CRITERION
CATALYSTS & TECHNOLOGIES

EPC
Euro Petroleum Consultants

2nd Russia & CIS
Bottom of the Barrel Technology
Conference & Exhibition
18 & 19 April 2007, Marriott Grand Hotel, Moscow

Correct catalyst selection leads to improved on-stream factor in high conversion Resid Upgrading units

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ABSTRACT

The next wave of major investment in the Russian refining industry is already underway, focused on greater bottom of the barrel upgrading to meet increasing domestic and export-market demand for transportation fuels, particularly diesel. Moreover, sustained high oil prices, growing sweet to sour differentials and shrinking fuel oil market outlets have seen a renewed rate of licence awards (including 2 in Russia) for H-Oil® and LC-Finer™ resid upgrading technologies. Accordingly, Russian resid upgrading refiners now find themselves in the advantageous position of being able to benefit from the valuable performance optimization lessons learned by the current worldwide 17 operating or announced Ebullated Bed units. Foremost amongst these lessons learned is how to better control sediment-induced fouling which has become the principal Ebullated Bed unit cycle limiting parameter and which becomes an even more limiting factor when processing feeds derived from Urals crude.

In this paper, the importance of correct catalyst selection and customization to achieve desired performance improvements is underlined using a range of examples from distinctly different commercially operated ebullated bed units. In all cases, the customised catalyst solutions developed in parallel with changing unit objectives focused first and foremost on incorporating better sediment (fouling) control in the reactor section to give improved unit operability. From there, meeting other targets such as achieving higher vacuum resid conversion levels to yield a product slate with ever tightening sulphur and stability limitations will be described.

1.0 INTRODUCTION

With the sustained strong economic emergence of countries such as China and India underpinning the projections for strong future growth in demand for refined products and in particular transportation fuels, the refining industry has received a new lease of life in recent years. In 2004 when the milestone of demand equaling supply was reached, refining margins reached record highs, which have remained healthy in some regions. This upturn in the industry's fortunes has spearheaded a wave of new investment with over 500 dedicated refinery projects including 160 major expansions underway as of March 2006 equating to 10 MMBPSD extra refining capacity to be on line by 2010.

In fact by 2020 the global demand for transportation fuels, weighted very much in favour of diesel, is projected to be double the 1990 figure of 66 MMBPSD. They are currently 900 million vehicles on the road. In 2050 this will rise to two billion with the world population at 9 billion, 50% higher than today's. The growing economic might of India and China will be accompanied by marked increases in vehicle ownership. In the same timeframe as this doubling of transportation fuels demand, the environmental and legislative drive to produce even cleaner transportation fuels coupled with even stricter control of refinery emissions will intensify further while the typical refinery crude slate will become heavier. Currently, 50% of the world's crude oil is heavy and sour **(1)**. The actual extent of this trend towards heavier crude diet varies per region based on factors such extent of local supply, opportunistic market crudes (light-heavy crude differential) on offer, and the degree of refinery complexity present.

A case in point is the North American refining industry where more oil sands derived synthetic crude is entering the east coast and mid-west regions on the one hand while an increasing percentage of processing of the more refractory Latin American crudes (Maya, Batchequero) is being observed on the Gulf Coast. This trend has helped to sustain very healthy margins due to the high degree of refining complexity present in that market capable of upgrading these crudes to lighter valuable products. In the European refining industry on the other hand, decreasing North Sea crude output has forced a greater reliance on Russian crudes such as Urals with associated properties, which generally lead to lower bottoms conversion. This combined with a lower degree of complexity (conversion capacity still very FCC-centric), compared to the North America refining industry, translates into higher fuel oil production and surplus.

Revamps/de-bottlenecking has been the major investment route followed in Europe to help meet the tighter specifications of Euro IV diesel with declining gasoline demand while a progressive switch from liquid fuel to natural gas in the refinery fuel system is helping to meet the new refinery emission standards. Tackling a decreasing local demand for fuel oil (especially high sulphur fuel oil, HSFO, bunker fuel with a typical S content of 2.8 wt.%) can be looked at in three different scenarios namely (i) find an alternative market (increase amounts exported), (ii) simply produce less through more selective crude processing or (iii) invest in best-fit Bottom of the Barrel upgrading technology to take advantage of the attractive Middle Distillate-Fuel Oil margin. While the last option gives the greatest long term processing flexibility, investing today means at least 5 years to implementation and at that stage the market dynamics may not be what they are today. Investing to squeeze more clean fuels out of the bottom of the barrel is not without risk, which needs to be effectively managed using a medium term forward curve at the project feasibility stage. This scenario re-emphasises the key underlining message with regard to investing in a resid upgrader namely it's all about 'the right project in the right place with the right base crude!'

The changing market dynamic scenario for a resid upgrading unit to be commissioned post 2010 can be best appreciated from the tighter cleaner fuels quality specifications, as part of the further evolution of on- and off-road transportation fuels, that are expected to be regulated in that timeframe. These include:

(a) further reduction of sulphur specifications for off-road (e.g. marine, agricultural, locomotive & construction machinery) diesel fuels currently mandated at 500–1000 ppmw to reach the on-road specification of 10–15 ppmw by 2010. See Table 1 below for regional variations for on and off-road diesel legislated/proposed specifications.

(b) a proposal by G-8 leading politicians for even more stringent legislated control of total refinery emissions legislated by 2009 as the successor to the 1997 signed Kyoto protocol for implementation by 2012 **(2).**

(c) agreement reached by European Union leaders in March this year to reduce CO_2 emissions by 20% from 1990 levels by 2020 and also to increase use of renewable fuels by 20% in the same timeframe **(3).**

(d) a provision to review range of non-sulphur mandated specifications such as aromatics and cetane for inclusion in EU 2008/9 clean fuels specification packages. A recent European Commission proposal calls for 10 ppmw Sulphur diesel for highway use by 1-1-09, off-road by 1-1-10 & marine use on inland waterways by 1-1-12. Additionally, polyaromatic content is recommended to be reduced from current level of 11 wt.% to 8 wt.% for highway diesel (ULSD) by 1-1-09 **(4).**

Legislated & Proposed Sulphur Levels - Diesel Fuels

On-Road

	S ppm			
	2004	**2005**	**2006**	**2008-9**
Singapore			🟩 **50**	
Japan	🟨 **50**			🟨 **10**
S. Korea			🟩 **50**	
Australia			🟩 **50**	🟨 **10**
China	🟩 **500**			
India		🟩 **350**		🟩 **50**
European Union		🟩 **10 & 50**		🟨 **10**
United States & Canada			🟩 **15**	

