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#### **REFINING DEVELOPMENTS**

### **SPECIAL**REPORT

# Is bottomless-barrel refining possible?

## Future energy demand will involve innovative methods that can upgrade residual products

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ith 193 countries worldwide, no nation is totally energy independent. Some nations are net energy exporters and export more energy than they import. Most countries rely on the few energy-producing nations that control abundant hydrocarbon reserves. And yet, even regions with vast raw resources import some form of energy.

So if energy independence is an unachievable goal, how does everyone get the fuel they need, especially in a world of rising demand, supply disruptions, natural disasters and unstable regimes? Global energy security can result through cooperation and engagement across the entire energy spectrum, from petroleum products to renewable energy such as biofuels. If we are willing to let investment and expertise flow freely across borders, prosperity will be fueled when innovation and technology converge and energy is available to everyone.

**Growing energy demand.** Looking forward to 2030, the forecast global oil demand is estimated to reach 116 million barrels/day (MMbpd) up substantially from the current 82 MMbpd global production (Fig. 1.) Curbing demand on

the consumer side while increasing available supply will require new innovative ideas, along with new methods to produce unconventional oil reserves and advanced processing technology supplemented with renewable fuels.

**Have we reached peak oil?** We do not believe that the world has reached peakoil production (Fig. 2). However, we are producing the maximum "easy oil." From this point forward, world oil reserves are becoming sourer, heavier, more acidic, harder to produce or recover—requiring increasing production costs and needing enhancedoil-recovery methods such as steam-assisted gravity drainage to produce heavy oils. Yet, heavy oil may be the short-term solution to energy issues (Fig. 3.) Producing sour, heavy oil while meeting increasing environmental and fuel specifications is the challenge confronting the refining industry.







**Where is the heavy oil?** According to the American Petroleum Institute, the largest known extra-heavy oil accumulation is Venezuela's Orinoco heavy oil belt (Fig. 4). The reserve boasts 90% of the world's extra-heavy oil when measured on an inplace basis. The Canadian province of Alberta contains 81% of the world's known recoverable bitumen. These two countries' reserves account for approximately 3.6 trillion bbl of heavy oil





FIG. 4 Global distribution of conventional crude oils and heavy hydrocarbons.



and bitumen in place. Based on forecast global demand and that 70% of the world's reserves are heavy, a technological movement is needed to upgrade the extra-heavy oil/bitumen feedstocks.

Reasonable analysis shows that sour heavy oil will make up an increasing share of the refineries' feed slate. Wood Mackenzie forecasts that by 2025, 25% (or 23.6 MMbpd) of world energy demand will be sourced from unconventional oil or heavy oil. Contrast this with the IEA's forecast that world oil sands/bitumen and heavy-oil production will be 6.4 MMbpd in 2030 up from 1.7 MMbpd in 2005.

Due to high oil prices, growing worldwide oil demand, globalization and continuing political destabilization in the Middle East, new technologies to upgrade bitumen and heavy oils will be important in meeting future energy demands (Fig. 5). While the global economy is forecast to grow 4%/yr, global primary energy demand, as projected by the IEA's 2006 forecast, is expected to increase by 53% between 2004 and 2030 or roughly 1.3%/yr. Over 70% of the new oil demand is attributed to developing countries; China alone will account for 30% of the new consumption.

**Renewables.** Ethanol is being politically promoted as the next great replacement for gasoline. Yes, it is a renewable fuel. However, if the entire North American corn crop was converted into ethanol, the volume produced would only replace 12% of the current gasoline while driving up corn costs for food applications. Ethanol consumes more energy to produce than the final product delivers, has a large carbon footprint, and has problems in pipeline transportation and degradation issues. All of these conditions will need to be addressed with future processing technologies.

Governments are under pressure to curb rising oil and transportation fuels costs. Rising energy costs are impacting natural gas/oil-based fertilizer manufacturing; food prices are increasing as corn-based ethanol is promoted as a replacement for petroleumbased products. Ethanol processing will require innovative technologies that allow mass production from nonfood stocks such as biomass.

