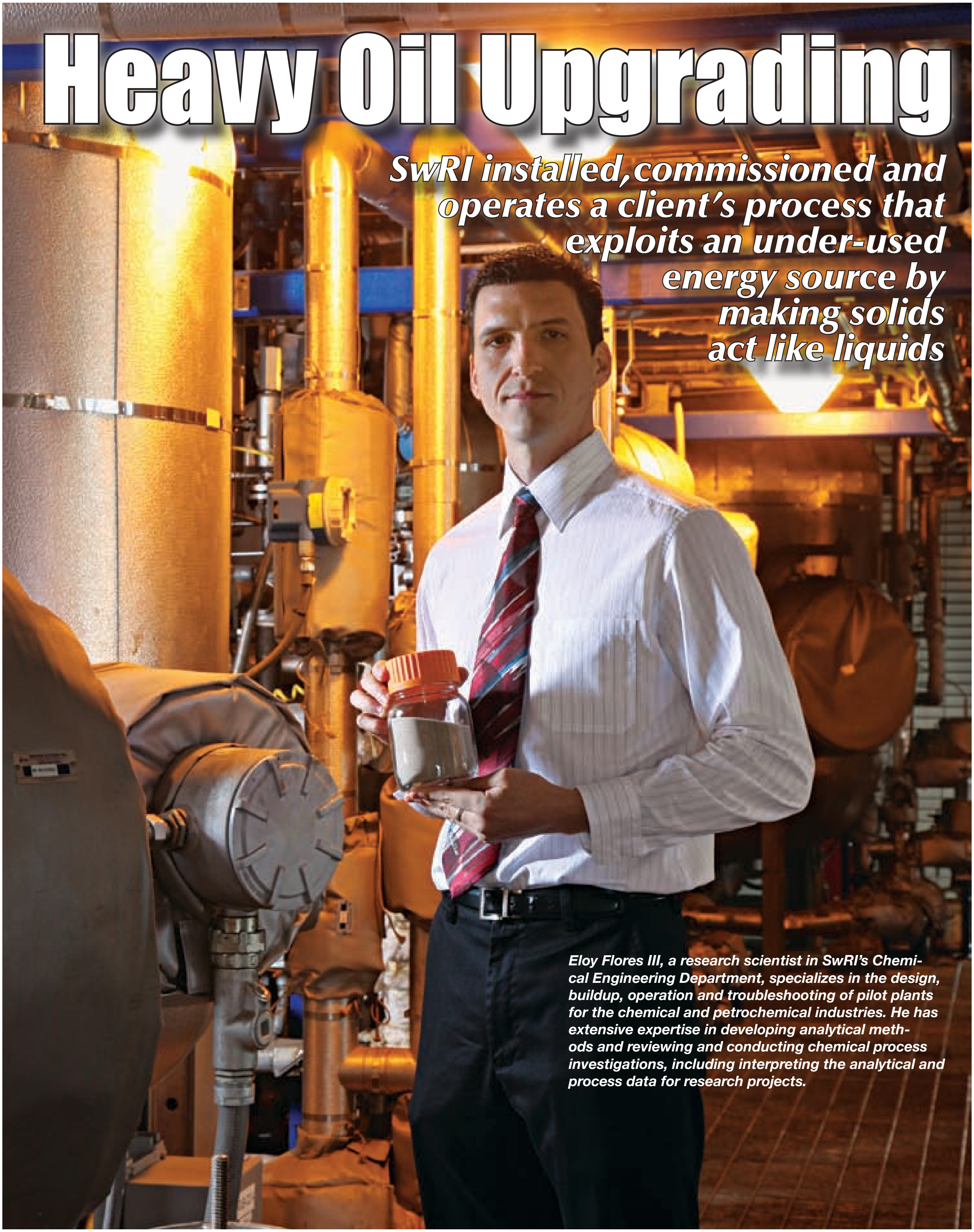
D1M017427

Heavy Oil Upgrading

SwRI installed, commissioned and operates a client's process that exploits an under-used energy source by making solids act like liquids



Eloy Flores III, a research scientist in SwRI's Chemical Engineering Department, specializes in the design, buildup, operation and troubleshooting of pilot plants for the chemical and petrochemical industries. He has extensive expertise in developing analytical methods and reviewing and conducting chemical process investigations, including interpreting the analytical and process data for research projects.