Off-Road

	S ppm			
			2007	**2008-9**
European Union				🟨 **10**
United States & Canada			🟨 **500**	🟨 **15**

🟩 **Legislated**
🟨 **Proposed/Expected or Voluntary**

Table 1: Current legislated and expected future specifications for both on and off-road diesel fuels

The principal effects of these expected extended regulations would be to reduce overall refinery operating flexibility even further. For instance where blending flexibility is concerned, these changes mean essentially zero disposal outlets remaining for blending away the traditional more refractory middle distillate streams (FCC LCO, Coker CGO) to the off-road distillate pool or indeed to the fuel oil pool. The more stringent refinery emission control measures also mean that higher bottom of the barrel conversion will be required with the domino effect of production of greater amounts of more refractory distillate streams not suitable for blending into on- and off-road pools without further severe and expensive integrated high pressure hydrotreating. Such extra hardware has to therefore also be included for any resid upgrading investment package on the table today with post 2010 implementation timing. The type and amount of total investment required per refiner will vary dramatically depending on degree of current conversion capacity but in all cases it is cl;ear that the investment will have to cater for the worse case 'ultimate clean fuels' scenarios painted by (a) to (c) above. For the existing resid upgrading hydro-conversion operators some form of retrofit or revamp may be required to not only meet the tighter product specifications but also to deal with the adverse effects on product stability and unit operability associated with pushing bottom of the barrel conversion even further above design.

Prior to such a revamp/retrofit, the true bottoms [conversion capability **–** product stability] balance of existing resid upgrading hydro-conversion units should be assessed by first ensuring that the correct choice of catalyst has been made. In Ebullated Bed resid upgrading units where 565°C+ conversions as high as 78 vol% are targeted, the choice of catalyst is critical to ensure sustained operation at such conversion levels without succumbing to fouling caused by excessive sediment formation resulting in premature unit shutdown. In this paper the role of unit customized sediment control catalysts in meeting the desired conversion and maintaining high unit operability by controlling the rate of fouling in the reactor section of such units is described. Specifically the role of the intrinsic properties of such catalysts in performing the chemistry required to maintain the necessary **S**aturates **A**romatics **R**esins **A**sphaltenes balance in the vacuum bottoms fraction to keep the main fouling precursor (asphaltenes) in solution will be described through specific case studies. Ahead of this, let's first examine the types of resid upgrading technologies available today and the role of the catalyst therein where applicable.

2.0 RESID UPGRADING LICENCED TECHNOLOGIES

The principal objective of a resid upgrading unit whether employing carbon-rejection ("coking") or hydrogen addition ("hydro-conversion") technologies is to convert lower value feedstocks such as Vacuum Tower or Atmospheric Tower Bottoms to higher value products such as transportation fuels or quality improved feedstocks for further upgrading in a downstream unit such as a hydrocracker, FCCU, or high pressure hydrotreater. The operation of a Resid upgrader can be further classified according to the 3 distinct product slates targeted namely:-

(i) Low Sulphur Fuel Oil production

(ii) High Quality Transportation Fuels production

(iii) Zero production of Fuel Oil

In the case of LSFO production this is traditionally accomplished in fixed bed resid hydroprocessing units geared to meeting sulphur specifications 0.27 to 0.7 wt.% in the blended product Fuel Oil, depending on the region's power plant SO_x emission specifications. The Middle and Far East represent the regions where this type of operation predominates. In fact 70% of the world's 50 fixed bed resid hydroprocessing units are located in the Far East with 16 units alone located in Japan. The resultant bottom of the barrel upgrading in these units is typically in 25-40 wt.% 520°C+.

For production of high quality transportation fuels, higher bottom of the barrel conversion is required in the dedicated resid upgrading unit with the final product quality specification being met by an integrated hydrocracker, FCCU or high pressure hydrotreater. This approach is becoming the new standard for more recently announced projects with the 'ultimate clean fuels' solution in mind. The advantage of achieving improved product quality specifications with hydrogen-addition resid technologies is achieving high quality transportation fuels specifications. Carbon-rejection technologies usually require an integrated hydrocracker in the basic design as well, for ultimate processing flexibility.

In the case of hydro-conversion technologies zero 'liquid' fuel oil production requires the combination of technologies approach. For instance some form of pretreatment technology of the ATB/VTB feed such as Solvent DeAsphalting can be applied whereas in the case of carbon rejection technologies the unconverted bottoms are simply transformed into 'solid fuel oil' the so denoted fuel-grade coke which is sold to local power plants or gasified. Representative lists of carbon rejection and hydro-conversion resid upgrading technologies together are presented below in Tables 2A and 2B below.

A REPRESENTATIVE LIST OF CARBON REJECTION LICENCED RESID UPGRADING TECHNOLOGIES			
Resid Upgrading Technology	**Principal objective**	**Principal Advantages**	**Principal Issues**
THERMAL CRACKING (Visbreaking)	Lower quality transportation fuels & MFO production at low Bottoms conversion	Low CAPEX option	Low bottoms conversion due to low coke tolerance Traditional disposal routes for MFO disappearing
DELAYED COKING	High Bottoms conversion (up to 80%)	No liquid bottoms (Fuel Oil) production Good feedstock flexibility Most applied Resid Upgrading technology with North American refining industry leading the way	Traditional market outlets for fuel grade coke by-product declining. Fuel grade coke has a bad CO_2 footprint as fuel for power generation plants w/o a flue gas scrubber Cyclic, energy- and labour intensive process
FLEXICOKING	High Bottoms conversion (up to 80%) with fuel gas production through integrated fluid bed gasifier	No liquid Bottoms (Fuel Oil) production No coke disposal issues as converted to clean burning flexigas	Higher CAPEX due to presence of gasifier and gas purification system (Flexsorb)

Table 2A: Representative list of carbon rejection based resid upgrading technologies highlighting typical bottom of the barrel conversion levels achieved with corresponding advantages/disadvantages of each technology. *(Other carbon rejection licenced technologies not listed above include Fluidcoking and Resid FCC)*

A REPRESENTATIVE LIST OF HYDROGEN ADDITION LICENCED RESID UPGRADING TECHNOLOGIES			
Resid Upgrading Technology	**Principal objective**	**Principal Advantages**	**Principal Issues**
FIXED BED HYDROTREATING [ARDS & VRDS Units]	Low Sulphur Fuel Oil and high quality FCCU feed production with resultant Bottoms conversion	Easily revamped for higher conversion via catalyst/internals retrofit or by having moving bed technology upfront Controlled operation to avoid product instability issues	Not suitable for processing highly refractory feeds (Ni+V > 150 ppmw) Susceptible to premature cycles due to sudden pressure drop increase LSFO specifications getting more stringent & feedstocks getting heavier
MOVING BED HYDRO-CONVERSION [Ebullated Bed Units]	High Bottoms conversion (up to 80%) depending on VR crude source	Constant catalyst performance	Fouling of work-up section especially at higher conversions Complex operation Crude processing flexibility Logistics with spent catalyst disposal
SLURRY HYDRO-CONVERSION (EST Technology)	High Bottoms conversion (claimed up to 99% with downstream integrated SDA)	Claims complete upgrading of the Bottom of the Barrel Excellent product quality	Still not commercially proven Recycling and Recovery of the catalyst can be a bottleneck to achieving economic cycles

Table 2B: Representative list of hydrogen-addition based resid upgrading technologies highlighting typical bottom of the barrel conversion levels achieved with corresponding advantages/disadvantages of each technology.

