The production of synthetic crude oil (SCO) from oil sands is expected to increase dramatically in the next decade. A hydrotreated synthetic crude sample was obtained from a refiner and characterized by standard methods, as well as by High Resolution Mass Spec (HRMS). The synthetic crude was distilled to 650°F+, blended at various levels with a conventional paraffinic VGO, and tested in an ACE unit over various types of FCC catalysts, in order to determine the effect of the feed properties and catalyst type on product yields. A range of catalysts with zeolite/matrix ratios varying between 1.3 and 3.8 were tested. Analysis of the sulfur species in the feed and the cracked products was also included.

Synthetic crude, produced from Canadian oil sands, is a growing feedstock source that is being utilized by an increasing number of refiners.* SCO from Canadian oil sands is projected to increase to 3.0 million bpd by 2015. With Canadian reserves of 170+ billion barrels of viable oil, economic forecasts predict that oil sands will continue to be a significant crude source for the foreseeable future.

Synthetic crude from oil sands has significantly different characteristics from traditional VGO feeds. Oil sands contain bitumen, which is separated out and then further processed to yield SCO. The unprocessed bitumen is highly aromatic, has low hydrogen content, low API gravity, and high levels of sulfur, nitrogen and metals. The final characteristics of the synthetic crude vary depending on the amount of processing the bitumen has undergone. Typically, after the bitumen is separated from the oil sands, it is upgraded in a fluid coker or an ebullating bed residue upgrader. The resulting product quality can be further improved by hydrotreating to remove additional metals, sulfur and nitrogen.

A paper presented by Grace Davison at the 2009 NPRA Annual Meeting ("Characterization and Catalytic Cracking of Synthetic Crude Feedstocks," AM-09-19) discussed the impact synthetic

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**Table 1.** Feed blend properties with standard VGO combined synthetic crude oil (SCO) at 0% SCO, 40% SCO and 80% SCO.

<table>
<thead>
<tr>
<th>Feed Name</th>
<th>Std VGO</th>
<th>60% Std VGO</th>
<th>40% Synthetic Crude</th>
<th>20% Std VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>28.5</td>
<td>22.9</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.37</td>
<td>0.40</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Total Nitrogen, ppm</td>
<td>0.12</td>
<td>0.13</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Basic Nitrogen, ppm</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Conradson Carbon, wt%</td>
<td>0.68</td>
<td>0.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>K Factor</td>
<td>11.94</td>
<td>11.73</td>
<td>11.62</td>
<td></td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.00</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Paraffinic Carbons Cn, wt%</td>
<td>63.6</td>
<td>67.5</td>
<td>52.3</td>
<td></td>
</tr>
<tr>
<td>Naphthenic Ring Carbons Cn, wt%</td>
<td>17.4</td>
<td>21.1</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td>Aromatic Ring Carbons Cn, wt%</td>
<td>18.0</td>
<td>21.4</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>Distillation, 10%</td>
<td>807</td>
<td>824</td>
<td>804</td>
<td></td>
</tr>
<tr>
<td>Distillation, 50%</td>
<td>816</td>
<td>807</td>
<td>791</td>
<td></td>
</tr>
<tr>
<td>Distillation, 90%</td>
<td>1034</td>
<td>1025</td>
<td>997</td>
<td></td>
</tr>
<tr>
<td>Distillation, End Point</td>
<td>1257</td>
<td>1266</td>
<td>1241</td>
<td></td>
</tr>
</tbody>
</table>

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**In This Issue...**

**FEATURE**
Effect of Synthetic Crude Feedstocks on FCC Yields

**PROCESS OPERATIONS**
- Sulfur Solidification Capacity Expanding
- Hydrogen Recovery from Ofigas
- Applying Model Predictive Control
- Processing Visbreaker Feeds in an FCCU
- Fouling and Corrosion in Overhead Systems

**INDUSTRY NEWS**
- Czech Refiner Tests Alternative Crude Oils
- Flint Hills Processing Higher Volumes of Eagle Ford Crude

**VALERO**
- Refining Facility Replacing Foreign Crude with Domestic Source
- Frontier Increasing Heavy Crude Processing
- Reliance Refining Reports 100%+ Utilization Rates
- Rompetrol Completes FCC Revamp
- Construction at Nghi Son Refinery Beginning this Month

**EDITORIALLY SPEAKING**
- Automation’s Role at the Front End of the Refinery

**CALENDAR OF EVENTS**

Cont. page 2
Global production of elemental sulfur passed the 50 Mt mark in 2008 and continues to rise. Virtually all this is by-product sulfur, recovered from oil refining and natural gas processing.