Author illustration; equipment in background is not operating.

By Eloy Flores III

Even though a global economic downturn has caused a year-to-year decrease in total liquid fuel consumption, liquid fuels — primarily petroleum-based transportation fuels — are still the primary world energy source. The United States is currently the largest liquid fuel consumer, but the Asian countries are forecast to surpass the U.S. by 2030. Although environmental concerns about hydrocarbon fuels are propelling efforts to curb carbon-based fuel consumption in the future, petroleum remains one of the least expensive energy sources to produce on the world market. The existing fleet of vehicles will rely on liquid hydrocarbon fuels for a very long time in the future. These reasons, plus petroleum's role as the starting point of thousands of everyday industrial and consumer products, will extend the worldwide demand for petroleum.

One variety of petroleum is heavy oil. Like the so-called "bottom of the barrel" of conventional petroleum, heavy oil is quite carbon-rich and very dense. The Energy and Information Administration (EIA) forecasts future heavy oil production to increase by 200 percent from 2006 to 2030. Of the world's total oil reserves, an estimated 53 percent are in the form of heavy oil or bitumen. Heavy oil and bitumen are terms used interchangeably to describe oil that is highly viscous (that is, it flows like thick honey), solid or near-solid at room temperature (like tar or asphalt), and has low hydrogen content. It also has a high mass density (API gravity of 20 degrees or less). Using the API gravity scale, oils with API gravity less than 10 sink in water and oils with API gravity greater than 10 float on water.

Refining heavy oil is a challenge; however, as the price of regular crude oil goes up, the economics for upgrading heavy oil to a synthetic crude oil continue to improve. A study released in 2004 identified 42 areas of research that could improve existing heavy oil upgrading technologies. With economics driving the heavy oil development, new technologies are being vigorously tested and piloted for commercial-scale applications.

Heavy oil production

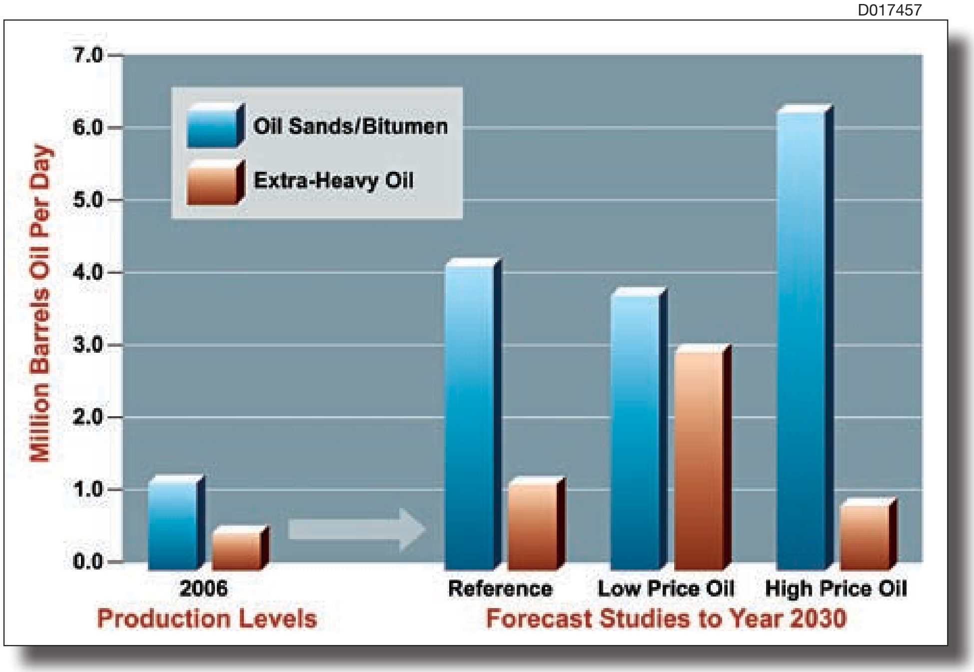
Heavy oil offers many challenges to traditional refining technologies. Where it is found, the lighter, more sought-after components of crude oil have slowly escaped underground strata over millions of years, leaving behind the heavier, precipitated bitumen or heavy oil. It could also be debated that the heavy oil is a younger, less mature oil that needs millions more years to mature. Regardless of how the heavy oil fields formed, they vary greatly in their accessibility depending on well depth, the remoteness of the location and the oil's fluid properties. All of this makes it difficult to use a single technology for upgrading the various kinds of heavy oil.