3.0 EBULLATED BED RESID UPGRADING LICENCED TECHNOLOGIES

In Germany during World War II, slurry-reactor technology was employed for the hydrogenation of coal and this later formed the basis for the development of the Ebullated Bed Reactor (as shown in figure 1 below) for heavy oil hydroconversion **(5)**. The EBR was invented by Hydrocarbon Research Inc. (HRI) (H-Oil Process) in the late 1950s to overcome the well-documented problems with upgrading of residual oils in fixed-bed reactors. The first H-Oil Process demonstration plant came on-stream in 1964 at Cities Service's Lake Charles, Louisiana refinery to be followed in 1968 by the first commercial (single-stage) unit at Kuwait National Petroleum's Shuaiba refinery. HRI licensed the first two-stage unit to Motiva (then Texaco) Convent refinery in Louisiana, USA, which started up in 1984. Subsequent H-Oil™ systems have been one or two-stage.

LC-Fining as developed by ABB **L**ummus **C**rest represents an off-shoot of the HRI technology which saw its first commercial operation come on line in 1984 at BP, Texas City refinery in the USA. The BP LC-Fining unit was the first three-stage ebullated bed unit. There are now one-stage, two-stage and three-stage LC-Fining units in operation.

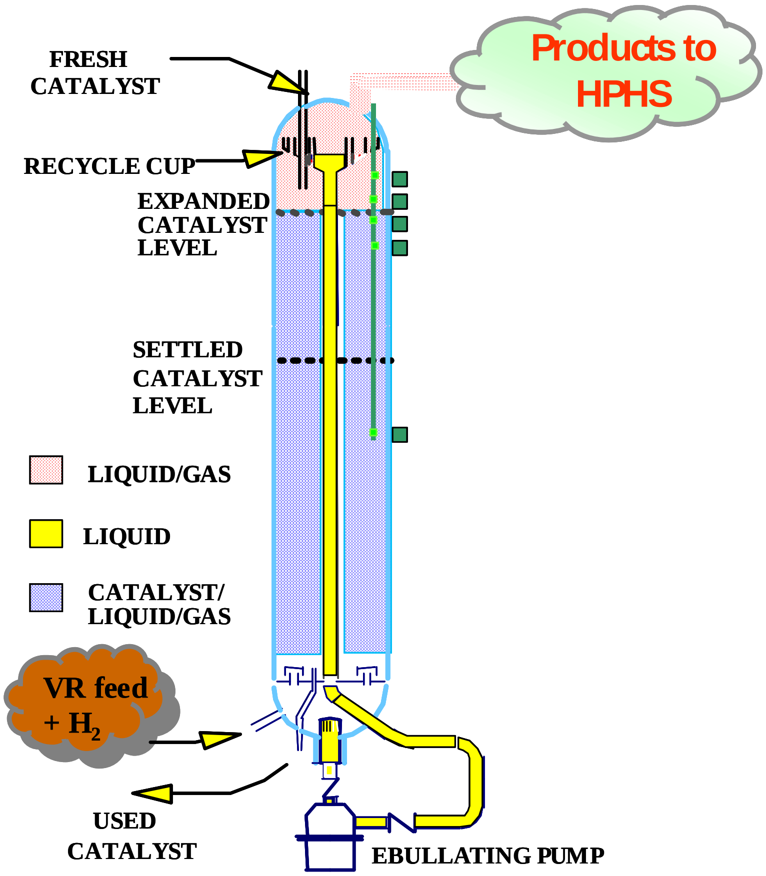

Figure 1: Example of one type of design of an ebullated bed reactor showing fresh catalyst addition from the top with feed entering from the bottom. The expanded catalyst bed is due to the high internal recycle. Used catalyst is withdrawn from the bottom.

More recently again, both H-Oil® and LC-Fining have introduced next generation Ebullated Bed process technologies whereby inter-stage separation between 2 reactors in a multi-stage unit **(6,7)** is introduced to positively influence the reaction kinetics in the last reactor to achieve higher overall unit performance. Inter-stage separation can be added in a revamp of an existing unit with the objective of overall higher conversion or higher throughput at exisiting conversion. Where a new grassroots unit is concerned inter-stage separation allows for a high degree of flexibility in design for instance a single train multi-stage design is sufficient to meet operating objectives or providing scope for downsizing of the EB reactor size to accommodate plot space, shipping or weight restrictions. All of these factors contribute to reducing the associated CAPEX required.

Table 3 below presents a list in chronological order of the 13 Resid Ebullated Bed units operating world-wide today and the 4 additional units to be commissioned by 2011.

REFINER	**EB Licenced Technology**	**Year Commissioned**	**Design Capacity (BPSD)**
1. KNPC, Shuaiba, Kuwait	H-Oil®	1968	24,000
2. PEMEX, Salamanca, Mexico	H-Oil®	1972	18,500
3. BP-Amoco, Texas City, USA	LC-FINING	1984	75,000
4. Motiva, Convent, USA	H-Oil®	1984	43,000
5. Syncrude, Canada	LC-FINING	1988	40,000
6. Husky, Lloydminster, Canada	H-Oil®	1992	32,000
7. Tonen, Kawasaki, Japan	H-Oil®	1997	25,000
8. Pemex, Tula, Mexico	H-Oil®	1997	50,000
9. ENI, Milazzo, Italy	LC-FINING	1998	25,000
10. PKN, Plock, Poland	H-Oil®	1999	34,000
11. Slovnaft, Bratislava, Slovakia	LC-FINING	2000	23,000
12. Shell Scotford (Trains 1 & 2), Canada	LC-FINING	2003	79,000
13. Neste Oy, Porvoo, Finland	LC-FINING	2007	40,000
Current total Resid EB capacity			**508,500**
14. Lukoil, Perm, Russia	*T-Star®*	*2004*	*70,400*
Shenhua, Outer Mongolia	*T-Star®*	*2007*	*69,500*
PetroCanada	LC-FINING	2009	50,000
Shell Scotford, Canada – Train 3	LC-FINING	2009	47,000
Mozyr, Belarus	H-Oil®	2010	60,000
Northwest Upgrading	LC-FINING	2011	29,000
Future total Resid EB capacity			**694,500**

