddeus Alderotti of Florence reported using the tubular condenser in the distillation of wine. This pioneer invention paved the way for the modern method of cooling and condensing the vapors outside (rather than inside) the still-head (top part of the retort).

Thus, the basic distillation technology, which is essential to achieve the full potential and value of crude petroleum, was available in the fourteenth century. But, five hundred years passed before the discovery of large deposits of oil in America and the excitement of science and technology during the Industrial Revolution in western Europe and America initiated the modern exploitation of this natural resource.

Oil in the Americas

In 1526, Oviedo, the Spanish explorer, reported the discovery of asphalt deposits in Cuba, and Havana soon acquired the nickname of “Carine” because all ships were careened (laid on their sides), overhauled, and coated with pitch. In his journal on 22 March 1595, Sir Walter Raleigh recorded that the stone pitch from Pitch Lake, Trinidad,
was excellent for waterproofing his ship because it did not melt in the sun as did the pitch from Norway. Two French missionaries, drafting their map in 1670, located an oil spring near what later became Cuba, New York. In 1755 Lewis Evans, the first American to put oil on a published map, called the site, Petroleum. Later it was called Oil City, Pennsylvania. George Washington wrote in his will that he had acquired a tract of land in western Pennsylvania because of “a bituminous spring which contains, of so inflammable a nature as to burn as freely as spirits, and is nearly as difficult to extinguish.”

As the focus of petroleum moved from France and Britain to the Colonies, the attention shifted from observation of occurrences of oil to methods of collection and use. Benjamin Franklin, who embodied this new scientific enlightenment, began in 1757 a study of oil culminating in his report to the Royal Society in London on 2 June 1774. His studies, although carried out with whale oil as the test material, anticipated by 100 years the use of oil on the waters of harbors to aid in the landings of ships in rough seas and also in the manufacture of bombs. In 1882 pipes were installed in Aberdeen Harbor to supply oil to calm the waves. Gordon’s oil-shells, shot at Montrose, Scotland on 6 April 1885, were effective in calming the waves. Hence, the expression “to pour oil on troubled waters.”

Eighteenth century missionaries and explorers reported that Indians dipped oil from springs, boiled out the water and used the oil as an ointment for toothaches, headaches, swellings, rheumatism, and sprains. It was also taken internally and used as fuel for lamps. Just as they tried the tobacco used by the Indians, American settlers tried and began to believe in the medicinal properties of this oil which was sometimes called rock oil. British Oil was patented in 1742 by Michael and Thomas Betton and, by the beginning of the nineteenth century, was widely distributed in England and America as a remedy for muscular ailments. Seneca Oil (from the Seneca Indians and Seneca Lake in New York) was promoted as an alternative to British Oil during the first half of the nineteenth century. Around 1825 on the Hughes River in Wirt County, West Virginia, petroleum was collected in sand pits about twelve feet deep. This oil was used for burns and as a liniment for horses. By 1843 as much as 20–30 gallons of oil could be gathered in two or three days from Oil Creek, Pennsylvania, and the price dropped from $16 a gallon in 1800 to about a dollar per gallon.
Salt Well Drilling

Up to this time shallow digging and oil springs were supplying the demand for medicinal oil. Drilling for oil has its origins in the salt well drilling in western Virginia. Salt was in great demand: 500 pounds were required to preserve a quarter-side of beef. Great quantities were required for preserving hides to make leather items. In 1806 the Ruffner brothers began drilling on their farm at the junction of Campbell’s Creek and the Great Kanawha River (now part of West Virginia) at the site of a large salt lick and a salt water spring. After overcoming drilling obstacles and developing a technique to bring in the brine (or salt water) well, it was contaminated with oil.

Their drilling successes, however, caused a rush into the area. By the 1820s, brine wells reached a depth of 2,000 feet. Many of these wells had crude petroleum as an unwelcome by-product. In the late 1830s, promoters in Burkesville, Kentucky used a “ruined” salt well as the source of thousands of barrels of oil for their American Medical Oil Company. In the 1840s, several hundred thousand bottles were sold in America and Europe.

Among the pioneers in the drilling for salt in Pennsylvania were Samuel Kier and his father, Thomas. They employed Joseph Doty, Sr., a veteran salt well driller from Kanawha. After striking brine at 465 feet, unwanted petroleum began to appear. For a time they simply dumped the unwanted petroleum into the Pennsylvania Canal. During the illness of his wife, Samuel Kier noticed that the American Medical Oil from Kentucky prescribed by his wife’s physician looked and smelled like the crude oil from his well. In 1849, he opened a business in Pittsburgh for the bottling and selling of his oil. He put peddlers on the road in decorated wagons and distributed handbills in the form of bank notes which made bold, unsubstantiated claims: three dosages a day internally and the lame might walk, the blind see. External applications would eliminate rheumatism, gout, and neuralgia. Many testified for its ability to cure cholera morbus, coughs, toothaches, corns, piles, urinary disorders, indigestion, and liver complaints. It gained support from many physicians. Samuel Kier received national notice from his huckstering, but not much profit because his sales distribution system and advertising schemes were too expensive.
A Growing Demand for Lamp Oils

Until the beginning of the nineteenth century, illumination in America was almost as primitive as it had been in ancient Rome or Greece. In the first half of the nineteenth century, the principal sources of lighting were tallow candles and lamps fed by whale oil. In the United States, whaling was a major industry both for the home market and for the lucrative export markets. Excessive hunting was, however, beginning to deplete the whale population. At the same time, a small amount of lamp oil was being produced from petroleum. Crude oil skimmed from ponds was distilled (See ChemTech 3) by about fifty small refineries in America to make a crude version of kerosene. Similar refineries were built in Rumania, Southern Russia, and other parts of the world where small surface supplies of petroleum were found. But in England coal was distilled to produce artificial gas for illumination. The process also produced a liquid, called coal oil, which was used as a fuel for lamps. In Scotland, oil shale was roasted to extract a thick liquid oil product which was then distilled to produce lubricating oils for machinery and kerosene for lamps.

The growing demand for lamp oil created strong incentives for entrepreneurs to produce more, but it was not until the 1850s that anyone thought of drilling for oil to find the sources of these seepages. Dr. Francis Beattie Brewer, a medical graduate of Dartmouth College, provided the initial momentum for the first oil well in America. He returned in 1851 to the family lumber firm of Brewer, Watson & Company in Titusville, and spent considerable time examining an oil spring on the company property. From his medical studies he had a continuing interest in the oil as a medicine. On 4 July 1853 the firm leased the spring to J. D. Angier of Titusville for five years. He was to gather the oil and divide the profits equally after deducting expenses. Next fall, while visiting friends and relatives in New Hanover, New Hampshire, Brewer took along a bottle of his oil to show his uncle, a professor of surgery and obstetrics at Dartmouth. The bottle passed to Professor O. P. Hubbard in the chemistry department, who predicted that it was valuable but would never become an article of commerce because of limited quantities.

A few weeks later the bottle came to the attention of George H. Bissell, a young New York lawyer, who was visiting Dartmouth, his alma mater. At this time, Bissell and some of his colleagues were
thinking about the possibility of distilling coal (similar to distilling the British coal oil) to produce a fuel for lamps. Petroleum was used in a very limited way to produce a fuel for illumination because there was no reliable commercial supply available in large quantities to serve the major populated cities such as New York. But, because of the similarities between coal oil and petroleum, Bissell probably guessed that a good illuminant might be produced from crude petroleum rather than coal. On the other hand, Bissell might have seen (through one of his legal contacts) the 1853 prospectus for Dr. Abraham Gesner’s North American Kerosene Company, which planned to produce kerosene from petroleum.\textsuperscript{10}

In any event, Bissell and his partner, J. G. Eveleth, made an agreement with Dr. Brewer to purchase the 100 acre Hibbard farm and to lease oil rights on 12,000 acres of Brewer, Watson & Co. timber land for $5,000. Because Kier’s popular handbills proclaimed his oil “discovered in 1848 in boring for salt water near the bank of the Allegheny River about four hundred feet below the Earth’s surface, pumped up with salt water,” Bissell wanted to look — not for medicinal oil — but for lamp oil in Pennsylvania. With financial backing from James M. Townsend, President of the City Savings Bank in New Haven, Connecticut, a group of investors formed the Pennsylvania Rock Oil Company on 30 December 1854.\textsuperscript{10}

The new company employed Benjamin Silliman, Jr., a professor of chemistry at Yale, to analyze samples of the oil and prepare a report. His father, Benjamin Sr., occupied the first chair in chemistry at Yale (1803) and performed the first distillation of oil in America (1833). Benjamin Jr. completed his report in April 1855, but he refused to release it until his bill of $526.08 was paid. Upon receiving the report, the financiers acted quickly — not because of any of Silliman’s chemical experimental results — but because of Silliman’s very optimistic conclusions that 50% of the crude oil could be distilled into lamp fuel and 90% of the crude would yield commercial products. By accident, Silliman’s report anticipated the possibility of cracking the petroleum as a result of the heating during the distillation process (See ChemTech 7). Because of unfavorable New York laws which held the stockholders liable for the debts of the company, Bissell reincorporated in Connecticut and sold more stock to raise capital. On 25 June 1855, the company was capitalized at $300,000 with the New Haven capitalists owning two-thirds. Unfortunately for Bissell
and Eveleth, several of the New Haven capitalists had paid for their shares with worthless stock and the new company quickly ran out of money. Townsend came to the rescue.

The First Oil Well in America

Townsend wanted someone to go to Titusville to begin the explorations for oil now that he was providing the needed new cash for the company. Edwin L. Drake had been residing at the Tontine Hotel in New Haven with his daughter since the death of his first wife in 1854. In the summer of 1857, he was recovering from an illness which caused his retirement after eight years as a conductor on the New York and New Haven Railroad. Drake had no experience in the oil business, but he was available and would be relatively inexpensive to employ since he had a railroad pass. In December 1857 at the age of 38, Drake made the trip to Titusville. Bissell wrote to Drake as "Colonel" Drake to impress the local folks in Titusville, and the title of Colonel stuck with Drake for the rest of his life. Because of favorable reports from Drake, appropriate leases were obtained, and Townsend with the New Haven group formed the Seneca Oil Company of Connecticut as the successor to the Pennsylvania Rock Oil Company and appointed Drake as the general agent.

Drake moved his family to Titusville in May 1858 and began oil recovery operations. At first Drake reactivated the old machinery of Angier and tried the old methods of accumulating the oil by enlarging the pits and gathering it through a system of baffle boards which he designed. He was so discouraged by the techniques, by the heavy spring rains, and by striking water in the excavations that he decided to try drilling.

Drake journeyed 100 miles toward Pittsburgh into the salt drilling country to find a temperate salt driller. Thinking that he had hired a driller, he returned to Titusville and designed and constructed an engine house for a six horsepower Long John stationary engine with a tubular boiler to power the drilling rig.

Using lumber from Brewer, Watson & Co., he designed and built a derrick in which to swing the drilling tools. It was 12 feet square at the bottom and tapered to 3 feet square at a height of 30 feet. Two dozen volunteers helped to raise the derrick from its horizontal to an upright position. Everything was now ready for the salt driller. Since no driller came, Drake suspended operations for the winter.
In April of 1859, Drake again went looking for a driller. In Tarentum, he found William A. Smith, both a driller and a blacksmith with experience making drilling tools. Earlier, Smith had made drill bits and salt pans for Samuel Kier. With $30.80 worth of iron from Drake, Smith made the drilling tools in his blacksmith shop. In May 1859, Drake sent a wagon to bring Smith, his son and daughter, and the new tools to Titusville to begin drilling at last. Drake's men had
already begun digging a hole and cribbing it with timber, the standard method for salt wells. Water kept flowing into the hole, even faster than a pump devised by Smith could carry it out. So Drake proposed that they stop the cribbing process at the current 16 foot level and, using a white oak battering ram, drive an iron pipe through the clay to rock. This method was successful to a depth of 32 feet, at which point Smith shifted to steam-powered drilling at a rate of 3 feet per day. By late August, after working seven days a week, Uncle "Billy" Smith had only a mud hole to show for his summer’s work. On Sunday, 28 August 1859, he went out to the well for a routine inspection. He noticed that the workmen had reached a depth of 69 feet the previous night and that the drill had fallen another 6 inches into a crevice. As Billy looked carefully into the pipe, he noticed a dark film floating on the surface of the water a few feet below the level of the derrick floor. Billy and his son began to collect the oil in whatever buckets they could find. Drake arrived the next morning and began to help with the collection of oil by attaching an ordinary hand pump to the walking beam. In the excitement of striking oil and faced with the immediate problems of storing so much oil, no one thought to gauge the well flow precisely. It has been estimated that this first oil well in America produced about 8 to 10 gallons a day.

Unaware of these results, Townsend and his financial partners in Connecticut decided about the middle of August that $2,347 was all that they could afford for a mud hole. They mailed Drake their final check with instructions to pay all outstanding obligations and close down the drilling operation. Fortunately, the mail moved slowly on the twice weekly stage from Erie to Titusville, and Townsend’s letter did not arrive until a few days after the oil strike.

Drake’s Accomplishments

Apparently, Drake did not appreciate the significance of his accomplishment; he simply carried out the job he was employed to do with great perseverance. As a driller he was an amateur. It took him two years to drill 69.5 feet through clay and rock; whereas, the Kanawha River drillers could bore through 1,000 feet of solid rock in six to eight months. His peak rate of 3 feet per day was only half the Kanawha rate ten years earlier. While others scrambled to lease drilling lands, Drake worked on improving the equipment for his first well. On 7 October 1859, his storage tanks and derrick burned to the ground. In the following months, he rejected all offers to lease or purchase
more land to expand his prospecting for oil. In June 1860, he was elected Justice of the Peace in Titusville and became a local oil buyer for Schieffelin Brothers of New York City. Three years later, he used his savings of $15,000–20,000 to become a partner in a Wall Street oil brokerage house. By 1866 he had lost all his money, and he spent the rest of his life in ill health, poverty, and obscurity. The State of Pennsylvania awarded him a pension of $1,500 in 1873, and he died in 1880.

In 1901 Henry H. Rogers, one of John D. Rockefeller’s major partners, spent $100,000 to build a monument to Colonel Edwin L. Drake in the Titusville Cemetery. On 2 September 1902, Col. Drake’s remains were interred during special dedication ceremonies. The inscription reads:

Col. E. L. Drake,  
born at Greenville, NY, March 29 MDCCCXIX,  
died at Bethlehem, PA, November 8 MDCCCLXXX,  
founder of the petroleum industry, friend of man,  
called by circumstances to the solution  
of a great mining problem.

He triumphantly vindicated American skill and  
and this spot laid the foundation of an industry  
that has enriched the state, benefitted mankind,  
stimulated the mechanical arts,  
enlarged the pharmacopoeia,  
and has attained worldwide proportions.

He sought for himself not wealth nor social distinction,  
content to let others follow where he led.  
At the threshold of his fame,  
he retired to end his days in quieter pursuits.

His highest ambition was the successful accomplishment  
of his task.  
His noble victory, the conquest of the rock,  
bequeathing to posterity  
the fruits of his labor and of his industry.

His last days oppressed by ills, to want no stranger,  
he died in comparative obscurity.  
This monument is erected by Henry H. Rogers  
in grateful recognition and remembrance.

Drake was the first person to demonstrate that one could drill for petroleum and produce this raw material in quantities adequate to sustain the development of a new industry — first as a source of illumination, later as a source of fuels for new forms of transportation, and finally as a source of petrochemicals for plastics and pharmaceuticals. Regardless of his shortcomings as a driller, businessman, or entrepreneur, his efforts removed the major barrier to the development of this new petroleum industry.
In primary production (or recovery), three types of drive mechanisms can operate. Water under the oil in the reservoir will displace the oil and push it to the wellbore. Second, if a gas cap exists above the oil, then its expansion will also drive oil up the wellbore. Third, dissolved gas will come out of the oil as production proceeds, and the expansion of such gas will also drive oil up the wellbore. The water drive mechanism is the most effective in bringing oil to the surface, and the dissolved gas mechanism is the least effective of these naturally occurring production techniques.

If these natural forces are not used properly, much of the oil will be wasted — left in an essentially unrecoverable state within the reservoir. Production may be high for a short period of time while the well operates as a gusher, but the reservoir pressure will be dissipated rapidly. The production rate will drop correspondingly, and as little as 15-20% of the oil may be recovered. Many processes have been developed to supplement these three natural production forces and increase the recovery of oil.

Waterflooding, or pumping water into selected wells, will increase the production from nearby wells as the water pushes oil to other wellbores in the same reservoir field. Various gases can be pumped into selected wells to enhance the production at other wells. Sometimes the natural gas which comes up the well with the oil is recycled back into the reservoir to increase the pressure. These secondary production (or recovery) methods, waterflooding and gas injection, may only yield about one-third of the available oil.

To increase production even more, enhanced recovery methods have been developed. Miscible liquids and gases are injected into the reservoir to act as detergents, “washing” the oil from the rocks. Injected carbon dioxide gas will dissolve in the oil and reduce its viscosity. The pressure of the carbon dioxide also helps to move the oil to the surface. Two thermal methods can be used to force more oil to the surface: steam can be injected into reservoirs containing very thick crude oil or a fire can be started in the well and fed by injected air and some of the oil. In both cases, the generated pressure and the reduced viscosity due to the elevated temperature will increase the yield of oil from the reservoir. See Figure 1-2.
More than 40% of the domestic oil production in the United States comes from fields using combinations of these various injection processes. Natural gas is produced in much the same way as crude oil, but it does require a different storage and transportation system. Gas is also transported from the fields to market in large pipelines.

The production of oil and gas has changed the source of energy for work in the last 100 years. There has been a dramatic decline in the dependence on the work from horses and man as the fuel from petroleum powered more and more machines in the period 1850–1959 (see Figure 1-3). Oil production increased ex-
ponentially during the period 1910–1967 (See Figure 1-4). In the last ten years, production of oil decreased in the OPEC countries, increased from the North Sea fields and Mexico, but remained about the same in the USSR and also in USA because of the production from the Alaskan North Slope fields (see FIG.1-5). Since 1859, when Colonel Drake drilled the first oil well in America, over 460 billion barrels of oil have been discovered and by 1980, 121 billion barrels had been produced. At least another 27 billion barrels are recoverable with present technology, giving an overall production efficiency of 32%. Perhaps another 46 billion barrels of oil will be recovered from future discoveries according to a US Geological Survey estimate. In 1986, crude oil reserves (in billion barrels) were: 27 in the USA, 49 in Mexico, 63 in the USSR, and 398 in the Middle East.
Predicting future worldwide energy demand is as uncertain as predicting future oil discoveries. The world market depends on the price and supply of oil as well as the price and supply of alternate sources of energy and the willingness to conserve energy. The search for new oil fields in the Arctic, the North Sea, the Far East, and other areas of the world must be tempered by the need to preserve the natural ecology of these remote areas. When the search leads into populated areas, the environmental concerns take on new dimensions.
Modern Production of Crude Oil

FIG. 1-5 Oil Production from major countries in 1979 and 1986

FIG. 1-6 Worldwide consumption of oil

FIGS. 1-5 and 1-6 adapted from data in TIME, 14 April 1986, p. 65 and Petroleum Intelligence Weekly, 1986
ENDNOTES


3. Ibid., pp. 37-46.

4. Ibid., pp. 49-60.


6. "Oil from the Earth."


CHAPTER 2

John D. Rockefeller Creates Standard Oil

The Rockefeller Family

John Davison Rockefeller was born on 8 July 1839 in the village of Richford, New York, 125 miles west of New York City.1 His great-grandfather, Johann Peter Rockefeller, emigrated from Sagendorf, Germany and settled his family in Somerville, New Jersey in 1722. His father, William Avery, grew up on farms in the lake region of New York. When William married Eliza Davison, the daughter of a prosperous Cayuga County farmer of Scottish decent, he purchased a farm in Richford. Eliza was spirited and slender, red-haired and blue-eyed, devoutly religious and straitlaced.2 She was a disciplinarian who believed in hard work, thrift, and austerity. She had little formal education but a great amount of common sense. To her son, John D., she transmitted a deep piety, a strong will, and a remarkable serenity.

William was opposite in character and personality. He was tall and muscular, with chestnut hair, expressive blue eyes, and a beguiling smile.3 He was filled with energy, an adventurous spirit, and an ostentatious temperament. He was the center of every gathering which he filled with talking, singing, or merrymaking. Lacking moral scruples, he did exactly as he pleased. He left the farm management to a hired man because he wanted to be away from home for extended periods. At times he was a trader in commodities such as salt and timber. Frequently, he returned from his mysterious trips with lots of money and expensive presents.

On 23 July 1849, William was charged by a hired girl in the Rockefeller household with rape.4 Because of his absence from home at the time of the accusation, the district attorney never endorsed the indictment and the case was never brought to trial. In absentia, William sold the Moravia farm in 1850 and moved the family to Oswego, New York for three years and then to Cleveland, Ohio. He advertised in the Cleveland directory as "Dr. William A. Rockefeller,
the Celebrated Cancer Specialist," an herbal doctor selling cancer treatments and medicines.\textsuperscript{5} William's character and activities are especially important because from the age of 10, John D. shouldered heavy responsibilities in the family. As the eldest son, Eliza relied increasingly on John D. for help with raising the younger children and for comfort in William's frequent long periods away from the home.

**Rockefeller, the Bookkeeper**

Upon graduation from high school at the age of 16 in 1855, John D. took a job as an assistant bookkeeper with Hewitt and Tuttle, a Cleveland firm specializing in the brokerage and shipment of produce.\textsuperscript{6} He applied himself to the business, utilizing many of the skills and traits acquired at home from his mother. Three years later he decided to start his own business. He and his partner formed the firm of Clark and Rockefeller and began operations as produce merchants in March 1859.\textsuperscript{7} From the beginning they were a financial success, as a result of increased orders and prices due to the Civil War. Both men were moderately wealthy by the end of the Civil War. Late in 1862, Samuel Andrews, an employee of a local refinery, asked Clark and Rockefeller to finance his proposal for a new refinery. They formed
a new partnership, Clark, Andrews and Company in 1863 and began operating the Excelsior Works. Andrews was in charge of the works and Clark's two younger brothers handled purchases and sales.