A novel technology that addresses the challenges or limitations of heavy oil upgrading is being operated by Southwest Research Institute (SwRI) for a commercial oil company. The technology has been demonstrated successfully, and the SwRI team continues to provide operational and technological support to improve, and provide technical data on, this process in tests with worldwide heavy oil feedstocks.

Heavy oil is considered an unconventional oil source primarily because it does not readily flow out of the earth like conventional petroleum crude oil. Heavy oil can be mined when it is close to the surface, or it can be heated and pushed out of the earth using steam or hot compressed gas. SAGD, or steam-assisted gravity drain, is one of the more common technologies for removing heavy oil, with about 15 commercial projects under way in Canada as of 2006.

The main requirement for SAGD is steam, which requires both heat (typically from natural gas) and water. Natural gas consumption is one of the most expensive parts of producing and upgrading heavy oil because it is used to generate steam.

Once it has been made mobile, heavy oil is removed from the earth, de-watered, purified and sometimes diluted with



Petroleum-based fuels remain the primary source for worldwide transportation needs. Although refining heavy oil is challenging, it is becoming economically viable as the price of regular crude oil continues to rise. Heavy oil production is predicted to increase by 200 percent in the next 20 years.

SwRI recently commissioned this heavy oil upgrade pilot plant facility to evaluate converting heavy oil or residual oil into high-quality synthetic crude oil.

condensate or diluent. The diluted heavy oil will then be sent to pipelines for transport, or it may be locally consumed in an upgrading process that converts non-transportable heavy oil into a lighter synthetic crude oil. This oil can be moved by pipeline and processed in conventional oil refineries. Because heavy-oil fields produce oil with varied properties, no single upgrading technology is best for all types of heavy oil.

One type of on-site upgrading technology relies solely on the availability of crude oil nearby. Heavy oil is removed from earth using one of the available extraction methods, and then is blended with nearby lighter crude oil for transport. Two other heavy-oil-using technologies employ off-site production facilities to deliver diluents, such as light oils from delayed coking or from nearby refineries, to heavy-oil fields where heavy oil can be diluted then pipelined back to upgrading facilities or refineries.

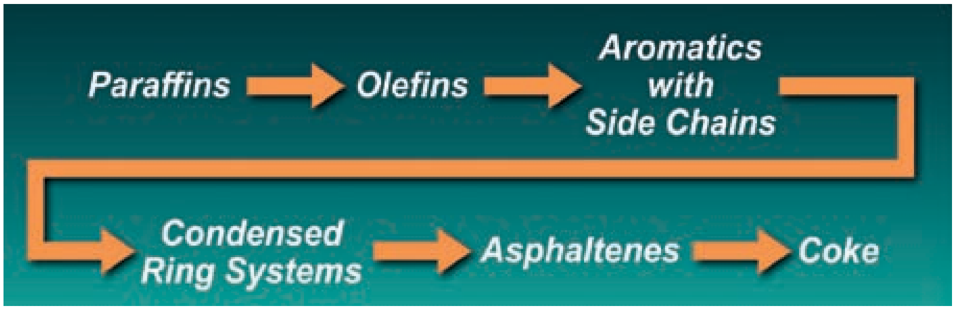
Heavy oil upgrading

Currently the most common unit operation for heavy oil upgrading is a refinery process, the coker. A coker operates on the principle of thermal "cracking," which converts large hydrocarbon molecules into smaller, more useful molecules by removing carbon while rearranging the chemical bonds of the original molecules. Cokers and other petroleum processes employ carbon rejection, wherein carbon is removed from the hydrocarbon molecules as coke in order to produce smaller, more valuable liquid hydrocarbon molecules.

