

ULSD PRODUCTION

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It is spoken about features ULSD production. Also in article shown technicals and economics point some of main hydrofining process diesel fuel.

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At last time question about development and application "clean fuel" is worldwide problem. Since 2005 ULSD with sulfur content 50 ppm is mandatory specification, next step to 10 ppm will be occur at 2009 [5].

Since 2000 most of refineries successfully complete upgrading program for produce new specification ULSD with 50 ppm sulfur content. Factors determine implementation this program is using new catalyst, using additional catalyst volume, optimization quality of feed, especially when feed is mix of cracking component.

In Russia and CIS specification for sulfur content in diesel fuel is 500 ppm. Conversion to sulfur content 350 ppm proposed in 2009, next reduction to 50 ppm in 2010.

Refineries in Russia and CIS are threshold of ULSD era, and most of refineries must adapt its hydrofining unit to new condition.

ULSD production determine as sulfur content with cyclic structure as aromatics [5].

If production diesel fuel with sulfur content 0,1-0,2 % wt. behavior hydrogenolysis reaction of mercaptans and sulfides with sulfur in alkyl branch, production diesel fuel with 350-500 ppm sulfur content by conversion cyclic compounds of sulfur with reaction ability change in line tiacyclan > naftenotiofen > alkytiofen > naftenobenzin-tiofen > benzenetiofen > dibenzentiofen.

ULSD production with sulfur specification 50 and 10 ppm mandatory condition is eliminated heteroatom sulfur compounds like 4,6-dimetyldibenzenetiofen. Reaction activity this molecule 20 times less compared with molecule of dibenzenetiofen. As opposed normal reaction desulphurization, more preferable is hydrogenation 4,6-dimetyldibenzenetiofen. Eliminated of 4,6-dimetyldibenzenetiofen depends on the hydrogen pressure [2].

Nitrogen removal follows a very similar reaction pathway, requiring a pre-hydrogenation step before heteroatom removal. It therefore competes with the hindered DMDBTs for active sites on the catalyst surface. Since nitrogen species, particularly basic nitrogen compounds, adsorb more strongly to that catalyst surface than sulfur species, near-complete removal of nitrogen is required when targeting sulfur levels <10 ppm. We discuss the importance of choosing a catalyst having this dual HDS/HDN functionality in subsequent sections [5].

Sulfur content depends on the crude nature and methods of refining and has quite different quantity.

LCO often add in diesel fuel like component of market fuel. Because LCO have a low efficiency in starting period and content a lot of sulfur, it is make impossible to use LCO as component for ULSD. Upgrading the specification of compounds with LCO is very difficult, especially high level content of aromatics and nature of sulfur compounds. A lot of molecules of sulfur is steric hinder, and therefore is eliminated difficult. Though refineries add LCO to gasoil (10-30 % vol.) and hydrotreated mix for obtain ULSD. Very important factor for LCO hydrotreated is end boiling point. If end boiling point of LCO increase at 5 °C it is increase temperature of reaction. As result cycle run of catalyst decrease and it is faster deactivation.

ULSD hydroprocessing unit design and optimization must take in to consideration the following factors:

- provide adequate control systems and tankage to ensure the correct feed quality to the unit;
- maximize reactor H₂ partial pressure;
- maximize reactor hydrogen-to-oil ratio;
- provide a reliable, adequate supply of high-purity make-up H₂;
- provide adequate recycle gas purity and unit pressure control systems;
- minimize H₂S and NH₃ in the recycle gas. Use only the best reactor internals and catalyst loading methods to ensure good catalyst/oil contacting;
- select the type of catalyst and provide sufficient catalyst volume to meet all product quality requirements and desired run length;
- design feed/effluent and feed/product exchangers and unit start-up/shutdown lines to minimize the potential for reactor bypassing;

- provide reliable operation of the product fractionator/H₂S stripper;
- minimize product contamination in off-site facilities: rundown lines, tankage etc.

More important point in ULSD production is:

- catalytic system;
- partial pressure of hydrogen;
- modern internal device in reactor;
- dense loading system.

Catalytic system. Using a new high-activity Ni-Mo catalyst having very high hydrogenation activity and is optimal way for elimination sulfur compounds. Leaders in hydrofining catalyst production is present in table 1.