Although it started as a sideline investment for Rockefeller, he became increasingly attracted to the refining business as he saw opportunities to use his management skills in a new industry with a good future. He began to encourage Andrews to improve their refining methods and to cut costs so that by 1865 they had one of the best equipped and operated refineries in Cleveland. As the War was drawing to a close, Rockefeller decided to get out of the produce business completely and devote his full attention to refining. He was not impressed with Clark's brothers, and he proposed that they auction the oil properties between themselves with the buyer taking the refinery and the other getting the commission business.

In February 1865, Rockefeller outbid Clark and bought the refinery for $72,500. Clark, Andrews and Company was dissolved and the new firm of Rockefeller and Andrews began business within a few days. In 1866, he hired Andrews' brother to go into the Pennsylvania region to purchase oil. John D. also hired his younger brother, William Rockefeller, to help with another new firm, Rockefeller and Company, which began by building another refinery in Cleveland. Within months William was sent to New York City to set up an office for export sales. The next year John D. persuaded Henry M. Flagler, a grain and produce merchant, to take an active role in the management of a new firm, Rockefeller, Andrews and Flagler. Stephen Harkness, Flagler's father-in-law, made a fortune in the California gold rush and served as a silent financial backer for Rockefeller, Andrews and Flagler.

**Rockefeller Forms Standard Oil**

Rockefeller's partnerships continued to prosper. In January 1870, the Standard Oil Company of Ohio was formed to consolidate all of his partnerships and capitalized at $1 million. Its 10,000 shares were divided as follows: John D. Rockefeller, President, 2,667 shares; William Rockefeller, Vice President, 1,333 shares; Flagler, Secretary, (1,333 shares); Andrews, Superintendent, (1,333) shares; Harkness, silent partner, (1,334 shares); O. J. Jennings, William's brother-in-law, (1,000 shares); and the firm of Rockefeller, Andrews and Company, (1,000 shares). Seven years after he entered the
Distillation is one of the most important unit operations in a chemical process because it can separate out of a complex liquid mixture one or more chemicals, called fractions, by heating the liquid mixture to vaporize some of the lower boiling chemicals from the liquid mixture. Then, some of the vapor is removed from the system and condensed to form a new liquid (a “fraction” of the original mixture). Distillation can only separate a mixture of chemicals if the composition of the liquid phase is different from the vapor phase. If this were not the case, the liquid formed in the condensation step would be identical to the original liquid, and therefore no separation of the chemical mixture into its components would take place.

As heat is applied to the liquid in the distillation process, the lower boiling chemicals absorb the energy and small bubbles of gas form in the liquid. As the temperature increases, some of these bubbles begin to escape from the surface of the liquid. The temperature levels off as all of the heat goes into vaporizing the low boiling chemicals and thermal equilibrium is established. In this dynamic equilibrium process, liquid molecules are vaporizing and vapor molecules are condensing back to a liquid at the surface of the liquid. At this stage in the distillation process, some of the vapor is removed and condensed back to a liquid in another vessel.

Figure 2-2 shows a schematic diagram of a simple distillation process. The temperature of the condenser is lower than the boiling point temperature and liquid forms in the collection vessel. This distillation process can be repeated on the newly formed liquid. With each repetition, the degree of separation improves. Theoretically, one could repeat this process an infinite number of times and obtain an infinitely small amount of 100% pure condensate and leave behind an infinitesimal amount of 100% pure liquid in the original distillation vessel. In practice, the percent purity required by the use of the product, the cost of constructing the distillation tower, and the cost of operating the distillation process all limit the number of steps (or plates) in the evaporation/condensation sequence.

In a chemical plant, these distillation columns are frequently called fractionating columns because they divide the original mixture containing many chemicals into components, or fractions, containing fewer chemicals of higher purity. These columns or cylinders, which can be several hundred feet tall, contain a series of plates, or trays, for contacting the
FIG. 2-2 Schematic diagram for the simple distillation, condensation, and collection of liquid.

Heat, Q, is applied to liquid, A, causing vapors, B, to form at the equilibrium boiling temperature, $T_{BP}$.

With the condenser temperature, $T_{CON}$, less than $T_{BP}$, vapors, B, condense into new liquid, C.

cont >>>>
liquid with the vapor so that equilibrium between the two phases can be reached very rapidly.

Figure 2-3 shows a diagram of a continuous fractionating column. Starting material, such as crude oil, flows into the middle plate. Each horizontal line in the column represents a separation stage (or plate) in the distillation process. The group of plates above the feed plate in the fractionating column is called the **rectifying** section of the column. Those plates below the feed tray form the part of the column called the **stripping** section. Liquid flows over each plate and through a down spout to the next lower plate. Vapors rise up through bubble caps to the next plate and equilibrate with the liquid on the plate. No liquid passes through bubble caps to the next lower plate.

Heat is supplied to the bottom of the column. The lighter boiling chemicals vaporize and form a liquid/vapor equilibrium mixture. As more heat is added, more vapor forms and rises up through the bubble caps to the first plate. A liquid/vapor equilibrium forms as some of the vapor condenses and transfers some of the heat from the lower plate to this plate. The new temperature is less than the temperature of the lower plate liquid/vapor equilibrium. The rising vapors transfer a decreasing amount of heat to each higher plate in the column. As a result, the equilibrium temperature decreases with increasing height of the column, and chemicals with lower boiling points move up the column while chemicals with higher boiling points move down the column.

Chemicals begin to segregate by boiling point ranges as the distillation process continues. Removal of liquid from the individual plates yields fractions of the original mixture with increased concentrations of chemicals within a narrower boiling point range. Adding more plates increases the degree of separation, or the number of fractions, by decreasing the boiling point range of each fraction. "Purer" fractions are produced, but at greater cost. Vapor rising from the top plate goes into a condenser, and part of the newly formed liquid is removed as the net **overhead** (or distillate) stream. But part of the condensed liquid returns to the top of the column as the **reflux** stream.

The reflux ratio is the amount of liquid returned to the column divided by the total amount removed from the fractionating column. This recycle stream completes the sequence of evaporation and condensation steps occurring at each plate throughout the length of the fractionation column.
Distillation: A Process to Refine Crude Oil

FIG. 2-3 Schematic diagram of a fractionating column for the distillation of crude oil illustrating seven major fractions removed from the column and their boiling point ranges.

1. Gases [Petrochemical Feedstocks] $T_1 < 90^\circ F$

2. Natural Gasoline [Straight-run gasoline or Light Naphtha] $T_2 = 90-200^\circ F$

3. Heavy Naphtha $T_3 = 170-400^\circ F$

4. Kerosene $T_4 = 350-550^\circ F$

5. Fuel Oil $T_5 = 390-620^\circ F$

6. Gas Oil $T_6 = >500^\circ F$

refinery business, John D. had now accumulated 60 acres of land and two refineries in Cleveland, timberlands and a barrel making plant, lake shore docking facilities, tank cars, railroad sidings, and warehouses in the oil regions and in New York City.  

As early as 1867, Rockefeller and Flagler negotiated a series of agreements with the Atlantic and Great Western, the Erie and Pittsburgh, the Lake Shore, the Pennsylvania, and other railroads that entitled Rockefeller to rebates on the railroad freight charges. The railroads made these concessions in exchange for Rockefeller’s promise to provide them with a steady supply of large oil shipments to eastern markets and also to refrain from constructing pipelines. From the very beginning trouble and controversy surrounded these agreements.

The drop in the price of illuminating oil, the serious cut into export demand because of the Franco-Prussian War, and the uneasy truce following the ensuing railroad rate wars combined to produce financial crises at refineries everywhere. At this time, the petroleum industry was typical of American business in general. There was vigorous competition among the small, independent producers, refiners, and marketers, most of whom were operating with limited capitalization. In 1870–71 the refining capacity of 12 million barrels annually was 2.5 times greater than the production of crude oil. This chronic lack of balance among the major segments of the industry (crude production, refinery capacity and production, and market demand) caused wide fluctuations in the prices of both crude and refined products.

Rockefeller’s business genius was his recognition that trimming the transportation costs, which could equal 20% of the final product cost, was the key to success in an operation of his size. He realized that obtaining more capital or product reputation and trademark would not contribute as much to his profits as would reducing transportation costs. The bargaining and rate wars followed a seasonal pattern. With the thawing of the Erie Canal each spring, the railroads would lose business to the canal, and as a result would begin to make rate concessions to keep their freight traffic. By late 1871, the railroads decided that they had lost enough money hauling oil.

On 2 January 1872, the Pennsylvania, New York Central, and Erie Railroads and a group of leading oil refiners led by Rockefeller met
to form the South Improvement Company. The railroads would charge the full freight rate to all, but members of the South Improvement Company would receive a rebate in exchange for shipping all their products via the member railroads.\textsuperscript{17} For the nonmembers the rates would in some cases be double previous rates, and the increase in rates would go to the South Improvement Company as a fund to eliminate further competitors. The new rate schedule was announced on 25 February 1872.

Two days later, 3,000 men gathered at the Titusville Opera House to begin the oil war between the producers and the refiners by forming the Petroleum Producers Union. Their plan was to embargo crude oil shipments and pressure the Pennsylvania legislature to repeal the charter of the South Improvement Company. Cleveland received 15,415 barrels of crude in March compared to 73,000 in February; 5,000 employees were idled. On March 25, the railroads cancelled their special contracts with the South Improvement Company. The Pennsylvania legislature revoked the charter of the South Improvement Company and passed a free pipeline bill on April 2. The Pennsylvania Railroad, however, lobbied to restrict the pipeline bill to eight oil producing counties and then set its new rates at what it would have netted under its old agreement with the South Improvement Company. The war ended on April 9 when the producers lifted the embargo.

**The Treaty of Titusville**

During these two months of confusion, speculation, and fighting in 1872, Rockefeller used fear of bankruptcy to enlarge Standard Oil's holdings. Five of the largest Cleveland refiners either sold or merged into Standard Oil, and sixteen smaller refineries were purchased, often at prices below the appraised value. By April Standard had gained control of all the refining capacity (12,000 barrels per day) in Cleveland.\textsuperscript{18} In addition he purchased Jabez A. Bostwick and Company to gain an export house and terminal facilities in New York City, and a refinery in Long Island. Rockefeller denied using the South Improvement Company as a threat. He claimed that he merely took advantage of the business conditions and paid a fair price for the excess refineries.

In August, Rockefeller tried one more time to organize the producers and the refiners by forming and becoming President of the
Kerosene, a liquid hydrocarbon mixture, was the first major commercial product of the new petroleum industry during the late 1800s. About the middle of the nineteenth century, candles and whale oil began to be replaced by kerosene and gas as the major sources of illumination in homes, shops, and factories. Using the process of distillation, the refineries of Standard Oil (and others as well) purified crude oil on a large scale to produce kerosene for mass marketing in the cities. Mixtures of hydrocarbon gases, produced from the distillation of coal, were also used as fuel for illumination. Today, kerosene is used as fuel in lamps and in stoves for heating and cooking, as a degreaser and cleaner, as a solvent in insecticidal sprays, and as a fuel for rockets, jets, and diesel engines.

Kerosene is a pale yellow or water-white oily liquid hydrocarbon mixture. A darker yellow indicates the presence of sulfur which causes it to smoke on burning. It is lighter than water with a density of 0.80 g/mL. It will not dissolve in water, but it is soluble in other organic solvents. Kerosene boils in the range 175–325 °C. It can irritate the skin; inhalation of the vapors can cause drowsiness or even coma.

Although kerosene is a complex chemical mixture, it is primarily composed of compounds formed from just two elements: carbon and hydrogen. When the maximum number of hydrogen atoms combines with a given number of carbon atoms, their combining ratios satisfy the empirical formula, \( C_n H_{(2n+2)} \). These hydrocarbons are called saturated alkanes, and for kerosene \( n \) ranges from ten to sixteen. The carbon chain may be straight or branched. For example, n-dodecane is a common, straight-chain alkane present in kerosene:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Alternate formula representations for n-dodecane:

\[
C_{12}H_{26}, \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

An example of a branched-chain dodecane is:

\[
\begin{align*}
\text{CH}_3 & \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\
\text{CH}_3 & \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3
\end{align*}
\]
One of the reasons for the complexity of kerosene is the possibility of isomers in the mixture. Isomers are compounds that have the same number of each type of element in the compound, but in each compound they are bonded to one another in different ways. The two compounds shown above are isomers; 12 carbons and 26 hydrogens bonded to one another in two different ways to produce a straight carbon chain or a branched carbon chain. Each hydrogen forms one bond with a carbon, but each carbon forms four bonds in various combinations with other carbons and hydrogens. Many other isomers of dodecane are possible.

If the hydrocarbons contain less than the maximum number of hydrogens per carbon, the compounds are called unsaturated alkanes. If double bonds are present in the compound, these types of unsaturated alkanes are called alkenes or olefins.

For example:

$$\text{CH}_3\text{CH} = \text{CH-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

Heptene-2

If the carbons form a ring rather than a chain with maximum number of hydrogens per carbon atom, they are called naphthenes. But six carbons in a ring with one hydrogen bonded to each carbon is called benzene. Kerosene contains many derivatives of benzene (also called aromatic compounds) in which one or more of the six hydrogens have been replaced by other groups of atoms.

Examples of aromatic hydrocarbon:

- cyclohexane, a naphthene

- benzene

- methyl benzene
Petroleum Refiners' Association, better known as the National Refin-ers' Association. The "Treaty of Titusville" was expected to bring equilibrium to the oil trade by regulating production, refining, and shipping according to market demand. But, the conditions could not be enforced; wildcat production, excess refining capacity, and an overextended railroad network were simply too powerful. In July 1873, the organization was dissolved by mutual consent of its members.

During this troubled year, Rockefeller and Flagler were constantly improving the Standard Oil Company. They consolidated refinery operations into the best six plants in Cleveland and scrapped the rest. With total capacity at 10,000 bpd, they dropped production to 3,400 bpd, only to raise it to 6,250 bpd in the second half of 1873. They purchased Devoe Manufacturing Company in New York City to strengthen their foreign sales of case oil from the Long Island refinery, and they purchased Chess, Carley and Co. in Louisville, Kentucky, a leading wholesaler in the southeast. Standard now controlled about 40% of the refining capacity in America.

Because his plan had worked so well in Cleveland, Rockefeller became convinced that he should apply the same procedure to the entire country, thereby making Standard Oil the one and only petroleum company in America. He anticipated the bitter opposition that would come as he carried out his plan of vertical integration which would make Standard Oil the only producer, refiner, and supplier of petroleum products. But to him, vertical integration and a monopoly on oil were necessary to stabilize and save the petroleum industry.

Transportation Problems: Pipelines Versus Railroads

Early in the 1870s the major technical bottlenecks in transportation of petroleum had been broken. A pipeline gathering system composed of over 2,000 miles allowed any producer in the Pennsylvania oil regions to move his crude from well head to railroad siding, canal bank or river port. Metal tank cars in the shape of cylinders replaced many of the barrels for long railroad hauls, but transportation cost were still among the industry's largest expenses. Preferential rail-road rates for the major refining centers and for personal friends only aided the expansion of the pipeline network. In an attempt to hold on to their position, the railroads tried to forge shipping agreements
with the gathering pipeline companies. But, the continuing rivalry among these groups prevented the development of a stable transportation system in the oil industry.

As early as 1868, Rockefeller hedged his bet on the transportation issue by acquiring a secret one-quarter interest in Gould's Allegheny Transportation Company (later PA Transportation Co.), a pipeline company. In 1873 he purchased a one-third interest in the United Pipeline Company and also its Imperial Refining Company at Oil City, Pennsylvania. Standard Oil controlled the refining capacity in Cleveland and New York City as well as all oil shipments into and out of New York City on all railroads except the Pennsylvania Railroad. So, Standard Oil influenced greatly any railroad agreement.

In general, Rockefeller followed the tactics that had worked so well in Cleveland. First, persuade the leading refiners in an area to join the Standard organization. Second, using his power in the transportation field, pressure the remaining independents to sell or merge into Standard Oil. In 1874 Rockefeller and Flagler found three major refiners who were receptive to their offer of a merger: William Warden and Atlantic Refining Co. in Philadelphia; Lockhart, Frew & Co. with seven refineries in Pittsburgh; and Charles Pratt and H. H. Rogers of Charles Pratt & Co. at Newtown, Long Island.

Two more acquisitions helped to consolidate his refining power. John D. Archbold, a vigorous opponent of Rockefeller during the South Improvement Company episode, was manager of the Porter, Morehouse & Co. in Titusville next to Standard's newly purchased Imperial Oil Refinery. After a year, Rockefeller convinced Archbold to join Standard Oil, probably because of the stability that Rockefeller was bringing to the transportation prices and also because Pratt and some of his other friends were joining the Standard group. Rockefeller made Archbold head of a newly formed company, Acme Oil Company of New York, in the fall of 1875. Later, Archbold rose to become one of the most influential officers at Standard Oil.

The other area in which Rockefeller wanted a presence for Standard Oil was West Virginia-Southern Ohio. He feared that the B & O Railroad would help to build up the power of the independent refiners in this area. So he convinced J. N. Camden, owner of J. N. Camden and Co. and the leading refiner in the area, to merge with Standard Oil.
Tidewater Pipe Company

Tidewater Pipe Company was formed on 22 November 1878 to transport oil the 100 miles from Coryville in the Bradford fields to Williamsport. From there the Reading Railroad would take the oil in tank cars to Philadelphia and New York. Tidewater planned to oppose Standard Oil's control of shipping oil by rail. The Reading Iron Works made 200 bulk cars for the Reading Railroad and National Tube made 5,000 tons of six inch wrought-iron pipe in 18 foot sections, each section weighing 340 pounds. Eleven-man gangs laid the pipe at the rate of 2 miles a day, all by hand except for horses to haul the pipe from the railroad terminals to sites up to 40 miles away.

In addition to coping with a five foot snowfall and the spring rains and mud, they designed a pump to lift the oil 22 miles up a 69 foot incline and a second pump to lift the oil 480 feet over a distance of 8 miles to the high point on the line. Then, the oil flowed downhill for 70 miles to Williamsport, 2,500 feet below the line's summit. Despite problems of variable line pressures, ruptures, and pumping problems, the $750,000 pipe line was completed on 22 May 1879, and 6,000 barrels of oil began to flow to Williamsport each day.

The other railroads and Standard Oil struck back with cuts in their gathering line and rail tariffs and with special charges against the Reading Railroad for the use of a short, but vital, stretch of rail into New York City owned by the Pennsylvania Railroad. The ensuing rate war hurt all sides. Within four months Standard laid its first 100 mile pipeline from Butler County to Cleveland. But Rockefeller knew that the markets were in the other direction. So, in December 1879, he offered the Erie Railroad $50,000 in cash, plus protection of its oil traffic, if he could lay a pipeline along its right of way from the Bradford fields to Bayonne and Weehawken, a distance of 400 miles. In 1880 Standard Oil began four other pipe lines and the Tidewater group became very uncomfortable.

Rockefeller refused Tidewater's offer to control the pipeline business as he felt comfortable with Standard's growing presence in the field. His newly formed National Transit Company controlled 3,000 miles of gathering lines and 30–40 million barrels of storage capacity, which fed into the Buffalo, Cleveland, and Bayonne trunk lines. Rockefeller's only competition was Tidewater and a few very small independents. By acquiring refining capacity and consolidat-
ing control over transport facilities, Rockefeller made it virtually impossible for independent refiners to survive in the 1870s.

**Standard Oil Trust Agreement**

By 1880 Rockefeller realized that some new type of organization must be created to unite his various companies now operating from Cleveland under the banner of Standard Oil of Ohio. Back in 1873, Standard controlled 10% of the total capacity of the 103 U. S. refineries; by 1880 Standard controlled 90% of the total refining capacity and the total number of refineries was down to 89. Production of crude oil reached 30 million barrels in 1883; refining capacity grew from 10.5 million barrels in 1873 to 28 million in 1884. Crude quoted at $2.50 a barrel at the wellhead in 1876, fell to $0.78 in 1879. Problems of communication, administration, governmental legislation, and public criticism needed attention.

Rockefeller had made good use of the trustee device up to this point. For example, when a company was acquired, its stock would be transferred to several major Standard Oil officers as trustees for the benefit of the stockholders of the Standard Oil of Ohio corporation. By a strict interpretation of the trustee concept, Rockefeller and his managers would deny under oath that they or Standard Oil of Ohio owned any of these properties. Rather, they claimed only to be holding them in trust for the stockholders of Standard Oil of Ohio. To avoid complications at the death of a trustee or a trustee getting mad and making trouble, groups of three employees at the Cleveland office were selected to serve as trustees of each company. Their main task was to apportion the profits each year to the stockholders of Standard Oil of Ohio in accordance with their relative holdings.

In 1882 the Commonwealth of Pennsylvania sued Standard Oil for $3,145,000 in nonpayment of taxes back to 1868 because it ruled that all capital stock of corporations doing any part of their business in Pennsylvania was fully taxable by Pennsylvania. Subsequently, the courts ruled that only property located in Pennsylvania was taxable. The Standard Oil Trust Agreement was drawn up and signed on 2 January 1882 by the 41 stockholders of Standard Oil of Ohio and the three trustees for each of the 40 named companies, valued at $70 million. The agreement also provided for corporations bearing the state names. Standard Oil of New Jersey and of New York were formed in 1882 and companies in Indiana, Iowa, Ken-
Almost immediately after oil began flowing to the top of the first oil well in America in 1859, collecting and transporting the oil from the fields to the refineries became a major problem. The quantity of oil quickly exceeded the available storage and hauling capacity of 6,000 Pennsylvania workers using wooden barrels, horse-drawn wagons, and river barges. Railroad tank cars, such as the Densmore (1865), were designed to move the oil in larger units.

Since rail lines could not be conveniently and economically constructed to each well site, transporters still had the problem of getting the oil to the nearest railroad siding. This problem was solved when a system of pipelines and pumps was employed to move such large quantities of oil in an efficient way. By the late 1860s, a system of gathering lines connected the wells of the northeast Pennsylvania oil fields with nearby railroad terminals. The Tidewater Pipeline was the first to bring oil from the Pennsylvania fields to the refineries on the east coast.