Petroleum coke, called "pet coke," is formed as a solid byproduct of a coker. It is mostly carbon with low hydrogen content and high sulfur content. Thirty to 60 percent liquid yield from the feed to a coker can be sent for processing in a hydrocracker/hydrotreater to yield synthetic crude oil. The balance is lost to coke.

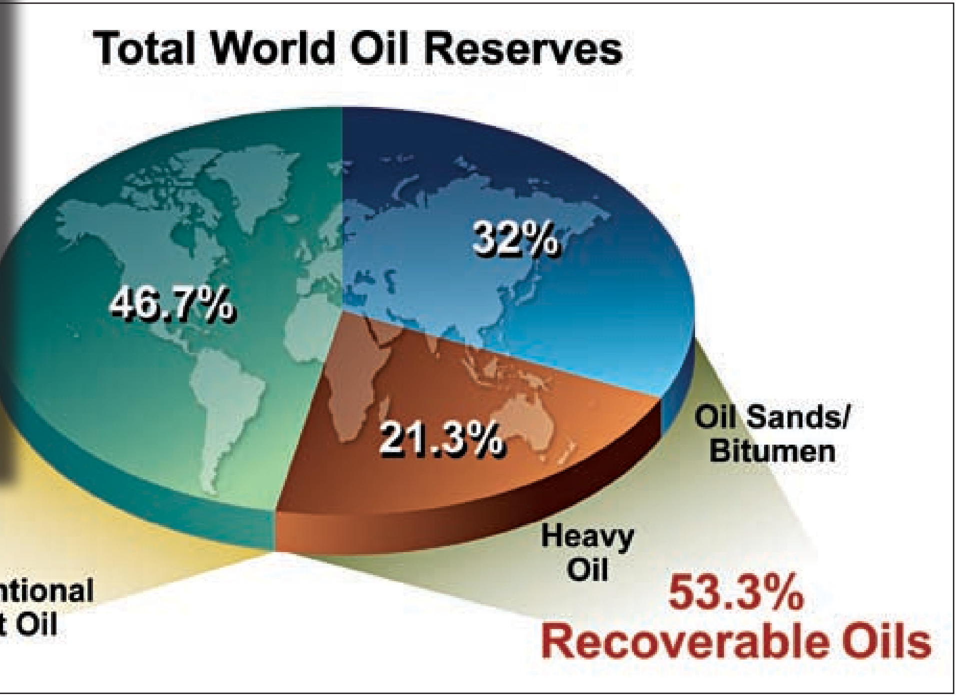
Cokers were first choice for upgrading heavy oil because they were used in petroleum refineries to process the heaviest and thickest material emerging from vacuum distillation towers. These so-called "vacuum distillation bottoms" flow like water at 300 to 400 degrees Celsius (three times the boiling point of water), but remain solid at room temperature and represent one of the most difficult materials in a refinery to handle and transport. Because of the similarity to heavy oil, the connection was made to cokers. However, upgrading heavy oil using a coker is limited to heavy-oil fields that have properties that are acceptable for cokers. Also, while cokers are efficient in upgrading vacuum bottoms from conventional crude oil, they are not necessarily as efficient with heavy oil.

The first company to use a coker on heavy oil was Great Canadian Oil Sands (now Suncor), in 1967. Another heavy oil upgrader, in operation since 1978, produces 12 percent of



This graphic illustrates the chemical route that produces coke during pyrolysis.

More than half of the world's oil reserves are from "recoverable" oils such as heavy oil and bitumen. Currently the challenge remains to make these recoverable oil sources usable by conventional refineries.



Canada's light crude oil, heavy oil bitumen that is mostly surface-mined; thus eliminating the need for a process to extract oil from thousands of feet below the surface. SAGD heavy oil is delivered as feedstock for the SwRI operation.

What makes heavy oil "heavy?"