Table 1

Catalysts for Deep Desulphurization and Aromatics Hydrogenation

Company	Co-Mo Type	Ni-Mo Type	Precious Metal Type
Akzo	KF-757	KF-848	KF-200
Criterion	DC-160, DC-185, DC-2000	DN-200	
Topsoe	TK-574	TK-573, TK-525, TK-555	TK-907, TK-908
UOP	N-40, N-108, N- 200	HC-H, HC-K, HC- P, HC-R, HC-T	AS-250
IFP	HR-416	HR-448	Platinum type
CCIC	CDS-LX6		
OCC	HOP-467	HOP-414	

Increasing the Hydrogen Partial Pressure. The hydrogen partial pressure is increased by increasing the reaction pressure, the hydrogen/oil ratio, and the purity of the hydrogen. In the United States the NPC has publicly released the responses of five companies - UOP, IFP, Akzo, Criterion, and Topsoe - to questions regarding the modifications of existing desulphurization unit, producing diesel fuel with a sulfur content of 500 ppm, for reducing the product sulfur content. The modification was estimated based on the use of feedstock with a sulfur content of 0.9 wt. %, a specific gravity of 0.861, and a T₉₀ value of 321 °C. The modifications required to reduce the sulfur content to 30 ppm are summarized in table 2 [1]. All of them regard an amine

scrubber as indispensable facility. UOP and IFP propose to minimize the cut down of LHSV by increasing the purity of circulating hydrogen. On the other hand, the other companies propose to decrease LHSV to the greater extent without increasing the hydrogen purity.

Table 2

Modification for reducing the sulfur content to 30 ppm from 500 ppm

	Current	UOP	IFP	Akzo	Criterion	Topsoe
LHSV	2	1.5	1.45	1.08	0.5	1
Amine scrubber installed	no	yes	yes	yes	yes	yes
Purity of circulating hydrogen (mol %)	75	90	91.3	75	75	75
Ratio of circulating hydrogen	1	1.9	3.649	1	1.6	1.16
Catalyst packing method	Sock	Dense	Sock	Sock	Sock	Sock

They require the significant sacrifice of LHSV. In addition, IFP says that a sulfur content level of 10 ppm can not be achieved at existing unit pressure and that new unit must be constructed. Criterion also says that although the data is tentatively shown, new unit is strongly recommended.

Table 3

Modification for reducing the sulfur content to 10 ppm from 30 ppm

	UOP	IFP	Akzo	Criterion	Topsoe
LHSV	1.5 ↓ 0.9	1.45 ↓ 1	1.08 ↓ 0.45	0.5 ↓ 0.4	1 ↓ 0.7
Ratio of circulating hydrogen	1.9 ↓ 2	3.694 ↓ ?	1	1.6 ↓ 1.85	1.16
Partial pressure, kg/cm ²	46	58	46	46	46

Distribution tray. To ensure efficient utilization of all the catalyst packed into the reactor it is essential to attain a uniform distribution of the feedstock and hydrogen throughout the entire catalyst layer. The misdistribution may also cause problems, such as occurrence of abnormally high temperature area (hot spots) due to uneven reaction temperature distribution or a rise in pressure differential across the reactor, that force sometimes discontinuance of operation. If the reaction fluid once begins to become deflected within the catalyst layer the normal state is hardly restored. Effective measures to avoid the misdistribution of reaction fluid include improvements of the reactor interior and the catalyst loading method.

When designing a high-performance liquid distribution tray, the following requirements should be borne in mind:

- the distributor nozzles should be spaced close together;
- pressure loss should be minimized;
- the tray should be configured so as to avoid deflection due to tilting;
- operation at a turn down ratio with a high liquid flow volume should be supported;
- operation with a wide range of gas-liquid volume ratios should be supported;
- good gas-liquid mixture performance is essential;
- the design should incorporate measures to prevent clogging due to scale.

Topsoe has developed a dense pattern flexible tray designed to ensure uniform dispersion. In tests using Topsoe's TK 554 catalyst the apparent relative desulphurization activity achieved with it was more than 2.5 times that with a simple chimney tray, and the average reaction temperature was reduced by 25 °C (table 4).