In 1960, crude oil moved through a massive U.S. pipeline system covering 160,000 miles with some pipes measuring over 48 inches in diameter. In addition, refined products derived from the crude oil moved through a 45,000 mile system of pipes. Millions of barrels of crude oil moved across the oceans in tankers and supertankers and on the rivers in giant barges each day. After World War II, crude oil moved across the Saudi Arabian mountains and desert in 42 inch diameter pipes from the fields near the Arabian Gulf to the shores of the Mediterranean Sea. Tankers then carried the crude to refineries in Europe and America.

After proven reserves exceeding 10 billion barrels of oil were discovered in the Prudhoe Bay area of Alaska, an 800 mile pipeline was constructed to move the oil across Alaska from Prudhoe Bay to the port of Valdez, and from Valdez by tanker to U.S. mainland refineries. About half (427 miles) of the pipeline is above ground, and 373 miles of the pipe is buried. Although Alaska covers 367,000 square miles, the pipeline right of way and pump stations occupy only 7.7 square miles.

The steel pipe was manufactured in Japan in 1969. The 40 foot sections, 48 inches in diameter and 1/2 inch thick, were sent to storage yards in Prudhoe Bay, Valdez, and Fairbanks, and in 1974 were welded into 80 foot sections, or double joints, before delivery to the installation sites. After each 80 foot section was welded into place, the welds were inspected with x-ray equipment to insure a good seal.
and the pipe was wrapped with 3M tape for protection against corrosion.

The pipe was either elevated above the ground or buried depending on how the heat from the oil might affect the soil. At the start of the pipeline the oil is 60°C, and friction from the flowing oil keeps it hot along its 800 mile journey. So, in those permafrost regions where it was necessary to bury the pipeline, it was insulated and the surrounding permafrost protected from thawing by refrigerated brine systems.

In most of the permafrost region, the pipeline was covered with a thick layer of fiberglass insulation and a galvanized sheet metal jacket and elevated at least 2 feet above the ground. Where necessary in the permafrost region, the support columns use a liquid ammonia refrigeration system to prevent thawing at the base of the support columns. In many of the more than fifty major river crossings, the pipe was coated in concrete and buried in the river beds. The pipeline reaches its highest point as it crosses the Atigun Pass at an elevation of 4,800 feet. At Thompson Pass, the pipeline climbs the mountain slope at a 70° incline.

The pipeline was installed in a zigzag pattern rather than in straight-line segments to allow for expansion and contractions during the extreme temperatures of Alaska. The 15 foot wide supports allow for a 12 foot lateral movement on Teflon coated beams and an 18 inch longitudinal expansion in each 1,200 feet of pipe over a temperature range of −70° to +145°F. Although designed for 12 pumping stations, only eight were constructed.

Each pump station is powered by a jet engine and electric power turbine using either natural gas or a liquid turbine fuel prepared by taking some crude oil from the line. A system of check valves prevents a backflow of oil from the higher elevations. The entire line has 175 block and check valves to reduce the size of a spill to not more than 50,000 barrels in case of a rupture along the pipeline. The pipeline can deliver 2 million barrels of oil per day to Valdez.

When the oil arrives in Valdez, it is stored in 500,000 barrel tanks, which are 272 feet in diameter and 59 feet high. Thirty of these storage tanks and the resulting tanker traffic make Valdez the largest crude oil loading terminal in the United States. Tankers, which can be loaded at the rate of 100,000 barrels per hour, take the crude to refineries in the Puget Sound, San Francisco, and Los Angeles-Long Beach areas.

The Trust decided to move into production of oil for the first time when it bought some of the Lima field in 1889. For the Trust, the Ohio-Indiana oil fields came at a perfect time. The cheap Lima crude helped the Trust deal with the declining yields of the Appalachian fields and the rising competition from the Russians in foreign markets. In the late 1880s, Herman Frasch solved the problem of high sulfur content in the Lima crude with his method to precipitate the sulfur. By the turn of the century, it became apparent that even more new fields must be found if the American petroleum industry was to maintain its worldwide leadership.

Petroleum at the Conclusion of the Nineteenth Century

Drake’s first oil well produced a few barrels in 1859, but a total of almost 60 million barrels flowed from all wells during the year 1899. Total output over this 40 year period reached one billion barrels. The basic production techniques were set during the first ten years of the petroleum industry by adapting the methods of salt well boring. The foundation for refining techniques was also laid. The methods of destructive distillation of coal to produce a liquid coal oil, and its refining, were transferred to petroleum and scaled up efficiently to produce kerosene in large quantities and then a series of by-products. Most of this output went to supply the world with kerosene, but about 200 by-products accounted for half of the industry’s sales, including naphthas for local anesthetics, solvents for industry, fuel for stoves and the internal combustion engines, waxes for pharmaceuticals and candles, oils and lubricants for machines, and heavy oils for the gas industry. No American innovation had more effect on the growth of the petroleum industry than the development of the long distance pipelines for the bulk transport of oil to refineries and markets. The Russians did, however, begin bulk shipments of oil to the world via ocean tankers late in the 1880s.

Unfortunately there was waste in production. Only a few geologists urged more responsibility in the placement of wells, the control of well pressures, the use of methods to prevent premature depletion
of the wells, and dealing with the dangers of flooding and fires. All these concerns were essentially ignored. Many of the explosions and fires from kerosene lamps were the result of refiners who did not monitor carefully their methods of distilling out the volatile gasoline fractions. Only when these fractions became more valuable as by-products did excessive dangers due to inferior grades of kerosene disappear in the late 1880s. Consumers certainly benefited from this competition as the cost of kerosene declined from $0.45 per gallon in 1863 to only $0.06 in the mid-1890s.

ENDNOTES

5. Flynn, pp. 53-54.
30. Private communication. Script to set of Exxon USA company slides.
32. Williamson, pp. 244, 466-470.
33. Williamson, p. 468.
34. Williamson, p. 469.
CHAPTER 3

Fuel for the Age of the Auto

As John D. Rockefeller increased his kerosene production and profits in the last third of the nineteenth century, three inventors began to change the course of his Standard Oil. Thomas Edison, with his electric light bulb and power networks, began to eliminate the need for kerosene. Nicolaus Otto developed a small internal combustion engine which began to compete successfully against large steam engines. Then, Henry Ford used the Otto engine in his Model T, which began to create new markets for petroleum products, especially gasoline.

Internal Combustion Engine: Nicolaus Otto

Nicolaus August Otto (1832–1891) began developing an internal combustion engine in the 1860s. In 1866, he and Eugen Langer obtained a German patent for a two-stroke per cycle atmospheric engine, the first successful internal combustion engine. They sold about 5,000 engines. At the Philadelphia Centennial in 1876, Otto exhibited a practical four-stroke per cycle engine which used kerosene or gasoline as its fuel. Otto’s new idea was the use of four strokes to achieve one power cycle — a major improvement over earlier engines. First, the piston goes down and draws the fuel and air into the cylinder; second, the piston moves upward to compress the mixture of fuel and air; third, the ignition (by a spark plug in today’s engine) causes the compressed mixture to ignite and drives the piston down in its power stroke; and fourth, the piston moves upward and pushes out the burned fuel mixture as the engine exhaust.

The 1876 Otto engine was a great commercial success because it proved that internal combustion (i.e., combustion within the cylinder itself) could serve as a fixed power plant in place of the steam engines. Furnaces and boilers were no longer needed to generate the steam to power the pistons. But the major advantage of the simpler engine was it could be used more easily in smaller vehicles.
The Model T: Henry Ford

Henry Ford (1863–1947) was born on his parents’ farm in Dearborn, Michigan, just outside Detroit. His father wanted Henry, the eldest son, to take over the farm, but Henry was intrigued by mechanical devices. As a young boy he was considered a wizard at fixing watches. In 1879 he left home, much to his father’s displeasure, to work as an apprentice in Detroit machine shops. Ford gradually gained a solid reputation as a skilled machinist who could repair steam engines. In Detroit during the mid-1880s, he repaired an Otto engine and also built for himself an engine modeled after the Otto engine to understand the principles of the internal combustion engine.

Between 1891 and 1899, Ford worked for the Edison Illuminating Company in Detroit, rising to become its chief engineer. During these years, he set up a shop behind his house to build a horseless carriage powered by an internal combustion engine. On 4 June 1896, he ran successfully on the streets of Detroit his first car, which he called a quadracycle. By 1899, he secured financial backing and formed a company, but it failed in 1901. He formed a second company in the same the year, but it too failed. Ford decided that he would have to produce a racing car to obtain more financial support and also to catch the imagination of the public. On 10 October 1901, he won a well publicized race in a car he built especially for speed. The next year Ford convinced the famous racer, Barney Oldfield, to drive Ford’s new “999” car in a race. The victory of the “999” car led directly to the founding of the Ford Motor Company on 16 June 1903.

Fortunately for Ford, by 1904 the country was in a period of rapid growth and high prosperity; and so he immediately found a good market for his cars. Ford’s original objective was to produce a low-priced family car that would sell to a wide market, but he could not convince his financial backers of this idea. In 1907 he bought them out and introduced his Model T the next year. In 1908 he produced 5,989 Model T Fords and sold them for $850 each. By 1916 he was producing 577,036 Model Ts per year and selling them for $360 each. This remarkable drop in price came about because of Ford’s decision to use a moving assembly line. On 1 January 1910 Ford began operation in a new plant at Highland Park, and by 1 April 1913 he had installed his first moving assembly line at Highland Park. His revolutionary manufacturing procedures became known as the
method of mass production. Not only had Ford succeeded in designing an inexpensive and simple car, but he had finally achieved his goal of designing an inexpensive and rapid means of producing his cars. He had designed both a new machine and a new manufacturing process.

Whiting Research Lab: William M. Burton

The introduction of Edison's electric light bulb and the spread of electric power networks greatly reduced the demand for kerosene as the illuminating fuel in lamps, but the rise in automobile sales created a new, strong demand for gasoline. As early as 1908, a few inventors recognized the need for new chemical processes that would provide substantial increases in the supply of gasoline. William M. Burton — the scientist, engineer and entrepreneur — was one of these few inventors. The heavy gas oil fraction of the crude oil, recognized by Benjamin Silliman in 1855 as a source of lighter hydrocarbons, was now available in large supply due to the weakening demand for kerosene.
Following Henry Ford’s introduction of the Model T, the need for gasoline increased dramatically. This once wasted by-product from the refining of kerosene became quite valuable. What is the chemical composition of this “by-product”? Gasoline is a liquid fuel mixture that must give off vapors which can be ignited by the spark generated within each cylinder of an internal combustion engine. A premium gasoline contains hydrocarbon chains with four to twelve carbons per compound which vaporize between 30 and 210 °C. Gasoline is a more volatile hydrocarbon mixture than kerosene. In fact, poor grades of kerosene containing some gasoline often produced explosions when burned in lamps in Rockefeller’s day.

This mixture of hydrocarbons is varied by the refiners to contain more of the lower boiling compounds as the weather conditions change from summer to winter. Too much of the lower boiling compounds, however, can cause vapor lock in the summer, but not enough of the lower boiling hydrocarbons in winter will make starting the automobile difficult.

The four classes of hydrocarbons found in gasoline are: alkanes, olefins (or alkenes), naphthenes, and aromatics. These are the same four classes of hydrocarbons in kerosene, only their chain lengths are shorter due to the higher volatility requirements (see ChemTech 4). For example, gasoline contains 3–4% of n-butane, a straight-chain alkane. Gasoline also contains about 6% n-pentane and 3.5% isopentane. These two pentanes are isomers:

\[ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \]

n-pentane

\[ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \]

\[ \text{CH}_3 \]

isopentane

n-Pentane is an example of a straight-chain alkane, but isopentane is an example of a branched-chain alkane. Branched-chain alkanes have more energy per carbon than straight-chain alkanes, so they contribute more to the total energy of the gasoline mixture as measured, in part, by its octane rating (see ChemTech 8). A modern refinery operation called reforming is used to convert some of the straight-chain hydrocarbons into branched compounds to enhance the octane rating of the gasoline.

cont >>>>
TABLE 3-1. Hydrocarbon Composition of a Typical Gasoline

<table>
<thead>
<tr>
<th>Type of Hydrocarbon</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Alkanes</td>
<td></td>
</tr>
<tr>
<td>a. Pentanes: n-pentane, iso-pentane</td>
<td>9.5%</td>
</tr>
<tr>
<td>b. Hexanes: n-hexane, 2-methylpentane, 3-methylpentane</td>
<td>12.0%</td>
</tr>
<tr>
<td>c. Heptanes: n-heptane, 2-methylhexane</td>
<td>3.5%</td>
</tr>
<tr>
<td>d. Octanes: n-octane, iso-octane</td>
<td>1.6%</td>
</tr>
<tr>
<td>e. Nonanes: n-nonane</td>
<td>1.8%</td>
</tr>
<tr>
<td>2. Naphthenes: cyclopentane, methylcyclopentane</td>
<td>from 4 to 40%</td>
</tr>
<tr>
<td>3. Olefins: Some pentenes, hexenes, &amp; heptenes</td>
<td>from 0 to 18%</td>
</tr>
<tr>
<td>4. Aromatics: benzene, toluene, ethyl benzene; ortho-, meta-, &amp; para-xylene</td>
<td>from 10 to 30%</td>
</tr>
</tbody>
</table>

TABLE 3-2. Hydrocarbon Composition by Grade and Season

(in Volume Percent)

<table>
<thead>
<tr>
<th>Type of Hydrocarbon</th>
<th>Premium Summer</th>
<th>Premium Winter</th>
<th>Regular Summer</th>
<th>Regular Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Alkanes &amp; Naphthenes</td>
<td>66.0</td>
<td>55.6</td>
<td>88.4</td>
<td>70.9</td>
</tr>
<tr>
<td>2. Olefins</td>
<td>7.0</td>
<td>14.6</td>
<td>1.4</td>
<td>9.5</td>
</tr>
<tr>
<td>3. Aromatics</td>
<td>27.0</td>
<td>29.8</td>
<td>10.2</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Adapted from Hancock, E. G. Editor. TECHNOLOGY OF GASOLINE. London: Blackwell Scientific Publications, 1985, pp. 43–52 (TABLE 3-1), p. 135 (TABLE 3-2).
FIG. 3-2 William Meriam Burton (1865–1954) Designed and developed the first chemical process for cracking crude oil to manufacture gasoline on a large scale.

courtesy of the Northwestern University Press

William Meriam Burton was born on 17 November 1865 (two years after John D. Rockefeller financed his first Cleveland refinery) and grew up in the town of East Cleveland, Ohio. Influenced by his father, Erasmus Burton, who was a physician, young William became interested in chemistry and set up a laboratory in his father’s barn. Charles F. Brush, a neighbor, enjoyed showing young Burton his mechanical and electrical devices. (The Brush magneto is an alternator with permanent magnets used to generate current for ignition in the internal combustion engine and for the telephone bell.) A sympathetic high school teacher helped Burton select Western Reserve University for college and later Johns Hopkins University, where Burton received his Ph.D. in chemistry in 1889.

From Hopkins, Burton went to work for the Standard Oil Company (Ohio), but after a year he was assigned to Standard Oil Company (Indiana). In the 1890s, the contributions that a Ph.D. chemist might make to the operation of a petroleum refinery were not obvious. In fact, William P. Cowan, the vice president in charge of refining, had no idea what he was to do with this newly assigned employee. On their first meeting at the Whiting Refinery, Cowan
asked Burton if he had brought his own set of tools (a common practice for newly employed machinists). Without telling Cowan, the directors of Standard Oil (Ohio) had decided that Dr. Burton would be the first head of the research laboratory that they wanted to create at their Whiting refinery. The laboratory was set up in the second story bedrooms of a farmhouse on the refinery property near the shore of Lake Michigan.

His first experiments, conducted with equipment and instruments which he made or had made in the refinery shops, determined the chemical and physical characteristics of refinery products: kerosene, waxes, greases, and lubricating oils. This testing led to the development of standardized analytical methods. These routine procedures were time-consuming and not very challenging. So he turned his attention from quality control to the manufacturing processes used to produce these chemicals that he had been testing. He began to experiment with changes in the processes that might improve the yields and the quality of these products.

**A Research Team: Humphreys and Burton**

The presence of sulfur in some of these products gave them an offensive odor and an undesired yellow color. For his success in eliminating sulfur compounds from some refinery products, Burton was promoted to assistant general superintendent of the Whiting refinery in 1892 and became the superintendent at the age of 31 in 1896. To fill Burton's place in the laboratory, a second chemistry Ph.D. from Johns Hopkins was employed. When he moved to Standard Oil (Texas) in 1904, a third Hopkins graduate, Dr. Robert E. Humphreys, joined the refinery research laboratory. Humphreys and Burton developed a strong, significant research collaboration which lasted for the rest of their professional careers.

Following Ford's introduction of his Model T in 1908, Burton recognized that there was a great need for more gasoline and that big profits could be made by increasing its supply. He predicted the general acceptance of the automobile and realized that in a few years the demand for gasoline would exceed the amount available from simple distillation of crude oil. He believed that the oil industry would have to adapt its processes and marketing activities to meet these challenges for more gasoline for the automobile. Otherwise, the petroleum industry would not continue to prosper in the face of the
declining kerosene market. In an age when few refinery supervisory personnel had any technical training, Burton was outstanding in his educational background and laboratory experience. As general superintendent of the Whiting refinery, he also had at his command all of the authority and refinery facilities necessary to test and develop his ideas about the cracking process.

With his laboratory now directed by the very capable Dr. Humphreys, Burton employed a fourth Johns Hopkins graduate, Dr. F. M. Rogers, as an assistant to Humphreys. From his position as superintendent, Burton could now orchestrate his new laboratory research team, direct his refinery shops in the construction of novel equipment, gather information on potential markets from his refinery sales force, and control the costs through his refinery accounting department. As the refinery superintendent, Burton also enjoyed access and support from the president and directors of Standard Oil (Indiana). In 1910, such a research and development operation could have only been carried out through the office of a refinery superintendent because only the office of the superintendent held the power necessary to coordinate such an effort.

Burton and Humphreys began their laboratory experiments with the knowledge that when a heavy petroleum fraction is heated to high temperatures, it decomposes into: (1) lighter products (which boil in the gasoline range); (2) a heavier, viscous liquid fraction; and (3) solid coke. For the raw material, they selected all of the fractions that boil above the kerosene range. Although these fractions constituted about two-thirds of the total crude oil coming into the refinery, they were much less valuable in the marketplace than the kerosene and straight-run gasoline fractions. The goal was obvious: discover processes to convert this entire heavy petroleum fraction into useful gasoline.

**Cracking Petroleum: The Burton Process**

In the laboratory during 1910-11, Burton, Humphreys and Rogers learned that moderate temperatures on the gas oil fraction produced the best cracking. But, in the plant under large-scale conditions, part of the gas oil evaporated in the heating process before the cracking reactions could reach the desired degree of completion. So, they used higher pressures to keep the gas oil in the reaction still for longer periods of time. At this time, not much was known about the high
pressure behavior of heated hydrocarbons, so the fear of explosions was justifiable. Also, little was known about catalysts except that some chemicals could accelerate reactions by some unknown mechanism without themselves being consumed in the reaction. (See ChemTech 10.) As the coke layer formed on the bottom of the still, the external temperature had to be increased to maintain the temperature of the cracking process within the reaction vessel. This increased heat could burn a hole in the bottom of the still, and set the petroleum inside the still on fire.

It was difficult to build large, high-pressure vessels. Vessels were constructed by riveting the steel plates with air hammers. Thus, the air pressure available within a particular refinery limited the thickness of steel plates used to fabricate the reaction vessels. (Ten years later, electric arc welding was developed, so thicker steel plates and higher temperatures and pressures could be used with greater safety.) Although Burton believed that he had a safety factor of four in his pressure calculations for the vessels, he actually only had a factor of 0.5 due to his poor estimate of the strength of his steel at the operating temperature. The still size was limited by the size of the largest steel plate: 30 feet x 10 feet. Because the bottom of the still had to be seamless, the largest Burton still was 8 feet in diameter and 30 feet in length.12

Against these odds, nevertheless, they tried some controlled bench-scale experiments. When Cowan, now president of Standard Oil (Indiana), learned of their "high pressure" (from 5 to 30 psi) experiments, he ordered them to stop such dangerous experiments and to pursue less hazardous research. While at a scientific meeting, Humphreys learned that heavy oils had been heated under a pressure of 50 psi without explosion. Humphreys and Burton renewed their requests and finally persuaded Cowan to give permission for them to resume their experiments. They ventured to 75 psi to discover that little of the gas oil vaporized from the still, the cracking proceeded with little coke formation, the yield of gasoline was 20–25%, and it burned well in the internal combustion engine.

If the cracking was allowed to run until 40% gasoline was produced, the amount of coke deposited was substantial. Cracking the residuum (the heaviest fraction of crude oil) at 75 psi produced more coke than gasoline.
FIG. 3-3 An Illustration from William M. Burton’s patent for cracking crude oil to manufacture gasoline, filed 3 July 1912, granted 7 January 1913

The crude oil (or a fraction from a distillation of crude oil) is placed in a reaction vessel (1), which is heated over a fire (2). The lower boiling chemicals (in the gasoline range) rise up a through take-off pipe (7) [Later, this becomes the Humphreys runback pipe.] and are carried to the condenser coils (9) in a cooling vessel (12). As the gasoline vapors condense back to a liquid, they are collected in a reservoir (10). Valves (3,4) control the pressure. Pressure and temperature regulate the extent of breaking (or cracking) the larger molecules into smaller ones used as gasoline.

At a temperature slightly less than 700°F and a pressure of 75 psi, the vapors from the cracking process were about one-fourth gasoline and three-fourths a mixture of kerosene and gas oil. Condensation of this mixture would require several distillations to remove the gasoline; and in the process, the kerosene would become partially cracked and worthless as an illuminant. Therefore, Humphreys invented the “run-back,” a simple but effective distillation pipe running at an upward angle from the still to the condenser. As the air cooled these 12 inch diameter pipes, the kerosene and gas oil would condense and run back into the still but the gasoline vapors would rise to the condensing coils. By 1911, they knew how to design and operate their process as efficiently and as effectively as the technology of the day permitted.
To construct a process plant, Burton had to convince management to allocate the money for a new plant.\textsuperscript{13} Burton journeyed to New York in 1911 to make a presentation to the Standard Oil Company (NJ) directors for $1 million to construct six batteries (ten pressure stills per battery) and their accessories. He estimated that about one year would be required for a return of this construction investment. The directors had little training or experience in the chemistry of petroleum, but they had lived through the age of steam boiler explosions on trains and steam ships.