The reasons for this growth are simple: a combination of increased fuel production to meet global demand; the refining of oil and gas with higher sulfur content; and ever more stringent environmental legislation, driving sulfur recovery efficiency levels as high as 99.9%. About two-thirds of this sulfur, which arrives from the extraction process in molten form, is then solidified. Why?

First, much of it has to be shipped elsewhere in the world for subsequent reprocessing (90% is converted into sulfuric acid, of which 50% is used in fertilizers and the rest for other chemical and production processes), and sulfur is easier, cheaper and safer to transport in a solid form.

**Editor’s Note:** A February 16, 2011 article in Wall Street Journal written by Liam Denning (“Profits for Oil Refiners Are More Than a Pipe Dream”) made mention to structural changes in the North American oil market coinciding with the recent development of Canada’s oil sands. For example, Denning wrote: “The upshot is blowout margins for any Midwestern refiner able to process heavier Canadian crudes [e.g., SCOs]...”. This seems to further validate the trend towards processing higher volumes of SCOs by various refiners.

More information on the application of GENESIS™ catalysts in processing SCO’s can be obtained by contacting Grace Davison or Rosann Schiller directly (rosann.schiller@grace.com).

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**PROCESSES OPERATIONS**

**Sulfur Solidification Capacity Expanding**

Global production of elemental sulfur passed the 50 Mt mark in 2008 and continues to rise. Virtually all this is by-product sulfur, recovered from oil refining and natural gas processing.

The reasons for this growth are simple: a combination of increased fuel production to meet global demand; the refining of oil and gas with higher sulfur content; and ever more stringent environmental legislation, driving sulfur recovery efficiency levels as high as 99.9%. About two-thirds of this sulfur, which arrives from the extraction process in molten form, is then solidified. Why?
A second increasingly important factor behind a growing need for solidification capabilities is a mismatch between supply and demand. Refineries have to retain sulfur until it can be sold. It therefore needs to be in a stable form that is both easy to stockpile, and then easy to load and ship.

A third reason for solidifying sulfur is the ability to cope with fluctuating throughput rates. If a refinery’s facilities are limited by the volume of molten sulfur that can be stored at any one time, then production capacity is finite. Once the tanks are full, that’s it. The ability to turn some of this molten sulfur into solid form – one that can literally be piled up outdoors – delivers an important degree of flexibility.

Sandvik’s experience in solidification systems stretches back over 75 years to the development of a steel belt cooler for resin/wax products and sulfur mixtures. But it wasn’t until 1980 that the company first introduced the Rotoform system, a process that would become the preferred sulfur solidification method for more processors than any other technology as shown in Figure 1, and will be discussed in more detail in the upcoming Innovations in Hydrocracking and Hydrotreating special report.

Hydrogen Recovery from Offgas

Demand for high purity hydrogen (H₂) in hydrotreating operations has led to increased pressure swing adsorption (PSA) capacity. Hydrogen recovery with PSA technology becomes favorable with offgases consisting of more than 40% hydrogen. Membrane-based technology instead of PSA technology may be preferable for lower hydrogen throughputs that don’t require high H₂ purity.

Basically, the PSA process of purification uses an adsorbent in a fixed bed to adsorb offgas impurities at high pressure, which are then desorbed at relatively low pressure into an offgas stream. Thus an extremely pure hydrogen product with purities in excess of 99.9% can be achieved by this process. The various licensors of PSA technology have developed modular skid mounted units for fairly rapid implementation.