The right combination of high boiling point hydrocarbons (including a class of compounds called asphaltenes) gives heavy oil the properties of being solid at room temperature with high density and high viscosity. Many factors affect the "heaviness" of oil, but high molecular weight compounds such as asphaltenes can be a big contributor. Asphaltenes are frequently characterized by their solubility in alkanes such as pentane and heptanes. Asphaltenes tend to agglomerate and precipitate, causing fouling in process equipment, and the oil will behave like molasses.

Coking

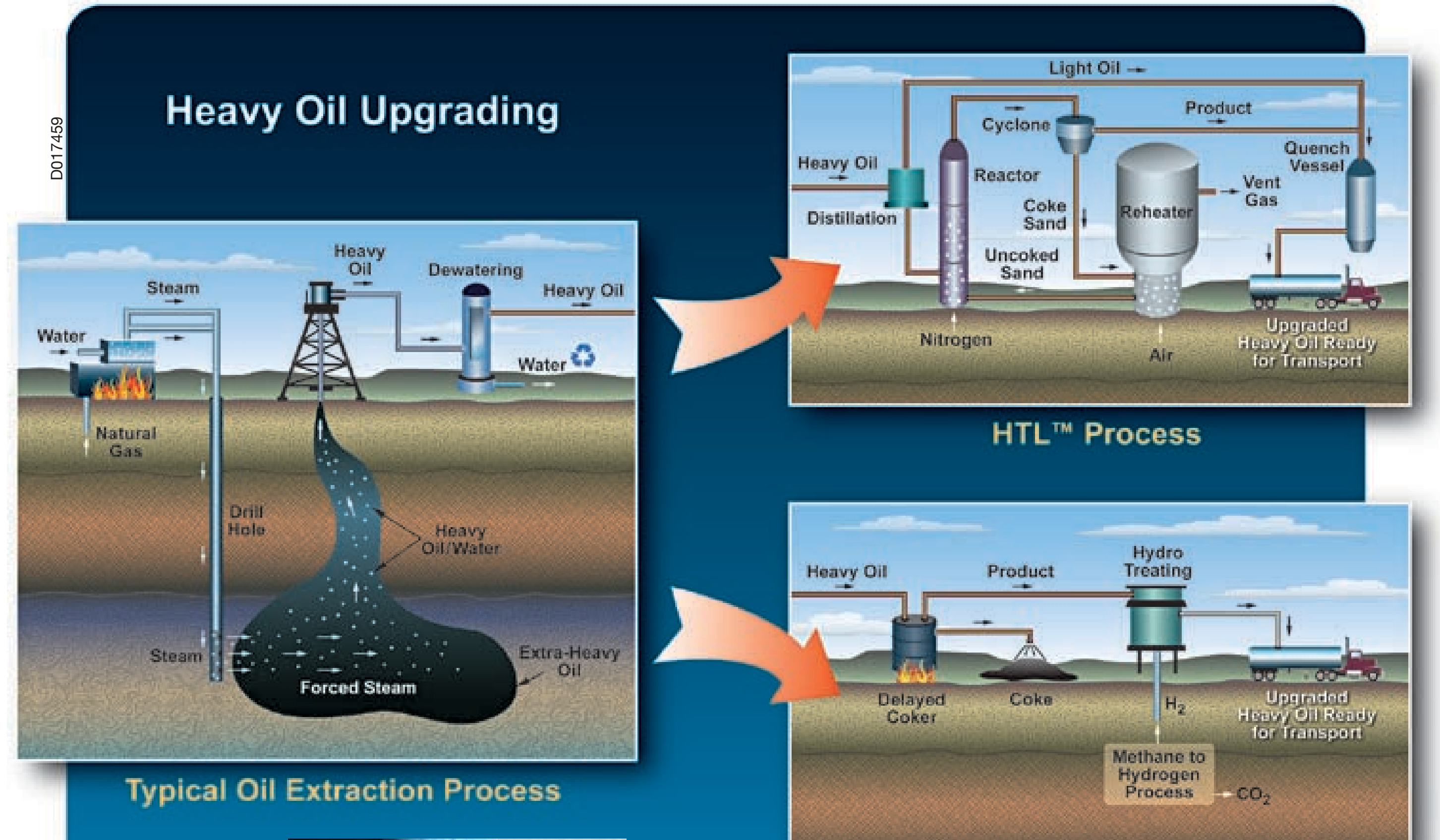
Coking is a fundamental reaction in petroleum and other industrial processes. In catalytic cracking processes, coking poisons the catalyst, so optimal equipment design is needed to minimize coking. Another kind of coking produces a solid, porous residue during the pyrolysis of coal to make coal tar and coal gases. During coal pyrolysis with oxygen, large hydrocarbons are broken down at high temperature in the cracking process. As highly reactive species, called free radicals, are formed, some of the carbon and hydrogen atoms are rejected and appear as elemental carbon and hydrogen rather than recombining to form other compounds. This carbon is termed coke, and coke is a very specific product of petroleum thermal cracking.

