Refinery Operations
Engineering Solutions, Maintenance, Reliability, Automation and Equipment

March 02, 2011 VOL: 2 ISS: 4

Effect of Synthetic Crude Feedstocks on FCC Yields

Selection of Appropriate Catalyst when Processing Combinations of Standard VGO with Synthetic Crudes are Analyzed., Rosann Schiller, Grace Davison

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.

Feed Name	Std VGO	60% Std VGO 40% Synthetic Crude	20% Std VGO 80% Synthetic Crude
API	25.5	22.9	20.5
Sulfur, wt%	0.37	0.40	0.42
Total Nitrogen, ppm	0.12	0.13	0.14
Basic Nitrogen, ppm	0.05	0.03	0.03
Conradson Carbon, wt.%	0.68	0.6	0.7
K Factor	11.94	11.73	11.52
Specific Gravity	0.90	0.92	0.93
Paraffinic Carbons Cp, wt.%	63.6	57.5	52.3
Naphthenic Ring Carbons Cn, wt.%	17.4	21.1	22.8
Aromatic Ring Carbons Ca, wt.%	18.9	21.4	24.9
Distillation, 10%	607	624	634
Distillation, 50%	818	807	791
Distillation, 90%	1034	1025	997
Distillation, End Point	1257	1266	1241

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

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 Cont. page 2

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crude has on hydrocarbon yields in the FCC unit. The study also examined the type of FCC catalyst that is most effective at cracking these feeds. Analyses of the sulfur species in the feed and the cracking products were also discussed.

For example, the paper noted that a major refiner in North America had been processing synthetic crudes for many years. It was noted that the synthetic crude has been upgraded and is then mixed into the facility's typical crude diet in ratios ranging from 20-40% (**Table 1**). In 2008, this refiner switched to an ADVANTA® catalyst. After turnover to ADVANTA® catalyst, the refiner realized a reduction in bottoms yield on the order of 0.3 lv% of feed, which is similar to the improvement observed in the ACE testing for ADVANTA® over AURORA® catalyst.

The processing of synthetic crude remains an important operating strategy for this refiner who, based on the test results, has reformulated to a GENESIS™ catalyst system to further drive bottoms reduction and unit profitability.

Lab data and extensive commercial experience show synthetic crude follows the same general cracking rules as more typical VGO feeds. Synthetic crude typically contains high levels of aromatics and naphtheno-aromatics. Porosity in the 100-600Å range is critical for the free diffusion of these large molecules into and out of the catalyst pores. The associated low feedstock hydrogen level makes the feed more difficult to crack and tends to increase coke levels. The use of an appropriately designed catalyst can mitigate these negative effects. The proper design of matrix activity and the interaction of matrix with zeolite ensures conversion of aromatic coke precursors into valuable liquid products. Grace Davison ADVANTA® and GENESIS™ catalyst technologies with low Z/M ratios demonstrate reduced bottoms, lower dry gas, and higher gasoline + LCO yields at constant conversion. Selective cracking of naphtheno-aromatics requires Grace Davison's matrix technology in ADVANTA® and GENESIS™ catalysts. Both systems possess coke selective matrix with high surface area and high pore volume in the 100-600Å region. Their high matrix porosity translates into excellent coke selectivity in commercial application and both are used successfully in several units operating with synthetic crude feed blends. ■

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).

PROCESS OPERATIONS

Sulfur Solidification Capacity Expanding

Hans-Georg Pohle, Sandvik

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?

Figure 1. Four Rotoform HS units in operation at a major refining facility.

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.

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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 (H_2) 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 H_2 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 H_2 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.

According to several licensors of PSA technology, the primary vessels of these units can last over 20 years provided that the feed to the PSA remains free of water and other corrosive elements. As previously noted, due to their typical design configuration based on several fixed bed reactors arrange in series, PSA units lend themselves to modular skid mounted designs. For example, Linde, the world leader in PSA units, installed a PSA unit at a Canadian refinery capable of processing 21,200 Nm^3/hr of offgas, which coincides with recent increases in hydrotreating and/or hydrocracking capacity. ■

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.[1] 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 C_5^+ (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 Pavilion 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. ■

1. E. Almeida, Neto, M. A. Rodriguez and D. Odloak, "Robust Predictive Control of a Gasoline Debutanizer Column," Brazilian Journal of Chemical Engineering, Vol. 17, No.s 4-7, Sao Paulo.

