
RAND DISCUSSION PARTICIPANTS

OPERATING COMPANIES

BP

Tom Bond
Manager, Global Fuels Technology

ChevronTexaco Products Company

Lance Gyorfi
Vice President, Refining

CITGO Petroleum Corporation

Jerry Thompson
Senior Vice President

Conoco, Inc.

L. Duane Wilson
Vice President, Fuels Technology

ExxonMobil Refining and Supply Company

Tom R. Eizember
Americas Regional Planning

Flying J, Inc.

Jeff Utley
Refinery Manager

Karl Judkins
Process Engineer

Frontier Oil Corporation

Gerald B. Faudel
Vice President, Corporate Relations and Environmental Affairs

Giant Industries, Inc.

Leroy Crow
Executive Vice President

Global Octanes Corp.

Ronald White
President

Marathon Ashland Petroleum

Mike Leister
Manager, Fuels Technology

Phillips Petroleum Company

Robert H. Pahl
Manager, Technology & Project Development

Joseph W. Kaufman
Director, Advanced Technologies & Ventures

Gary A. Schoonveld
Fuel Regulation/Asset Development

Brian Evans
Manager, Fuels Technology Division

Shell Oil Products US

Carmine Falcone
Vice President, Refining

Dave Jacober
Manager, Clean Fuels

Bill Palmer
Business Development Coordinator
Los Angeles Refinery

Sinclair Oil Corporation

Kevin Brown
Senior Vice President, Operations

Sunoco, Inc.

Joel H. Maness
Senior Vice President, Refining & Supply

Tesoro Petroleum Corporation

Stephen L. Wormington
Executive Vice President
Tesoro Refining, Marketing & Supply Company

James L. Taylor
Senior Vice President, Manufacturing
Tesoro Petroleum Companies, Inc.

Texas Petrochemicals LP

Bill Waycaster
President and Chief Executive Officer

Larry Goodwin
Director, Technology & Asset Evaluation

Valero Energy Corporation

John F. Hohnholt
Senior Vice President, Development and Technical Support

Williams Energy Services

Randy M. Newcomer
Vice President, Refining and Marketing

Michael N. Mears
Vice President, Transportation and Terminals

Bruce W. Heine
Director, Government Affairs

TECHNOLOGIES AND SERVICES PROVIDERS

CD Tech

John Adams
Managing Director
Chemical Research & Licensing Company

Lawrence A. Smith, Jr.
Director of Research
Chemical Research & Licensing Company

Criterion Catalyst and Technology Company

Richard Stade
President

Arthur Suchanek
Vice President

Grace Davison

Robert H. Bullard
Managing Director
Advanced Refining Technologies, LP

Richard J. Nozemack
Vice President, Refining Catalysts
General Manager, Americas

Joanne Deady
Director of Planning

Equity Engineering Group

Greg Alvarado
Business Development Manager

Fluor Daniel

Ed Godlewski
Vice President, Sales
North Americas Energy & Chemicals

Arnie Smith
Executive Director

Bob Henderson
Director, Process Engineering

Halliburton KBR

Martin Van Sickels
Vice President & Chief Technology Officer

Timothy H. Wasp
Vice President, Technology Sales

HSB Reliability Technologies

Keith Buress
Senior Vice President

KBC Advanced Technologies, Inc.

Ramon C. Loureiro
Executive Vice President, Business Development

UniPure Corporation

Robert Levy
Senior Vice President

Donald Jackson
Vice President, Business Development

UOP

Carlos Cabrera
Senior Vice President and General Manager
Refining and Petrochemicals