They lacked confidence in this new idea and feared a major explosion, in part, because they were removed from the laboratory and were not familiar with the research details which led to Burton's proposal. Also, they could not afford any other risks as the United States Circuit Court in a landmark decision had ordered Standard Oil to dissolve its trust composed of thirty-three subsidiary companies. Since the existence of the Standard Oil empire was in jeopardy, the directors felt that they could not assume the liabilities for possible explosions of these new Burton stills, even if the potential return on their investment might be quite large. So they did not grant start-up monies to Burton.

**Construction of First Burton Stills**

**Follows Standard Oil (NJ) Breakup**

Disappointed, Burton returned to Chicago.\textsuperscript{14} Within a few weeks the U.S. Supreme Court upheld the dissolution decree from the Circuit Court, and on 15 May 1911 the breakup of the Standard Oil Company (NJ) was confirmed. On 1 September 1911, the parent company distributed to its stockholders all of the equities in its thirty-three subsidiaries. Now, Burton could try his proposal again, but this time he was in a much more favorable position. He would be seeking approval from his fellow directors of the newly independent company, Standard Oil (Indiana). What seemed like a risk in New York City was now a necessity in Chicago.

Standard Oil (IN) found itself after the breakup with excess refining capacity and a great dependence on others for its supply of crude oil. It was, therefore, essential to reduce its dependence on outside suppliers of crude by getting more products from each barrel of oil processed in its refineries. Burton trimmed his request to $800,000. The project was approved in Chicago because the Standard
Oil (IN) directors knew Burton well, respected his ability to run the Whiting refinery, trusted his scientific research results, and simply felt that they could rely upon Burton's recommendation because he was one of them.

Construction of the first six batteries of sixty stills began at the end of 1911. Each still was a drum on its side, 8 feet by 30 feet, built to withstand a pressure of 75 psi. From the top of each still rose the Humphreys run-backs, two 12 inch diameter pipes inclined toward the condensing coils. Connected to the condensing coils were vessels in which the liquid gasoline, separated from the light gases, was collected. A tall smokestack, exhausting the flue gas of the furnaces, rose above each battery. Construction was completed in November 1912, and the first stills began operation in January 1913. (See FIG. 3-5)

Success was apparent from the beginning. The Burton units performed as expected and doubled the yield of gasoline from crude oil. Within two years Standard Oil (IN) recovered the money spent on the first sixty units. The price of gasoline did not fall due to this doubling of the production capacity, but rose due to the increasing popularity of the automobile. In 1913, another sixty units were installed at the Whiting refinery, sixty units at the Wood River, Illinois refinery (across the river from St. Louis), and sixty units at the
In the Burton process, a gas oil reaction from the distillation of crude oil passes through tubes in a furnace and is heated to temperatures in the 700°F range for several minutes. Depending upon the pressure, as much as half of the hydrocarbons are vaporized and some are cracked; that is, chemical bonds in some of the larger hydrocarbons are broken in a series of thermal reactions to produce smaller hydrocarbons.

Burton discovered that there are many possible reaction pathways for these chemical processes and that the final product distribution can be controlled to some degree by variations in the temperature, pressure and heating times.

When Burton received the Willard Gibbs Medal from the American Chemical Society on 17 May 1918, he said, “Although we know very little about the reactions that occur when petroleum is distilled under pressure, it may be interesting to speculate a little on this subject. Let us start with the paraffin (or alkane), C_{14}H_{30} and see what might happen.”

**Cracking Reactions**

Breaking larger hydrocarbons into smaller ones:

\[ \text{C}_{14}\text{H}_{30} = \text{C}_{12}\text{H}_{26} \text{ (dodecanes)} + \text{C}_2\text{H}_4 \text{ (ethylene)} \]

\[ \text{C}_{14}\text{H}_{30} = 4\text{CH}_4 + 4\text{C}_2\text{H}_2 \text{ (acetylene)} + \text{C}_2\text{H}_6 \text{ (ethane)} \]

\[ 2\text{C}_{14}\text{H}_{30} = \text{C}_8\text{H}_{18} \text{ (octanes)} + \text{C}_{20}\text{H}_{42} \]

\[ \text{C}_{20}\text{H}_{42} = \text{C}_8\text{H}_{18} + \text{C}_{12}\text{H}_{24} \text{ (olefins)} \]

\[ \text{C}_{12}\text{H}_{24} = \text{C}_{10}\text{H}_{22} \text{ (decanes)} + \text{C}_2\text{H}_2 \]

“We feel confident that the finished gasoline contains such paraffins (or alkanes) as \text{C}_8\text{H}_{18} \text{ (octanes)}, \text{C}_{10}\text{H}_{22} \text{ (decanes)}, and \text{C}_{12}\text{H}_{26} \text{ (dodecanes)}, but one of the most interesting results is the formation of free hydrogen....”

\[ \text{C}_{14}\text{H}_{30} = \text{C}_{14}\text{H}_{28} + \text{H}_2 \]

[which can then react with some of the lighter gases in alkylation type reactions such as:]

\[ \text{C}_2\text{H}_2 + 2\text{H}_2 = \text{C}_2\text{H}_6 \]

“It also seems probable that, under the influence of heat and pressure, the gases of the different series polymerize to form saturated...
products that are useful [in alkylation type reactions]."

\[2\text{CH}_4 + \text{C}_2\text{H}_2 = \text{C}_4\text{H}_{10} \text{ (butanes)}\]

\[3\text{CH}_4 + 2\text{C}_2\text{H}_2 = \text{C}_7\text{H}_{16} \text{ (heptanes)}\]

[from Willard Gibbs Medal Address, "Chemistry in the Petroleum Industry" by William M. Burton. J. Industrial & Engineering Chemistry, 10, 486 (1918)]

In its early days, this new cracking process had its problems. For example, the amount of cracking, and hence the amount of gasoline produced, increased with temperature; but so did both the amounts of very light, gaseous hydrocarbons and the solid coke. With Burton’s equipment, it was very difficult to purify and improve the quality of any gasoline that was produced at very high temperatures. Also, as the coke built up during the cracking, it was very difficult to get good heat transfer in the stills and pipes. Cleaning the coke from the still and pipes at the end of each batch processed was a very expensive and time-consuming process.

Nevertheless, for the first time, the Burton Process synthesized, via chemical transformations, new smaller hydrocarbons from some of the larger hydrocarbons which occur naturally within crude oil. Up to this time, various hydrocarbons were only separated (not chemically changed) out of the crude oil mixture by distillation into fractions according to boiling point ranges to produce various refinery products such as kerosene, straight-run gasoline, greases and waxes. Burton’s thermal cracking process doubled the yield of gasoline from a barrel of oil and launched the petroleum industry into a new phase: the production of petrochemicals, the building blocks for synthetic polymers, plastics, and pharmaceuticals in the twentieth century.
Sugar Creek, Missouri refinery. In 1914, Standard Oil (IN) installed twenty Burton units at the Casper, Wyoming refinery and purchased gas oil from other refiners in the Wyoming crude oil field.

**Burton Process: Problems and Improvements**

In spite of these successes, there were difficulties with the Burton process.\(^{15}\) To minimize the possibilities of fires and explosions and maximize the efficiency of cracking, still operators were carefully trained by Dr. Humphreys on a commercial-size unit at the Whiting research laboratory. Except for fires at leaking joints, which could usually be extinguished without great damage, the operators had few problems. The slow step in the process was the cooling time and cleaning out the coke after each batch. The hot residual oil had to be pumped out, and then steam was blown through the tank to remove hydrocarbon vapors. Next, a man in an asbestos suit with a pick and shovel entered the still to clean out the coke. A compromise was reached between the desire to return the still to service and the heat that the cleaner must suffer. It was agreed that the cleaner would enter when the temperature dropped to 250°F.

The cracked gasoline had a yellow color due to some sulfur contamination. Customers were suspicious of the unusual color, having been cheated on other occasions by refiners who produced poor-quality gasoline as a result of inadequate quality control. Also, in many cars such as the Model T, the gasoline tank was located under the driver’s seat. The sulfur odor made it unpleasant to be in the driver’s seat if one had spilled a little gasoline during a fill-up. To overcome these problems, cracked gasoline was given a new name, “Motor Spirit,” and a reduced price (10.5 cents per gallon versus 13.5 cents per gallon for straight-run gasoline in 1913). The public, however, was not willing to accept the odor and strange yellow color at any price under any new name. Fortunately, Burton and Humphreys were able to make a few minor changes at the refinery to correct the color and odor problems. Cracked gasoline soon became indistinguishable from straight-run gasoline.

Improvements to the Burton process followed.\(^{16}\) In 1914, the first 120 stills were equipped with perforated plates to catch some of the coke before it settled on the bottom of the still. This enabled the still to operate longer under more controlled heating conditions, thereby increasing the gasoline produced by about 10%. The new fractionation-
ing techniques of the air cooled radiator in place of the two run-back pipes and the distillation tower, developed by Frank R. Lewis and Thomas S. Cooke in 1915, improved the process. (See FIG. 3-6). Fifty Burton stills, operating at 90–95 psi, were equipped with these new distillation (or bubble) towers in 1918. The bottom temperature of the tower was kept at 595°F (equal to the endpoint of kerosene distillation) so that all kerosene and lighter products would be in the overhead fraction. The distillation tower increased the amount of gasoline produced and the rate of production. However, only a few Burton units were built with these towers because the company lost too much money shutting down old units to retrofit them. In January 1922, two towers ruptured simultaneously, from corrosion not from pressure; twenty men were killed and the rest of the installations were condemned. Then, Indiana Standard was found in violation of the original Globe Oil of California patent for the use of these towers in the distillation of petroleum. The Burton process was abandoned during this decade as more profitable processes were developed.

**The Tube Still: Edgar M. Clark**

One major improvement to the Burton process in addition to the false-bottom plate, the radiator, and the distillation tower was the tube still designed by Edgar M. Clark while he was manager of the
A crude oil fraction is cracked in the still (1) due to pressure and heat from the furnace (2). The vapors rise up through a pipe (3) and enter the base of the bubble tower. Liquid/vapor mixtures are formed in the plate/bubble cap compartments (6, 7, 8, 9) of the tower (4) according to boiling point ranges of the fractions. Some of the liquid runs back into the still via the reflux pipe (11), while vapors are removed from the top of the tower (13) and carried to the condenser (14) and then to storage (16).

Standard Oil (IN) refinery at Wood River, Illinois. Unlike Burton and Humphreys, he had no formal academic training beyond elementary school. He began working as a railroad station agent, but in 1890 joined his father as an hourly laborer at Standard Oil. Because of his mechanical aptitude, energy, and inventive genius, he was promoted rapidly. First, he served as assistant superintendent under Burton at the Whiting Refinery; and in 1907, he was named manager of the new Wood River refinery. This assignment separated him from Burton and Humphreys, but he kept in touch with them because of their friendship. While separated from Burton and Humphreys, he gained a new perspective on the problems that they all faced during
the developmental years 1909–11. He tried some new approaches in his spare time. On his way to the office each morning, he would fire up a small experimental still, extinguish the fire on his way to lunch, relight it after lunch, and then collect and analyze his products in the evening.

He borrowed from the design of steam boilers because he recognized the similarities of producing pressure by heating water to create steam and by heating the oil to create oil vapors. The increased pressure then holds the mixture at an elevated temperature for the time required for cracking. He designed a series of pipes that send the oil back and forth across the length of the furnace a number of times, providing the time delay required for the cracking reaction. The rapid flow of the oil in a liquid-vapor mixture sweeps a larger portion of the coke along with it into a Burton type still located above the furnace and the tube stills. Because his results were promising and Burton stills were to be installed in his Wood River refinery in 1912–13, he ran the experimental still on a 24-hour basis and tracked the increase in gasoline output.

**Burton-Clark Process**

By 11 September 1914, he had perfected his design, applied for a patent, and started construction of the first twenty Burton-Clark units, which began operation in April 1915. Within four months, twenty units were installed at the Whiting refinery, and by December 1920, a total of 250 units were in operation at the Wood River, Whiting, Sugar Creek (Missouri), and Casper (Wyoming) refineries. In the furnace were 45 cracking tubes, each 4 inches in diameter and 29 feet in length.

These tubes lay along an inclined plane, lowest in the convection section of the furnace and rising through the convection and radiation sections. Circulation was aided by the natural flow of the heated oil in the inclined tubes. By the time that the oil reached the inclined section of the furnace, it had begun to crack. The cracked vapors were forced through the tubes by the hydrostatic pressure of the heavier liquids above them at a rate which carried much of the coke out of the reaction tubes and into the Burton still. Because the Burton still was now above the furnace, it served as a reservoir from which the cracked vapors could flow up the Humphreys run-back line and the partially cracked liquid could run back to the bottom and be returned
FIG. 3-7 A battery of Burton-Clark stills with Lewis-Cooke bubble towers which increased the production of gasoline and other products from the cracking and distillation of petroleum to the tube still with additional fresh crude and continue the cracking process.

The 4 inch diameter pipes of the tube still could be cleaned quickly with a mechanical router while hot. The Burton-Clark still could operate for 48 hours, rather than 24, before it had to be cleaned. It could process more oil in a semi-batch process, rather than a batch process. (See ChemTech 9.) The still was first filled with 9,150 gallons; then another 7,500 gallons of fresh gas oil was added to the recirculating steam and cracked before the formation of solid coke forced a shut down. By increasing the surface area of the gas oil relative to its volume in the furnace and sending the hot oil under pressure to the reservoir still, cracking occurred over a longer period in both places and efficiency was improved. If a pump adequate to
handle the hot oil had been commercially available, it is quite likely that Clark would have made a breakthrough to a continuous process. Before the end of 1916, Clark was running his stills at 100-110 psi and requesting permission to operate at any pressure up to 400 psi.

**Beginning to Produce Gasoline on a Big Scale**

The Burton process reigned supreme from 1913 to 1919, producing essentially 100% of the cracked gasoline. With its four modifications, the Burton Process achieved significant cost reductions for Standard Oil (IN) as Table 3-3 shows.19

<table>
<thead>
<tr>
<th>Process</th>
<th>Year Intro</th>
<th>Cost $/gal</th>
<th>Total % Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Distillation</td>
<td>before 1913</td>
<td>0.187</td>
<td>(Basis)</td>
</tr>
<tr>
<td>Burton Process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell Still</td>
<td>1913</td>
<td>0.135</td>
<td>27.8</td>
</tr>
<tr>
<td>with False-bottom Plate</td>
<td>1914</td>
<td>0.124</td>
<td>33.7</td>
</tr>
<tr>
<td>with Radiator</td>
<td>1915</td>
<td>0.114</td>
<td>39.0</td>
</tr>
<tr>
<td>Tube Still</td>
<td>1915</td>
<td>0.111</td>
<td>40.6</td>
</tr>
<tr>
<td>with Bubble Tower</td>
<td>1916</td>
<td>0.098</td>
<td>47.6</td>
</tr>
</tbody>
</table>

Adapted from Enos, p. 42. (in 1913 US $)

The Burton Process and its modifications gave Standard Oil (IN) the greatest return on its investment in the history of the petroleum industry. Approximately one-half of its profits of $366 million during the period 1913-1922 came from the Burton process (R&D costs $236,000).20 With such profits, Standard Oil (IN) executives had no fear that any competitive process could threaten them. They believed that the Burton Process was the best possible way of producing gasoline from the inexpensive gas oil fraction and that their patent position was strong and secure.

By 1918, this attitude, plus the problems of World War I, caused Standard Oil (IN) to lose its leadership role in research.21 In 1925 only half of the cracked gasoline was produced by the Burton process and in 1929, only 10%. Because Burton and his colleagues were chemists, trained in the batch process of the lab bench, their attention was focused more on the starting material and the resulting final product
than on the mechanics of the process. In the 1920s, the chemical engineers, who were more interested in the process, as a process, would lead these chemists and the industry from batch processes to continuous processes in a renewed effort to produce even more gasoline from each barrel of oil.

ENDNOTES


5. Enos, pp. 4-5.


8. Enos, pp. 6-10.


15. Enos, pp. 24-27.


CHAPTER 4

Solving the Gasoline Shortage of the 1920s

The Rise of Roads and Autos in the 1920s

By the decade of the 1920s, the automobile and the road — one a product of private industry and the other a product of public agencies — were restructuring the American landscape in significant ways. There was one automobile on the road for every 4.5 persons (by 1967 one auto for every 2.3 persons), and 55% of American families owned automobiles. By 1927, when Ford stopped production of the Model T and began to meet the competition from General Motors under the direction of Alfred P. Sloan, the automobile was America's leading industry in terms of the value of the product.

The construction of roads accounted for the second largest expenditure of public funds in the 1920s. In 1921, the United States had 2,713,000 miles of dirt roads, but only 447,000 miles of roads surfaced with paving stone, gravel, concrete, or asphalt (by 1965, the proportions were almost reversed). The success of the automobile created a huge new market for asphalt to improve many of these dirt and gravel roads. The demand for gasoline by automobiles, and also by the new aviation industry, frequently exceeded the available supply. Public fears of shortages were widespread. Also, the higher compression ratios of the improved internal combustion engines required higher octane ratings to avoid engine knock.

Origins of the Dubbs Process

As news of the Burton process spread throughout the industry, other inventors were stimulated by the promise of big profits to develop competing processes to satisfy this increased demand for gasoline. In two years, ten new commercially successful processes were introduced: the Coast, Dubbs, Emerson, and Fleming processes in 1920; and the Cross, Greenstreet, Holmes-Manley, Isom, Jenkins, and Tube and Tank processes in 1921. The Dubbs process stood out among all the others because of its remarkable successes.
The absence of knock is one of the most important requirements for high quality gasoline because engine knock can be annoying, waste fuel and damage the engine. A good-quality gasoline must have a high antiknock value, or octane number, to prevent engine knock at all speeds and loads. Ideally, the spark plug should ignite the vapors of the fuel-air mixture, and the combustion should proceed smoothly and evenly down the cylinder. Knock results because chemical reactions begin in the fuel-air mixture as soon as it is drawn into the cylinder during the intake stroke.

As the mixture is progressively heated by the cylinder walls, by compression prior to the power stroke and by burning gases after the spark plug fires, some of the hydrocarbons undergo a series of cracking and oxidation reactions producing unstable molecules. The spreading flame front sweeps across the cylinder, heats and compresses the unburned portion of the fuel, and causes these unstable molecules to autoignite and to detonate throughout the cylinder instantaneously.²

Rather than being pushed down in a smooth power stroke, the piston is given a sharp, hard rap by the sudden pressure changes to which it cannot respond because it is physically connected to the crankshaft. Throughout the cylinder, this autoignition causes high-frequency pressure fluctuations in the audible range. The human ear hears the sharp, pinging metallic sound called knock or spark knock. Fuel energy is wasted in the form of these pressure waves and in increased heat radiated to the surrounding engine parts and the cooling system.

Prolonged knocking overheats valves, spark plugs, and pistons and contributes to their wear. Knock can be thought of as one possible outcome in a race between the flame front advancing down the cylinder and the generation of unstable intermediates in the precombustion gas. If the precombustion gas reactions get ahead of the flame front, knocking will result.

In 1919, Charles F. Kettering and Thomas Midgley, Jr. at General Motors began a series of experiments to determine the cause of engine knock and to discover how to prevent it. Their work led to the discovery of tetraethyllead as a significant antiknock compound.

In 1926, Graham Edgar at the Ethyl Corporation developed the octane scale to measure in a quantitative way the antiknock characteristics of various gasolines. When the alkane, n-heptane, is burned in a standard internal combustion test engine (single-cylinder, four-stroke, variable compression ratio), it produces a large amount of knocking. So n-heptane was selected as the fuel to set the zero reference point on this new numerical scale. If 2,2,4-trimethylpentane (also called iso-
Octane Number Scales at the Gas Pumps

octane) is used as the fuel in the standard test engine, no knocking is heard. So, pure isooctane was assigned the value of 100 on this scale. To standardize the test engine, various reference fuel mixtures of n-heptane and isooctane were assigned values equal to the percent isooctane in each mixture. For example, the amount of knock from a reference fuel mixture of 13% n-heptane and 87% isooctane was assigned an octane value of 87.

To determine a fuel's anti-knock characteristics, the test engine is operated with the test fuel under one of two sets of standard conditions. Auxiliary equipment detects pressure impulses from the detonation and records the knock intensity. This knock intensity is bracketed by two reference fuel mixtures. The octane value of the test fuel is determined by interpolation between the octane values assigned to the two reference fuel mixtures.

These two sets of standard test conditions give rise to two octane scales. The Motor Octane Number (MON) was developed for fuels and automobiles in use in the 1930s. The Research Octane Number (RON) uses a less severe set of test conditions to reflect the improvements in fuel and auto performance since World War II. The difference between RON and MON is called the sensitivity (SEN = RON - MON). For two fuels with the same value of RON but different values for MON, a smaller sensitivity (RON - MON) indicates good antiknock performance. Aikanes do not contribute to sensitivity since they are also the reference fuels, but olefins and aromatics do. Today, the average of the RON and MON values are reported on the pumps at gasoline service stations as the "octane number" (or antiknock index), since taken together they are a better predictor of the gasoline's antiknock quality than either one individually.

If the compression ratio of the engine can be increased, then the power obtained from the combustion of the gasoline-air mixture in the engine can be increased. Increasing the compression requires work. The fuel supplies the necessary energy for this work, but the power produced by the engine exceeds the work required for the compression step. Less heat is rejected to the cooling system; more of the heat (energy from the fuel) goes to useful work, increasing the efficiency of the engine.

The octane scales are not linear with respect to compression ratio (see the right side of Figure 4-1.) In the 1930s, car engines operating with a compression ratio of 5:1 required gasoline with octane ratings of 70–75. During the 1960s, car engines operating with a 10:1 compression required gasolines with an octane rating of about 100 to avoid knocking. Because of the oil crisis in cont >>>
Octane Number Scales at the Gas Pumps

1973–74 and the resulting changes in engines, the autos of the 1980s and 1990s operate at lower compression ratios and require fuel with octane ratings between 87 and 93.