Table 3: Chronological list of current 13 operating Ebullated bed units and 4 additional units planned to be commissioned from 2009 thru 2011. Ebullated bed technology is also applied to upgrade other feeds such as VGO in the case of the Perm T-Star unit and hydrogen donor solvent liquid derived from a coal liquefaction process in the case of the Shenhua unit planned in Outer Mongolia. [Information in this table obtained from references **(6), (10),** & **(11)**]

4.0 OVERVIEW OF EB CATALYSTS DEVELOPMENT

1st generation Ebullated Bed catalysts were designed with focus on maximizing HDS performance in a high pitch/bottoms (538°C+/1000°F+) conversion environment. At that time it was assumed that all of the 538°C+ conversion was thermal-based with the role of the catalyst solely to provide the hydrogenation function necessary for the HDS reaction. 2nd generation EB catalyst development maintained this focus while targeting even higher bottom of the barrel conversions. Achieving these higher conversions also led to more noticeable fouling of downstream equipment and product instability. In many cases the sediment formation responsible for the fouling phenomena resulted in shorter unit cycles and increased frequency of cleaning of hardware such as pump strainers or product filters while the asphaltene precipitation responsible for Fuel Oil instability required uneconomic back-blending with a more valuable (high aromatic content) based component such as FCCU LCO. Moreover, sediment formation and thereby cycle-limiting fouling in EB units was not seriously taken into account in grassroots unit design until the mid nineties. Fortunately development of dedicated sediment control EB catalysts was commenced at Criterion in the late eighties which resulted in the commercialization of the first dedicated sediment control EB catalyst, TEX-2710, in 1992 **(9)**. Since that time continuous improvements have been made in sediment control catalysts culminating in commercial catalysts such as our TEX-2720 catalyst.

In recent years, Criterion has been developing high activity catalysts with sediment control function customized to the particular EB unit operation. The main factors taken into account in this EB catalyst customization involve the 'Four C's approach' **(12)** which is also successfully applied in catalyst development for other refining applications such as ULSD production. Firstly, a firm understanding of the **C**hemistry of the reactions required to take place in the EB unit coupled with any inhibiting/de-stabilisation reactions (such as asphaltene flocculation) is required. Secondly, the chemistry required needs to be linked to the **C**omposition of the various VR feeds (crude source) with and without diluents such as HCO etc. being processed from which a distribution and relative reactivity of the reactants is obtained. At this point the unit operating **C**onditions (H_2 partial pressure, LHSV, CAR, Mode of catalyst addition (parallel or cascade) are added to the mix to give an idea of the extent of desired/un-desired reactions achievable under process conditions. Matching of the latter combination of information ultimately leads to a more definitive selection of the best type of sediment control **C**atalyst to be applied. This is then checked in dedicated pilot-plant testing versus a reference catalyst, which is usually the incumbent material.

This approach led to the development of the first customized higher conversion with enhanced sediment control catalyst, used in the early 2000's in the Motiva, Convent H-Oil™ 2-stage Ebullated Bed unit. This catalyst has since been further optimized in line with changing Middle East crude slate. Newer generation catalysts demonstrate higher conversion combined with associated higher degree of sediment control, customised to each individual refiner's feed and operation. These include catalysts for processing of vacuum resid feeds derived from Oil Sands (used by a North American refiner and a catalyst, which is specifically designed for use with Urals derived feedstocks (to be used in late 2007 by a European refiner)). Criterion has also developed new generation catalysts tailored specifically for the two-stage operations on vacuum resid streams derived from the heavy Mexican crudes used by Pemex and a catalyst tailored for one-stage operation for upgrading of heavy bitumen feed with unique properties and dispositions in Syncrude in Canada. Lukoil-Permnefteorgsyntez have also been using Criterion catalyst in their Ebullated Bed VGO upgrading T-Star unit since start-up in November 2004. Representative performance of this catalyst is described in section 7.0.

5.0 FOULING ASSOCIATED WITH SEDIMENT FORMATION IN EB UNITS

Given the nature of the operation of Ebullated Bed units whereby constant catalyst performance (by monitoring for first signs of decrease in reaction exotherm) is targeted through constant addition of sufficient fresh catalyst, in most cases the typical cycle length achieved on the unit is dictated more by fouling of downstream equipment (HP/LP separators, Atmospheric or Vacuum Towers, Heat Exchangers, AT/VT Heaters etc..). Consequently, the key to operating any EB process lies in the control of fouling precursors. Fouling mitigation is performed as part of the standard unit monitoring by measuring and controlling sediment (generally measured by the IP-375 method)

A typical definition of sediment is 'everything that won't pass through a filter apparatus' and this can be both inorganic (e.g. catalyst fines, iron oxide, iron sulphides and clay minerals from high ash content feeds) and organic (e.g. coke and/or agglomerated precipitated asphaltenes) in nature. In more general terms sediment is made up of inorganics + coke + insoluble Asphaltenes. In figure 2 below a optical micrograph of a sample of inorganic sediment, taken from a product strainer basket in a EB unit, is presented. The sample was first washed in toluene to remove any residual oil and then calcined to burn off residual coke. The resultant magnified image in figure 2 shows that the inorganic sediment present primarily consisted of a mix of fresh catalyst fines (white - yellow particles) and cinders (corrosion products, primarily present as Fe_2O_3 after calcination).

Figure 2: Optical micrograph of sample of toluene treated and calcined inorganic residue (sediment) removed from a product strainer of a North American Ebullated Bed unit

Sediment formation begins in the reactor section especially under high severity conditions applied to achieve either higher Vacuum Resid/Bottoms (538°C+/1000°F+) conversion or higher throughput at a fixed conversion. Reactor section WABTs as high as 454°C can be applied to meet these objectives. Under such extreme conditions destabilisation of the unconverted vacuum bottoms due to precipitation of asphaltenes, which is the least soluble fraction in heavy oils, occurs. This destabilization of the unconverted feed can also occur in the recovery section as a result of progressive asphaltene precipitation/flocculation. The first fingerprint on the likelihood of sediment formation and thereby fouling tendency during operation comes from a range of analyses of the heavy oil fractions in the downstream work-up sections namely Atmospheric (ca. 350°C+) and Vacuum Tower (ca. 538°C+) Bottoms. A representative list of these analyses is tabulated below in Table 4. Note also that crude characterisation methods exist which allow for determination of the maximum conversion level achievable at the point where onset of product instability (due to asphaltene precipitation) occurs. It is well documented **(6)** that Vacuum Resid feeds derived from Urals (Russian Export Blend) have lower maximum achievable residue (538°C+/1000°F+)

conversion limits compared to typical Middle East crudes before sedimentation-induced fouling occurs at unacceptable rates.

