Appendix A — Overview of Petroleum Refining

Refining petroleum is the process of separating crude oil into useful hydrocarbon-based substances. These substances include fuels (gasoline, jet fuel, diesel, kerosene, and fuel oils), petrochemical feedstock (naphtha, ethylene, benzene, and xylene), and other products (lubricating oils, greases, waxes, bitumen, white oils, and petroleum coke).

The first refinery opened in 1861 and produced mostly kerosene, tar, and naphtha (gasoline). The last major refinery built in the U.S. was completed in 1976. The number of refineries in the U.S. hit a high point in 1981, when 315 were operating. Many closed during that decade because they were small and inefficient or because prices for petroleum products were historically low for the latter 1980s and much of the 1990s. Since then, the number of operating refineries in the U.S. has continued to shrink. Even in the 1990s, as the industry faced growing requirements for cleaner fuels and improved environmental performance along with rising demand for gasoline, the number of refineries continued to drop, from 194 in 1990 to 155 at the end of the decade. Currently, the capacity of domestic refineries is considered inadequate to meet the demand for products.

How Refineries Work

A refinery carries out a number of processes to produce products from the "crude" or unprocessed oil that comes out of the ground. These processes are organized into several categories: physical separation, chemical conversion, purification or treatment, and blending. These processes combine to create a variety of products that are more than the sum of their parts: the output from a refinery actually exceeds the input. This appendix discusses the steps that are involved in refining crude oil, as well as potential impacts to the surrounding community.

Crude Beginnings

Crude oil often is delivered to the refinery by barge and, as a result, refineries are concentrated in coastal states. It also can be delivered by pipeline, and so refineries are located near current or historical sources of crude oil and near heavily industrialized regions. Crude oil would be delivered from Canada to the MHA Nation Clean Fuels Refinery by pipeline.

Crude oils are used to create a wide variety of substances because they contain "hydrocarbons," a mix of hydrogen and carbon in various chemical structures. The crude can range in color from clear to black and in texture from like water to nearly solid. Crude oil is a fossil fuel, meaning that it was created from the natural decay of plants and animals that lived in ancient seas: anywhere crude oil is found was once a sea bed.

The atoms in hydrocarbon molecules are arranged in a variety of ways, from straight chains to rings, and contain a varying number of carbon atoms. A hydrocarbon with one (methane, a gas that is lighter than air) or only a few carbon atoms will be a gas; slightly longer "chains" of carbon molecules will create a liquid, and a long chain will be a solid, such as wax or tar. When they are refined, these chains are combined in a number of ways to produce anything from gasoline and jet fuel to plastic and nylon. These chains also control how quickly the substance will evaporate and so how it will be processed when it is refined. Throughout the process, intermediate steps continuously remove unwanted components, such as sulfur and excess gas, which often can be used in other portions of the refining process.

Crude oil contains hundreds of different types of hydrocarbons mixed together that must be separated to be useful. The various types are separated in an oil refinery: the various hydrocarbon "chains" boil at different temperatures — from barely above room temperature to more than 1,112 ºFahrenheit — and so can all be separated by distillation.

Basic Processes

The most common method used to separate the crude oil into the various components is to heat the oil, allow it to boil and vaporize, and then condense the various vapors into a variety of products. Atmospheric distillation was the first refining process developed (in 1862) and produces mainly kerosene and some diesel fuel that can be further refined. After the initial atmospheric distillation step at MHA, the refinery will use hydrotreating, hydrocracking, and alkylation to process the crude oil.

The major classes of hydrocarbons in fuel oil include the paraffins and, unlike a paraffin candle, are usually gas or liquid; the aromatics, which refers to the chemical "rings" that make them up and not to the smell; naphthenes or cycloalkanes, which are usually liquid; and other categories that can be liquid or gas and that include alkenes, dienes, and alkynes.

Desalting

Before certain varieties of crude oil can be processed at all, they must go through a process called "desalting." This process removes water, salts, and other solid materials that otherwise could damage the equipment at a refinery. Desalting essentially means that the crude oil is dehydrated (water is removed) so that the impurities settle out.

Synthetic crude is crude that was processed at the source. It does not require desalting at the refinery. Thus, the waste water and contaminants that are a byproduct of desalting are not an issue for refineries that use synthetic crude oil.