## **TABLE 1.** Product testing results using various upgrading methods with Canadian bitumen

Properties	Feed	Hydro- visbreaking, a	Hydro- visbreaking, b	Hydro- conversion, a	Hydro- conversion, b
Gravity, °API	12.5	14.0	14.3	22.2	25.0
Density @15°C	981.5	972.5	970.5	919.8	903.0
S, wt%	3.26			0.46	0.28
Viscosity, cp @20°C	3,749	904	340	103	45
C <sub>5</sub> asphaltenes, wt%	12.2			7.4	3.3
Nickel, wppm	36			18	13
Vanadium, wppm	52			25	18
Viscosity reduction, %		76	91	97	99
Desulfurization, %				86	92
Demetallization, %	)			51	65
Pressure, psig		750	1,725	1,700	1,700
Temperature, °F		770	800		

### SPECIALREPORT REFINING DEVELOPMENTS

**Biodiesel is another promising renewable fuel.** It can be produced from products that do not directly compete with foodstocks and is economically cost-competitive with petroleum diesel. There are environmental advantages to using biodiesel blended with petroleum diesel; it burns cleaner and has less carbon dioxide (CO<sub>2</sub>) and particle matter (PM) emissions. B20—20% biodiesel blended with petroleum based diesel—has 20% less carbon monoxide (CO), 30% less unburned hydrocarbons, 22% less PM, 20% less sulfates emission, and has a higher cetane number and built-in oxygen content. B20 burns fully, contains no sulfur (S) or no aromatics. Blending biodiesel with petroleum diesel can stretch the current supply and is an environmentally friendly and cleaner burning transportation fuel.



FIG. 6 A stand-alone hydroconversion/upgrader unit processes bitumen into SCO and syngas.



FIG. 7 Configuration for hydroconversion pilot-plant and testing facility located in Two Hills, Alberta, Canada.



**Other technology options.** A new processing scheme integrates hydroconversion/upgrader technology to upgrade very heavy crude with a biodiesel and downstream refining operation. Hydrogen for the upgrading can be produced by using glycerin derived alcohol; thus eliminating the need to produce hydrogen from residue oil, coke or natural gas. By combining the different processing operations within the facility, a small carbon footprint is used and less energy is imported for transportation production. The new design has fewer environmental impacts to the community.

**Hydroconversion technology.** The upgrader/hydroconversion processes can better utilize the increasing refinery feed slate of very heavy oils and can manage the bottom-of-the-

### **TABLE 2.** Product upgrading improvements using hydroconversion and hydrovisbreaking methods

Properties	Feed	Hydro- conversion	Hydro- visbreaking
Gravity, °API	8.5	24.8	17.0
Density @15°C	1,009.9	904.7	952.5
S, wt%	5.14	0.24	3.32
N, wppm	2,680	1,430	3,060
Conradson carbon, wt%	12.75	2.59	8.24
C <sub>5</sub> asphaltenes, wt%	17.3	1.6	8.9
C <sub>7</sub> asphaltenes, wt%	12.6	1.2	7.8
Nickel, wppm	77	8	61
Vanadium, wppm	196	18	163
Viscosity, cSt	2,399 @60°C	10.04 @40°C	29.85@40°C
Residue (524+°C), wt%	55.8	11.68	26.39
Desulfurization, %		95	35
Demetallization, %		90	18
Residue conversion, %		79	53



barrel residual products. Technologies such as carbon rejection or deasphalting lose significant portion of the barrel profits. Asphalt or high-S bunker fuels are dwindling markets; many countries are requiring marine operators to use low-S bunker fuel for ships.

The demand for hydroconversion/upgrading technology will grow as the global oil supplies get sour, heavy and more acidic. At the refinery, the hydroconversion process can be used to upgrade sour, heavy crude before entering the refinery or upgrade refinery residual streams into higher quality oil for transportation fuels production and to reduce coke make.

This technology is a hydrogen-addition method using oncethrough, single-pass operations (Fig. 6). Originally, the processing goal was to upgrade heavy crude and residual oils to a higher quality, higher value products. Hydroconversion technology can be used to upgrade refinery-generated residual streams such as residual oils into naphtha and distillates. An additional processing benefit is that hydroconversion can drastically reduce contaminant levels of sour heavy-oil products, especially lowering levels for S, nitrogen (N) and metal levels.

The hydroconversion processing applies unique mixing methods to optimize combining hydrogen with the hydrocarbon feedstock. With such a blending method, this process has inherently higher mass-transfer efficiency and can operate under less severe operating conditions (pressure, temperature and catalyst volume) than traditional hydroprocessing technologies. Lower pressure and temperatures condition enable lowering capital and operating costs with a hydroconversion unit up to 25% reduction as compared to traditional hydroprocessing units.