William Keesom
Senior Consultant
Refining & Petrochemical Services

Christopher D. Gosling
Manager, Alkylation & Oxygenates Technologies

ASSOCIATIONS, GOVERNMENT, OTHER

American Association of Oil Pipe Lines

Benjamin S. Cooper
Executive Director

American Petroleum Institute

Edward H. Murphy
Downstream General Manager

James E. Williams
Products Issues Manager

Clean Fuels Clearinghouse

Clayton McMartin
President

Hart/IRI Fuels Information Services

Frederick L. Potter
Executive Director

Nicholas L. Economides
Director, Refining and Fuels Issues

Terrence S. Higgins
Director, Refining & Special Projects

Stacy R. Klein
Deputy Director, Alternative Fuels & Vehicle Technology

Paul Argyropoulos
Director, International Fuel Quality Center

Tammy Klein
Deputy Director, International Fuel Quality Center

National Petrochemical & Refiners Association

Urvan Ruiz Sternfels
President

Bob Slaughter
General Counsel and Director, Public Policy

Tim Hogan
Technical Analyst

Jeffrey L. Hazle
Director, Lubricants & Waxes and Maintenance Programs

Stillwater Associates Downstream Consulting

David Hackett
President

Thomas E. Gieskes
Vice President

U.S. Department of Energy

Joanne Shore
Head of Analysis, Refineries
Energy Information Administration

Barry McNutt
Policy Analyst, Office of Policy

Thomas H. White
Policy Analyst, Office of Policy

UNIVERSITIES

Georgia Institute of Technology

Ronald W. Rousseau
Chair, School of Chemical Engineering

Massachusetts Institute of Technology

Jefferson W. Tester
H. P. Meissner Professor of Chemical Engineering

Texas A&M University

Rayford Anthony
C. D. Holland Professor and Chair, School of Chemical Engineering

University of California, Berkeley

Enrique Iglesia
Professor of Chemical Engineering

University of Texas

John G. Ekerdt
Dick Rothwell Endowed Chair in Chemical Engineering

DISCUSSION PROTOCOL

BUSINESS ENVIRONMENT

1. What are the most important business trends governing your market segment? How are they affecting your operations?
2. What are the greatest threats to your current and future (beyond 5 years) viability?
3. What is your strategy for meeting the market challenges of the future?

CRITICAL OPERATIONS TRENDS & DEVELOPMENTS

4. What are the recently available (or emerging) innovations critical to the success of your firm?
5. What impact do these innovations have in terms of
 - enhancing productivity
 - meeting market demand
 - managing new and emerging environmental, health, and safety regulations?
6. Are technology and services supplier capabilities adequate to your anticipated needs? What about engineering and construction capacity?
7. Do you have an adequate supply of trained personnel?
8. Is capital availability a major problem in the near-term? The long-term?
9. The industry faces a number of operational changes requiring attention over the next five years. Beyond that period, what do you believe will be your company's greatest challenges?

ROLE OF THE FEDERAL GOVERNMENT

10. What value has federal research and development provided to your operations in the past?
11. What role should the federal government play in the future?
 - For the U.S. Department of Energy?
 - For other agencies?

PETROLEUM REFINING PROCESSES AND PRODUCTS

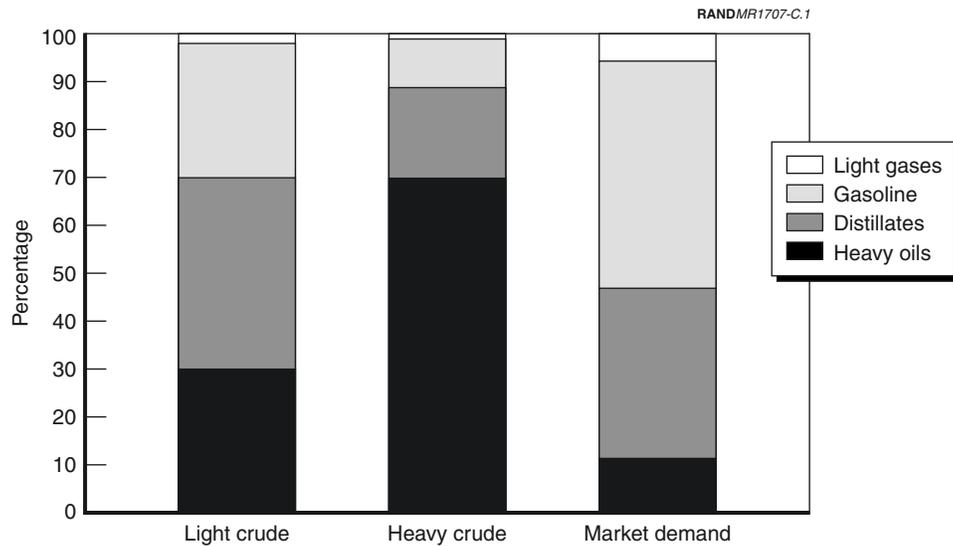
Petroleum refining is a mature industry with a well-established infrastructure and technology base. It employs a complex array of chemical and physical processing facilities, developed and evolved over the past century as required by petroleum product demand, environmental regulations, and business economics. (Figure 3.1 shows a generic refinery flow diagram indicating several types of processing steps and the flow of products.) Every refinery in the United States is unique: The types, size, number, and flow sequences for each refinery vary, depending on crude oil input quality, output product slate and quality, and environmental, safety, economic or other constraints.