Distillation

The first and most important step in the process is called fractional distillation. The various components of crude oil boil at different temperatures and so can be separated in the process. First, the crude oil is heated, usually with steam, to a temperature of 700º to as high as 1,200º Fahrenheit. All but the heaviest components "flash" into gas ("vapor") that cools as it rises. The vapor enters the "fractionating tower, a steel tube about 120 feet high, that contains trays at various heights. As the vapor rises in the column, it cools, condenses back to a liquid, and collects on the trays. Each tray contains holes that allow the vapor to flow up through the tray; some liquids collect and are returned to a lower level where they evaporate again. This recycling action makes the product more pure. Because the various components of crude oil boil at different temperatures, they condense at different temperatures and heights in the column. The column is coolest at the top and hottest at the bottom, so the components with lower boiling points condense back to liquid farther up the column. At successively higher points, the products include lubricating oil, heating oil, kerosene, gasoline, and gases. The liquids — called "fractions" — that are collected are either sent to condensers to cool them more, or move on to other areas of the refinery for more processing.

					Product	Carbons
Crude Oil	20º C				Gas	4
	40º C			Reformer	Naphtha	8
	70º C				Gasoline	8
	200º C				Kerosene	12
				Alkylation Unit	Gas Oil or Diesel	16
	300º C			Cracking Unit	Lubricating Oil	36
					Heavy Gas Oil	44
Boiler	600º C	Distillation Column			Residual	80

Two types of crude oil distillation are in use at refineries. "Atmospheric" distillation operates under pressure that is ambient (in other words, at normal air pressure) or slightly above. Some refineries also follow this step with distillation under vacuum. These vacuum towers tend to be wider than the atmospheric columns, but operate under generally the same principle; they often produce usable products from the thick residual that remains from atmospheric distillation.

Almost none of the products that come out of the fractional distillation column is ready for market. Instead, they must be processed further, usually by:

- Solvent extraction or dewaxing
- Cracking: breaking large hydrocarbons into smaller ones
- Unification: combining smaller pieces
- Alteration: rearranging the various pieces.

Solvent Treating

Solvent treating involves methods to remove the impurities that remain after the initial distillation step. These methods usually are used both at intermediate stages in the process and just before the product is sent to storage. Essentially, these processes remove the impurities by adding solvents (a liquid that can dissolve another substance). Depending on the specific processes, the impurities either clump up and fall to the bottom by chemical reaction (known as precipitating), are evaporated away along with the solvent, or the product is chilled so that the impurities precipitate.

Cracking

Cracking may be "thermal," which uses heat to break apart large hydrocarbon molecules into smaller compounds, or "catalytic," which uses a catalyst to cause a reaction in and change the hydrocarbons.

Developed in 1913 — when it was known as the Burton Process — in response to the increase in demand for gasoline, the thermal cracking technology uses a combination of pressure and intense heat to physically break large molecules into smaller ones to produce additional gasoline and other fuels. The initial process, however, produced unwanted byproducts and eventually evolved into methods that produce materials that are more desirable. Thermal cracking also may use high-temperature steam to break hydrocarbons into raw materials that are used to manufacture chemicals.

Visbreaking

Two other techniques are used to treat the residuals that remain in the distillation tower. The first is "visbreaking," considered a "mild" form of thermal cracking. In this process, residuals from the atmospheric distillation tower are heated, and then the resulting product is cooled with gas oil and rapidly burned or "flashed" to make heavy oils flow more easily. The process, originally developed in the 1930s, also produces tar.

Coking

In the second technique, "coking," the residual that is left behind in the distillation tower is heated until is breaks down into oil, gasoline, and naphtha (which is further processed to make gasoline); the process leaves behind an almost pure residue of carbon called "coke," which is sold. It is not the same as the coke produced in steel making.

Hydrocracking

In general, catalytic cracking has replaced most uses of thermal cracking. All forms of catalytic cracking break down complex compounds into simpler structures to increase the quality and quantity of the desirable products and decrease the amount of residuals. A similar process that is not as common as "catalytic cracking," is called "hydrocracking." It is a two-step process that uses a different catalyst — a substance that helps cause a reaction but that does not take part in it — than catalytic cracking, as well as lower temperatures; it also involves high pressure and introduction of hydrogen ("hydrogenation"). It breaks down heavy oil into gasoline and jet fuel or kerosene. Hydrocracking was developed in the 1960s to increase production of gasoline and forms the basis for the modern petrochemical industry. It is used for feedstock that is difficult to process by either catalytic cracking or reforming because they contain substances that are considered "poisons" for the catalyst.