During World War II, the U. S. Army and Navy developed a linear scale, called the Performance Number (PN), to rate the antiknock quality of aviation gasoline used in supercharged aircraft engines. The PN scale is related to the MON scale (See the left side of Figure 4-1). Although modern methods of expressing gasoline knock characteristics such as highest useful compression ratio (HUCR), aniline equivalent, and benzene equivalent have been developed, the empirical RON and MON scales have served as excellent methods to evaluate the quality of gasoline for over sixty years.

Table 4-1 Performance Characteristics of Some Gasolines

<table>
<thead>
<tr>
<th>Process</th>
<th>Date</th>
<th>Boiling Range °F</th>
<th>RON</th>
<th>PN</th>
<th>Ton-Miles at 40 mph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burton</td>
<td>1913</td>
<td>430–750</td>
<td>55</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>Dubbs</td>
<td>1922</td>
<td>430–1000</td>
<td>73</td>
<td>52</td>
<td>29.2</td>
</tr>
<tr>
<td>Houdry</td>
<td>1936</td>
<td>430–750</td>
<td>87</td>
<td>71</td>
<td>39.5</td>
</tr>
<tr>
<td>Fluid Bed</td>
<td>1955</td>
<td>430–1000</td>
<td>95</td>
<td>85</td>
<td>49.5</td>
</tr>
</tbody>
</table>


Table 4-2 Octane Numbers for Typical Grades of Gasoline

<table>
<thead>
<tr>
<th>Grade:</th>
<th>PREMIUM</th>
<th>REGULAR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summer</td>
<td>Winter</td>
</tr>
<tr>
<td>Research Octane Number (RON)</td>
<td>97.0</td>
<td>97.7</td>
</tr>
<tr>
<td>Motor Octane Number (MON)</td>
<td>88.6</td>
<td>87.3</td>
</tr>
<tr>
<td>Sensitivity (= RON – MON)</td>
<td>8.4</td>
<td>10.4</td>
</tr>
</tbody>
</table>

FIG. 4-1 Gasoline octane ratings on the MON and PN scales vs. the minimum compression ratio for no engine knock

The story of the Dubbs process begins in California in 1909.4 Jesse A. Dubbs, a Pennsylvannia oil refiner, built a small skimming plant near Santa Barbara, California to produce asphalt from heavy crude oil in the nearby Santa Maria oil field. His three sons, Leland A., E. J., and Carbon Petroleum (C. P.) worked with him to design a new process that would break the emulsion formed between the salt water and the crude oil. It was almost impossible to handle this Santa Maria oil by the ordinary distillation methods of his day. Jesse Dubbs invented a tube still in which the pressure increased due to the vaporization of some of the chemicals in the crude oil as the temperature increased. His goal was to break the emulsion, to separate the asphalt from the salt water, and produce a good paving material for roads.

Apparently, he did not realize that some cracking of the heated oil under pressure was also occurring. In his first patent application filed in November 1909, he did not claim cracking in his process to manufacture asphalt. In a second patent application, filed in June 1911, he again failed to claim any cracking upon heating with pressures as great as 600 psi. The appearance of the Burton process in 1913 and a visit from Frank L. Belknap, an attorney for Jonathan Ogden Armour who wanted to purchase his patents, changed Jesse Dubbs’ view of his asphalt process.

Armour and Dubbs

As a freshman at Yale in 1901, Jonathan Ogden Armour was called home at the death of his father, Philip Danforth Armour.5 Since his father had owned 72% of the stock of Armour and Company, the giant Chicago meat products company, Ogden took control of the company. Aided by World War I, efficient utilization of the meat by-products, vertical integration of the company, and his enterprising management, Armour and Company’s annual sales increased from $100 million in 1901 to a peak of $1 billion in 1918. J. Ogden’s personal share of the profits in 1917 alone was $15 million out of the $21 million total. With such riches beyond any conceivable private needs, Armour began to invest in novel enterprises.

Armour was attracted to the new petroleum industry. He saw a parallel between the improvements that had been made in the meat processing industry and possible improvements in the petroleum industry. Great profits were made in meat processing by
changing from a batch process (one person butchering a whole animal) to a continuous disassembly line. The carcass was moved down a line as each worker performed one task in the butchering process.

If the petroleum industry could change from a batch process to a continuous process, then greater profits might result. This would require a change from cracking and distilling one charge at a time in a Burton unit to a new process with crude continuously flowing into a unit reactor, the same chemical reaction occurring at each point in the flowing system, and gasoline continuously flowing out.

One of J. Ogden’s first investments outside the meat industry was the purchase of the Standard Asphalt and Rubber Company in Independence, Kansas in 1913. The company was started in 1906 to manufacture asphalt and a synthetic rubber out of the inexpensive heavy residues left by various petroleum refining processes. Air was blown into the liquid residue of a Kansas crude especially rich in asphalt. This oxidation process improved the quality of the asphalt. Standard Asphalt licensed this oxidation process to a number of oil companies, but it steadily lost money, due primarily to inadequate storage facilities. By 1914, its deficit reached $300,000. At this point, Armour felt something should be done, so he sent Hiram J. Halle to rescue the operation. Halle had been an effective troubleshooter for Armour in the past, saving two other dying firms. After taking charge in November 1914, Halle enlarged the plant at a cost of $250,000, improved its operating efficiencies, and generated a profit of $350,000 in the next year. Armour made him president of Standard Asphalt and Rubber Company in 1916.

Universal Oil Products Formed

In 1913, Armour purchased from Jesse A. Dubbs for $25,000 a group of patents which would help to protect his investment in Standard Asphalt. The purchases were made through Frank L. Belknap, Armour’s attorney at Standard Asphalt. Armour had given Belknap the assignment to purchase, if possible, all U.S. patents related to the manufacture of asphalt. Because Belknap was from Chicago, he was familiar with the Burton process and recognized immediately the similarities between the Dubbs process (patent filed in 1909 but not granted until 1915) and the Burton process (patent filed and granted in 1913). Carbon Petroleum Dubbs, who was now working for
Standard Asphalt, helped Belknap to persuade his father to sell the patents to Armour. Belknap began a yearlong process of amending and consolidating the pending Dubbs patents to broaden and modify them. Walter M. Cross (the 1921 Cross Process), a chemistry professor at Kansas University Medical College, appeared as one of Belknap's expert witnesses before patent examiners on 29 October 1914. When the final patent was granted on 5 January 1915, it was for the treatment of oil with heat and pressure. The original goal of breaking the emulsion to produce asphalt had now become a very minor part of the final patent.

On 24 November 1914, Universal Oil Products (UOP) was created to hold these newly acquired patents. J. Ogden Armour held 20% of UOP's stock, Jesse A. Dubbs, 30%; Armour gave the other half of the stock to five business associates, including 2% to Belknap. Later these gifts were to grow and to number among the largest in history. With the patent in hand, Halle immediately brought suit against Standard Oil (IN) for patent infringements in the operation of the Burton process. A sixteen year legal battle began.

UOP needed to construct and operate a process according to its patent claims to demonstrate that it could produce gasoline just as the Burton process did. Such activities required money and engineering
By either chemical or physical operations, a chemical process transforms the raw materials (input stream or feedstock) that enter a reaction vessel into desired products (output stream). These chemical processes are classified as batch, semi-batch, or continuous.

In a batch process, the feedstock is added to the reaction vessel at the beginning of the operation, and the products are removed in a single step after the processing of the feedstock is complete. In a continuous process, the feedstock flows continuously into a reaction vessel, and the products flow continuously out of the reaction vessel. The reaction vessel for a batch process may be a vat holding several hundred to over 20,000 gallons of reactants (e.g., 7,000 gal. Burton cracking still). The reaction vessel for a continuous process might be a column several hundred feet in height (e.g., a distillation column) or a length of piping which provides the time delay for the reaction to take place (e.g., fluid bed catalytic cracker).

A batch process is typically used when small amounts of product are desired, whereas the more efficient, continuous processes are frequently used when great quantities of products are desired. A semi-batch process has characteristics of both batch and continuous processes: either the feedstock input stream or the product output stream operates continuously and the other stream operates in an almost instantaneous mode (e.g., Dubbs clean circulation).

Continuous processes are usually operated at steady-state conditions, while batch and semi-batch processes are operated under transient, or unsteady-state, conditions. In a steady-state operation, all of the process variables (e.g., temperature, pressure, volumes, flow rates, etc.) do not change with time. But in a transient operation, the process variables do change over time.
skill. Cities Service Company agreed to purchase Standard Asphalt for $3 million in 1916, and Armour turned over his share ($2 million) to UOP so that Halle could transform UOP into a research and development laboratory located on part of the old Standard Asphalt refinery property. Carbon Petroleum Dubbs was appointed principal research engineer on the new laboratory staff because of his refinery experience, energy, and enthusiasm.8

After two years, the company laboratory moved to the Chicago area (Riverside), and Carbon Petroleum built a laboratory in his home at Wilmette, Illinois.9 In his home laboratory, he conceived the idea of "clean circulation," which became his major improvement to his father's process. In the clean circulation process, a part of the cracked distillate (or reflux), which is heavier than gasoline, was circulated from the condenser of the fractionating tower back to the cracking tubes for additional cracking. This cleaner distillate was lighter than the incoming fresh feedstock of gas oil. It diluted the gas oil and reduced the formation of coke. With less coke formed, the process could also accept crude oil as a feedstock. Recall that the Burton process could only accept the gas oil fraction or other distillates produced during the first distillation of the crude oil. This advantage, plus the continuous flow feature from Jesse's first patent, were the two major improvements over the Burton process.

While research continued in Riverside, two pilot plants were constructed in Independence, Kansas. The first followed Jesse's patent, and the second in 1918 incorporated the clean circulation concept as designed by Carbon P. Dubbs. The feedstock was heated as it passed through a bank of horizontal pipes in the furnace and then rose through a split run-back pipe to a fractionating tower. A reflux stream from the fractionating tower mixed with incoming feedstock for additional cracking and the gasoline fraction was condensed and sent to storage tanks. Gas oil leaving the heating coils was held at a temperature of 820°F and 135 psi. Note the similarities to the Burton process, but the important difference of continuous processing at higher temperature and pressure.

UOP Licenses the Dubbs Process

In 1919, Halle decided it was time to show the process to prospective licensees. He approached Shell Oil Company, which operated a refinery in Wood River, Illinois called Roxana Petroleum Company.
Halle chose Shell because it was large, competed with Indiana Standard, and was not permitted to use the Burton process. Others were interested and Halle arranged a public display of the process for twelve days beginning on 22 June 1919. At this display, Halle announced that the Dubbs process would be available to all refiners without reservation or discrimination. This included guaranteeing performance and yield, and sharing all technical information and updates. The royalty rates would be the same for all, based on barrels processed not on profits generated by the licensee. Also, UOP would defend all suits brought against a licensee for patent infringement.

On 12 December 1919, Roxana Petroleum purchased a license to operate the Dubbs process, following Halle's guarantee that the Roxana unit would have a capacity of 250 barrels per day (Burton = 89 barrels, Burton-Clark = 225 barrels per day). Construction of unit No. 1 at Roxana was completed in March 1921. Dubbs could not reach the guaranteed output of 21% gasoline on the basis of 250 barrels of charge per day because they were unable to clean out the unit within the required 24 hour time period.
An Explosion Leads to a New Design

On the tenth run of the unit in December 1921, the unit exploded and killed two men. This was a severe, costly blow to the young process design company. Although C. P. felt personally responsible, he replaced the design engineer with two new ones and made a major break from his father's design. He decided that a single, large diameter reaction vessel could replace the small diameter soaking tubes designed by his father. It would be less likely to become clogged with coke leading to ruptures, fires, and explosions. He also added two vents and a safety valve to the reaction chamber, a cylinder 4 feet in diameter and 30 feet long. The furnace was redesigned to contain nine rows of tubes, alternating between three and four tubes per row. The dephlegmator (or fractionating tower) was raised higher to increase the pressure in the recycle leg. The single receiver house was replaced with a pump house having a pressure distillate condenser on its roof. Roxana No. 1A did not look like No. 1 in process design or appearance. These design changes and setbacks cost Armour another $4 million.

By 1921, Armour's financial condition had deteriorated significantly. Armour and Co. and its Sutter Basin project (a large scale irrigation project in the Sacramento Valley) had a combined deficit of $31 million. By the end of 1922, Armour's personal debt soared to $56 million, but at UOP the financial picture was beginning to improve. Having run deficits in prior years, UOP earned a $5,000 profit as Roxana No. 1A began to operate satisfactorily. Just as the UOP royalties began to flow in, Armour passed into the hands of his creditors. UOP's annual royalty income topped $2 million in 1925. Even so, UOP needed more cash to meet the continuing costs of designing and testing additional Dubbs units. To help, a friend loaned Armour $150,000 of Liberty Bonds. Using the bonds as collateral, Halle borrowed $135,000 for UOP. UOP never needed to borrow money again.

The second unit at Roxana cost $60,000 and had a 500 barrel capacity. Buying a standardized unit from what was now becoming a well-recognized process design company was a great aid to the small refiner. They could attract investor capital by using standard units from UOP, and they could operate using a variety of feedstocks. By the end of 1926 the Dubbs process was well established in the industry, and many companies, working as licensees, had contrib-
uted to its improvement (e.g., Shell of California's design of a hot oil pump). The capacity of the Dubbs unit increased to 4,000 barrels per day in 1931, aided by improvements such as electric arc welding. The size of the Burton still was limited because electric arc welding was not available until the 1920s. By 1926, great enhancements in fractional distillation, notably by Warren K. Lewis of MIT, had been made so that the production of a specific type of gasoline from a cracking unit was possible. By cracking less severely and removing the cracked oil from the soaking chamber more quickly, refiners could reduce the coke formation and the down time for cleaning.

The Big Five Purchase UOP

Standard Oil (CA), dissatisfied with the results from its license to operate the Burton process, purchased a license for the Dubbs process in 1924. Its royalties to UOP rose from $32,000 in 1926 to $1 million in 1929. With even bigger units coming on stream in 1930, Standard Oil (CA) expected to pay over $2 million the next year. Shell Oil had paid $3 million in 1929 and also expected to pay even higher royalties. At first, Shell and Standard Oil (CA) chose to pay the royalties rather than try to develop their own processes because they expected the
Burton-Dubbs patent dispute to nullify both patents, putting the processes in the public domain. They did not anticipate that the legal battle would last sixteen years and then be settled out of court. But with the legal battle dragging on they changed strategies.

On 6 January 1931, Shell and Standard Oil (CA) negotiated a deal with three other oil companies to purchase UOP for $25 million. Shell paid $10 million; Standard Oil (CA), $5.4 million; Standard Oil (IN), $3.3 million; Standard Oil (NJ), $3.3 million; and The Texas Company (later Texaco), $3 million. Mrs. Armour received $10 million for her 400 shares; Halle, $3.2 million; C. P. Dubbs, $3.6 million; Belknap, $1.1 million, with the balance going to the remaining shareholders. During the 1930s the royalty rate was reduced in several steps from 15 cents per barrel to 5 cents, and in 1944 to 3 cents.

After its purchase by the big five, UOP retained its independence. The agreement called for Halle to remain as president for fifteen years; and UOP continued to reflect, under his leadership, its founding ideas of open research and development. Unlike Standard Oil (IN), it believed that such an open sharing of research aided UOP and the petroleum industry in general. As early as 1927, it recognized the need for research in catalysis and oxidation. Not able to afford research in both fields, Halle chose catalysis. In 1929, UOP recruited the famous Russian expert in catalysis, Vladimir Ipatieff, who in turn recruited Hans Tropsch, the German chemical synthesis expert. The result of UOP's research team was catalytic polymerization (1935) and catalytic reforming (1949); they also played a prominent role in fluid catalytic cracking (1942) pioneered by the French engineer, Eugene Houdry.

In 1944, the five owners of UOP set up the Petroleum Research Fund, which was to hold the UOP stock with the income passing to the American Chemical Society to sponsor research in petroleum chemistry and chemical engineering. Now, the royalties paid by the licensees returned to the industry in the form of new research. In 1959, the American Chemical Society sold the stock in UOP to the public for $72.5 million, returning UOP to its original status as an independent company, and created a diversified endowed fund. The Petroleum Research Fund continues today with a program of research grants to colleges and universities to support technological progress in the broad area of petroleum.
ENDNOTES


3. Enos, p. 60.


5. Enos, pp. 61-63.


8. Enos, pp. 69-70.


10. Enos, pp. 78-79.

11. Enos, pp. 80-81.

12. Enos, pp. 81-87

13. Enos, pp. 87-89.

CHAPTER 5

Catalytic Cracking of Petroleum

French Origins of Modern Catalytic Cracking

Eugene Jules Houdry was born in Domont, near Paris, on 18 April 1892, and died in Philadelphia on 19 July 1962. He was educated as an engineer because his father wanted him to join the family firm which manufactured structural steel. After three years of experience in the firm and being made a partner, he was called into French military service in 1914. After duty in the artillery, he was transferred to the tank corp and took part in the first tank battle of World War I. He was seriously wounded in the Battle of Juvincourt on 16 April 1917. After the war, he returned to the family business, now called Houdry & Son, and was elected a director of several other companies, including one which manufactured automobile parts.

He was fascinated with auto racing, especially the mechanical and technical aspects. Auto racing placed great demands on both the machinery and the fuel. Racing, as we have seen with Henry Ford, was used to popularize the automobile and to test improvements in the fuel and the design of the auto. While visiting the United States in 1922, Houdry attended the race in Indianapolis and visited Ford's assembly plant in Detroit. Houdry recognized that additional improvements in engine design could not be made until the quality of the fuel was increased. Also, from his military experiences and observing the importance of the airplane, he knew that great quantities of high-quality gasoline would be essential to defend France in another war. Motivated by patriotism, he wanted to improve gasoline so France would be strong enough to stay out of another world war.

During and after World War I, many researchers tried to make gasoline out of a variety of abundant starting materials: the distillation of bituminous coal at a low temperature, the destructive hydrogenation of bituminous or lignite coals or the oils derived from these coals, and the hydrogenation of carbon monoxide (also called the water-gas synthesis). Houdry and his father had invested in some
of these processes, including a process developed by E. A. Prudhomme. When the results of using metals such as nickel and cobalt as catalysts in the water-gas reaction did not lead to a commercially viable process, Houdry and his father bought out the Prudhomme group so that Eugene could take over the catalysis research. Prior to Burton’s thermal cracking, which doubled the amount of gasoline produced from a barrel of crude, there was widespread fear of a shortage of crude oil. World War I renewed such fears. After the war, demand for gasoline again exceeded available supplies. Houdry realized that catalytic cracking might meet this new increased demand if it could increase the yield of gasoline per barrel of oil to even higher levels.

First Attempts at Catalytic Cracking

The Houdry family had the financial resources necessary to support Eugene in such a major research effort. And Eugene had the necessary skills, energy, and enthusiasm for the project. He often stayed in the laboratory around the clock, monitoring his experiments and napping on a nearby bed. His background in engine fuels and in mechanical engineering prepared him for the evaluation of each new batch of gasoline and for the fabrication of the new equipment to handle the catalyst in the cracking vessels. Within his new process company, he created a research team composed of a chemist, a mechanical engineer, and a civil engineer who would conduct many of the daily experiments on catalytic reactions. A large amount of Houdry’s time was spent trying to obtain funding by promoting the potential benefits of a catalytic process to the French government.
Houdry and the team studied fundamental catalytic reactions of hydrocarbons from various sources because little was known about catalysis in 1925. Both of the two known types of catalysts (pure metals used for hydrogenation and aluminum chloride) retarded the cracking of petroleum. Nickel, cobalt, and iron were known to be catalysts, but they produced large quantities of coke (or carbon) which coated the metal pellets and eliminated their catalytic activity. But Houdry was not discouraged. In a procedure similar to one used by Edison, who tried hundreds of substances as filaments for his electric light bulb, Houdry spent three years in the empirical testing of hundreds of chemicals for their catalytic activity in the cracking reaction.

At three in morning one day in April 1927, he noticed that a charge of low grade heavy crude petroleum was producing a clear distillate from a column packed with the oxides of silicon and aluminum (silica and alumina). It tested well in his automobile on a nearby hill, meeting Houdry’s high standards of performance. Of course, carbon was deposited on the catalyst during the reaction. Having found a suitable catalyst, Houdry now had to solve the problem of developing a process to remove the carbon, regenerating the catalyst for re-use.

Houdry decided to take the simplest approach to removing the carbon coating from the silica and alumina granules. He drained the oil from the reaction vessel and burned the catalyst in the presence of air to oxidize the carbon to carbon dioxide. The cracking reaction is endothermic (requires heat), but the oxidation of carbon is exothermic (gives off heat). Using some of the heat liberated in the regeneration of the catalyst could make the overall cracking process more economical. But a number of design problems remained to be solved, such as the down time for the still while the catalyst was being regenerated. The competing hydrogenation process of I. G. Farben in Germany seemed to have more promise; so interest in the Houdry process at this point was limited. Even so, several oil companies, including Standard Oil (NJ), did visit Houdry’s laboratory soon after his first success was announced.

By 1929, Houdry and the team had also demonstrated a commercial process to produce gasoline from lignite coal. But the cost of the process was very high, and the French government withdrew its subsidy, forcing Houdry to close his plant at St. Julien.
In a chemical process designed to manufacture a product, the rate of the chemical reaction must be controlled so that product is produced in a reasonable amount of time. The chemical engineer can control the rate of the reaction by varying the concentrations of the reactants and products, by changing the temperature, by changing the pressure, and by using a catalyst.

A catalyst is a substance that changes the rate of a chemical reaction without being consumed in the reaction. If the catalyst is not poisoned, it can be used over and over. It is possible to regenerate a poisoned catalyst, restoring its ability to alter the rate of a reaction. In the manufacture of gasoline, a catalyst can increase the rate of conversion of crude oil feedstock into desired product at constant temperature, pressure, and reactant concentrations. Note that not all catalysts are accelerators of reaction velocities; some slow reaction rates (e.g., inhibitors in food products to retard spoilage).

Catalytic processes can be grouped into two categories: homogeneous catalysis, if the catalyst is in the same phase as the reacting substance, or heterogeneous catalysis, if the catalyst is in a different phase from the reactant. Solid oxides of aluminum and silicon plus various metals in pellets and powders are used in the heterogeneous catalytic cracking of petroleum since the catalyst is a solid and the reactants are liquids and gases.