To mitigate operating cost, a large percentage of the molecular sieve adsorbent used in PSA-based H₂ purification is reused depending on the unit’s operating history. Refiners and suppliers of PSA technology use certain criteria and testing procedures to determine if the adsorbent’s activity is sufficient for reuse. However, many refiners opt to replace the entire molecular sieve adsorbent inventory as the cost of this material is relatively inexpensive.

Applying Model Predictive Control

Many refiners have applied model predictive control (MPC) to major refinery units. Selective application of model predictive control (MPC) technology has been typically applied to linear refinery processes. The benefits come from determining and controlling the optimal properties and relative sizes of the various product streams. A study by Petrobras’ Almeida et al discusses the application of MPC to moderately nonlinear processes. The system used in this work is an industrial gasoline debutanizer column. In the debutanizer column, several nonlinearities are present in the advanced control level when the manipulated inputs are the reflux flow and the reboiler heat duty. In most cases the controlled outputs are the contents of C₅⁺ (pentane and heavier hydrocarbons) in the LPG and the gasoline vapor pressure. The Almeida approach considers several process models representing different operating conditions where linear models are identified. The results show that the multi-model predictive controller is capable of controlling the process in the entire operating window while the conventional MPC has a limited operating range.

According to a Pavillon Technologies blog provided by Michael Tay, Manager of Sales Engineering, he noted that MPC could move beyond the traditional linear applications and into more complex systems such as blend optimization. “These are highly non-linear in nature, which has led to mixed results when attempted with linear methods. There can be very large benefits in making blend quality control better by reducing blend give-away or by responding in real-time to blend component shifts as the blend component units shift in real-time,” according to Tay.

Another complex application according to Tay is to control the CDU actively during crude switches. “These are also nonlinear and include challenging dynamics, but the value of success can be quite high,” says Tay.

Processing Visbreaker Feeds in an FCCU

An investigation was recently carried out and published by Stratiev et al to test the feasibility of processing a 360-510 °C visbreaker fraction in the FCCU, in order to maximize high-value product yields.\(^1\) In summary, Stratiev et al reported the following:

It was found that addition of 25% of the visbreaker 360-510 °C cut to the FCC feed does not negatively affect the FCC yield pattern. Deriving the 360-510 °C fraction from the visbreaker and processing it in the FCC unit could increase the crude oil conversion by 2.8%. The yield of high value LPG and gasoline could increase by 0.8% and 2.6% of the crude oil, respectively, while reducing yields of fuel oil and FCC LCO by 3.7% and 0.6% respectively. Characterization of the 200-360 °C visbreaker cut showed that this material is more suitable as a component for transportation diesel than FCC LCO because of the lower aromatics content, 41% versus 72% of FCC LCO and higher cetane index - 42 versus 21 of FCC LCO.\(^1\)


Fouling and Corrosion in Overhead Systems

High performance alloy applications in areas of refinery processing that are known to be corrosive, such as the FCC main fractionators overhead systems and flue gas desulfurization equipment can benefit from use of Hastelloy® alloy in select areas. This nickel-chromium-molybdenum wrought alloy is considered the most versatile corrosion resistant alloy available. It is resistant to the formation of grain boundary precipitates in weld heat-affected zones, thus making it suitable for most chemical process applications in an as-welded condition. This alloy is designed to resist pitting, stress-corrosion cracking and oxidizing atmospheres up to 1900°F, and is one of the few alloys resistant to wet chloride gas, hypochlorite and chlorine dioxide solutions.

Acidic corrosion-erosion in an FCC main fractionator overhead circuit may result from some units frequently being in a catalyst recirculation (CRO) transient phase. CRO is used to allow quick start-ups after short shutdowns. Process water sampled during those phases exhibit a very low pH due to the presence of sulfuric acid. Sulfur trioxide (SO\(_3\)) is formed during catalyst recirculation operations. The SO\(_3\) goes up in the main fractionator overhead and condenses as H\(_2\)SO\(_4\) with the water vapor. This media easily corrodes carbon steel equipment. According to one expert familiar with this type of problem, a way to mitigate this corrosion is a condensed water pH control during those periods.
INDUSTRY NEWS

Czech Refiner Tests Alternative Crude Oils

In a press release from late February, Česká rafinérská, a.s., Litvínov, noted that it has processed in its two refineries an amount of crude oil feedstock close to 7,318 thousand tons. Next to the record set in 2003, this is the second-highest amount from the conversion to the processing mode.