Hydrotreating

"Hydrotreating," is a process that removes certain constituents — nitrogen, sulfur, oxygen, and metals — that are considered "contaminants" in the liquid petroleum. These materials can damage the refinery equipment and impair the quality of the finished product. It also is used in advance of catalytic cracking to improve yields and to upgrade the quality of the product. Essentially, the process works by mixing the feedstock with hydrogen, heating it, and then passing it through a catalytic reactor. The reactor converts the contaminants to other forms that can be separated; the result is a gas stream that, after treatment, can be used to fire the furnaces at the refinery, and a liquid stream that can be blended or used as feedstock.

Practically all the naphtha that is fed to catalytic reforming units is hydrotreated to remove arsenic, sulfur, and nitrogen that would damage the catalyst. The resulting product, called reformate, is fed to the gasoline blending pool. Byproducts of this process include hydrogen, which is recycled within the refinery and used in hydrotreating or hydrocracking.

Unification

Unlike cracking, which separates the large hydrocarbons into smaller ones, "unification" does the reverse. The process creates compounds that are used in making chemicals and in blending gasoline, and generates hydrogen, which may be used in hydrocracking or may be sold.

Reforming

The major process is "catalytic reforming," which converts low-octane products into components that can be blended into high-octane gasoline. It also produces hydrogen that can be recycled and used in other processes. Reforming is the result of a number of reactions that occur simultaneously. The reformer includes a reactor (which may consist of alternating furnaces and fixed-bed reactors) and a section for product recovery. Most processes use platinum as the catalyst, although it may be combined with a second substance.

Alkylation

Finally, the structure of the hydrocarbon may be rearranged, rather than broken or combined, to produce a product. At MHA, the alteration process is known as "alkylation." In alkylation, certain gases (known as "low molecular weight") are mixed with a catalyst. This catalytic process was developed in the 1940s to produce high-octane aviation gasoline, clean-burning fuels, and materials to produce explosives and synthetic rubber.

Treating and Sweetening

Some intermediate and finished products may be treated and sweetened, in most cases to remove unwanted sulfur. Treating is a means to remove certain substances that are considered "contaminants" in the finished product. These contaminants can include sulfur, nitrogen, oxygen, certain metals, and salts. Sweetening is a major refinery treatment for gasoline and improves color, odor, and stability; it also reduces the concentration of carbon dioxide. These processes can be accomplished by addition of acid or other compounds, by heating the product, or through use of catalysts.

Saturate Gas

A saturate gas plant separates components of the refinery gas, including butanes that will be used in the alkylation process; pentanes that will be used to blend gasoline; and ethanes that will be used to produce petrochemicals.

Asphalt Production

The residual materials from the refining process can be used to produce asphalt. Asphalt for roads is processed in vacuum distillation, where it is heated and sent to a column under vacuum to prevent it from cracking (further separating into other materials). When the asphalt will be used for shingles or other roofing materials, it is produced by air blowing. It is heated almost to the point where it will evaporate and then sent to a tower, where hot air is injected. A third process is solvent deasphalting. This process uses propane or hexane as a solvent; it produces lubricating oil, materials that can be recycled in other parts of the refining operation, and asphalt. The process feeds the material and propane into a tower at closely controlled mixtures, temperatures, and pressures, and separates the material on a rotating disc. The products are evaporated and exposed to steam to recover the propane, which is recycled in the operation.

Blending

Blending is the physical mixing of a number of different hydrocarbons to produce a product. Products can be blended through manifolds or in tanks and other vessels. The products can be blended by injecting the correct amounts of each component; additives to improve performance can be added both during and after blending to provide specific characteristics that would not otherwise be present.