Heterogeneous catalysis involves four steps: first, the reactant diffuses to the surface of the catalyst; second, the reactant is adsorbed onto the surface of the catalyst; third, the adsorbed reactant is converted into an adsorbed product; and finally the adsorbed product diffuses away so the process can be repeated with a new reactant. This process lowers the energy required so that the reaction can proceed at a faster rate to its equilibrium point. In the cracking of petroleum, coke is one of the products formed on the surface of the catalyst. The coke poisons the catalyst with a coating that blocks other molecules from being adsorbed on the surface of the catalyst. So the rate of the reaction is reduced. Eventually, the coke buildup is so great that the catalyst must be regenerated by removing the coke. If a reactor design, such as the fluid bed catalytic cracker, can increase the surface area of the catalyst exposed to a given amount of petroleum, the efficiency of the process is enhanced.
Houdry Moves from France to America

In the six years from 1923–1929, Houdry spent a large amount of his and his wife’s money. Houdry anticipated that the stock market crash in 1929 and the business recession would probably reduce demand for gasoline. So he expected it would be difficult to obtain additional funds to continue his research. However, Harold F. Sheets, a European representative of the Vacuum Oil Company, was impressed by the potential of the Houdry process and persuaded his company to take out a license. Because Houdry needed more financial support, Sheets was able to convince Houdry to move his research to the Paulsboro, New Jersey laboratories of the Vacuum Oil Company in October 1930. The next year, Houdry and Vacuum Oil formed the Houdry Process Corporation; Houdry and his French associates held two-thirds of the stock and Vacuum Oil, one-third. Now, Houdry could concentrate on his laboratory work since he had financial security in the new company.

But the security did not last long. Later that year, Vacuum Oil merged with Standard Oil of New York (Socony, later to become MOBIL). Because Houdry’s pilot plant results were not as good as expected, he lost some support from the new managers. So, Houdry approached Arthur E. Pew, Jr. and Clarence H. Thayer of Sun Oil Company about a collaboration. They realized the potential of the process and purchased half of the shares held by Houdry and his French associates. In exchange, Houdry moved his research operations to the refinery and laboratories of Sun Oil in Marcus Hook, Pennsylvania.

Since the depression caused a drop in the heavy fuel oil market price, Houdry shifted his research from cracking the gas oil fraction (Burton’s feedstock) to cracking the heavy fuel oil fraction. As Burton had discovered, using the heavy fuel oil as the starting material in the cracking process increased significantly the formation of coke. But Pew and Houdry were willing to take the risks of attempting to design processes and equipment which would cope with the buildup of coke on the catalyst and with the crucial regeneration cycle to remove the coke from the catalyst.

Quite unexpectedly, the demand for gasoline remained stable during the depression, and competition within the industry centered around improving the quality of the gasoline. As the country began
to come out of the depression, demand for gasoline increased and the need to replace thermal cracking as the standard process was obvious to all in the industry. Sun Oil, a smaller refinery with close contact between its owners and managers, marketed a single grade of gasoline superior to the general grade of gasoline widely sold. Sun Oil's interest in the Houdry process was driven by its desire to be first with a new process to produce even better gasoline so as to maintain its competitive advantage in the marketplace.

The Pew Family Creates Sun Oil

J. Newton Pew, Sr., a former school teacher, founded Sun Oil as a result of his interests in the transmission of natural gas via pipelines and became a a competitor of John D. Rockefeller. In 1877, Pew purchased natural gas from the oil wells in Pennsylvania and piped it to Olean, New York, and five years later through another pipeline to Pittsburgh. In the 1890s, he and his friend formed Pew and Emerson Company to enter the liquid oil business. After Emerson dropped out, the company became Sun Oil and built its first refinery in Toledo, Ohio. In 1901 Sun Oil constructed its Marcus Hook, Pennsylvania refinery to process Mexican crude for the northeast market. After the great Spindle Top field in Texas began producing crude the next year, Mexico was dropped. Oil from Spindle Top, a source of high-quality oil with a good lubricating oil fraction, was brought to Pennsylvania in Sun's schooners, ocean tankers of the period, which carried about 30,000–40,000 barrels of oil.

J. Howard Pew, one of J. N. Pew's three sons, attended Grove City College and the Massachusetts Institute of Technology as his father had, and returned home to manage the Marcus Hook Refinery. In 1910 J. Howard became president and devoted his attention at first to the lubricating oils part of Sun Oil's business. Because the Spindle Top field in Texas provided Sun Oil with a high octane gasoline for its special markets and because of the high gasoline prices after World War I, he changed his attention from lubricating oils to gasoline in 1920. Sun's refinery could produce 3,000 bpd of gasoline, dyed blue to give it a distinctive color, and marketed it as Blue Sunoco for the first time in 1927.

Fixed-Bed Catalytic Cracking

To protect Sun's market during the 1930s, J. Howard Pew supported the recommendation from his nephew Arthur E. Pew, Jr. (vice
FIG. 5-2  Houdry fixed-bed catalytic cracking process diagram

president of manufacturing) to buy into the promising Houdry Process.\textsuperscript{10} By 1936, Houdry's research led to increasing the yield of gasoline from 23% of the crude oil to 43% from his catalytic cracking process. Both Sun and Socony constructed Houdry fixed-bed catalytic cracking units. The octane rating increased from 72 for thermally cracked gasoline to 88 for gasoline from the catalytically cracked process.

Socony constructed a Houdry unit at Paulsboro, New Jersey which would process 2,000 bpd of light gas oil in June 1936.\textsuperscript{11} The following year Sun Oil's Houdry unit at Marcus Hook began processing 12,200 bpd of heavy gas oil. In 1939 Sun constructed a two-stage process, one for the first crude distillation and the second stage for catalytic cracking at the Marcus Hook and Toledo refineries. The unit size was quickly increased from 28,000 bpd to 45,000 bpd of crude. By the end of the year, Sun and Socony had spent $35 million to construct fifteen catalytic cracking units having a combined capacity of 221,675 bpd. In three years these two companies increased the industry's
total cracking capacity by 10%. The cost of cracking by the Houdry process was 24.5 cents per barrel of gas oil compared to 31.5 cents via thermal cracking in 1938. Like the Burton process, the Houdry process was a significant technological advance. With the patent protection, each company was able to invest large sums of money very quickly to capture a significant share of the market.

The actual manufacturing process to produce the catalysts in pellets had its origins in some of the early work of J. Howard Pew in Marcus Hook before World War I. Sun had developed a silica-alumina gel for decolorizing its lubricating oils and, in a similar way, coprecipitated silicon and aluminum salts in pellets for use as the synthetic catalyst in the fixed beds of the Houdry Process in 1940. These fixed-bed units operated by Houdry and others were crucial to the World War II effort because they produced high-quality gasoline and aviation fuel (90% of all the catalytically cracked aviation fuel during the first two years of the war).12 After the war the Houdry fixed-bed process yielded to the fluid-bed process.

FIG. 5-3
Houdry fixed-bed catalytic cracking plant with three reactors

Courtesy of the Houdry Process Corporation
Thermofo r Catalytic Cracking

Both the Thermofo r Catalytic Cracking (TCC) and Houdriflow pro-
cesses grew directly out of the Houdry fixed-bed catalytic process. Both of these catalytic processes replaced the Houdry fixed-bed process within ten years. The Houdry fixed-bed process equipment was expensive to construct. The metals and materials for reaction vessels were in short supply due to World War II. Like the thermal cracking processes, it could not handle very heavy fractions or stocks with a high sulfur content. But the principles demonstrated by Houdry were applicable to the development of a new continuous process with a circulating or moving-bed catalyst.

Research on a moving-bed catalytic process actually began back in 1935 at the laboratory of Socony-Vacuum Oil Company in Paulsboro, New Jersey. By this time, Houdry and his team were across the river working on the fixed-bed process in the Marcus Hook laboratories of Sun Oil. The TCC process was composed of two separate zones, each designed for its unique function in the process, cracking or regeneration. But Houdry's fixed-bed design required the reaction vessel to meet the requirements of both the cracking and the regeneration of the catalyst. In the TCC process, the catalyst would flow down through the cracking zone, and be lifted mechanically to the top of the regeneration zone. Then, the catalyst would flow down the regeneration furnace and be lifted again to the cracking zone in a continuous recycle process. In commercial units, 100–150 tons of catalyst per hour would be circulated.

It was difficult to design equipment which would distribute evenly this quantity of catalyst and the motion of the catalyst caused it to grind itself into dust, or "fines," which had to be removed. The temperature of the reaction vessels was regulated by varying the rate and temperature of the air supplied to the burning zone and by circulating water through cooling coils within the catalyst bed. The kiln, or oven used in the regeneration cycle, was similar to the kiln that Socony-Vacuum Oil had used for a number of years to purify clay for another process. Since this kiln had been called Thermofo r, this new process for the manufacture of gasoline was named Thermofo r Catalytic Cracking (TCC).

Socony's affiliate, Magnolia Petroleum in Beaumont, Texas, completed the installation of two units in October 1943. The needs of the
Allies in World War II caused Socony to skip from the 250–500 bpd process in a small pilot plant at Paulsboro to a 10,000 bpd unit without an intermediate pilot plant stage. The upper limit on the capacity of the plant was controlled by the capacity of the elevators to lift the catalyst from the bottom of each zone to the top of the next. The best mechanical equipment available could just lift the desired 100–150 tons per hour, achieving a catalyst velocity of 0.5–1.0 feet per minute. While Magnolia was constructing its two units, an outside license was given to Gulf Oil to build three units. By June 1944, less than one year later, eighteen large TCC units were in operation at the refineries of eight major oil companies.

**Houdriflow Process**

The Houdriflow process attempted to overcome the weight limitation of the mechanical lift equipment and the crushing of the catalyst into "fines" by lifting the catalyst pneumatically. Large volumes of catalyst can be lifted upward by blowing a gas and/or a liquid from the bottom of the solid catalyst upward. Houdry used flue gas from the regenerator and Socony used air as the transporting fluids in the initial experiments in columns 16–20 inches in diameter and 200 feet in height.

The Houdriflow process increased the catalyst to oil contact ratio from 1.5 : 1 in the original bucket-TCC process to 7 : 1. As a result, more and hotter catalyst came into contact with the oil producing more cracking and allowing more oil in the liquid form to be added to the reaction vessel. The higher rate of catalyst recirculation also provided additional heat and reduced the regeneration time. The reactor was placed above the kiln so that spent catalyst could flow by gravity from the reactor to the regeneration unit and then was lifted pneumatically to the top of the reactor.

In the spring of 1948, the first license was granted to Tidewater Oil Company of Oklahoma. Sun Oil went on stream with 4 units at its Toledo, Ohio refinery in 1950. In October of 1950, Magnolia converted to air lift on its TCC processes in Beaumont, Texas. Many TCC air lift units were installed with capacities up to 30,000 bpd. Simplifying the process equipment and mode of construction permitted small refiners to install small TCC and Houdriflow units (1,500 bpd and higher). Houdry and Socony were the only companies with consecutive innovations in the cracking process because they were
able to see the limitations and the merits in their first process and to shift their design efforts accordingly. TCC and Houdriflow were among the most important developments in the manufacture of gasoline.

**Suspensoid Process**

Standard Oil (NJ), like Houdry, had also been working on catalysis in the 1920s, including both catalytic cracking and catalytic hydrogenation. Standard Oil (NJ) concentrated on the destructive hydrogenation process because the raw materials — coal, heavy oils, tar, and hydrogen — were in abundant supply at good prices. The better grades of petroleum in the 1920s were thought to be in very limited supply, even close to being depleted. With an abundant supply of coal and an advanced chemical industry, Germany had done a significant amount of research on hydrogenation. For example, during World War I, Dr. Friedreich Bergius was able to produce oil in the laboratory by the hydrogenation of coal under high temperature and pressure.

In the 1920s, a catalyst was used to improve the hydrogenation process. Standard Oil Development (later Esso Research and Engineering Company) knew of these results and entered into a cooperative research program with I. G. Farbenindustrie. In 1929 I. G. Farben sold to Standard Oil Development the right to use all their hydrogenation expertise throughout the world, except in Germany, for $35 million in Standard Oil (NJ) stock. Standard Oil (NJ) constructed hydrogenation plants in Linden, New Jersey, Baton Rouge, Louisiana, and, Baytown, Texas. These plants were small and did not play a significant role in the refinery operations during the 1930s.

Standard's process used the catalyst in a powdered form and the mixture of powdered catalyst and oil vapors was called **Suspensoid**. The powdered catalyst was propelled into a stream of vaporized oil by means of a rotating screw. The mixture was then fed into a cracking coil, similar to ones in the Tube and Tank units [a version of the Burton process developed by Standard Oil (NJ)]. In the next stage, the light cracked fraction was separated from the heavy fraction with the catalyst, then the catalyst was filtered from the heavy fraction and discarded. The finished product gave a higher yield of gasoline with a higher octane number than the thermal cracking process. Of course, removal and discarding of the catalyst

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were problems and increased the cost. By 1934, a 12,000 barrel per day unit had been designed, but was not built. In 1940, Imperial Oil Company of Canada did convert a Tube and Tank unit to Suspensoid cracking. Four more were constructed during World War II and operated until 1953 when they were replaced by fluid-bed units.

**Fluid Catalytic Cracking Process**

In 1938 Professors Warren K. Lewis and E. R. Gilliland in the Department of Chemical Engineering at MIT suggested, while consulting for Standard Oil Development, that the reaction tubes be moved from their traditional horizontal position to a vertical one.\(^{17}\) They were asked to investigate the behavior of finely divided particles in vertical tubes, and thus began research on the modern fluid-bed crackers. Under certain conditions, finely divided powders in contact with vapors can exhibit the properties of a fluid.

The fluid bed will flow in any direction given a slight differential pressure, will reach a uniform temperature with agitation, and is relatively compressible. Oil vapors mixed with the solid powder catalyst in the right proportion and with the proper pressure can
cause the mass to flow just like a liquid along any desired path. After cracking, the solid catalyst can be separated easily from the oil vapors before the vapors are condensed into a liquid stream. The first successful laboratory experiments on this project were performed by two of Professor Warren K. Lewis’ graduate students, John Chambers and Scott Walker. Standard Oil (NJ) quickly took over the project, and within six months it was producing gasoline in its laboratories at the Bayway, New Jersey refinery.

Houdry was asking a very high price to license its process, so Standard Oil (NJ), M. W. Kellogg Company, Standard Oil (IN), British Petroleum Company, Ltd., the Royal Dutch/Shell group, Texaco Corporation, and Universal Oil Products entered into a cooperative research and development program designed to circumvent the Houdry patents. This approach to process development was unlike previous ones which often took the form of very independent firms with only a few engineers who worked in secret and attempted to protect their results with patents. This was a friendly multi-company effort conducted by large groups of engineers and scientists, many of whom were specialists in very narrow areas.

Whereas thermal cracking was marked by secrecy and nasty, long-term patent litigations, the new group pooled its information and patents from the beginning of its fluid-bed research. The major problems of fluid catalytic cracking were all technological in origin.
and did not include those additional problems of finance, administration, and promotion of the product which were significant in the development of thermal cracking. Fluid catalytic cracking demonstrated the benefits resulting from the creation of research and development laboratories at all the major oil companies beginning in the 1920s and the steady accumulation of knowledge about process design. Like TCC and Houdriflow, developments in fluid catalytic cracking were accelerated by World War II and also proceeded from small pilot plants to large-scale commercial units without constructing intermediate units.

On 25 May 1942, the first fluid-bed unit with a capacity of 12,000 bpd was placed on stream at the Baton Rouge refinery of Standard Oil (NJ). Units at Bayway, New Jersey and Baytown, Texas followed later in 1942. The U.S. military demands for gasoline rose from 33,000 bpd in December 1940 to 507,000 bpd in October 1942, and the fluid-bed units helped to meet this demand for aviation gasoline in the 100+ octane range. By 1956 seven refineries in the United States were processing between 200,000 and 343,000 bpd at

FIG. 5-6 Percentage of Cracking Capacity by Process from 1918 through 1963.
each location. The fluid catalytic cracker became the industry standard for cracking petroleum to produce gasoline and continues to be so today.

<table>
<thead>
<tr>
<th>Process</th>
<th>Cost of Innovation</th>
<th>Returns from Innovation</th>
<th>Returns/Cost Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burton</td>
<td>1909-17 $0.236</td>
<td>1913-24 $150.+</td>
<td>600+</td>
</tr>
<tr>
<td>Dubbs</td>
<td>1909-31 7.00+</td>
<td>1922-42 135.+</td>
<td>20</td>
</tr>
<tr>
<td>Tube &amp; Tank</td>
<td>1913-31 3.487</td>
<td>1921-42 284.+</td>
<td>80+</td>
</tr>
<tr>
<td>Houdry</td>
<td>1923-42 11.00+</td>
<td>1936-44 39.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Fluid</td>
<td>1928-52 30.00+</td>
<td>1942-57 265.+</td>
<td>9</td>
</tr>
</tbody>
</table>

Adapted from Endnote 1, p. 243

FIG. 5-7 Growth in capacity of a single cracking unit by type of process in barrels of raw material per day from 1918 through 1958

Adapted from Endnote 1, p. 242
A modern oil refinery operation has three essential parts: (1) **input of feedstocks**, (2) **physical and/or chemical processing**, and (3) **output of products**. The very complex procedure of physical and chemical processing can be subdivided into a series of fundamental processes called **unit operations**. These individual building blocks of refinery processing are based on either a physical or a chemical change in the feedstock to produce a product. Only one type of physical or chemical transformation (i.e., operation) is performed in a given unit operation. Examples of unit operations involving a **physical change** include: distilling, condensing, drying, extracting, evaporating, melting, and absorption. Examples of unit operations involving a **chemical change** include: thermal cracking, catalytic cracking, alkylation, reforming, isomerization, oxidation, reduction, hydrogenation, hydrolysis and combustion.

A series of these unit operations can be linked together to form a **unit process** which might produce a single chemical product such as kerosene or tetraethyllead. In a like manner, a series of unit processes can be linked together to form a plant process such as a complex oil refinery which produces a large number of chemical commodities.

The first step in the operation of an oil refinery is to separate the liquid crude oil, which contains several thousand different hydrocarbons, into fractions. Some, if not all of these first fractions, will be mixtures, too, but they will contain fewer hydrocarbons per fraction than the original crude oil. Since this separation, or fractionation, only requires a physical change, the unit operations of **distilling** and **condensing** are frequently used. These unit operations can be repeated over and over until a particular fraction contains only the desired mixture (e.g., kerosene or straight-run gasoline) or a pure chemical (e.g., octane).

Chemical unit operations allow the refiner to synthesize new molecules from those present in the original crude oil. For example, **thermal cracking** is a chemical unit operation that breaks bonds in some of the larger molecules, producing smaller ones. By controlling the temperature, pressure and reaction time, the cracking reaction can make more molecules suitable for gasoline. A **catalytic cracking** can give even greater control over the reaction and increase the amount of gasoline produced. In the **catalytic reforming** unit operation, straight chain alkanes in the C₆ - C₁₂ range with low octane numbers are chemically changed into branched chain alkanes, olefins, cyclic structures. When these compounds are added to gasoline, they increase the octane number.

**Alkylation** is another chemical unit operation which improves the octane number of gasoline by combining small, volatile molecules...
and hydrogen into larger molecules in the gasoline range. The alkylation unit operation can synthesize branched-chain molecules with octane numbers greater than 100. These unit operations are combined to create four unit processes to provide the feedstocks necessary to produce the synthetically blended gasoline purchased by the motorists.  

(1) **straight-run gasoline** — separated from crude oil by direct distillation;

(2) **catalytically cracked gasoline** — chemically synthesized using various fractions produced from the first distillation of crude oil (sometimes cracked in the presence of excess hydrogen gas to improve the yield);

(3) **catalytically reformed gasoline** — chemically synthesized by rearranging the structure of hydrocarbons, such as the alkanes (also produces hydrogen gas); and

(4) **gasoline from alkylation reactions** — chemically synthesized by combining small, volatile molecules created in the catalytic cracking process in the presence of excess hydrogen.

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**FIG. 5-8** Simplified oil refinery flow sheet diagram, Input: 100 barrels, Output: major products (in barrels produced per 100 barrels of input)
ENDNOTES

2. Enos, pp 132-133.
3. Enos, p. 133.
4. Enos, pp. 133-134.
5. Enos, pp.136-137.
7. Enos, pp. 137-140.
8. Enos, pp. 140-141.
12. Enos, p. 159.
13. Enos, pp. 163-175.
17. Enos, pp. 200-201.
18. Enos, pp. 204-206.
CHAPTER 6

An Example of Chemical Process Calculations

From Feedstock to Products

The refining of petroleum to obtain a variety of useful products — from gasoline and asphalt for our cars and roads to a host of chemicals used to make plastics, fibers, paints, drugs, lubricants, solvents, heating fuels, and the many other synthetic products which surround us in our everyday lives — is a very large and complex operation. The design, operation, and mathematical analysis of even a part of an oil refinery all require knowledge, skill, and a systematic approach.

From historical case studies and analyses of the figures and diagrams presented in the preceding chapters, we have discovered the overall purpose of the oil refinery and some of the details of the chemical processes taking place within it. We can also enhance our general understanding of refinery operations by making some simple calculations that show the results of chemical transformations taking place in various processes within an oil refinery. Rather than dealing with the refinery as a whole, we can focus on individual parts, called unit operations, especially those required to make gasoline. What follows is a simple mathematical procedure to make some of these quantitative calculations.

Balances: Mass and Energy

From what you already know, a logical first question might deal with how much of a particular product can be produced, via some process, from a barrel (42 gallons/barrel) of oil and at what price can it be sold by the owners of the refinery to make a profit? Such questions bring to mind the picture of crude oil flowing into some reactor and the product flowing out the other side to satisfy some market demand.

\[ \text{Input Stream} \rightarrow \text{IDEAL REACTOR} \rightarrow \text{Output Stream} \]  

(1)
Of course, in the real world we would have to add at least one more stream, since it would be a rare process, indeed, which produced only the desired product in 100% yield.

\[\text{Input Stream} \rightarrow \text{NOT SO IDEAL REACTOR} \rightarrow \text{Product Stream} \quad (2) \rightarrow \text{Waste Stream}\]

Refer to the process flow diagram for a typical refinery FIG. 6-2 to see how crude oil as the input stream is processed through a number of reactors to generate a series of product streams, most of which contain mixtures of chemicals. These mixed-product streams are further separated into product streams having fewer chemicals in higher concentrations and into waste streams.