In 2010, Česká rafinérská managed to successfully test processing of alternative crude oil types at the Litvínov refinery, while also optimizing automotive fuels formulations. The number of unscheduled facility shutdowns at both Česká rafinérská facilities has decreased. However, this new “norm” got complicated in late 2010 due to operating limitations put in place at both refineries.

The Company has fulfilled its obligation to add bio-components to automotive fuels released into the Czech Republic tax circuit (i.e., bioethanol was added to gasoline, and FAME was added to diesel fuel, namely in volumes imposed by amendment effective within the period from January 1 to May 31, 2010, and subsequently from June 1, 2010 onwards.)

Flint Hills Processing Larger Eagle Ford Crude Volumes

Wichita, Kansas based Flint Hills Resources LP recently reported that it will add the capability to ship up to 200,000 bpd of crude oil and condensate from its terminal in Ingleside, Texas, which is integrated into the Port of Corpus Christi navigation network. According to recent comments from Brad Urban, senior vice president of crude oil for Flint Hills Resources, “With this approval we will be able to proceed with permitting and complete our plans to modify and integrate these assets into our crude terminal that is already receiving Eagle Ford production. Flint Hills Resources expects to begin outbound waterborne shipments of Eagle Ford from the retrofitted assets by the middle of 2012.”

“We believe the Eagle Ford Shale play will produce a large volume of crude oil for a long time – and in amounts that will exceed what local refiners can use,” Urban said. “Due to the proximity to Eagle Ford production, we believe Corpus Christi and Ingleside are the best locations for shipping Eagle Ford crude to other markets on the Gulf Coast.” The API gravity of Eagle Ford crude oil is roughly between 30-50 °API.

Valero Refining Facility Replacing Foreign Crude with Domestic Source

A report from Reuters dated February 10 quoted Valero Energy Corp. Chief Executive Bill Klesse as saying that Eagle Ford shale crude from south Texas was replacing foreign crude at the company’s 93,000 bpd Three Rivers, Texas refinery. The refinery, located 74 miles south of San Antonio, is running 27,000 bpd of Eagle Ford crude currently, and is expected to run 40,000 bpd of the oil by May, Klesse said in a recent conference call. Within the year, the refinery will be running 60,000 bpd of Eagle Ford.

Frontier Increasing Heavy Crude Processing

Houston based Frontier Oil Refining Corp. will shut an FCCU and an alkylation unit for planned work from late March into April at its Cheyenne refinery in Wyoming, a company executive said in a conference call to reporters on February 24. “Planned work on an alkylation unit at the company’s El Dorado refinery in Kansas has been postponed from this fall until the spring of 2012,” said James Stump, vice president of refining operations at Frontier, during the conference call.

The crude throughput rate during the first quarter at the Kansas refinery is expected to average 134,000 bpd, according to Stump. Oil processing at the Wyoming plant is expected to average 42,000 bpd in the same period.

Frontier is increasing the amount of heavy crude it processes at El Dorado by about 25% and at Cheyenne by about 60% for a combined total of approximately 60,000 bpd, Stump said.
EDITORIALLY SPEAKING

Automation’s Role at the Front End of the Refinery

Refineries are looking for ways to improve profits through better utilization of current assets and deference of major expenditures. However, refinery utilization rates for many refiners have improved significantly along with margins as discussed in the Industry News sections of this issue, predating a higher level of automation and control investment.

It is probably not feasible to expect to continue cutting costs at the same level as 2009 and 2010. Nonetheless, decreasing “cost structures” in the downstream refining business mandate hard economic justification for major expenditures and new investments, including new automation systems.