This appendix provides a brief overview of the major processes and technologies involved in refining. It is intended as a primer for those in the policy community who have an interest in the industry and in products supply but who are not familiar with the technical aspects.

CRUDE OIL INPUTS

Raw crude oil is a complex mixture of chemicals classified as hydrocarbons—molecules consisting primarily of carbon and hydrogen. Crude also contains small amounts of non-hydrocarbon chemicals, such as sulfur, which can affect refining requirements as well as product quality. The quality, or chemical makeup, of crude stocks varies significantly depending on their upstream source. This affects the type and degree (conversion requirements) of the downstream refining required to produce a desired slate of finished products.

The primary quality parameter used to characterize crude oil is its gravity (density)—an indication of how heavy the crude is. Lighter crudes contain a larger portion of the smaller and more hydrogen-rich molecules needed to manufacture higher-value gasoline and other transportation fuels. Heavier crudes contain a greater portion of larger and more carbon-rich molecules found in heavy industrial fuels, asphalt, etc., for which there are more-limited markets and, thus, lower prices. Figure shows the distribution of the natural



SOURCE: Higgins (2003).

Figure C.1—Range of Products in Light and Heavy Crude Oils Prior to Refining and the Market Demand for Refined Products

yield of light gas, gasoline, middle distillate, and heavy oils in light versus heavy crude prior to processing. Also shown is a breakdown of the market demand for the same product categories. The yield of heavy product from either type of crude is greater than demand, but this product can be transformed to lighter material through the refining process. The yield of heavy oils from the heavy crudes is more than twice the yield from light crudes. To render these crudes economical (i.e., attractive to the market), greater refinery conversion requirements and, thus, greater refinery complexity is needed to generate higher-value lighter final products.

Crude oils are also classified by sulfur content, which varies significantly across crude types. Sulfur is a natural crude oil contaminant that has a negative impact on both refinery processing and final product quality. Within a refinery, high sulfur levels can lead to more-rapid corrosion and can degrade equipment performance; it can also increase emissions of sulfur compounds into the air. Sulfur in refined products also leads to undesirable emissions of sulfur compounds from the transportation fleet and can interfere with the performance of automotive emission control systems. The sulfur content of finished products is highly controlled and is the primary constituent of concern in past and future environmental regulations.

SEPARATION

Separation processes involve segregating crude or intermediate streams into different molecular collections, or *fractions*, based on their physical properties, without changing the molecules. The most common process is *crude distillation*, in which raw crude is separated into groupings characterized by volatility (boiling) range. Distillation is the first step in the refining process; all crude oil undergoes this step.

Crude is first treated in a desalting process to remove trace quantities of water, salt, and sediment, which can be detrimental to subsequent processing. The crude is then heated and sent to a distillation column. There, lighter fractions with lower boiling points condense and are collected toward the top, and heavier fractions are collected toward the bottom. The distillation operation yields light gas and refinery fuel, naphthas, distillates, gas oils, and residue (*bottoms*). *Naphthas* are gasoline-boiling-range molecules typically sent for octane improvement and then gasoline blending. *Distillates*, including kerosene, usually undergo further treatment and then are blended into jet fuel, diesel fuel, and home heating oil. The heavier “gas oil” is sent to downstream processing for conversion into lighter (gasoline, distillate) streams. Finally, the bottoms are blended to generate heavy industrial fuel or asphalt or routed to final heavy residue processing.

CONVERSION

Conversion operations, usually called *cracking*, involve chemical reactions that “break” large, heavy hydrocarbons (of limited market value) into smaller, lighter hydrocarbon molecules suitable for gasoline or other fuels or for further processing. Conversion operations allow a refinery to adjust natural crude fractions to match refined product demands.

Fluid catalytic cracking is the second most prominent U.S. refinery process in terms of throughput. The feedstock is heated to a high temperature and is mixed at low pressure with a solid catalyst on which cracking reactions occur to convert heavy gas oils to light gases, gasoline, and distillates. The products are separated first from the catalyst and then into gases and light and heavy liquids. Over time, the catalysts are deactivated by carbon (coke) contamination. Deactivated catalyst is sent to a regenerator section where air is introduced and coke burned off the catalyst.