Table 4

Distribution tray effectiveness

	Simple Chimney Tray	Topsoe
Average reaction temperature, °C	346	321
Feedstock sulfur content, % wt.	0.7	0.9
Product sulfur content, % wt.	0.05	0.035
Relative desulphurization activity	1	2.5

Catalyst Loading Systems. If the catalyst is loaded in such a way that the top surface of layer is at an incline on the way of the loading, the catalyst particles become slanted along the inclination. It is known that the oil tends to flow along the inclination and may be deflected by the slanted portions, even if the top surface of the catalyst is packed flat.

In the past, to keep the surface flat during the catalyst loading, the work was halted periodically and the surface was leveled by manpower. However, there were limits to the effectiveness of such techniques, and the frequent interruption of the loading work lowered the efficiency. In order to get around these problems a catalyst loading system has recently been developed that incorporated monitors which allow real-time measurement of the flatness of the catalyst surface without interrupting the work and a catalyst loading machine which is able to constantly control the incline of the surface.

Increasing requirements to quality for diesel fuel become development hydrofining technology ULSD production (table 5).

Table 5

High-quality diesel fuel production technology

Process	Licensers
SynSat	Criterion, ABB Lummus, Shell
Ultra Deep HDS	Topsoe
MAK Fining	Mobil, Akzo, Kellogg, Fina
MQD Unionfining	UOP
Deep HDS, HDAr	IFP

SynSat Process. The SynSat process uses either one reactor or two reactors in series and divides the reaction zone into two stages. In the first stage both feed oil and hydrogen flow downward, while in the second stage direction of hydrogen flow can be set upwardly or downwardly depending on conditions. The SynSat process is being used commercially in Sweden, Germany, and the United States (table 6).

Table 6

Commercial application of SynSat Process

Company	Pro- cessing volume	Feedstock characteristics				Product characteristics			Reaction type
		Sulfur content	T ₉₅	Den- sity	Aroma content	Sulfur content	Den- sity	Aroma content	
		BPSD % wt.	°C	g/cm ³	% vol.	ppm	g/cm ³	% vol.	
Scanraff	48000	0,54	32 3	0,841	22,1	100	0,835	11,3	Co/Cnt
		0,34	28 6	0,827	21,5	1	0,812	4,4	
Preem	37000	0,14	33 8	0,866	-	100	0,858	-	Co/Cnt
		0,1	27 7	0,827	21,8	2	0,815	3	
Lyondell- Citgo	50000	1,38	36 7	0,902	58,2	<5	0,861	34,8	Co/Co

Topsoe Ultra Deep HDS process. Topsoe's Ultra Deep HDS (UDHDS) process is a two-stage process for producing low-sulfur and low-aromatic diesel fuel. In the first stage reactor Ni-Mo catalysts are used. The second stage reactor employs a precious metal catalyst, TK-907. The San Joaquin refinery in the United States provides an example of the commercial application of this process (table 7).

Table 7

Commercial application of Topsoe Ultra Deep HDS

	Density, g/ml	Sulfur, ppm	Nitrogen, ppm	Aromatics, % vol.	Reaction temperature, °C
Feedstock	0,91	6,515	775	33	-
First stage output	0,88	9	3	24	367
Second stage output	0,87	1	0	3,5	287

MAK Fining process. MAK Fining is a hydrorefining process licensed by ExxonMobile, Akzo Nobel, Kellogg, and Total-Fina. It can be designed to match the current diesel fuel standards as well as the upgraded standards in years ahead by combining the following processes and catalysts:

- 1) UDHDS: Ultra-deep hydrodesulphurization (Co-Mo catalyst);

- 2) HDHDC: Mild hydrocracking of heavy distillate (Ni-Mo catalyst);
- 3) HDAr: Hydrogenation of polycyclic aromatic compounds (precious metal catalyst);
- 4) MIDW: Dewaxing by hydroisomerization of Paraffin;
- 5) CFI: Cold-flow improvement by selective hydrocracking of n-paraffin.

OMV Germany (Burghausen refinery) uses a system combining UDHDS and MIDW. Although the details of the feedstock properties are not clear, diesel fuel with a sulfur content of 10 ppm or less and a cloud point of -11 °C or less (improvement of 18 °C) was reportedly being produced.