The first, and absolutely essential, step in the analysis of an oil refinery process, or of any chemical process, is the careful accounting of this flow of material through the reactor. It is the key to monitoring the rate of production, the yield of the desired product, and the profits available from the sale of the chemicals. This accounting process is called a **material balance**. It is actually a restatement of the Law of Conservation of Mass: matter cannot be created or destroyed, only transformed from one state to another within the reactor. From the masses (or volumes) involved, chemical engineers begin to get a feel for the overall size of the chemical process, and hence the size and cost of reactors, compressors, pumps, piping, heat exchangers, distillation and fractionation towers, and other processing equipment necessary to construct the complete plant.

We could also consider an **energy balance** using the same technique. Briefly, as the name implies, an energy balance is similar to a material balance. It is equally important in the total analysis of an oil refinery. The energy added to the system to operate pumps, compressors, heaters, cooling towers, etc. must be equal to the energy consumed by the process reactions. Likewise, this is just a restatement of the Law of Conservation of Energy: energy cannot be created or destroyed, only changed from one form to another. The management of the energy required by endothermic reactions or generated by exothermic reactions in the chemical process is just as critical to the safety and the efficiency of the process as is the material balance. Improper control of the energy in a process can lead to a
runaway reactor, to loss of product and profits, and to spoiling our environment.

**Systems and Flows Across Boundaries**

A balance of any kind is made with respect to a definite entity, which is called the *system*. The choice of definition for the system is arbitrary, but you should be very clear about your definition of what constitutes the system at the very beginning of your analysis of the system. For example, let us refer to FIGS. 5-8 and 6-2 and select the following mixer as our system.

\[
\text{Heavy Naphtha} \rightarrow \text{MIXER} \rightarrow \text{Mixed Heavy Naphtha}
\]  

(3)

The double lines around the mixer form the *system boundary* and clearly define those process streams which cross the boundary, flowing either into, or out of, the system. The sum of all materials flowing into the system minus whatever accumulates within the system must equal the sum of all materials flowing out of the system.

\[
\text{[Input]} - \text{[Accumulation]} = \text{[Output]}
\]  

(4)

This accounting of materials will always be valid regardless of the units of mass which we use (e.g., tons, pounds, kilograms, grams) in a mass balance, and likewise, it will also be valid if we formulate the balance in terms of an atom balance. In the case of mixing heavy naphtha "A" with "B," we could formulate a carbon and/or hydrogen balance for the mixing of these hydrocarbons.

**Steady-State Operations**

We can simplify this process further if we operate the process under steady-state conditions. This means simply that we operate the process in such a way that there is no change in the conditions at any point within the process over time. At various points along the mixing process for the two naphthas, you obviously have different concentrations of the naphthas, but because the flow rates are constant over time and the mixing is constant over time, the concentration of each naphtha will not vary with time at a particular point.
within the process stream. In such a case, equation (4) becomes:

\[ \text{[Input]} = \text{[Output]} \]  \tag{5} 

because we have eliminated the start-up, all speeding up, all slowing down and the stopping of the process from our analysis. Under steady-state conditions, the process is simply running (or “cruising”) at a constant rate during a given time period.
A. General Procedure for Solving Balance-Type Problems

To illustrate the general procedure for solving problems, let us select a simple distillation problem and apply the principle of material balance to calculate the quantity and composition of the product stream for this distillation (or fractionation) unit operation.

**Example Problem:** A mixture of 50% hexane and 50% heptane is being separated by fractional distillation into an overhead product that has 10.0 mole-% heptane and a bottoms product that has 0.5 mole-% hexane. If 10,000 gal/day of the blend is fractionated, how many gallons of each product are produced?

**Step 1:** Classify the Type of Problem.

This is a material balance problem since we are asked questions about the amount and composition of the product stream.

**Step 2:** Draw a Flow Sheet.

FIG. 6-1 is the flow sheet for this distillation problem. Since the overhead contains 10.0 mole-% heptane, it must also contain 90 mole-% hexane. Likewise, the bottoms must contain 99.5 mole-% heptane. Mole-% is simply the number of moles of a substance divided by the total number of moles of all substances in the system, multiplied by 100 to convert the ratio to percent. Thus, the sum of all the individual mole-% within a mixture must equal 100.

**Step 3:** Select a Basis for the Calculation.

It is convenient to choose 100 gallons of the feed stream as the basis since we are asked for the distillate and bottoms outputs in gallons.

**Step 4:** Construct an Input-Output Table.

This is simply a bookkeeping ledger sheet to account for all materials entering and leaving the system in some common units such as gallons, pounds, moles, or even atoms. The input followed by the output of each process stream is listed left to right, and the components of each stream are listed top to bottom forming a matrix.

On the ledger sheet, let D represent the total number of lb-moles of hexane and heptane in the distillate, the product of the distillation process.
Let B represent the total number of lb-moles of hexane and heptane left in the bottom of the distillation vessel after the distillation is completed.

**Input-Output Table**

<table>
<thead>
<tr>
<th></th>
<th>Chemical</th>
<th>Gals</th>
<th>Density</th>
<th>Lbs. Mol. Wt.</th>
<th>Lb-Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>50.0</td>
<td>5.526lb/gal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>50.0</td>
<td>5.727lb/gal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Moles-%</th>
<th>Lb-Moles</th>
<th>Lbs</th>
<th>Gals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>90.0</td>
<td>0.90 * D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>10.0</td>
<td>0.10 * D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillate</td>
<td>100.0%</td>
<td>D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hexane 0.5 0.005 * B
Heptane 99.5 0.995 * B
Bottoms 100.0% B

**Step 5: Formulate Material Balances.**

5a. Since the compositions of the product streams are given on a molar basis and the reactants on a volume percent, calculate the number of lb-moles of each reactant (hexane and heptane) and enter the results in the Input Table. This step will require you to look up the density and the molecular weight (or formula weight) of each reactant in a handbook.

**Input**

<table>
<thead>
<tr>
<th></th>
<th>Chemical</th>
<th>Gals</th>
<th>Density</th>
<th>Lbs.</th>
<th>Mol. Wt.</th>
<th>Lb-Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>50.0</td>
<td>5.526lb/gal</td>
<td>276.3</td>
<td>86 lb/lb-m</td>
<td>3.21</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>50.0</td>
<td>5.727lb/gal</td>
<td>286.4</td>
<td>100 lb/lb-m</td>
<td>2.86</td>
<td></td>
</tr>
</tbody>
</table>

5b. Formulate two simultaneous, independent equations in the two unknowns (D and B) using the [input] = [output] material balance equation twice.

\[ \text{Eqn} \quad \text{Chemical} \quad [\text{Output}] = [\text{Input}] \]

1. Hexane: \( 0.90 \times D + 0.005 \times B = 3.21 \) lb-moles
2. Heptane: \( 0.10 \times D + 0.995 \times B = 2.86 \) lb-moles

**Solution:**

- Distillate, D = 3.56 lb-moles
- Bottoms, B = 2.52 lb-moles

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5c. Record these values in the Output Table and simply calculate the remaining entries in the table, converting lb-moles of product back to pounds and then to gallons using molecular weights and densities a second time.

<table>
<thead>
<tr>
<th></th>
<th>MOLE-%</th>
<th>LB-MOLES</th>
<th>LBS</th>
<th>GALS/BASIS</th>
<th>GALS/DAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>90.0</td>
<td>3.20</td>
<td>275.</td>
<td>49.8</td>
<td>4980.</td>
</tr>
<tr>
<td>Heptane</td>
<td>10.0</td>
<td>0.356</td>
<td>35.6</td>
<td>6.2</td>
<td>620.</td>
</tr>
<tr>
<td>Distillate</td>
<td>100.0%D</td>
<td>3.56</td>
<td>310.8</td>
<td>56.0</td>
<td>5600.</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.5</td>
<td>0.013</td>
<td>1.08</td>
<td>0.19</td>
<td>19.</td>
</tr>
<tr>
<td>Heptane</td>
<td>99.5</td>
<td>2.50</td>
<td>250.</td>
<td>43.8</td>
<td>4380.</td>
</tr>
<tr>
<td>Bottoms</td>
<td>100.0%B</td>
<td>2.51</td>
<td>251.</td>
<td>44.0</td>
<td>4400.</td>
</tr>
</tbody>
</table>

5d. Interpretation of Results.

As a cross-check, observe that the sum of the distillates and bottoms equals the original input in gallons per day.

What has been accomplished by this fractional distillation process?

1. A single solution that was originally 50% hexane and 50% heptane (by volume) has been separated into two different solutions.

2. One of these solutions, the bottoms, is now 99.5% heptane and only 0.5% hexane. So the bottoms fraction is now a relatively pure chemical.

3. The other solution, the distillate, is now 88.9% hexane and only 11.1% heptane. If you want a solution that is essentially pure hexane, the distillate fraction can be distilled a second time to decrease the amount of heptane in the hexane. You could continue to repeat the distillation procedure until the hexane solution has the desired level of purity. Of course, each additional distillation will increase your production costs as well as the purity of the hexane solution.

Some Practice Problems

Problem 6-1. On the flow sheet (Figure 6-2) we see that heavy naphtha from the crude fractionator after desulfurization (called A) is combined with the heavy naphtha from the catalytic hydrogen cracking fractionator (called B) and that after mixing this combined
feed enters the catalytic reformer. Suppose it is known that A contains 60% \( \text{C}_6 \) and 40% \( \text{C}_8 \) hydrocarbons, while B contains 50% \( \text{C}_6 \) and 50% \( \text{C}_8 \) hydrocarbons. If 200 kg of A and 100 kg of B are mixed per minute; (a) how many kilograms of mixture are produced per minute; and (b) what is the composition of the product mixture?

**Problem 6-2.** Atom balances are based on the concept of conservation of atoms. Input of some species of atom, such as carbon, must equal the output of the same species (carbon in this case) regardless of the types of chemical reactions that might take place.

\[ \text{Input (of carbon)} = \text{Output (of carbon)} \]
Consider again catalytic cracking. The number and types of compounds and reactions occurring in the catalytic cracking process make it very difficult to analyze the process in detail. But the number of moles of product relative to the number of moles of reactants will increase as the cracking process produces molecules of smaller molecular size from the larger organic molecules of the crude petroleum. So, calculating the relative increase in the total number of moles of product versus reactants will give a measure of the extent to which the cracking reaction has occurred.

Suppose we analyze the input and output streams and find the following compositions:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Feed Stream</th>
<th>Product Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_6H_{14}</td>
<td>.0 mol per cent</td>
<td>5 mol per cent</td>
</tr>
<tr>
<td>C_7H_{14}</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>C_8H_{18}</td>
<td>3.0</td>
<td>20</td>
</tr>
<tr>
<td>C_9H_{24}</td>
<td>7.0</td>
<td>20</td>
</tr>
<tr>
<td>C_{10}H_{24}</td>
<td>20.0</td>
<td>10</td>
</tr>
<tr>
<td>C_{12}H_{32}</td>
<td>35.0</td>
<td>10</td>
</tr>
<tr>
<td>C_{18}H_{36}</td>
<td>35.0</td>
<td>15</td>
</tr>
</tbody>
</table>

From these data, calculate the ratio of the number of moles of product to the number of moles of feed. Make your calculations first using a carbon balance, and then repeat your calculations using a hydrogen balance. Did you get the same answers? Why or why not?

**Problem 6-3.** One of the techniques for producing the hydrogen required for various synthetic reactions in the refining and petrochemical process operations is to react hydrocarbon gases, such as methane and ethane, with steam in the presence of a nickel catalyst. The analysis on a dry basis of the gases leaving such a reactor is:

- CH_4: 4.6 mol per cent
- C_2H_6: 2.3
- CO: 18.6
- CO_2: 4.6
- H_2: 69.7

Even though steam is present in the reaction mixture, the analytical methods used to detect these gases did not detect the presence of water vapor. Assuming that methane and ethane are the only hydrocarbons present in the input stream to the reactor, what is the molar ratio of these two gases in the feed? Also, how many pounds of steam react in the reactor per 1,000 standard cubic feet (scf) of hydrocarbon feed gas?
Problem 6-4. To improve its octane number, a natural gasoline is topped in a distillation column to produce a medium octane gasoline. The composition of the natural gasoline, the overhead distillate and the medium octane bottoms are given in the table:

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>NATURAL GAS</th>
<th>MED. OCTANE GAS</th>
<th>OVERHEAD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FEED</td>
<td>BOTTOMS, B</td>
<td>DISTILLATE, D</td>
</tr>
<tr>
<td>Hexane C₆H₁₄</td>
<td>25.0 mole-%</td>
<td>0</td>
<td>60.0 mole-%</td>
</tr>
<tr>
<td>Heptane C₇H₁₅</td>
<td>25.0 mole-%</td>
<td>22.0 mole-%</td>
<td>30.0 mole-%</td>
</tr>
<tr>
<td>Octane C₈H₁₈</td>
<td>50.0 mole-%</td>
<td>78.0 mole-%</td>
<td>10.0 mole-%</td>
</tr>
</tbody>
</table>

How many liters of medium octane gasoline can be produced from 50,000 bbl of natural gasoline? The density of each stream is 0.80 g/cm³. One barrel equals 42 gallons. (FIG. 6-3 is the basic diagram for this system.)

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1These problems, some of the figures, and part of the notes were taken from INTRODUCTION TO CHEMICAL ENGINEERING by Edward V. Thompson and William H. Ceckler, New York: McGraw-Hill Book Company, 1977, and used with permission of the authors.
APPENDIX I

GENERAL REFERENCES


APPENDIX II

Glossary of Key Terms

Aliphatic hydrocarbons. Compounds of carbon and hydrogen (and their derivatives) which may be straight-chain, branched-chain, or cyclic. The saturated aliphatic compounds have the general formula, \( \text{C}_n \text{H}_{2n+2} \), and the unsaturated ones have fewer hydrogens per carbon than given by this formula.

Alkanes. Hydrocarbons containing the maximum number of hydrogen atoms per carbon atom.

Alkene. An aliphatic hydrocarbon containing one or more double bonds.

Alkylation. A chemical unit operation in the manufacture of gasoline that combines small, volatile organic molecules and hydrogen into larger molecules.

Anticline. A geological formation of stratified rock layers in the shape of a dome or hill, normally underground, in which oil is frequently found.

Antiknock index. See octane number.

Aromatic hydrocarbons. Compounds of carbon and hydrogen containing benzene or its derivatives. Many have odors.

Artificial lift. Any technique, such as injecting fluids or gases into oil wells, that brings additional oil to the surface after naturally occurring pressures have been exhausted.

Asphalt. A solid, liquid or semi-solid mixture of high molecular weight hydrocarbons and their derivatives which occurs in natural bituminous deposits and is a residue in the refining of petroleum.

Barrel. The unit of measure in petroleum production. One barrel (brl) is equivalent to 42 US gallons or 5.61 ft³ or 158.8 liters.

Batch process. A chemical operation in which reactants are mixed in a reaction vessel and then products are removed from the vessel at the conclusion of the reaction.

Bitumen. A substance containing primarily carbon and hydrogen, but also very small amounts of nitrogen, oxygen and sulfur, that occurs in nature and can be produced by chemical decomposition of petroleum.

Bottoms. Any liquid that collects at the bottom of a tank or fractionating column after distilling off the lighter fractions.

Branched-chain hydrocarbons. Hydrocarbons that contain carbon chains branching off from the main carbon chain.
British oil. A kerosene exported from Britain to America in the 19th century.

Catalytically-cracked gasoline. Gasoline manufactured by using catalysts to break bonds of larger molecules into smaller ones within the gasoline range. The process is similar to production of thermally-cracked gasoline except it uses lower temperatures and pressures.

Catalytically-reformed gasoline. Gasoline manufactured by a chemical process that rearranges the molecular structures of hydrocarbons into molecules within the gasoline range.

Catalyst. A chemical substance that changes the rate of a chemical reaction without being consumed in the reaction. In homogeneous catalysis, the catalyst is in the same phase as the reacting substance (both catalyst and reacting substance are dissolved in same solvent). In heterogenous catalysis, the catalyst and the reacting substance are in different phases (e.g. solid metal catalyst reacting with liquid crude oil).

Christmas tree. A collection of control valves, pressure gauges and piping used to cap off the top of a producing well and regulate the flow of oil from the reservoir to the surface.

Coal. A solid mineral produced from decomposed organic vegetable matter which has been subjected to high temperature and pressure in the absence of air over millions of years. It is used as a fuel and in the production of coke, coal gas, water gas and coal-tar mixtures such as coal oil. Major types of coal are: anthracite (86-98% C), a hard black coal that burns with much heat and little smoke; bituminous coal (40-80% C), a soft black coal that produces tar or pitch when burned; lignite (30-40% C), a soft brown-black coal showing some of the texture of the original wood/vegetable matter.

Coal gas. A gas produced by the destructive distillation of bituminous coal and used as a fuel for illumination and heating.

Coal oil. A form of liquid crude oil produced by the destructive distillation of coal.

Coke. A solid residue, composed primarily of carbon, remaining after the distillation of petroleum or coal.

Compound. A chemical substance formed by the union of two or more elements in definite proportions. The smallest part of a chemical compound that can exist in a free state and still retain its properties is a molecule. Some elements also exist as discrete molecules.

Condenser. A heat exchanger, such as a cooling coil or radiator, containing a circulating fluid at a low temperature. As hot vapors contact the condenser, heat flows from the vapor into the cool liquid causing the vapor to condense into a liquid.
Connate water. A thin film of water retained in the pores spaces at the formation of the rock.

Continuous process. A chemical process in which reactants flow continuously into a reaction vessel (which may be a long pipe to provide the time delay for the reaction to take place) and products flow continuously out of the reaction vessel. If it is operated as a steady-state process (omitting the starting up and the stopping operations), the reaction is invariant with time and very efficient for producing large quantities of products.

Core. A cylindrical sample of rock produced in a drilling operation and then analyzed to assess the production potential of a well.

Cracking. A petroleum refining process using heat, pressure and catalysts in various combinations to break large molecules into smaller ones. Two major types are thermal and catalytic cracking.

Crude oil. Unrefined, naturally occurring liquid petroleum composed of hydrocarbons and their derivatives with colors ranging from yellow to black. Crude oil containing a high percentage of sulfur is called sour crude, while crude with a low percentage of sulfur is called sweet crude. The terms petroleum and crude oil are frequently used interchangeably, and almost all liquid crude oil reservoirs contain natural gas deposits and some solid petroleum such as asphalt.

Cyclic hydrocarbons. See naphthenes.

Dephlegmator. An older term for a fractionating (or distilling) tower.

Derrick. A tall, load-bearing structure built over a well platform to raise, lower and store the pipe necessary for drilling and to bring a well into production.

Destructive distillation. The distillation of coal under heat and pressure in the absence of air to produce mixtures such as coal oil and coal gas.

Distillate. Any fraction of a mixture removed during a distillation process; usually characterized by its boiling point range. Fractions removed from the bottom of the fractionating tower are called bottoms; fractions from the top of the tower (or still) are called the overheads. The lower portion of the tower is called the rectifying section; and the upper portion of the tower is called stripping section. Heavy gasoline and light kerosenes are also called distillates.

Distillation. A physical separation process in which components of a mixture of chemicals in the liquid state are vaporized and condensed according to various boiling point ranges as heat is applied to the original mixture. The resulting condensates (also
called distillates or fractions) are new, simpler mixtures, each containing fewer numbers of chemicals in higher purity because the vapor phases of the distillates have concentrations of the components different from the original liquid mixture.

Drilling mud. A mixture of clays and chemicals put down the well stem during the drilling operation to cool and lubricate the drilling bits, to remove the rock fragments produced during the drilling process, and to help prevent a blowout or gusher when oil is struck.

Endothermic reaction. A reaction that requires heat.

Enhanced oil production (or recovery). Modern, artificial techniques used to removed additional oil from a well after primary and secondary production (or recovery) techniques have been exhausted. They include flooding techniques such as injecting liquids (e.g. water) or gases (e.g. carbon dioxide) or thermal methods such as injecting steam or creating a fire front underground to increase the flow of oil to the production well.

Enhanced recovery. See enhanced oil production.

Exothermic reaction. A reaction that produces heat.

Extraction. A process of separating one chemical from another using two immiscible solvents.

Fault. A geological formation in which sections of rock have moved up and while others have moved down creating discontinuities in the various layers of rock. Oil migrating in one layer of rock becomes trapped at the discontinuity, or fault, leading to the formation of an oil reservoir.

Feedstock. The input stream to a chemical process.

Fluidized-bed catalytic cracking. A process that cracks crude oil by flowing a catalyst through the hot oil under pressure.

Fraction. See distillate and distillation.

Fractional distillation. See distillation.

Fractionating columns. See distillation.

Gas cap. A free-gas phase occupying the upper portion of the rock layer in an oil reservoir.

Gas injection. The injection of a gas (natural, air, etc.) into a reservoir to maintain pressure in the reservoir.

Gas oil. A liquid distillate of crude oil that boils higher than kerosene (450-800°F), but lower than lubricating oils. Originally used as an enriching agent in the production of city or manufactured gas, it is now the main feedstock for catalytic cracking units.
Gasoline. A volatile, flammable, liquid hydrocarbon mixture which is produced in the refining of crude oil and used as the fuel in the internal combustion engine.

Gusher. A well that is using all of its natural pressure to bring oil from the reservoir to the surface as rapidly as possible in the form of a geyser or a blowout.

Heterogeneous catalyst. See catalyst.

Homogeneous catalyst. See catalyst.

Hydrocarbon. See aliphatic and aromatic hydrocarbons.

Hydrogenation. A chemical process of adding hydrogen to centers of unsaturation in hydrocarbons and their derivatives.

Internal combustion engine. An engine in which the power is produced within the cylinder as a result of the pressure created by burning a fuel such as gasoline to produce a gas explosion directly within the cylinder. Before the internal combustion engine, steam was generated externally and then its pressure was used to power an engine.