Other Products

Lubricants, waxes, and grease also are refined from the residuals that remain after atmospheric and vacuum distillation. The primary objective of this process is to remove the asphalts, certain other compounds, and waxes. In creating this process, the asphalt is first removed from the reduced crude, which is combined with lubricating oil and treated to produce a compound called a "raffinate." This raffinate contains wax that is continuously removed by mixing the material with a solvent; the mixture is cooled, the wax is removed, filtered, and washed to remove oil. This wax can be used to make paraffin candles, in cosmetics, and in petroleum jelly.

The dewaxed raffinate is blended with other materials in extraction processes that use solvents to create lubricating oil. Additives help the finished product meet the characteristics that are needed for motor oils, industrial processes, and oils for metal working.

Finally, grease is produced by blending what are known as "metallic soaps" (they contain calcium, sodium, aluminum, lithium, or other metals, depending on the intended use for the grease) and other additives into lubricating oil at a temperature of 400º to 600º Fahrenheit.

Other Operations

Most processes at a refinery require tremendous amounts of energy to create the steam, power, water, hydrogen, and heat required for the various processes. Thus, most include methods for heat integration, recycling of some constituents, heat regeneration, and energy savings. Some of the major processes are discussed in this section.

Heating

Process heaters and heat exchangers preheat the product in various processes so that it reaches reaction temperatures. Heat exchangers use either steam or hot hydrocarbons that have been transferred from some other section of the process. The heaters are usually designed for specific operations. They may be fired by refinery or natural gas, distillate, and residual oils.

Cooling

Heat may be removed from some processes by air and water exchangers, fans, gas and liquid coolers, and overhead condensers, or by transferring heat to other systems. Mechanical refrigeration units may use water, mixtures of alcohol and water, or various glycols (antifreeze) as coolants.

Steam

Heat from flue gas or other sources generate steam at various points in the process. These systems include the furnace and an enclosure where heat is transferred and that seals the system to prevent flue gas from escaping. Other parts of the system supply fuel — refinery gas, natural gas, fuel oil, or powdered coal — distribute the heat, and supply water to create the steam. The water is treated to remove sediment and contaminants that could damage the system.

Pressure Relief

Refineries include a variety of processes that will release pressure when necessary. Pressure relief is automatic and occurs when operating pressure reaches a preset level. The term "blowdown" is used to describe an intentional, and not automatic, release of pressure, such as during startup, shutdown, or in emergencies. All systems incorporate safety relief valves, used for air, steam, and gas, to release any excess pressure in a system.

Flaring

Flaring is the controlled and safe burning of gas that cannot be used for commercial or technical reasons. The tall flame can be highly visible, especially at night, but emissions from the flare are closely controlled under the terms of federal and state air quality permits that govern the refinery.

Waste Water Treatment

Waste water treatment is used for process, runoff (usually rain), and sewage water before it is discharged or recycled. Wastewater usually contains hydrocarbons, dissolved and suspended materials, and other compounds that can be both alkaline and acidic.

The waste water is first pretreated by separated hydrocarbons and solids from the water, usually by gravity separation, skimming, and filtration. In some cases, heat is needed to separate the oil and water. The water is also neutralized so that it is neither acidic nor alkaline.

After the pretreatment step, suspended solids are removed by sedimentation or air flotation. (Many refineries use a technique called dissolved air flotation, known as "DAF.") Like a municipal treatment plant, this step involves screening or filtering water and then using processes that biologically degrade organic matter and remove oils and chemicals. In addition, advanced techniques such as chlorination, ozonation, ion exchange, reverse osmosis, and activated carbon may be used to remove specific contaminants and meet the limits set under the refinery's water permit.

Cooling Towers

Cooling towers at a refinery remove heat from process water, either by allowing air to pass perpendicular to the flow of water, or by allowing the water to cascade down through a tower. In either case, the water must be treated before it can be re-used.

Electric Power

Refineries may receive power from the local grid or may generate it on the site with steam turbines or gas engines. Substations that receive power and route it to distribution stations within the refinery are located away from sources of explosive vapors, as are most transformers, circuit breakers, and switches.

Compressors

Systems that include air and gas compressors, coolers, receivers and dryers, controls, distribution piping, and blowers provide air to operate air-powered tools, to regenerate catalyst, and to supply heaters and other operations. Air also must be provided for certain instruments and controls, some motors, and some connections.

Loading

The refinery must be equipped with facilities for loading the product into tank cars, trucks and, where possible, ships and barges.