Other technologies, such as the one currently being operated at Southwest Research Institute, also rely on thermal cracking. When heavy oil is fed into the upgrading reactor, it is dispersed into small droplets. These droplets collide with moving sand particles in the reactor to give the oil a place to crack. The droplets will begin to vaporize and, depending on temperature and other factors, the remaining unvaporized material on the sand is the starting point for forming coke. The asphaltenes in heavy oils are a main contributor to what makes heavy oil difficult to flow. The SwRI client's fluidized sand technology can take advantage of minimizing the contact and residence time of the sand and heavy oil. This increases the selective thermal cracking of asphaltenes, resulting in high yields of stable liquid products. In contrast, a conventional coker operates at long residence time, which results in poorer yields of unstable liquid products.

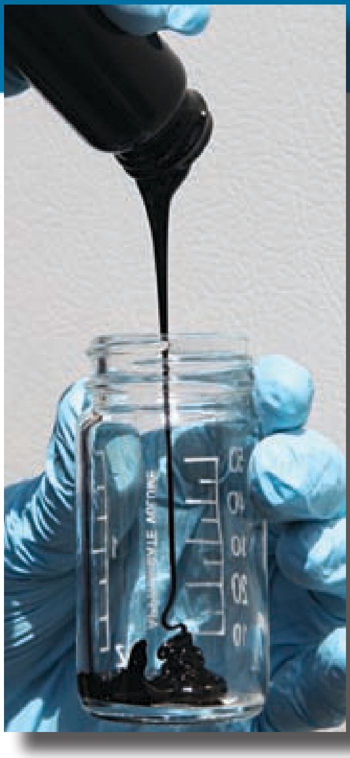
Upgrading heavy oil with fluid sand

No one-size-fits-all technology exists for upgrading heavy oil because of the variability in its properties from oil field to oil field. This makes possible new technologies to process a larger range of heavy oils and to improve process efficiency and reduce the need for electricity, water, natural gas and diluent. One such technology, known as HTL™, has been successfully installed and operated at SwRI for a commercial client in what is known as the Feedstock Test Facility (FTF). The facility processes whole, heavy crude oils with API as low as 6. The unit has atmospheric and vacuum distillation columns and a reaction section and can recycle unconverted bottoms to create an essentially bottomless, synthetic sour-crude product. The core proprietary hot section was designed to process pure vacuum bottoms with API gravity as low as minus-2. The FTF can process 10 to 15 barrels per day of heavy oil on a continuous basis.

The technology is analogous to a fluidized catalytic cracking unit in a standard petroleum refinery to upgrade highly variable, low-value petroleum without the use of catalyst. While catalyst technologies continue to improve, they are not ideal for upgrading heavy oil because



SwRI's client has patented a fluidized sand circulation process to upgrade heavy oil. Oil enters the reactor where it is atomized (mixed with a carrier gas or steam to produce small droplets of liquid) and injected parallel to the lift gas and fluidized solids flow. Here the oil contacts silica sand at high temperature, causing the heavy oil to thermally "crack" or break down chemically on the sand surface producing lighter, upgraded hydrocarbons and depositing coke on the surface of the sand. The sand and upgraded hydrocarbon gas are separated in a cyclone after which the coked sand can now be burned off in the reheater using normal air. The newly regenerated sand is then sent back in its hot state into the reactor to upgrade more heavy oil. The product can be collected or recycled for further processing to meet specifications.