***Feed* and Product *Property* Analysed**	**Description/Function**
Standard bulk properties such as Density, Viscosity S, N, MCR, Distillation	*Provide initial fingerprint on feed and product refractive and coking natures*
Nickel and Vanadium content	*Contributors to catalyst deactivation*
Shell Hot Filtration Test (IP375) "SHFT"	Principal measurement technique used to quantify sediment levels
C_7 (Toluene) Insolubles	Measure of coke content Precipitated Asphaltene content = SHFT – Toluene Insolubles
SARA Analysis	**S**aturates **A**romatics **R**esins **A**sphaltenes matrix fundamental for product stability (tendency to flocculate and form sediment)

Table 4: Representative list of feed and product analyses carried out to monitor fouling tendency in Ebullated Bed Resid upgrading units.

An increase in any of the properties (with the exception of Sulphur and Resin content), analysed as listed in Table 4, means increased sedimentation downstream. This leads not only to overall reduced unit operability (in terms of throughput, maximum achievable conversion and cycle length) but can also lead to product instability (e.g. blended fuel oil instability). The 12 most frequently encountered operational barriers in Ebullated Bed units are listed in Table 5 below.:

Typical Operability barrier in an EB unit
1. Fouling and plugging of Feed Heater
2. High radial temperature profiles (hot spots)
3. Plugging of Ebullating pumps
4. Fouling of HP/LP Separators
5. High cleaning frequency of product filters
6. High cleaning frequency of AT suction pump strainer
7. High cleaning frequency of VT suction pump strainer
8. Fouling of Vacuum Tower heater
9. Coking of Vacuum Tower
10. High cleaning frequency of VTB heat exchangers
11. Plugging of Fuel oil chiller
12. Fuel oil instability and off-spec

Table 5: Representative list of main equipment adversely affected by sediment-induced fouling in EB units leading to reduced unit operability **(8)**.

Accordingly, any measure of enhanced sediment control, such as a change to an improved sediment control catalyst will have an immediate positive impact on the overall operability of the unit including extending cycle length. Not only is the structural/chemical make-up/design of the catalyst important in controlling sediment (organic based) but it also has to be characterized by excellent physical integrity/mechanical strength properties so as to not contribute to inorganic sediment in the form of catalyst fines.

The improved unit operability offered by Criterion's first dedicated sediment control catalyst, TEX-2710, was demonstrated **(9)** by TEXACO general engineering department (a former licensor of H-Oil® technology) who performed a 55-day customer specific pilot-plant test versus the first-generation catalyst installed in the customer's H-Oil® unit at that time (Criterion HDS-1443B catalyst). The sediment formation versus 538°C+ conversion data presented in figure 3 for processing a 85/15% Vacuum Resid/FCC HCGO feed blend shows the far superior sediment control of the TEX-2710 catalyst which allowed for 538°C+ conversion as high as 83 vol.% compared to a 65-68 vol.% maximum operable conversion for the incumbent system. More notable is the factor 3 lower sediment level with the TEX-2710 catalyst at a 15% higher absolute 538°C+ conversion level. This much enhanced sediment control performance not only facilitated the higher temperature operation to maximize conversion and distillate yields but also led to overall improved product quality due to improved HDS/HDN/HDCCR and also improved fuel oil stability due to 4 times less sediment present. Given this very positive pilot-plant test data the customer conducted a trial and then switched to the TEX-2710 catalyst shortly thereafter in 1994 and the first visible advantage of the sediment control properties of TEX-2710 in action was manifested in much reduced frequency of cleaning of the Vacuum Tower Bottoms heat exchanger. Prior to the introduction of the TEX-2710 catalyst, 538°C+ conversion was limited (generally to ca. 60%) by the high frequency of cleaning of this VTB heat exchanger The use of TEX-2710 produced a very clean system with minimized cleanings. Since that time the same refiner has continued to use Criterion newer generation customized sediment control catalysts including those with enhanced conversion activity in his H-Oil® unit.

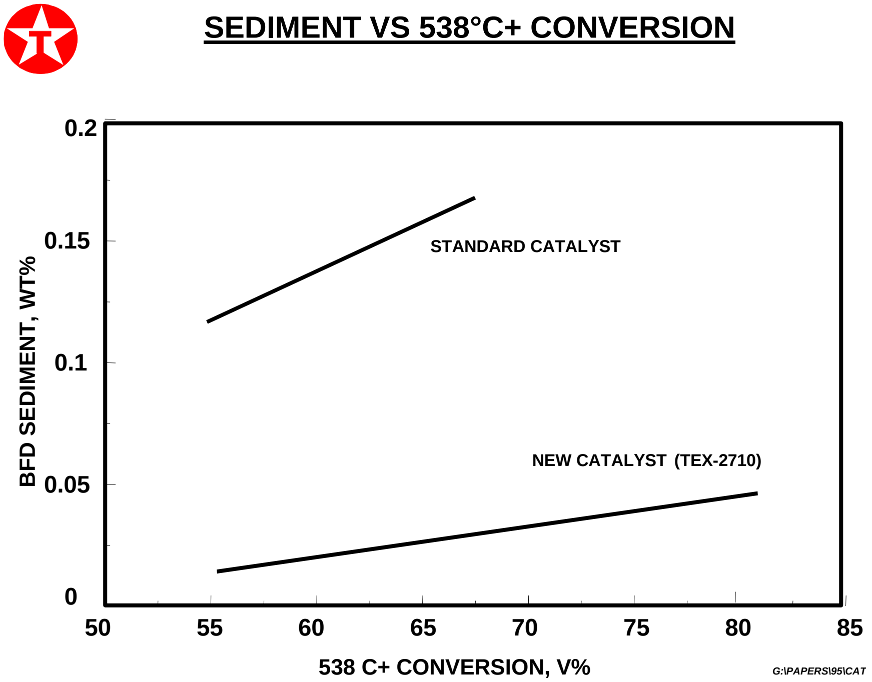

Figure 3: Texaco General Engineering Department comparative customer specific 55-day pilot-plant evaluation of Criterion TEX-2710 sediment control catalyst versus the incumbent reference catalyst in terms of sediment formation as a function of 538°C+ conversion [from reference **(9)**]. "BFD" stands for "Bottoms Flash Drum" liquid, which had a boiling range similar to commercial Atmospheric Tower Bottoms.