**Oil-field applications.** A series of field tests were conducted at a pilot plant (Fig. 7) using the hydroconversion process. Field tests investigated upgrading possibilities for heavy Canadian bitumen feedstock (12.5°API) at temperatures between 725°F and 805°F, pressures from 500 to 1,725 psig, hydrogen/oil ratios between 5,000 and 10,000 scf/b, without catalyst (hydrovisbreaking) and with catalyst (hydroconversion). The initial purpose of these tests

## **TABLE 3.** Product results of hydroconversion processing of heavy oil (17.5° API)

At the selected	operating condi	tions	Bitumen feed		Syncrude product	
API gravity			17.5	35.0	35.0	
Specific gravity			0.9497	0.849	0.8498	
S, wt%			1.22	0.03	0.038	
Metals, wppm			77	<1.	<1.5	
Conradson carbon, wt%			7.4		<1	
N, wt%			0.286		0.135	
Aromatics, %			42.4		-	
369+°C, wt% (vol%)			75.75 (77.9)		-	
509+°C, wt% (vol%)			50.92 (51.8)		-	
535+°C, wt% (vol%)			41.74 (42.1)	5.04 (4	5.04 (4.23)	
Crude product yields	Full-range naphtha*	Kerosine	Heavy diesel	Vacuum gasoil	Vacuum residue	
TBP, °C	IBP-200	200–300	300–350	350–535	535+	
TBP, °F	IBP392	392–572	572–662	662–995	995+	
Wt%	20.18	30.89	16.45	27.44	5.04	
Vol%	22.77	31.32	16.01	25.67	4.23	

\* IBP = Initial boiling point

was to reduce the bitumen viscosity sufficiently to meet pipeline viscosity targets without requiring diluents. A 75% reduction in bitumen viscosity was achieved at a moderate pressure of 750 psig. The bitumen viscosity was reduced by more than 90% at higher temperatures and pressures (800°F, 1,725 psig). However even at these conditions, the °API gravity was increased by 2°, and the S level was reduced by 10%.

To further improve upgraded-oil quality, a high-activity hydrotreating catalyst was added to the system. With such a catalyst, API gravity improvements up to 12.5° were achieved together with desulfurization levels of 92% and a viscosity reduction approaching 99% (Table 1.) For severe service, a large demonstration unit, with a 10-bpd design capacity, was constructed to operate at 1,700 psig.

In another testing series, very heavy ( $8.5^{\circ}$ API) and very sour (5.14 wt% S) Canadian bitumen feedstocks were evaluated at pressures up to 2,000 psig, a hydrogen/oil ratio of 6,000 scf/b, and a high space velocity of  $0.5 \text{ v/v.hr}^{-1}$ . These evaluations considered improvement achieved with a hydroprocessing catalyst (hydroconversion) and without a catalyst (hydrovisbreaking).

With a high-activity hydrotreating catalyst, an API gravity improvement of 16.3° was achieved with desulfurization levels to 95%, demetallization to 90% and a vacuum residue (524+°C) conversion of almost 80% (Table 2.) These are outstanding results at such a high space velocity and operating temperatures. The product obtained through hydroconversion was stable, while the hydrovisbreaking product was not (high bromine number.) Figs. 8 and 9 summarize the true boiling point (TBP) distillation curves for this bitumen feed and upgraded syncrude product.

In 2005, a series of 12 pilot-plant runs were conducted for a major international oil producer. The testing focused on required operating conditions to upgrade a heavy oil from 17.5°API to a minimum of 34.0°API gravity, while decreasing the S content from 1.22 wt% to below 0.6 wt%. These tests were conducted at pressures between 1,700 psig and 1,825 psig (120 kg/cm<sup>2</sup> to 128 kg/cm<sup>2</sup>), and at average catalyst temperatures between 710°F and 806°F (377°C to 430°C). The overall catalyst space velocity was 0.40 v/v.

 $hr^{-1}$  for a one-year catalyst cycle. At the previous temperatures and pressures, the desulfurization ranged from 75% to 97%, denitrogenation from 37% to 53%, metal removal from 76% to 98%, Conradson carbon reduction from 47% to 87%, and the pitch (535+°C) conversion from 37% to 95%. The hydroconverted products were stable at all conditions, even with the high space velocity vs. testing results obtained with traditional hydroprocessing processes.

Table 3 summarizes testing results for upgrading 17.5°API sour crude via hydroconversion upgrading methods.