The catalytic cracker is central to the operation and economics of a refinery because of its high yield of gasoline and distillate, its ability to adjust feed types and product yields, and the higher product profits it produces. Typical yields of gasoline plus distillate will exceed 60–70 percent of the feed and account for

over 60 percent of total refinery gasoline plus distillate output. Cracking also produces significant quantities of light gases categorized as *olefins*. Light olefins are relatively reactive chemicals that are valuable petrochemical feedstocks and can be further processed to produce high-octane gasoline and oxygenated gasoline components. The fluid catalytic cracker is the unit most responsible for gasoline sulfur. Accordingly, sulfur reduction strategies focus on technologies to desulfurize this stream.

A second conversion application found in a significant number of complex refineries is *hydrocracking*. Like catalytic cracking, this technology is used to convert heavy oils to gasoline and distillates blending streams. Hydrocracking differs from catalytic cracking in that hydrogen is introduced and consumed, operating pressures are substantially higher (in excess of 2,000 pounds per square inch) and temperatures are lower. Hydrocracking feed is heated and then flows to a two-stage reactor system along with high-purity hydrogen, which is produced elsewhere in the refinery. The first reactor section is typically a high-severity hydrotreating operation, reducing sulfur and nitrogen to near-zero levels. The second reactor provides for cracking and subsequent hydrogenation reactions. Both reactors consist of fixed beds of solid catalyst particles. The products and remaining hydrogen are later separated, after which the products are fractionated into gases, gasoline, and distillate. Catalysts become deactivated with coke (as in catalytic cracking but to a lesser extent), which is subsequently burned off under controlled conditions.

Hydrocrackers can produce high-quality gasoline intermediates with volumetric yields of 100 percent of feed. Alternatively, yields of 85 to 90 percent jet fuel plus diesel can be produced concurrently with a small amount of gasoline. Products from hydrocracking are particularly useful blending components for cleaner-fuel applications. They are nearly free of sulfur and are low in *aromatic compounds*, which are ring-shaped molecules that have poor diesel fuel performance and emission characteristics. Hydrocracking reactions open up and convert heavy aromatic components, producing jet fuel and diesel products with excellent fuel characteristics. Because of this capability, the hydrocracker is commonly used to upgrade low-quality, high-sulfur distillate streams from catalytic cracking and coking (see below). Hydrocracking is more effective than fluid catalytic cracking in converting heavy gas oils and producing low-sulfur products, but hydrocrackers are more expensive to build and operate, in part due to the need for supplies of hydrogen.

Coking is the final means of converting the heaviest portion of the crude barrel as well as the refinery bottoms (residual upgrading). The feedstock is heated and cracks into light gases, low-quality gasoline and distillates, and gas oils, which are further processed into final product. The remainder is by-product petroleum coke, which contains almost all of the metal and ash components, a

good part of the sulfur, and much of the asphaltic materials from the crude being refined.

Thirty five refineries, most of them in California, Texas, and Louisiana, accounted for 70 percent of U.S. coke production in 2002. Most U.S. coke is high in sulfur and metal and has a limited domestic market. It is sold abroad as a low-quality fuel for cement kilns, electric power generation, and other uses—often at zero or negative net revenue to the refinery. A number of projects to build new cokers and expand existing plants are under way and more are anticipated. These are largely associated with a push by refiners and heavy crude producers to increase the capability to process heavy, high-sulfur crudes, such as those from Venezuela. A declining market for heavy oil as an industrial fuel has also driven this trend.

COMBINATION

Combination processes join two light gaseous streams to form a larger high-value fuel product. At least one of the gas streams used in the combination process consists of olefin hydrocarbon molecules produced from fluid catalytic cracking, coking, or an outside petrochemical operation.

Alkylation is a process developed in the 1940s to produce aviation fuel to support the military efforts in World War II. The product, called alkylate, is a high-octane gasoline component with other valuable clean-fuel properties. It is widely used in industry, accounting for about 20 percent of the gasoline pool. There are about 60 alkylation units in the United States, and almost every refinery with a catalytic cracker also has an alkylation unit.