6.0 CUSTOMISED SEDIMENT CONTROL CATALYSTS FOR PROCESSING OF FEEDS DERIVED FROM URALS CRUDE

(I) GETTING TO GRIPS WITH THE ASPHALTENE CHEMISTRY

Many of the more recently announced licences for Ebullated Bed units involve processing of Vacuum Resid derived from Urals crude. Neste Oy in Finland are commissioning their three-stage LC-Finer this year **(11)** while Mozyr in Belarus will be commissioning a 2-stage H-Oil® residue conversion unit in 2010 **(12)**. Processing of Urals-derived feeds presents extra challenges where sediment control is concerned given the different asphaltene complex macromolecule make-up and chemistry present in such VR feeds. A typical heavy oil contains up to 10^6 molecules with the asphaltene fraction the most difficult to characterize as it tends to self-associate **(13)**. Moreover, the asphaltene structure under EB unit reaction conditions is vastly different from what is analysed as present in the VR feed at room temperature. In fact, data from light scattering experiments have shown that asphaltenes are not truly in solution in petroleum but rather exist in colloidal suspension in the oil. The degree of interaction/self-association between asphaltenes in heavy oil is governed by properties such as polarity, H_2 content, aromaticity of the oil. In actual EB processing of VR feeds addition of highly aromatic diluents such as LCO or HCO helps to keep the asphaltenes in solution by acting in a similar solvent function as the Resins. Upon heating of the oil the degree of self-association of asphaltenes decreases and this re-inforces the concept why asphaltene flocculation also occurs in the work-up section of an Ebullated Bed unit as the reactor effluent is progressively cooled in F/E heat exchangers leading to the well-established fouling.

Some extensive characterization **(6)** of the asphaltene solubility in Vacuum Resid derived from Urals crude shows that it has a higher relative solute (asphaltene)/solvent (maltene) ratio compared to middle east crude derived VR feeds and as such Urals based asphaltenes have overall lower solubility in the associated SARA matrix characterizing all heavy oils. This means that in Urals derived VR feeds there is a higher degree of self-association of the asphaltenes which means greater tendency to form sediment as lower severity conditions.

As part of the Four C's approach to EB sediment control catalyst customization, Criterion has perfomed mulitple analyses of several Urals derived VR feeds from many Ebullated Bed users . This data shows that Urals-derived feed generally has low asphaltene contents as defined by the n-heptane insolubles test (generally 5-8 weight % as compared to say 9-13 weight % for Arabian feeds processed in Ebullated Bed units). At first sight this characteristic would be expected to benefit stability. However the feed resin content (the R in the SARA matrix), defined as the n-pentane insolubles minus the n-heptane insolubles and representing the heavy aromatic fraction responsible for dispersing asphaltenes and keeping them in solution, is much lower in Urals derived resid feeds (typically at 4 wt. % versus 8 wt % for Arabian feeds processed in Ebullated Bed units and up to about 13 wt. % for some bitumen derived feeds as processed in Canada). In addition, the lower sulphur content of Urals derived VR feeds only helps to accentuate the asphaltene instability phenomenon. Lower feed sulphur means lower sulphur containing products which translates into lower polarity, another important consideration in maintaining stability in helping to slow down the rate of asphaltene agglomeration which ultimately produces sediment.

(II) EUROPEAN REFINER CASE STUDY

The asphaltene solubility for Urals derived feeds decreases at faster rates as 538°C+ conversion is increased leading to earlier precipitation/flocculation of asphaltenes in the unconverted 538°C+ bottoms product. This greater instability as a function of 538°C+ conversion behaviour of VR feed ex Urals crude means that both maximum upgrading of the feed and cycle length achievable in the EB unit are dictated more by rate of sediment formation than units processing VR feeds derived from middle east crudes. As such the sediment control catalyst applied for processing VR feeds derived from middle-east crudes may or may not be the best suited for the processing of Urals-derived VR feeds. This is the reason why Criterion's employs the customized approach to Ebullated Bed catalyst development as highlighted previously in section 4.0 and in so doing has set the standard in the Ebullated Bed catalyst marketplace.

A critical component part of this customized approach is dedicated pilot-plant testing using targeted customer feed and conditions. A recent example of such a study featured a 40-day pilot plant test performed at the Criterion R&D facility in Houston using feed and conditions from a European refiner processing a 90/10 Vacuum Resid / diluent feed blend derived from Urals crude in his Ebullated Bed resid upgrading unit. A pilot-plant test duration of 40 days without fresh catalyst addition was specifically performed to simulate steady state equilibrium catalyst performance. Moreover, Robinson-Mahoney CSTR reactors were used as they show similar back-mixed kinetics as present in the commercial Ebullated Bed units. The properties of this 100% VR feed are presented below in Table 6.

Feed Property ***(100% Vacuum Resid ex Urals crude)***	**Units**	**Value**
Density at 15°C	Kg/m^3	1011
Sulphur content	Wt.%	2.95
Total Nitrogen content	ppmw	6713
Nickel content	ppmw	60
Vanadium content	ppmw	184
CCR content	Wt.%	16.6
% 538°C+ (1000°F+) fraction	-------	85.9
Temperature profiles applied for targeted conversion in 40 day test	Day 1-20 ….. 404-406C Day 21-30 … 414C Day 31-40 … 404-406C (backcheck)	

Table 6: Properties of Vacuum Resid feed ex Urals (Russian Export Blend) crude as processed in an Ebullated bed unit of a European refiner experiencing reduced unit operability due to sediment-induced fouling

The refiner was experiencing unacceptably short cycle lengths due to the need to shutdown to clean critical downstream hardware that was being severely fouled. Furthermore during actual operation, 538°C+ conversion was controlled at lower than design levels as a means of better controlling the rate of fouling in the unit. The main objective of the pilot-plant test was to demonstrate that Criterion's latest generation, high activity sediment control TEX-2731 catalyst, specifically developed for processing Urals-derived VR feeds, was more suitable compared to the previous generation TEX-2730 catalyst, previously evaluated with the same feed and conditions. The refiner requested measuring comparative sediment behaviour in his targeted 538°C+ conversion window of 52 (Winter) to 66 (Summer) vol%.