Tanks

Tanks are located throughout the refinery and may be at normal atmospheric pressure or can be pressurized. They store the crude oil, intermediate components, and the finished product, as well as water, additives, and other chemicals.

What are the Major Products of a Refinery?

Refineries produce a number of products. Figure A–1 below shows the proportions of the various products; each is explained briefly below.

Gasoline: Currently the most important product of refineries, gasoline may contain additives to enhance performance and protect against rust.

Kerosene: The first major product of a refinery, kerosene is used in jet fuel and for cooking and space heating.

Liquefied Petroleum Gas: Known as “LPG,” this product is produced for use as fuel (usually as “bottled gas”) and as a material to manufacture other chemicals.

Distillate Fuels: These products consist primarily of diesel, used to power vehicles and generators, and domestic heating oils.

Residual Fuels: These “leftover” fuels are used in ships, power plants, and commercial and industrial facilities.

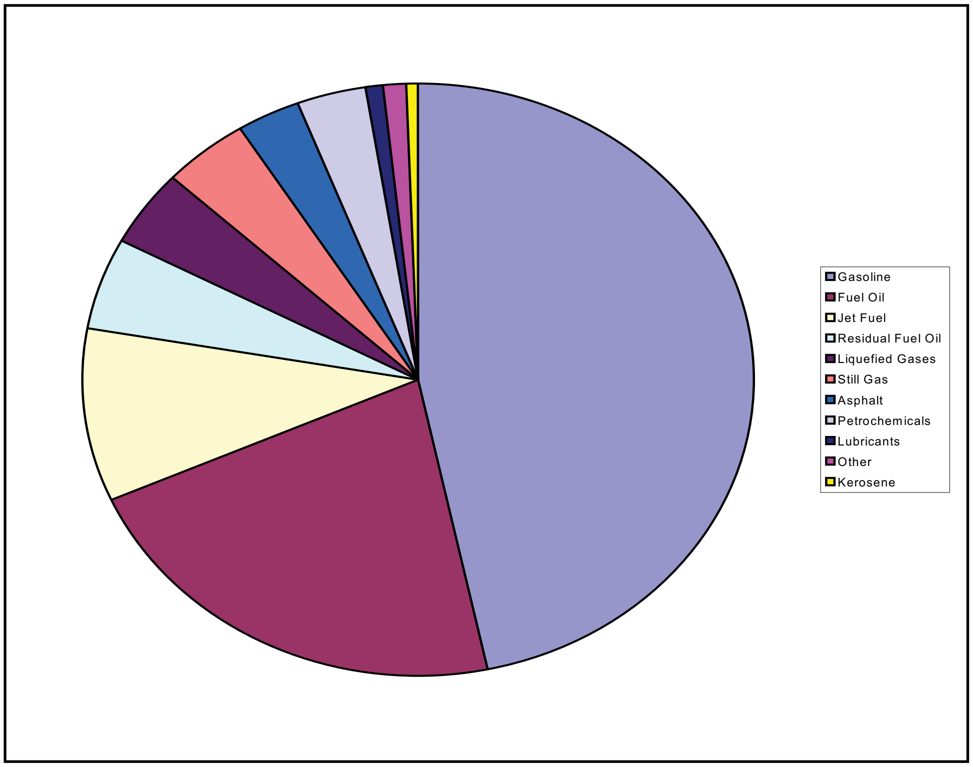

Figure A–1 Distribution of Petroleum-based Products from Refining

Coke and Asphalt: Coke is almost pure carbon and may be used in anything from electrodes to charcoal for home grilling. Asphalt is used in roads and roofing.

Solvent: The term encompasses of variety of products used for purposes such as cleaning and degreasing.

Petrochemicals: These products are primarily intended to produce plastics and synthetic fibers and rubbers.

Lubricants: These products are the result of special refining processes. They are used in motors and as industrial greases and cutting oils.

Regulations and Health and Safety

Petroleum refining has been called one of the most heavily regulated industries in the United States. In addition to the environmental impacts of operations, refineries must deal with the complex regulations that involve their products. For example, gasoline must be formulated different depending not only on season but on geographic location: the industry now produces more than 20 variations of reformulated gasoline to meet the requirements set for specific climatic and geographic areas.