Alkylation combines an olefin, usually butylene or a mixture of butylenes and propylene, with a non-olefin to produce a high-octane gasoline stream. Olefins and isobutanes are made to react in the presence of a strong liquid acid, and the final products are separated in a fractionation section. The two conventional alkylation processes are differentiated by the type of acid catalyst used—hydrofluoric acid or sulfuric acid.

There is likely to be increased production of alkylate as a cleaner fuel component in the future, as a partial replacement for MTBE and to lower the vapor pressure of gasoline. However, alkylation poses potential environmental and public health concerns. Hydrofluoric acid is a volatile compound with cloud-forming tendencies upon release. It is a very hazardous and toxic substance that may cause serious injury or death on exposure. There have been a number of initiatives by environmental groups or local communities to ban its use in refineries. Sulfuric acid is less hazardous but nevertheless presents handling, storage, and transportation concerns.

Etherification combines various light olefins with alcohols through a low-temperature and low-pressure process resulting in oxygenated compounds called ethers. The process employs a solid catalyst. The primary ether used in gasoline is MTBE. Approximately 40 percent of MTBE production capacity is represented by refinery facilities designed to utilize olefins supplied by the catalytic cracking unit.

MTBE is a gasoline additive with a high octane number, and it is the primary source of gasoline oxygen required in cleaner gasoline regulations. As of 2002, MTBE was blended into about 25 percent of U.S. gasoline and made up about 3 percent of the U.S. gasoline supply, but it has come under attack in a number of states because of public health concerns over contamination of drinking water from releases of gasoline containing MTBE from underground storage tanks and even surface spills.

Polymerization combines two light olefins, also to produce a high-octane gasoline component. The process employs a fixed catalyst bed operating at low temperatures and pressures. The process is relatively inexpensive and the product is less desirable than alkylate or ether. Polymerization products consist primarily of olefins, which are toxic and unstable in gasoline forming gums.

REFORMULATION

Reformulation processes alter the chemical composition of hydrocarbons in refinery intermediate streams and are widely used to increase the octane of gasoline blending components and, hence, to improve the performance characteristics of the final fuel.

Catalytic reforming upgrades low-octane gasoline boiling streams (naphthas) to high-octane blending streams. There are a number of chemical reactions in the reforming process, but the primary reactions involve production or rearrangement of compounds called *aromatics*. Aromatics are ring-shaped molecules that exhibit high-octane characteristics and in pure forms constitute valuable feedstocks for the petrochemical industry. In reforming, naphtha is heated and passed through a fixed bed of catalyst in a hydrogen-rich atmosphere. The catalyst is platinum-based or platinum with another precious metal and must be protected from lead, nitrogen, sulfur, and other contaminants. The process therefore includes an initial hydrotreating of the feed to reduce these contaminants and protect the catalyst.

Catalytic reforming has traditionally been the primary octane generator and control process for most gasoline-oriented refineries. It is capable of producing a gasoline stream at over 100 octane and can vary product octane over a broad range with minor operating adjustments. However, the aromatic compounds

produced, particularly benzene, have recently been found to be unacceptably toxic, resulting in regulatory pressure to utilize lower-octane aromatic sources. On the other hand, catalytic reforming also produces byproduct hydrogen, which is required for hydrotreating and hydrocracking operations. Reformers provide a majority of refinery hydrogen requirements, which continue to increase as new rounds of environmental fuel specifications are introduced.

Isomerization involves chemical rearrangement of low-octane straight-chain hydrocarbons to branched-chain forms to take advantage of enhanced chemical characteristics or higher octane. The process involves heating the appropriate liquid stream and passing it over a fixed bed of catalyst in the presence of hydrogen.

During the final stages of gasoline lead phasedown, isomerization became widely used to provide an incremental source of replacement octane. More recently, there has been additional interest in isomerization to control the toxic properties of gasoline, namely reducing benzene. Isomerization is also used to reduce the benzene content of gasoline components as a toxic control measure. Currently, about 40 percent of U.S. gasoline refineries employ naphtha isomerization. As the value of isomerization for cleaner fuel production has increased, the technology has gradually improved.

TREATING

Treating processes involve the removal of undesired chemicals (i.e., sulfur, nitrogen, heavy metals) from refinery streams. The primary treating process is *hydrotreating* (also referred to as *hydrodesulfurization* and *hydrorefining*), which typically employs hydrogen under medium- to high-pressure conditions to desulfurize various intermediate gas-oil streams before they are further processed into gasoline or diesel blendstocks. It is also used on a wide range of intermediate or final product streams from naphtha to heavy residue.