Iso. A prefix attached to a chemical name to indicate a different bonding arrangement of the same number of atoms making up a compound. Frequently, petroleum chemists use iso to denote any type of branched-chain hydrocarbon. One of the standards used to determine the octane rating, iso-octane, contains eight carbons; but because of branching, the longest straight chain contains five carbons. So its proper name is 2,2,4-trimethylpentane.

Kerosene (or kerosine). A pale yellow, flammable hydrocarbon liquid used as a fuel for lamps and heaters and also as a solvent. It is less dense than water and does not dissolve in water.

Molecule. See compound.

Motor Octane Number. See octane number.

Naphtha. A fraction (or distillate) from the distillation of crude oil with a boiling point range lower than 400-500°F (occasionally up to 650°F). Naphtha includes the fractions used to formulate gasoline and the lighter grades of fuel oils such as kerosene and diesel fuel oil. But, as a finished product, naphtha denotes a product with a much narrower boiling point range, e.g. varnish makers' and painters' (VM&P) naphtha with a 200-300°F boiling point range.

Naphthene. Any cyclic aliphatic hydrocarbon.
Octane number (or antiknock index). An empirical measure of the amount of knocking in the cylinder of an internal combustion engine when a particular grade of gasoline is used. The Motor octane number was developed in the 1930s by assigning a value of zero to the knock produced when n-heptane is the fuel, and a value of 100 to the knock produced when pure isooctane (also called 2,2,4-trimethylpentane) is the fuel. Reference mixtures of these two fuels were assigned motor octane numbers equal to the percentage of isooctane. A test gasoline that produced a knock equal to one of the reference fuel mixtures was then assigned its motor octane number equal to the percent isooctane in the reference fuel. The Research octane number uses a less severe set of test conditions to reflect the improvements in modern gasolines and automobiles. The octane number on the gas pumps reported to the consumer is the average of the motor and the research octane numbers. Sensitivity is the research octane number minus the motor octane number. Performance number was developed by the US Army and Navy during World War II to rate aviation fuel.

Oil-shale. See shale.

Olefin. See alkene.

Overhead distillate. See distillate.

Oxidation. A chemical process in which a substance loses electrons. Reduction is the reverse of oxidation.

Performance number. See octane number.

Permeability. A measure of the ease with which fluids, such as crude oil, flow through the interconnected pores of rock formations.

Petrochemicals. Chemicals manufactured from petroleum and natural gas or from any raw materials derived from petroleum and natural gas. They are the intermediate building blocks in the manufacture of many finished products.

Petroleum. A naturally occurring mixture of hydrocarbons and their derivatives in gas, liquid and solid states, depending upon pressure and temperature. See crude oil.

Plates. Stages or steps in the distillation of a mixture; the number of plates is a measure of the degree of separation achieved by a distillation. In geological formations, layers of subterranean rock (tectonic plates) that can shift or slide, causing earthquakes.

Polymerization. A chemical process of joining monomers into repeating units of long chains called polymers.

Porosity. A measure of the openings or spaces within a rock formation.
Primary Production. The first stage in the production of oil from a reservoir which uses the natural reservoir drive forces (gas pressures) to recover the oil.

Primary Recovery. See Primary Production.

Process Operation. A series of unit operations combined in a special sequence to carry out a chemical transformation in a chemical process.


Rectifying section. See distillate.

Reduction. A chemical process in which a substance gains electrons. Oxidation is the reverse of reduction.

Reflux. That part of the distillate from a distillation that is returned to the still for additional distilling.

Reforming. A cracking process in which low octane naphthas and gasolines (hydrocarbons with low molecular weights and straight chains) are converted into high octane products using combinations of high temperatures and pressures, and catalysts.

Research octane number. See octane number.

Retort. A vessel in which substances are distilled or decomposed by heat.

Rock oil. Crude oil or petroleum.

Salt well. A well producing brine (water with a high concentration of sodium chloride).

Saturated hydrocarbon. A hydrocarbon containing the maximum number of hydrogens per carbon atom.

Saturation. In a reservoir formation, a state in which the pore spaces are filled to capacity with crude oil. It also refers to a crude oil containing the maximum amount of dissolved gases. A reservoir is characterized, in part, by the percent or degree of saturation.

Secondary production. The first artificial pressure maintenance methods used to boost oil production after the primary production methods are exhausted. Waterflooding is an example.

Secondary recovery. See secondary production.

Seneca oil. A crude oil extract from New York State marketed in the 19th century.

Sensitivity. The research octane number minus the motor octane number.
Shale. A fine-grained sedimentary rock composed of silt and clay or mud. Oil-shale contains petroleum that cannot be removed by ordinary well techniques. The oil-shale must be mined and heated to extract the petroleum.

Shale-oil. Oil that is extracted from oil-shale.

Sour crude. See crude oil.

Spark knock. A knocking or pinging in the cylinder of the internal combustion engine due to a shock wave getting ahead of the flame front during the incomplete ignition of the gasoline and compressing the unburned fuel against the cylinder. This pressure causes unstable molecules to autoignite and detonate throughout the cylinder. The resulting high-frequency pressure fluctuations are in the audible range.

Steady-state process. Operating a process so that the process variables do not change with time.

Still head. The top of the distillation column.

Straight-chain hydrocarbon. See Aliphatic hydrocarbons.

Straight-run gasoline. The naturally occurring gasoline in petroleum deposits. Crude oil contains about 10% straight-run gasoline.

Stratigraphic trap. A petroleum reservoir formed by the misalignment of layers of rock of different porosity or permeability. The petroleum migrates in the porous rock until it is stopped by a layer of rock with low porosity.

Stripping section. See distillate.

Sweet crude. See crude oil.

Suspensoild. A Standard Oil of NJ process that used the catalyst in a powdered form to crack oil in the manufacture of gasoline.

Synthesis gas. See water gas.

Theromofor catalytic cracking. A Houdry process to crack oil to manufacture gasoline. The catalyst was circulated from reactor to regenerating vessel using a mechanical conveyor system.

Transient process. Operating a process so that the process variables change with time.

Unit operation. A fundamental process operation divided into two types: physical changes such as distillation, extraction, condensing, drying; and chemical changes such as cracking, reforming, alkylation, oxidation, combustion. Unit operations are the building blocks of a process operation.
Unsaturated hydrocarbon. A hydrocarbon containing less than the maximum number of hydrogen atoms per carbon atom. For example, each double bond within an alkene reduces the total number of hydrogens within the hydrocarbon by two.

Waterflooding. Injecting water into an oil reservoir to remove additional oil after primary methods have been exhausted.

Water gas (or synthesis gas). A mixture of carbon monoxide (CO) and hydrogen (H₂) gases produced by the destructive distillation of coal or coke.

Water-gas synthesis. The hydrogenation of carbon monoxide to form methane (CH₄, a gas) and water.

Wildcat well. A well drilled in an area where no oil or gas producing wells are located on the chance that oil will be found. About one out of every nine wildcat wells produces some oil; an even smaller number are profitable. The name comes from the wildcats often heard howling in the hills of Pennsylvania when the first oil wells were drilled.
APPENDIX III

QUESTIONS AND PROBLEMS FOR REVIEW
AND FOR ADDITIONAL STUDY

A. REVIEW QUESTIONS

1. Describe the three major types of geological formations in which one might expect to find reservoirs of crude liquid petroleum.

2. What are the natural forces that cause oil in reservoirs to come to the surface of the earth?

3. In addition to these natural forces, what processes/procedures can be used to drive more oil to the surface?

4. Can all of the oil in a reservoir be forced to the surface of the earth by some combination of natural and artificial methods? Explain.

5. Why is it more expensive to obtain crude oil from shale and sands than from reservoirs of oil found in the limestone deposits located in Saudi Arabia?


7. List the four types of gasoline, obtained either directly or by synthetic processes, which are blended to produce the gasoline sold at your local service station. Explain how each type of gasoline is produced.

8. An octane number is displayed on the pump at your local service station, and the higher the octane number, the higher the cost of the gasoline per gallon. What is the significance of this octane number and how is it determined for a blend of gasoline such as “unleaded regular”?

9. A gasoline is a complex mixture of chemicals. What types of compounds are found in gasoline? Do oil refineries vary its composition as the seasons of the year change? Explain. What types of “additives” are put into gasoline? Explain the purpose of each major type.
10. What is the difference between “sweet” and “sour” crude oil? What process is used to remove sulfur from crude oil before it is transported over any great distance, and why is this necessary?

11. Compare and contrast the trans Saudi Arabian Pipeline with the trans Alaskan Pipeline. Why are pipelines so important to the petroleum industry?

12. Define in your own words each of the following terms as they relate to the production of gasoline: heterogeneous catalysis, batch process, continuous process, cracking reaction, and fractional distillation.

13. Label each of the following statements as true or false:

   _ Crude oil occurs in large underground pools or lakes called reservoirs.

   _ When you strike oil in a drilling operation, it is best to let the gusher flow at maximum pressure because this will bring the largest amount of oil to the surface.

   _ About 2/3 of all the oil in a given reservoir can be brought to the surface using special techniques called artificial lift.

   _ The use of oil by societies around the world is relatively new — since the beginning of the Industrial Revolution.

   _ Although oil shale contains a lot of oil, the total amount of oil in shale is less than the proven reserves of Saudi Arabia.

   _ The fluid bed catalytic cracker was put into operation during World War II due to the great demands for 100+ octane aviation gasoline, but it is no longer used to manufacture gasoline.

   _ America has more tar sand deposits but less oil shale deposits than Canada, even though Canada has a commercial plant which produces synthetic crude oil from its Athabasca tar sands near Edmonton, Alberta.

   _ Rockefeller got his start in business as a produce salesman during the Civil War, but switched to drilling for oil in northwest Pennsylvania after the Civil War.

   _ Three types of geographical faults which can lead to oil reservoir formations are: anticlines, domes and stratigraphic traps.

   _ Synthetic gasoline can be made in any of the following processes: alkylation, reforming, catalytic cracking, and hydrocatalytic cracking.
14. Match each phrase or sentence in Part Y with the one best term from Part X. Use each term in Part X only one time.

**PART X**

1. Alkylation
2. Aromatics
3. Artificial Lift
4. Atomic Weights
5. Blooey Line
6. Bottle type Submersibles
7. Bubble Caps and Trays
8. Burton, William M.
9. Butylene
10. Cable-tool Drilling
11. Canada
12. Catalyst
13. Catalytic Cracking
14. Christmas Tree
15. Columbia
16. Convergence Zone
17. Cracking
18. Dehydration
19. Densmore
20. Derrick
21. Drake, Col. Edwin L.
22. Drawworks
23. Drill Ships
24. Drilling Mud
25. Dubbs, Carbon P.
26. Dubbs, Jesse
27. Endothermic
28. Enhanced recovery techniques
29. Enthalpy
30. Equilibrium Constant
31. Ethylene
32. Exothermic
33. Formation Pressure
34. Formula Weights
35. Heat Capacity
36. Houdry, Eugene
37. Hydrocracking
38. Hydrostatic Pressure
39. Hydrotreating
40. Big Inch
41. Little Big Inch
42. Independent Marketer
43. Inland Barges
44. Internationals
45. Iran
46. Iraq
47. Isomerization
48. Jackups
49. Warren K. Lewis
50. The Majors
51. Mexico
52. Mole
53. Molecular Weights
54. Naphthenes
55. OAPEC
56. Oil Shale
57. Olefins
58. OPEC
59. Paraffins
60. Pennsylvania Rock Oil Co.
61. Petrochemicals
62. Plate Tectonics
63. Platform, rigid
64. Posted Barges or compliant
65. Propylene
66. Reservoir Drive Mechanisms
67. Rotary Drilling
68. Rotary Table
69. Saudi Arabia
70. Seismograph
71. Seismometer
72. Semisubmersibles
73. Smith, Uncle Billy
74. Soviet Union
75. Stoichiometry
76. Tar Sands
77. Temperature
78. Thermal Cracking
79. Titusville
80. Townsend, James M.
81. Van Syckel, Samuel
82. Venezuela
83. Vertically Integrated
PART Y

_ built the first oil pipeline in 1865
_ straight-chain compounds of carbon and hydrogen containing the maximum number of hydrogens per carbon (i.e., saturated hydrocarbons)
_ cyclic, unsaturated hydrocarbons
_ developed the process for catalytic cracking of oil
_ made significant improvements in distillation of oil into fractions of higher purity
_ key components in the fractional distillation column
_ the chemical rearrangement of straight-chain hydrocarbons to branched chain hydrocarbons, especially isobutane

Exxon, Chevron, Mobil, Gulf Oil, Texaco, Royal Dutch Shell, and British Petroleum

_ developed a batch process for the thermal cracking of various crude oil fractions
_ developed one of the first processes for the continuous thermal cracking of crude oil and its various fractions
_ a substance which alters the rate of a chemical reaction without itself being affected
_ a process of making oils of a lower boiling point range from oils of a higher boiling point range
_ a process producing gasoline at a lower temperature and pressure than the Burton Process
_ a theory to explain the movement of sections of the earth’s crust
_ invented by David Milne in 1841; a few years later, the Italian, L. Palmieri, set up a similar instrument on Mount Vesuvius
_ site of the drilling of the first oil well
_ an unemployed railroad conductor who founded a new world-wide industry
_ a blacksmith who drilled the first oil well
_ a method of drilling that led to the successful Lucas well, the first of the great wells at Spindletop, Texas
_ its purpose is to support the traveling and crown blocks and the enormous weight of the drill stem and to store drill pipes and collars
_ pressure exerted by the drilling mud in the hole
_ used to control the flow of oil from a completed well and to monitor the pressure within the well
_ water flooding, immiscible gas injection, miscible gas injection, chemical flooding
_ an early railway tank car

Amoco, Conoco, ARCO, Sun Oil, Phillips Petroleum, and Marathon Oil

_ Saudi Arabia, Iran, Iraq, Kuwait, and Venezuela
_ This country has more proven gas reserves (40% of World supply) than any other country.
_ This country has more proven crude oil reserves (22% of world supply) than any other country.
_ This country has more oil in tar sands than any other country.
_ must yield at least 10 gallons of oil per ton of rock and some deposits contain over 100 gallons per ton of rock
B. ADDITIONAL STUDY

15. Gasoline can be produced from sources other than crude oil. Prepare a short (2-3 pages) research paper on each of the following topics:

   a. Gasoline from Coal: A South African Process
   b. Gasoline from Natural Gas: A New Zealand Process
   c. Gasoline from Tar Sands: A Canadian Process
   d. Gasoline from Oil Shale: An American Process for the 21st Century

16. Tetraethyllead was the first antiknock compound added to gasoline. Other “octane enhancers” include: toluene, t-butyl alcohol, methyl-t-butyl ether (MTBE), methanol, and ethanol.

   a. Write the chemical structures of these compounds.
   b. Compare the octane numbers of these “octane enhancers” to the octane numbers for n-heptane, n-hexane, n-pentane, and 2,2,4-trimethylpentane (isooctane).
   c. Is there a relationship between the chemical structures and the magnitude of the octane numbers? Explain.

17. All grades of gasoline have about the same energy content (115,000 Btu/gal or 32,000 kJ/Liter).

   a. If all of the energy contained within a gallon of gasoline could be turned into useful work (ideal 100% efficient combustion) and if it takes about 5.5 hp to maintain a 2-ton car at a constant speed of 20 mph on a level road without wind and tire-to-road resistance, how many miles could the car travel on one gallon of gasoline?

   b. In actual practice, only 30% of the available energy within a gallon of gasoline is converted into useful work (45% is lost in the cylinders, 20% to cooling water and other engine parts, and 5% to friction in engine parts). Continuing to neglect wind and tire resistance, what is the reasonable upper limit on the miles per gallon at 20 mph on a level road?

   c. Is 200 mpg possible for any car under any normal road conditions?

   \[ 1 \text{ hp} = 550 \text{ ft-lbf/sec}, \quad 1 \text{ Btu} = 778 \text{ ft-lbf} \]

18. Analyze and comment on the statement: “This premium gasoline is too hot for my car’s engine.”
19. Explain:

a. Is high octane gasoline more dangerous to the consumer than low octane gasoline?

b. Why is an "empty" gasoline container more dangerous than a filled one?

20. Suppose that gasoline could be considered just a mixture of the octanes and that, in the cylinder of the internal combustion engine, it is burned according to the following chemical equation:

\[ \text{C}_8\text{H}_{18} + \_ \text{O}_2 = \_ \text{CO}_2 + \_ \text{H}_2\text{O} \]

a. Balance this chemical equation for the combustion of gasoline.

b. Calculate amount of carbon dioxide, \( \text{CO}_2 \), that would be produced in the exhaust emissions if a gallon of gasoline were burned in the above reaction. [Assume that the gallon of gasoline weighs 2.65 kg since density = 0.70 for n-octane.]
APPENDIX IV

Visual Resources

1. Sources of Slides
   a. Commercial Slides

The slide collection used in this unit includes several sets of slides purchased from vendors.

The History of the AIChe. American Institute of Chemical Engineers, 345 East 47th
   Street, New York, NY 10017. (AIChe)

The Periodic Table. Denoyer-Geppert Audio-Visuals, Times Mirror, 1972. Chicago, IL.
   Reorder No. 68971. (G)

Oil from the Earth. Society of Petroleum Engineers of AIME, P. O. Box 64706, Dallas,
   Texas 75206. (OPTE)

Oil Production in the Los Angeles Basin. James L. Ruhle Associates, P. O. Box 4301,
   Fullerton, CA 92631. (OPLAB)


Tar Sands. James L. Ruhle Associates. (TS)

   b. Slides from Books and Articles

The 100 and 200 Princeton slide series are sources of pictures dealing with the internal
   combustion engine, the automobile and the development of electricity. The 800
   series is a source of petroleum related pictures assembled for this unit.

130 Sears, Stephen W. The American Heritage History of The Automobile in America.


135 Shackett, Sheldon R. The Complete Book of Electric Vehicles. Chicago: Domus


   Putnum's Sons.


252 Cunningham, John T. Thomas Edison: They Called Him Wizard! Newark, NJ:
   Public Service Electric & Gas Company.

253 Ellis, Keith. Thomas Edison: Genius of Electricity. Priory Press Ltd.


257 World Book Encyclopedia.

* * *

801 Nivens, Allan. Study in Power: John D. Rockefeller. New York: Charles
   Scribner's Sons, 1953.

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Appendix IV


822 Offshore Technology Conference


951 Charles Sheeler Exhibit, National Collection of Fine Arts.

2. Video Tapes

a. Films for the Humanities and Sciences

The series, "Experiment: Chemistry" is a set of ten laboratory experiments performed on video tape. The students record the results, make calculations, and prepare a report. I use five experiments to introduce basic chemical ideas of chemical
formulas, chemical energy, isotopes, measurement of atomic weights, chemical equilibrium and rates of chemical reactions, which are essential background material in order to understand the chemistry of petroleum. The titles are:


They also offer a series called "Chemistry in Action." I use five of these to illustrate some chemical process technologies and to give the students "plant tours":

Aluminum, Chemicals from Sodium Chloride, Part I, Chemicals from Sodium Chloride, Part II, Polyethylene, and Iron and Steel.

All are available from Films for the Humanities and Sciences, P. O. Box 2053, Princeton, NJ 08543.

b. American Institute of Chemical Engineers

Video tapes are also available from the American Institute of Chemical Engineers. Two that you might consider are:

Chemical Engineering: Measurements for a Competitive Age — highlights the work of the National Bureau of Standards program in chemical engineering (20 minutes). Borrow for $5.00 and then make your own copy for free with their permission.

Century 21 — Discovering the New America. A discussion of the pros and cons of modern technology (25 minutes). Borrow for $5.00 or purchase for $14.00 from DAVKORE Company, ATTN: Dave Lewis, 1300 D Space Park Way, Mountain View, CA 94043

Write to the Public Relations Department of the American Institute of Chemical Engineers, 345 East 47th Street, New York, NY 10017 for a recent catalog.

c. Out of the Fiery Furnace

The seven-hour PBS Television series, "Out of the Fiery Furnace," is also excellent. The TV producer, Robert Raymond, has also written an excellent companion book, Out of the Fiery Furnace: The Impact of Metals on the History of Mankind (published by The Pennsylvania State University Press, University Park and London, 1986) which contains many beautiful pictures from the video tapes. His history of metals from ancient to modern times includes many topics in history of chemical engineering. You may want to use segments of this program.

3. Computer Programs

a. Project SERAPHIM

Programs that I have used from Project SERAPHIM, an NSF sponsored software development project, include:

3. Refinery — No. 806. Tutorial on operation of an oil refinery; economics of operation.

Project SERAPHIM is an excellent source of computer programs at affordable prices ($5.00 per diskette; many diskettes contain several programs). In addition, they offer written material on ways of using their programs. For example, "Teaching Tips IV" gives detailed information about using the programs in the 800 Series [Cat. No. TT 004]. Write for their catalog: Project SERAPHIM, Dr. John W., Moore, Director, Department of Chemistry, Univ. of Wisconsin-Madison, Madison, WI 53706 (608) 263-2837

b. The American Institute of Chemical Engineers

The American Institute of Chemical Engineers publishes a catalog of computer programs, "AIChE Applications Software Survey for Personal Computers." The Institute’s address is: 345 East 47th Street, New York, NY 10017. (212) 705-7657.
APPENDIX V

Answers to Questions and Problems in Chapter 6 and Appendix III

CHAPTER 6

6-1. a. 300 kg/min, b. 56.7% C₆ and 43.3% C₈.

6-2. a. 1.32 to 1.00, output to input, b. Yes, basis choice cannot change results.

6-3. a. 2.76 moles methane per mole of ethane in the input stream, b. 51.3 lb steam per 1000 ft³ feed gas.

6-4. 5.49 x 10⁶ liters of medium octane gasoline produced per 50,000 barrels of natural gasoline distilled. (2.45 x 10⁶ liters of overhead distillates also produced)

APPENDIX III

1.-12. See text and glossary.

13. All are false except last two statements.


17. a. 164 miles/gal, b. 49.2 miles/gal, c. no

20. a. 2C₅H₁₀ + 25O₂ = 16CO₂ + 18H₂O

b. 186 moles of CO₂ (or 8.17 kg)