A snapshot of the main findings from this case study is presented below in figures 4 and 5. Figure 4 demonstrates that both TEX-2731 new generation and TEX-2730 previous generation catalysts achieved the required 538°C+ conversion levels at acceptable temperatures with TEX-2731 operated at 2°C higher WABT and therefore approximately 2 vol% higher conversion. Both catalysts have the same intrinsic rate constants for 538°C+ conversion. The Shell Hot Filtration Test (IP-375) measurement of sediment formation data presented in figure 5 emphatically illustrates that improved sediment control performance of the TEX-2731 at both the minimum and more importantly maximum 538°C+ conversion levels. The superior sediment control performance of TEX-2731 can be recognized all the more by the fact that its ATB SHFT data at 414°C is lower than TEX-2730's ATB SHFT data at 404°C. Moreover, at the max. specified 538°C+ conversion level of 66 vol.%, TEX-2730 is already at the max.allowed ATB SHFT specification of 0.15 wt.% while TEX-2731 there is clearly scope to push conversion further before hitting that max. ATB SHFT spec.

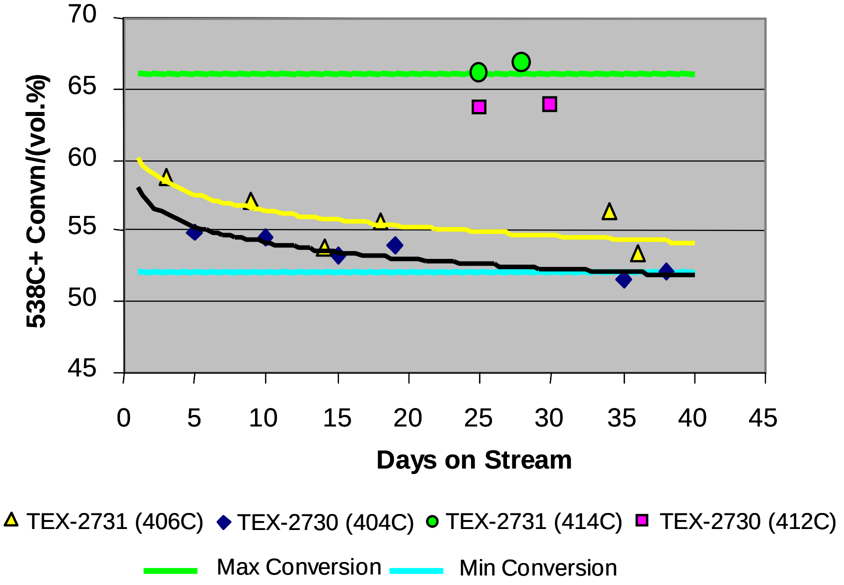

Figure 4: 538°C+ conversion profiles of Vacuum Resid ex Urals crude in comparative TEX-2731 vs. TEX-2730 sediment control catalyst evaluation for European refiner with EB operability constraints

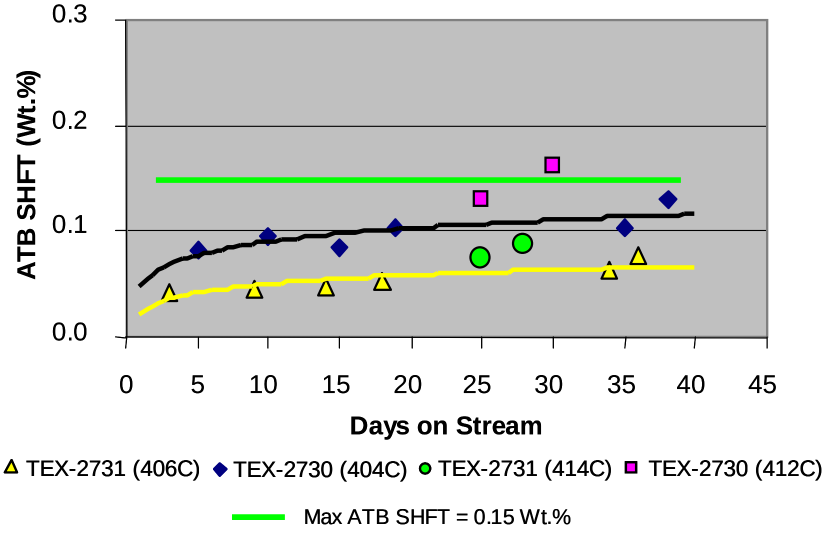

Figure 5: Comparative Atmospheric Tower Bottoms SHFT data for TEX-2731 versus TEX-2730 catalysts at the 538°C+ conversion levels presented in Figure 4.

7.0 LUKOIL PERM T-STAR OPERATION WITH CRITERION LK-1 CATALYST

The former Texaco (now Axens)-licenced T-Star VGO upgrading unit was commissioned at Lukoil's Perm refinery in November 2004 as the heart of their deeper conversion complex which also features an ADIP (MEA-based) recycle gas scrubber, dedicated Hydrogen manufacturing and sulphur recovery plants and a sour water stripper (14). The T-Star complex features an ebullated bed T-Star operation followed by a two-stage fixed bed Synsat® HDA reactor system for the saturation of polyaromatics in the T-Star product diesel stream to meet Euro IV specifications. Perm avail of the design capacity of the T-Star unit by co-processing what otherwise would be orphan streams in the refinery namely Heavy Coker Gas Oil, LCO and aromatic extracts at typically 61,000 BPSD. This still leaves scope to process imported VGO if required. The VGO/Distillate blended feed consists on average of 73% straight run material. The properties of this feed compared to the original VGO/Cracked Gasoil design blended feed are presented in Table 7 below.

Feed Property	Units	2006 Typical	2003 'Updated' Design	Original Design
Feed description	------	73/27% VGO/Cracked Gasoil blend	VGO/Cracked Gasoil blend	VGO/Cracked Gasoil blend
Density at 15°C	Kg/m^3	899	914	912
Sulphur content	Wt.%	1.56	1.64	1.93
Total Nitrogen content	ppmw	N.M.	N.M.	N.A.
Nickel content	ppmw	0.03	<0.2	1.6
Vanadium content	ppmw	0.2	<0.5	4.4
MCR content	Wt.%	0.15	N.M.	0.90
ASTM D1160/*D86* Distillation	°C			
IBP/50/95/FBP (Vol.%)		218/395/519/535	*271/376/467/491*	N.A.