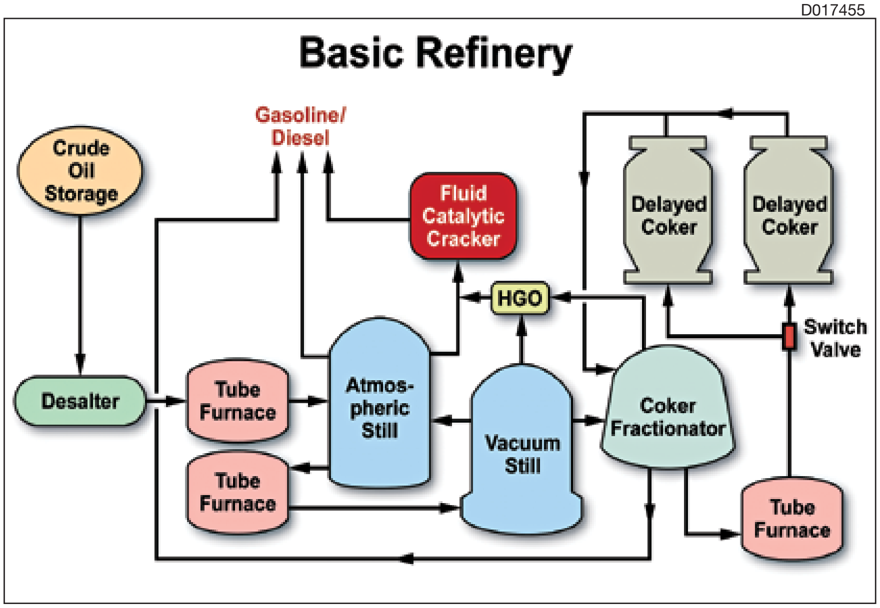
of the large amount of coking that occurs and thus inactivates the catalysts. Also, catalysts are high-cost compared to common silica sand used in this new process. Because coke is a detriment to catalytic processes, the key to the SwRI plant's carbon rejection technologies is the absence of a catalyst. This upgrading makes a syncrude that is flowable, less dense, and with fewer contaminants in the form of sulfur and metals compared to the starting heavy oil.

The SwRI client's technology uses ordinary silica sand for thermal cracking in a fluidized bed process. The FTF is a small version of a heavy oil upgrading facility, with the fluidized bed system as the center of the technology. The technology relies on short residence-time coking on the surface of individual sand particles, and during a subsequent continuous burn-off stage the coke-laden sand can produce high-quality heat. This heat source can eliminate the need for natural gas and thus could reduce costs as well as allow installations at remote locations with limited resources.

Heavy oil upgrading facility

Designed by SwRI's client and constructed by a company specializing in pilot plant construction, the FTF unit was built in five modules and shipped to the Institute in September 2008. In turn, the Institute worked with the client's technology team, prepared a site and supplied utilities to support the FTF. The project team was able to process its first batch of oil less than four months after the components arrived.

The multi-purpose FTF will be used to support the engineering and design of commercial facilities, generate commercial product for marketing, test heavy oils from around the world, optimize and enhance the upgrading process, generate new intellectual property and patents and showcase the technology as a world-class operation.



The varied properties of oil produced from heavy-oil fields prevent a single-technology solution to refining it. Basic refineries include a coker process unit, but upgrading heavy oil using a coker is limited to heavy-oil fields with properties acceptable for existing cokers.

The SwRI team used its experience in chemical process integration, operations and troubleshooting to provide operating manuals, process improvement and characterization and analytical support tailored to the plant's FTF process.

FCC unit as a pattern for FTF processing

The operation of an FCC unit is similar to the FTF heavy oil upgrading technology being operated at SwRI. The robustness and technological advantages of FCC units are important to the analogous operations of the FTF.

FCC units convert low-value, heavy-end refining byproducts to high-value petroleum products such as gasoline, diesel and kerosene. Fluidized catalytic cracking units utilize a solid catalyst by making the solids behave like liquids as they move under gas pressure in the reactor (hence the term "fluidized.") About half of conventional petroleum is in the boiling point range of today's liquid fuels. FCC units are the most critical part of a modern refinery because they allow refiners to utilize more of the crude oil by converting the high-boiling-point portion of the feedstock to the boiling point range of specifications fuels. This conversion also modifies product parameters to produce more valuable products in the refinery. The FCC units are designed to handle the heavy byproducts from other parts of crude oil refining.