Properties of feedstock and products processed at a pilot plant of the combination of HDS and HDHDC using a zeolite containing catalyst are shown in table 8.

Table 8

MAK Fining process

	T ₉₅ , °C	Sulfur, ppm	Total aromatics, % wt.	Polycyclic aromatics, % wt.	Cetane number
Feedstock	356	16,6	39	15	51
Case 1	353	25	22	1,2	57
Case 2	349	3	19	0,7	58

MQD Unionfining Process. UOP's MQD Unionfining employs either single-stage or two-stage reactor system. It produces high-quality, low-sulfur diesel fuel by combining hydrogenation process with other processes such as hydrocracking, catalytic dewaxing, aromatics hydrogenation and hydroisomerization.

IFP Prime-D30 Process. IFP's Prime-D30 is a process for producing diesel fuel with ultra-low sulfur content, reduced polycyclic aromatic compounds, and a boosted cetane rating. Two-stage hydrogenation is required to accomplish aromatics hydrogenation aimed at increasing the cetane index. In the first stage an Ni-Mo catalyst and comparatively high pressure (6 to 8 MPa) is used to reduce the sulfur content of cracked diesel fuel to 50 ppm wt. or less. After fractional distillation of the reaction products, the diesel fuel fraction containing virtually no sulfur and hydrogen sulfide is

sent to the second stage, where aromatics hydrogenation takes place. The precious metal catalyst used in the second stage is a highly active hydrogenation catalyst. It is capable of processing even feedstocks containing significant amounts of sulfur. When LCO with a sulfur content of 1.58 wt. % is subjected to the two-stage process, the sulfur content is lowered to 3 ppm in the first stage, and then the aromatic content is reduced to 1.4 % in the second stage, according to reports (table 9).

Table 9

IFP Prime-D30 Process reaction

	T ₉₅ , °C	Sulfur, ppm	Nitrogen, ppm	Aromatics, % wt.	Cetane number
Feedstock	319	15,8	1,1	66,4	27,5
First stage output	288	3	1	34,2	45
Second stage output	283	<0,5	<0,5	1,4	53,4

ULSD production need a lot of investment for reconstruct existing unit (table 10). It is reason why special technical regulation attachment at 31.12.2009 in Russia.

Table 10

Costs of upgrading conventional equipment for Ultra-Deep Desulphurization

Upgrade Item	Sulfur, ppm	Amount of Investment, \$ million
Standard	500	-
Catalyst change (50% increase in activity)	285	-
Gas recycle/scrubber	180	1,8
Increasing purity of makeup hydrogen	140	2,4
Increased EOR temperature + reactor	120	0,6
Reactor	30	1,4
Change of operating duration from 2 years to 1 year	20	-

The costs of building a new ultra-deep desulphurization unit, presented by the licensors, are shown in table 11. They vary widely, running anywhere between \$1,100 and \$3,000 per BPSD, depending on the feedstock properties and the refinery's environment. This investment is equivalent to between \$60 and \$150 million for a plant with a capacity of 30,000 to 40,000 BPSD.

Table 11

Costs of installing Diesel fuel ultra-deep desulphurization equipment

Process	Processing volume (BPSD)	Quality target	Equipment cost (\$/BPSD)
SynSat (two-stage)	30000	S: 10 ppm, Ar: 5 % vol	3330
IFP (two-stage)	30000	S: <5 ppm, Cetane rating	2070
MAK Fining	35000	S < 10 ppm	1100-2000
MQD Unionfining	45000	S: 10 ppm, Ar: 2 % vol.	3310
IFP HYC	40000	S: <10 ppm, Ar: <8 % vol.	2500-3000

ULSD production have feature. This feature activate by high quality requirements and problems in reconstruct existing system.

The refiner's goal is to produce ULSD that not only meets the regulatory requirements of 10 wppm sulphur, but also the additional commercial requirements of a high quality product.

High severity hydrotreating is known to produce color-unstable products. A variety of reasons are given for the occurrences of poor product color stability, but one common factor is the reactor outlet temperature: at reactor outlet temperatures as low as 360 °C, diesel begins to become color sensitive. Although color is not a regulatory specification, it is a "workmanship" issue and poor color stability will adversely affect customer satisfaction.