Table 7: Comparative properties of VGO/Cracked Gasoil feeds typically processed in 2006 versus original and 2003 updated design feed blends for Lukoil-Permnefteorgsyntez's T-Star unit

The comparative feed data in Table 7 shows that both the 2006 actual and 2003 updated design feed blends are less refractory than the original design feed. This reflects backing out some of the heavier VGO 'Surgut -550°C' feed and replacing it with the lighter VGO 'Surgut+Kunghur 490°C' feed. Lukoil-Permnefteorgsyntez took economical advantage of this change in feed by operating the T-Star unit at much lower WABTs than in the original design but still targeting the original 36 wt.% 350°C+ conversion and product quality specifications. This was accomplished by fine-tuning of the fresh and regenerated catalyst (Criterion LK-1) addition rates. Note that inherent in the design of T-Star units is the re-use (following appropriate regeneration) of the used catalyst withdrawn from the bottom of the reactor. The processing of the less refractory feed blend containing far less contaminant metals (Vanadium in particular) also served to accommodate a higher quality and thereby higher residual activity performance of the regenerated catalyst added. This meant that almost twice as much regenerated LK-1 catalyst compared to fresh was added to the unit in 2006 processing period. Figures 6 and 7 below illustrate the 350°C+ conversion performance achieved in the 2006 processing period and also the constant high HDS performance respectively. Table 8 presents the typical product yield structure obtained in the 2006 processing period with in addition a comparison of product sulphur quality showing actual performance superior to design specifications.

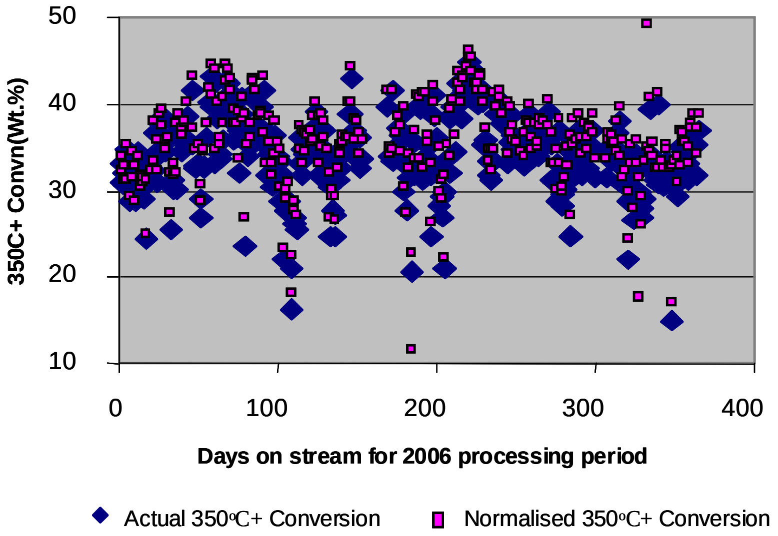

Figure 6: Actual versus normalized 350°C+ conversion profiles in Lukoil-Permnefteorgsyntez's T-Star unit achieved on Criterion fresh and regenerated LK-1 catalyst for 2006 processing period.

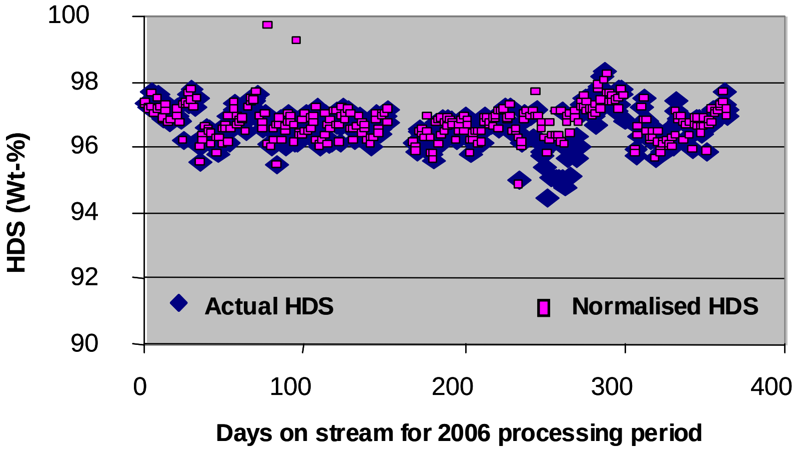

Figure 7: Actual versus normalized HDS performance achieved in Lukoil-Permnefteorgsyntez's T-Star unit achieved on Criterion fresh and regenerated LK-1 catalyst for 2006 processing period.

Product Fraction	Yield (tons/hr)	Actual Sulphur Content/ppmw	Original Design Sulphur Specification/ppmw
C5-	3.2	-------	-------
Naphtha (80-175°C)	20.2	57	<200
Distillate (175-350°C)	132	181	<300
350°C+	201	781	<900

Table 8: Typical product yield profile achieved in Lukoil-Permnefteorgsyntez's T-Star unit achieved on Criterion fresh and regenerated LK-1 catalyst for 2006 processing period. A comparative product sulphur quality (actual versus original design) is also presented.

With now over 2.5 years of processing experience under their belt successfully operating their deep conversion complex, Lukoil Permnefteorgsyntez are now looking to further optimize the conversion in the T-Star unit operation to produce more middle distillates from more refractory streams. Sound like a familiar story?

8.0 CONCLUSIONS

1. With the on-going legislative and market driven requirement for greater upgrading of both the bottom of the barrel and its product streams the operation of existing and to be commissioned resid upgrading units such as Ebullated Bed units will become more challenging especially in combating fouling of downstream hardware due to enhanced sediment formation.

2. Refiners who process Vacuum Resid feeds derived from Urals crude face the extra hurdle of lower asphaltene stability in the feed itself and a faster rate of flocculation of these macromolecules and thereby even more accelerated sediment formation/fouling as severity is increased.

3. Russian and CIS refiners can benefit from the experience of the 3 current Ebullated units upgrading such Urals derived feeds and indeed from homegrown units such as Lukoil-Permnefteorgsyntez's T-Star which has now successfully operated for over 2.5 years processing VGO blend.

4. Economic upgrading of Vacuum Resid feeds derived from Urals crude starts with use of a customized sediment control catalyst in the ebullated bed reactor. Criterion's is recognized as having set and continuing to set the industry standard for such catalysts with this approach. The latest generation Criterion customized state of the art catalyst designed for processing Urals derived VR feeds at high conversion without succumbing to the adverse effect of sediment formation is TEX-2731.

5. Customer specific comparative pilot-plant testing of TEX-2731 for a European Ebullated Bed Urals operation unequivocally demonstrated the sediment control attributes of the catalyst while meeting all the unit objectives. Consequently, the first commercial application of TEX-2731 in a European refinery Ebullated Bed unit will take place in late 2007 as the key first step to combating the fouling of major equipment experienced since commissioning of the unit a number of years ago.

9.0 ACKNOWLEDGEMENT

Criterion would like to acknowledge Lukoil-Permnefteorgsyntez's Chief Engineer, Mr Vladimir Yakunin and Chief Technologist, Mr Valery Krylov for their valuable contributions to section 7.0 of this paper.

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