The FCC unit is the primary conversion unit in most U.S. refineries. An estimated 45 percent of worldwide gasoline production comes from FCC units. Fluidized catalytic cracking units have evolved to become the workhorse of modern refining operations. Utilizing the basis of FCC technology while eliminating the catalyst can provide a simpler, more versatile system for upgrading heavy oil.

Fluidization of sand particles takes place when gas rises through a sand bed and propels the sand particles in the moving gas. The gas traveling upward will form bubbles, further mixing solids and gas. At certain gas flows, the gas and solid move smoothly together and the solids are now said to be fluidized. Once fluidized, the solids can flow just as water would, either down pressure gradients or in response to gravity as with a waterfall. Fluidized beds are used for many chemical processes: coal gasification, industrial combustion and liquefaction, as well as the disposal of organic, biological and toxic wastes. The current design and operation of fluid beds is based on many years of experimentation and commercial experience. Advances in computer technology and a better description of all the forces involved have made fluidization science a continued area of interest and research.

Even though fluidized bed technology is over 60 years old, there continue to be areas for improvement. Some of the more recent advances come from feed nozzle injection systems, standpipe optimization for increased solid circulation, and riser baffle designs for improved distribution of fluidized solids in the reactor. With continuing advances in computer software and computation power, more accurate models will be able to help predict and improve upon the efficiency of such systems. ❖

Questions about this article? Contact Flores at 210-522-2547 or eloy.flores@swri.org.

REFERENCES

- Energy Information Administration (EIA), "Short-term Energy Outlook," June 9, 2009
- Energy Information Administration (EIA). "Office of Energy Markets and End Use. 2030:EIA Generate World Oil Balance Model," 2009.
- Attanasi, D., Meyer, R., "U.S. Geological Survey Fact Sheet 70-03." August 2003 - Online Version 1.0, "Heavy Oil and Natural Bitumen--Strategic Petroleum Resources." http://pubs.usgs.gov/fs/fs070-03/fs070-03.html.
- ASTM D 3142, Standard Test Method for Specific Gravity, API Gravity, or Density of Cutback Asphalts by Hydrometer Method.
- Yeung, K.C., "An Overview of Alberta *In Situ* Recovery Methods," Petroleum Society of CIM Lloydminster Section 2007 Heavy Oil Technical Symposium, September 20, 2007, Suncor Energy Inc.
- Pavel, S.K., Silverman, M.A., "Heavy Oil Upgrading with HTL Technology," AiChE Spring Meeting, March 24, 2010.
- Ellis, P., Christopher, P., "Tutorial: Delayed Coking Fundamentals." Great Lakes Carbon Corporation, Port Arthur, TX. Prepared for presentation at the AIChE 1998 Spring National Meeting, New Orleans, March 8-12, 1998., Topical Conference on Refinery Processing Tutorial Session: Delayed Coking, Paper 29a, Copyright 1998 Great Lakes Carbon Corporation. UNPUBLISHED., March 9, 1998.
- American Association of Petroleum Geologists., "Petroleum Provinces of the Twenty First Century." February 1, 2002.
- Acevedo, S., Castro, A. et al, "Relations between Asphaltene Structures and Their Physical and Chemical Properties: The Rosary-Type Structure." Energy and Fuels 2007, 21, 2165-2175.
- Johnstone, R., Berry, A.G.V., "Petroleum Coke Formation and Properties."
- Trinidad Leaseholds Ltd., Pointe-a-Pierre, Trinidad, BWI. "Industrial and Engineering Chemistry," Vol. 36, No. 12, December 1944.
- Flint, Len., "Bitumen & Very Heavy Crude Upgrading Technology." LENEF Consulting Limited, March 31, 2004.
- Chen, Ye-Mon, "Recent Advances in FCC Technology." Powder Technology, 163, 2006 (2-8).