Investment in hydroprocessing applications has frequently been driven by yield improvement (i.e., economic) objectives: Throughout the 1980s, economic incentives in crude oil markets motivated refiners to process crude oil with a progressively increasing sulfur content and to “dig deeper into the crude barrel” to convert higher percentages of lower-valued, heavy fractions into premium gasoline and distillate products. Hydrotreating also is used to address reliability, emission control, and cleaner fuel concerns. In the role of treating intermediate product, it is used before reforming to remove sulfur to protect the catalyst and before catalytic cracking to reduce sulfur emissions, eliminate nitrogen and metal contaminants, reduce product sulfur, and improve cracking yields. On the product side, it is used to meet final product sulfur specifications for gaso-

line, jet fuel, and distillates. Hydrotreating can also improve other product characteristics (i.e., diesel cetane or lubricating oil properties).

Other treating processes are used to eliminate specific sulfur molecules from final gasoline and jet fuel products. In addition, newer sulfur-reduction technologies are being introduced to remove sulfur from fuels without requiring the hydrotreating process.

SUPPORT OPERATIONS

A number of miscellaneous processing facilities of varying complexity and purpose are required to support the refinery operation, produce specialty products (lubricants, asphalt, etc.), and provide for environmental control. Major support facilities include hydrogen systems, sulfur recovery facilities, light gas handling, product blending, utilities (steam, electricity, and water), and wastewater treatment.

High-purity hydrogen is required for a number of refinery processes, such as hydrotreating and hydrocracking. Hydrogen that can not be supplied via reforming is generated by steam-reforming of light fuel gases or by partial oxidation of heavier streams. In steam-reforming natural gas, refinery fuel gas or other light gas feed is heated, mixed with steam, and passed through solid catalyst at high temperature and moderate pressure. In the oxidation process, heavier feeds are sent to a combustion chamber where they are partially burned in the presence of steam. The carbon monoxide combustion product is then passed through a solid catalyst bed with steam to produce hydrogen and carbon dioxide.

Sulfur removed in refinery processing flows into refinery gas streams in the form of hydrogen sulfide. Hydrogen sulfide is subsequently converted to elemental product sulfur in a two- or three-step process. First, the hydrogen sulfide is removed by absorption using an alkaline solution and then stripped out of the solution with steam. Next, the hydrogen sulfide stream is sent to a sulfur recovery facility, where a portion is combusted to sulfur dioxide. The resultant combustion products are then passed over a solid catalyst, which converts them to elemental sulfur and water. Sulfur is used as a chemical and fertilizer feed stock.

Primary sulfur recovery typically recovers about 95 percent of the hydrogen sulfide feed stocks. For environmental compliance, the remainder is processed in a third sulfur recovery step, or tail gas treating unit in which a number of different technologies may be employed.

Light gas streams, consisting of compounds ranging from hydrogen to butane, are produced throughout the refinery. These are typically collected and separated for various product or refinery uses. The gases are liquefied by compression and cooling and then separated via fractionation. Products include hydrogen streams, fuel gas, liquid propane gas, butane, and a number of petrochemical feeds.

In many areas of the refinery, oil comes in contact with water, through steam use or water washing. The resultant water is collected and treated to remove oil and other contaminants prior to discharge or recycling. A typical wastewater treatment unit contains a number of upgrading steps including an oil-water separator to physically recover free oil, dissolved air flotation, biological treatment, filters, and settling basins. Some odorous water streams are treated separately prior to recycling in the wastewater facilities. Sulfur compounds, ammonia, and a few other hydrocarbons are stripped out with steam in a sour water-stripping unit. The stripped gases are then sent to sulfur recovery facilities.

Steam and electricity are used in processing operations for feedstock heating and pumping and compression energy. Refineries purchase steam and electricity or generate them on-site with steam boilers and traditional power generation facilities. Cogeneration, the efficient integrated production of electrical power and steam, is often used to optimize refinery energy usage.

The final step in the refinery process is blending refinery streams into final products. In gasoline blending, an automated system meters and mixes blend stocks and additives. Product properties are tested with online analyzers supplemented by laboratory facilities, and computer control is employed to adjust blends to target specifications.