Very important point in ULSD production is lubricity. Lubricity has been defined as "a liquid's intrinsic ability to prevent wear on contacting solid surfaces in the absence of any hydrodynamic lubricating films". This property has been a concern due to problems experienced with accelerated jet engine failures for low sulphur jet fuels.

The problem was linked to severely hydrotreated jet fuels having both low sulphur and low aromatics contents.

Each major ULSD project, especially new unit designs, should include a sensitivity analysis to determine the equipment modifications and associated investment needed to meet possible future ULSD requirements for a higher cetane index and reduced aromatic content. Cetane index is strongly correlated to aromatics content. Significant increases in the diesel product's cetane index requires significant reductions in its aromatics content.

An important consideration is that aromatics reduction, and therefore cetane "lift", in the reactor can be either kinetically or equilibrium limited. This is especially true for low-pressure units. The aromatics saturation reaction rates increase with increasing partial pressure.

Since this minimum is affected by the reactor outlet hydrogen partial pressure, potential future ULSD cetane index and aromatics specifications may be the over-riding consideration that sets the reactor pressure for a new ULSD unit. Unfortunately, revamped, lower-pressure units are unlikely to be able to produce a significantly higher cetane index or significantly lower aromatics content.

Catalyst selection and reactor sizing for a new ULSD unit may be strongly influenced by the catalyst aromatics saturation activity. A catalyst with a higher aromatics saturation activity will require a lower reactor temperature to reach the aromatics equilibrium, and a lower equilibrium aromatics level is possible at a lower reactor temperature. New catalyst improvements in aromatics saturation activity could shift the reactor temperature required to reach the equilibrium aromatics concentration, and thereby, reduce the minimum achievable product aromatics level for a given reactor.

Tankage and blending facilities need to be considered in a new light. Blending strategies must focus on achieving the sulphur target while minimizing giveaway on other specifications, such as API gravity and viscosity. Concerns about contamination between higher sulphur products and ULSD involve every step of the transportation process from refinery tankage to final customer use. All of the options being considered are additional steps, which add costs to the delivered products.

FCC conversion and catalyst management needs to be evaluated to determine the impact on distillate (LCO) quality and quantity. The FCCU LCO cut point strategies need evaluation to determine the optimum for ULSD.

Crude and vacuum unit optimization can provide opportunities to increase ULSD production. Improving fractionation efficiency and stripping strategy, optimizing crude tower cut points, increasing distillate recovery in vacuum tower, and making deeper cut-points in the vacuum tower (for more FCCU feed and LCO production) are all options to be explored.

It is important to provide high level of reliability when we construct new unit or revamp existing unit. The reliability of each individual clean fuels unit becomes a key refinery driver. The outage of one of these units could lead to inability to deliver product to the market. This scenario is a significant change from normal past practices where the refiner could still produce saleable products, although at a lower rate and/or price, if a single unit was shutdown. Under the clean fuels requirements, the refinery cannot produce fuels until that individual unit is repaired. The risk to the refinery is a complete refinery outage from the shutdown of one unit. As a result, high reliability for each clean fuels unit is crucial for financial success [4].

References

1. Yutaka Mukai, Toshiaki Hisamitsu, Yoshihiro Mizutani. Survey of Petroleum Refining Technology for High-quality Diesel Fuel., 2001. URL (review date: 26.12.2008): <http://www.pecj.or.jp/japanese/report/report02/report-pdf/01surv4-3e.pdf>
2. S. Mayo, E. Brevurd, L. Geritsen, F. Platengo. Process for produce ultra low sulfur diesel // Oil and Gas Technology. 2001, No 3.
3. Salvatore Torrisi Jr., Tom Remans, Justin Swain . The challenging chemistry of ultra-low-sulfur diesel // World Refining. 2002, Vol. 12, No 12.
4. Scott Sayles, Jim Bailor, Robert Ohmes. ULSD problems and solutions. // Petroleum Technology Quarterly. 2004. Vol. 9, No 5.
5. F. Stoop, L.G. Leliveld, S.L. Lee . Transition to ultra low sulfur diesel // Sixth world refining conference about oil refinery technology in Russia and CIS. 27 September 2006.