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Published biweekly by
NEMESIS MEDIA GROUP, LLC
PO BOX 5416
Kingwood TX 77325. USA
Phone: (713) 344-1379
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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. Stratiev, D., D. Minkoy and G. Stratiev, "Synergy Between Fluid Catalytic Cracking and Visbreaking to Increase High-Value Product Yields," Lukoil Neftochim Bourgas AD, Bourgas, Bulgaria.

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_2SO_4 with the water vapor. This media easily corodes 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. ■

Reliance Refining Reports 100%+ Utilization Rates

During the nine months ended December 31, 2010, 49.9 million tonnes of crude was refined by Reliance Industries Limited (RIL) refineries reflecting an average utilization rate of 107%, according to information available on their website. This was perhaps the highest in the world. In comparison, average refinery utilization rates were 84.6% in North America, 78.6% in Europe and 85.9% in Asia. During this nin month period, refinery utilization rates improved in all the major markets of US, Europe and Asia due to increased product demand and improving economic environment. ■

Rompetrol Completes FCC Revamp

Rompetrol Rafinare, company member of The Rompetrol Group, has registered in 2010 a consolidated turnover of over $3.5 billion, 12% larger than in 2009, and shows a significant improvement of the operational results (EBITDA), of $16 million, on the increase compared to a $3.25 million result registered in 2009.

The financial results achieved were influenced primarily by external factors, such as closing/reducing refining capacities. In addition, other factors included the difficult conditions in obtaining working capital and related financing, the differences in the exchange rate, the impact of macro- economical measures like VAT increasing to 24%, increase of inflation rates (from 4,75% in 2009 to 7.90% in 2010) or the amount of different taxes can be added.

Among the major projects completed in 2010 included an FCCU revamp, allowing a significant increase in production yields. Also completed was the integration of new systems for monitoring process unit performance. ■

Construction at Nghi Son Refinery Beginning this Month

Vietnam has picked France's Technip, Japanese engineering firm JGC Corp. and Spain's oil engineer Tecnicas Reunidas for a $5 billion deal to build Nghi Son oil refinery, the country's largest, a state-run newspaper reported.

Petrovietnam Construction Corp, a subsidiary of state oil group Petrovietnam, will join the three foreign firms in the engineering, procurement and construction contract for the 200,000 bpd refinery, the Vietnam Economic Times newspaper quoted Petrovietnam Chairman Dinh La Thang as saying earlier this year.

He said the selection of partners in the EPC contract would enable construction of the refinery, which has a total investment of $7 billion, to start in March, as reported by Reuters earlier this year.

Petrovietnam has been developing the Nghi Son refinery in the northern province of Thanh Hoa in a venture with Kuwait Petroleum International, Japan's Idemitsu Kosan Co and Mitsui Chemicals.

Nghi Son's operation is scheduled in 2014, and together with Dung Quat oil refinery, the country's first refinery, the two will meet half of domestic oil product consumption, the newspaper reported.

Petrovietnam also recently noted that it has also picked JGC Corp. as adviser for a plan to raise Dung Quat refinery's capacity to 200,000 bpd from 130,000 bpd now, and the project is expected to be completed in 2016. Following the successful test-run completion of Dung Quat refinery and the handover to its owner Petrovietnam in late May 2010, the state oil group now already runs the refinery at more than 100% of its capacity. ■

EDITORIALLY SPEAKING

Automation's Role at the Front End of the Refinery

Rene Gonzalez, Editor
Refinery Operations

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, predicating 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

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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 hydroprocessing 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 crudes 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

13-17, *2011 AIChE Spring Meeting & 7th Global Conference on Process Safety*, American Institute of Chemical Engineers, Chicago, Illinois, +1 203 702 7660 , www.aiche.org.

20-22, *NPRA Annual Meeting*, National Petrochemical and Refiners Associatio, San Antonio, Texas, +1 202 457 0480, www.npra.org

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

30-31, 14th Annual ARTC Meeting, Singapore, Incisive Media & Global Technology Forum, +852 3411 4829, www.gtforum.com

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.

24-27, *NPRA Reliability & Maintenance Conference & Exhibition*, NPRA, Denver, Colorado, +1 202 457 0480, www.npra.org.

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.