Wherever possible, marginal projects and plant upgrades have been shelved while still trying to sustain efforts to improve efficiency and reliability. At some point beyond 2011, the industry may reach a plateau in efficiency improvements. Thereafter, new automation systems

Cont. page 7
will be necessary for supporting optimization strategies such as predictive asset management.

At the same time, enabling technology will also be needed in support of low carbon technologies ---- a new challenge for even the most experienced professionals. In other areas, the major automation suppliers are providing effective partnerships with operating companies and technology licensors. In many cases, the automation experts pursue a parallel track with the technology supplier/licensor and the refinery to implement control systems in key conversion units, such as with reducing the variability in hydrogen purity from pressure swing adsorption applied to refinery offgas. This has become just one of the many important tasks targeted for improvement by most refiners, as they increase hydrosprocessing capacity and severity.

Refiners expecting improved margins and utilization rates between now and mid-2013 know that they only have a short window to implement the technology needed to turn a profit. In many cases, the basis of making a profit over the next two or three years means avoiding unplanned shutdowns, safe operations and higher throughputs compared to what we have seen since late 2008. One of the most efficient ways of achieving these goals is by improving automation and control of existing assets.

To be sure, it would be nice to have the capital to build a new crude/vacuum unit with upgraded metallurgy, the latest in fired heater design, additional desalting capacity and all the other metrics needed to process the heaviest and most hydrogen-deficient crude on the market, but the reality is that much of the capital outlays planned over the next two years has already been committed to revamping downstream conversion units, such as the FCCU, hydrocracker, etc.

There are compelling arguments for justifying higher-than-planned investment in upgrading crude units for a variety of reasons, such as increasing diesel production directly from the vacuum unit, increasing atmospheric gas oil production to FCC and/or hydrocracking operations. However, it’s no secret that the refining industry is neoconservative about “experimenting” with new types of technology, such as application of multi-variable predictive (MPC) control, well proven in linear processes, to non-linear processes such as crude unit “switching” operations.

Optimal crude unit switching operations are becoming a “do it right the first time” priority as more refiners in disparate locations, from the Midwest US to the Czech Republic, are documenting the introduction of feedstocks that they have not traditionally processed in the past. For example, one refiner as noted in this issue’s Feature article by Grace Davison’s Rosann Schiller noted that processing of various percentages of synthetic crude oil (SCO) combined with traditional VGO have been effectively converted to high quality products with the latest hydrotreating catalyst systems. But first, these feedstocks had to be processed through the crude unit. For example, one of the two facilities that Ceska Rafinerski operates in the Czech Republic has successfully processed an “alternative crude” through its facility.

All of these facilities have no doubt found ways to improve crude unit flexibility, perhaps without the level of investment needed to upgrade downstream thermal conversion and catalytic conversion units. In any case, there was probably an automation aspect to the upgrade as will be discussed in more detail in the Innovations in Crude Unit Optimization special report scheduled for publication this October. ■
CALENDAR OF EVENTS

MARCH


27-31, ACS Spring 2011 National Meeting & Exposition, American Chemical Society, Anaheim, California, +1 508 743 0192, www.acs.org


APRIL

3-6, The Middle East Downstream Week, 12th Annual Meeting, World Refining Association, Paris, +44 (0) 20 7067 1800, www.wraconferences.com

13-16, 6th Russia & CIS Bottom of the Barrel Technology Conference & Exhibition, Euro Petroleum Consultants, Moscow, +44 (0) 20 7357 8394, www.europetro.com

MAY

2-6, Coking Safety Seminar, Coking.com, Galveston, Texas, +1 360 966 7251, www.coking.com

17-18, China Downstream Technology & Markets Conference & Exhibition, Euro Petroleum Consultants, Tianjin, +44 (0) 20 7357 8394, www.europetro.com


JUNE

13-14, The Global Catalyst Technology Forum, Euro Petroleum Consultants, Dubrovnik, Croatia, +44 (0) 20 7357 8394, www.europetro.com

15-16, 9th International Bottom of the Barrel Technology Conference, Euro Petroleum Consultants, Dubrovnik, Croatia, +44 (0) 20 7357 8394, www.europetro.com