There are emissions from refineries — that's the nature of refining. But from 1992 to 2001, the industry spent about $98 billion on various measures to protect the environment. (These expenditures include capital expenses for pollution controls, research and development, operations, maintenance, and administration, and a small portion for cleanups and spills.) Overall, more than 99.7 percent by weight of crude oil that arrives at a refinery is converted to product or fuel for the refinery.

Almost all components of a refinery are considered "closed" systems, meaning that all of the product that is being refined is enclosed within some kind of container. These closed systems are designed both to limit waste and to prevent emissions. As a result, the potential for exposure by humans is limited and would occur mostly on the site, where safe work practices and personal protective equipment protect the health and safety of workers.

The most visible emissions from a refinery occur when gas is "flared" (burned), usually to release pressure in one part of the system or to burn waste gases. Although the flame can be seen for a considerable distance, flaring occurs only under a permit issued by a state or federal agency that strictly limits the compounds that can be released from the refinery. Most of the emissions consist of sulfur dioxide.

Of the emissions that refineries must report under the Toxic Release Inventory, about three-quarters are to air and the rest to wastewater. The major sources of environmental risk include:

- Air: Refinery emissions contain several precursors to ozone. The impacts are most significant near and downwind of a facility.
- Water and soil: Refineries pose a potential for contamination from leaks and spills. Refineries are, however, required to have in place a Spill Prevention Control and Countermeasures Plan that describes in detail how to contain a spill; in addition, refineries are designed with containment structures that would enclose a leak or spill.
- Health: Air emissions from refineries can contain benzene.
- Global warming: The products from refineries — although not the refineries themselves — may contribute to global warming. The overall risk associated with global warming is still being studied, however.

Bibliography

American Petroleum Institute. 2001. U.S. Refining Industry: A System Stretched to the Limit [Web page]. Located at http://api-ep.api.org/. Accessed: September 20, 2003.

American Petroleum Institute. 2003. Environmental Commitment: Crude Oil Provides Tools to Color our World; Gasoline Boutique [Web page]. Located at http://api-ep.api.org/. Accessed: September 20, 2003.

American Petroleum Institute. 2003. U.S. Oil and Natural Gas Industry's Environmental Expenditures, 1992-2001. American Petroleum Institute, Washington, DC.

Arizona Clean Fuels Refinery. 2003. The Arizona Clean fuels Refinery [Web Page]. Located at http://www.arizonacleanfuels.com/refinery/htm. Accessed: October 7, 2003.

Bull and Bear Financial Report, The. 2002. Oil and Gas Sector Glossary [Web Page]. Located at http://www.thebullandbear.com/resource/RI-archive/gloss-oil.html. Accessed: October 7, 2003.

Chevron. 2003. Processing Crude Oil [Web Page]. Located at http://www.chevon.com/about/pascagoula/refiningprocess/proccrude/shtml. Accessed: September 22, 2003.

Conoco, Inc. 2003. How does an oil refinery work? [Web Page]. Located at http://www.midwestnpioneer.org/central/conoco.html. Accessed: October 6, 2003.

Environmental Defense Fund. 1999. Oil Refining: Pollution Prevention Solutions for the Oil Refinery in Your Community [Web Page]. Located at http://www.environmentaldefense.org. Accessed: October 6, 2003.

Environmental Roadmapping Initiative. 2003. Petroleum Refining: Impacts, Risk, and Regulation [Web Page]. Located at http://ecm.ncms.org/ERI/new/IRRpetref.htm. Accessed: October 6, 2003.

Freudenrich, Craig C. 2003. How Oil Refining Works [Web Page]. Located at http://www.howstuffworks.com/oil-refining.htm. Accessed: September 30, 2003.

Occupational Safety and Health Administration. 2003. OSHA Technical Manual, Section IV, Chapter2: Petroleum Refining Processes. U.S. Department of Labor [Web Page]. Located at http://www.osha-slc.gov/dts/osta/otm/otm_iv_2html. Accessed: September 24, 2003.

U.S. Environmental Protection Agency. 1994. EIA Guidelines for New Source Petroleum Refineries and Coal Gasification Facilities. U.S. Environmental Protection Agency, Office of Federal Activities, Washington, D.C.