**Cost of upgrading bitumen.** Table 4 summarizes data on similar Alberta bitumen feedstocks before and after upgrading by either coking or hydroconversion processing. The coker products must be hydrotreated to remove S, which is a corresponding additional cost.

**Refinery applications.** The hydroconversion upgrading can provide a unique means to yield more middle-distillate fuels and low-S products. As mentioned earlier, the global crude supply is becoming sourer, heavier and more acidic; refining these crudes generates greater amounts of residues with high contaminants levels of S and N. In addition, environmental legislation for cleaner-burning fuels limits available markets for heavy, high-S refinery products.

A potential long-term solution is installing a hydrogenaddition upgrading process to increase light-product yields from refinery heavy, low-value, sour residues. By using hydroconversion methods to upgrade these residues, refiners can change their refinery product slate, generate higher margins and reduce amount of high-S residues. Refiners will have better management of the bottom-of-the-barrel residuals.

The hydroconversion process can be integrated within an existing refinery. All residues and a new heavy crude are blended and preheated by the reactor effluent, mixed with recycle gas and further heated to the reactor temperature in a fired heater. The heated hydrogen/oil mixture is sent to hydroconversion/upgrader reactors where hydroconversion and hydrogenation yield gases and light hydrocarbons. After cooling, reactor effluents are sent to a high-pressure separator where the overhead vapors are mixed with makeup hydrogen and reused as recycle gas. The makeup hydrogen is provided by the synthesis-gas unit and is recovered by a membrane unit or supplied through a regional pipeline.

Naphtha, kerosine and heavy-diesel production will increase respectively by about 60%. The hydroconversion process feed, refinery residue and new sour heavy crude supply oils are upgraded into lighter transportation fuels. Furthermore, the refinery's total capacity will increase approximately 20,000 bpd with the processing of low-value residual streams and sour heavier feedstock. The liquid volume increase (swell) will depend on the conversion level of the upgrader and operation severity.

**Benefits of upgrading residuals.** The per-barrel product-cracking spread is determined by adding the value of the refined products produced by the upgrading unit, subtracting

#### **TABLE 4.** Upgrading results for Alberta bitumen using delayed coking and hydroconversion upgrading methods

	Delayed coking <sup>1</sup>	Hydroconversion process
Bitumen feedstock		
Gravity, °API	7.8	8.5
S, wt%	5.10	5.14
N, wt%	0.45	0.27
Syncrude product		
Gravity, °API	28.7	24.8
S, wt%	3.20	0.24
N, wt%	-	0.14
Product yields, % feed		
Light crudes	82.0	90.5
Heavy crudes	0.0	17.5
Coke	18.0	0.0
Light crude prices, \$/bbl <sup>2</sup>	51.51	51.51
Heavy crude prices, \$/bbl	31.57	31.57
Gross revenues, \$/bbl	42.24	52.14
Bitumen prices, \$/bbl <sup>2</sup>	30.73	30.73
Operating costs, \$/bbl	4.00	3.50
Hydrogen costs, \$/bbl	0.00	6.50
Total costs, \$/bbl	34.73	40.73
Net Income, \$/bbl feed	7.51	11.41

<sup>1</sup> Gray, M. R., "New technique defines the limits of heavy oils, bitumen," *Oil & Gas Journal*, Jan. 7, 2002.

<sup>2</sup> Alberta Energy and Utilities Board: 2005.

the price for residual fuel-oil feedstock, and dividing by the number of barrels sent to the hydroconversion unit. To illustrate, if the per-barrel prices of naphtha are \$60, \$50 for distillates and \$30 for residual fuel oil, then the per-barrel cracking spread would be about \$26.60, minus the operating cost of \$8.50/bbl, for a net profit increase of \$18.10/bbl.

Bottom-of-the-barrel options. Refineries will need to find new methods to convert the bottom-of-the-barrel residuals into lighter products. Hydroconversion/upgrader methods are effective processing options to convert residuals steams into transportation fuels and middle distillates. In addition, hydroconversion methods can be applied to decrease the imbalance between the high availability of residual fuels (atmospheric and vacuum residues) and the increasing demand for transportation fuels (gasoline, distillates). Such practices enable refiners to better manage the bottom-of-the-barrel residuals, convert low-value products into higher-value products and increase profitability. HP



James Runyan has 25 years of direct hydrocarbon experience as a project manager and outage program construction manager. Mr. Runyan is responsible for all engineering and operation functions and has significant engineering, procurement and construction experience. His refining experience and work with refining managers to improve production has been a great asset for Genoil.

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