Workshop on
"Cleaner liquid fuels and improved vehicular technologies"

Pathways to Ultra Low Sulfur Fuels – Role of oil companies

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Talk outline….

- Fuel specs
- Present status
- Technical issues in the production of ULS fuels
- Approaches to deep desulfurization
- Challenges in implementing ULS specifications
- Summary

Diesel Specifications: Euro Norms

Sulfur, ppm	2500	500	350	50	10
Cetane number		48	51	51	51
PNA, vol%		--	11	11	8
Density @15°C, kg/cm^3		820-860	845	845	845
Distillation, T95°C, max		370	360	360	360

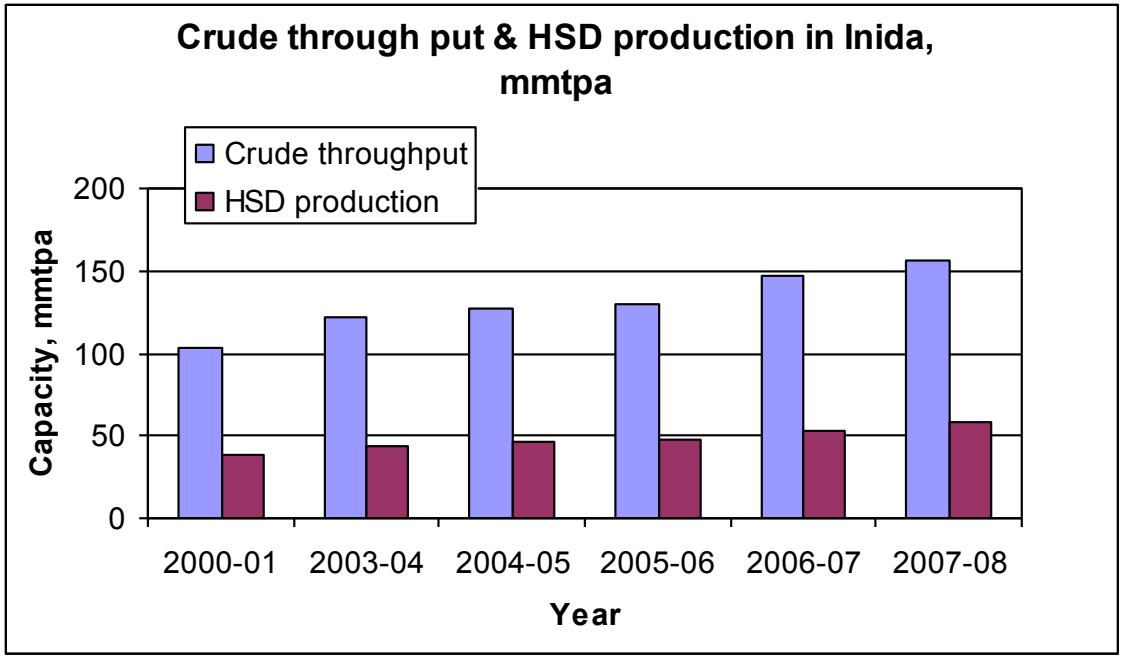
Present Status

- In the last few years Indian refineries made large investments to upgrade technology for producing Euro III/IV fuels
- About 40% of the crude processed in Indian refineries is hydroprocessed (hydrotreated or hydrocracked)
- Challenges are being faced with respect to handling, storing, transportation of Euro IV fuels with 50ppm S

Hydrotreating capacity

	Crude dist. cap, mbpd	Hydrotreating cap, mbpd
World*	85 (4250 mmtpa)	43 (2150 mmtpa) / ~51%
India#	3.6 (180 mmpa)	1.4 (70 mmtpa) / ~39%

- HDT process is growing @4% per year
- HDT cat market US $ ~1 billion & forms 1/3 of total refining cat market.



* Data for 2005; Ref: R.P. Silvy, App. Cat A: Gen 261, 247-252 (2004)

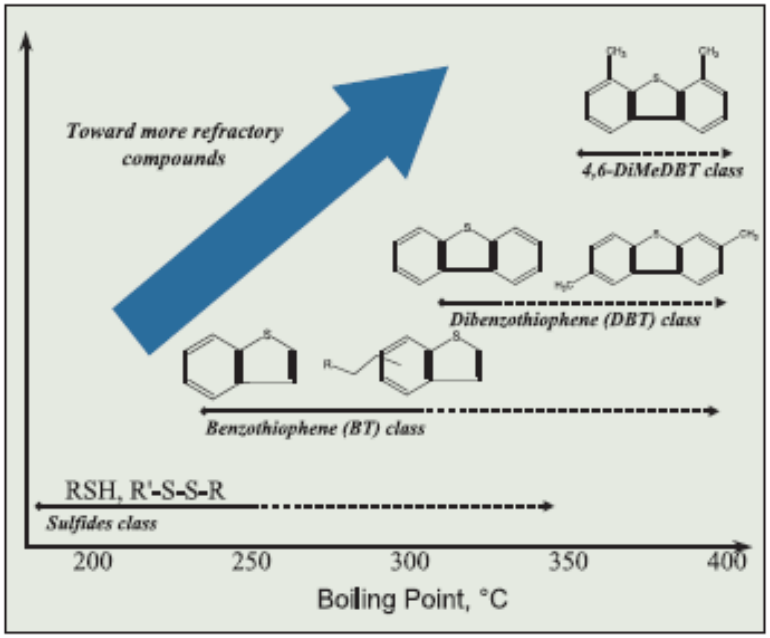
Data includes RPL's new plant; Data for graph – from Petroleum & NG statistics 2008, GOI

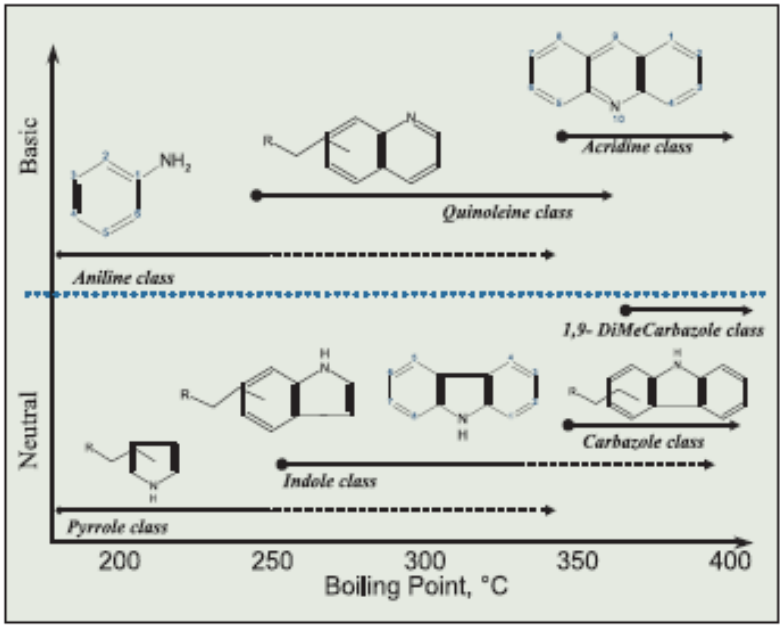
Technical issues in producing ULS fuels

Distribution of S compounds in different cuts of crude
(with 1.2% wt feed sulfur)

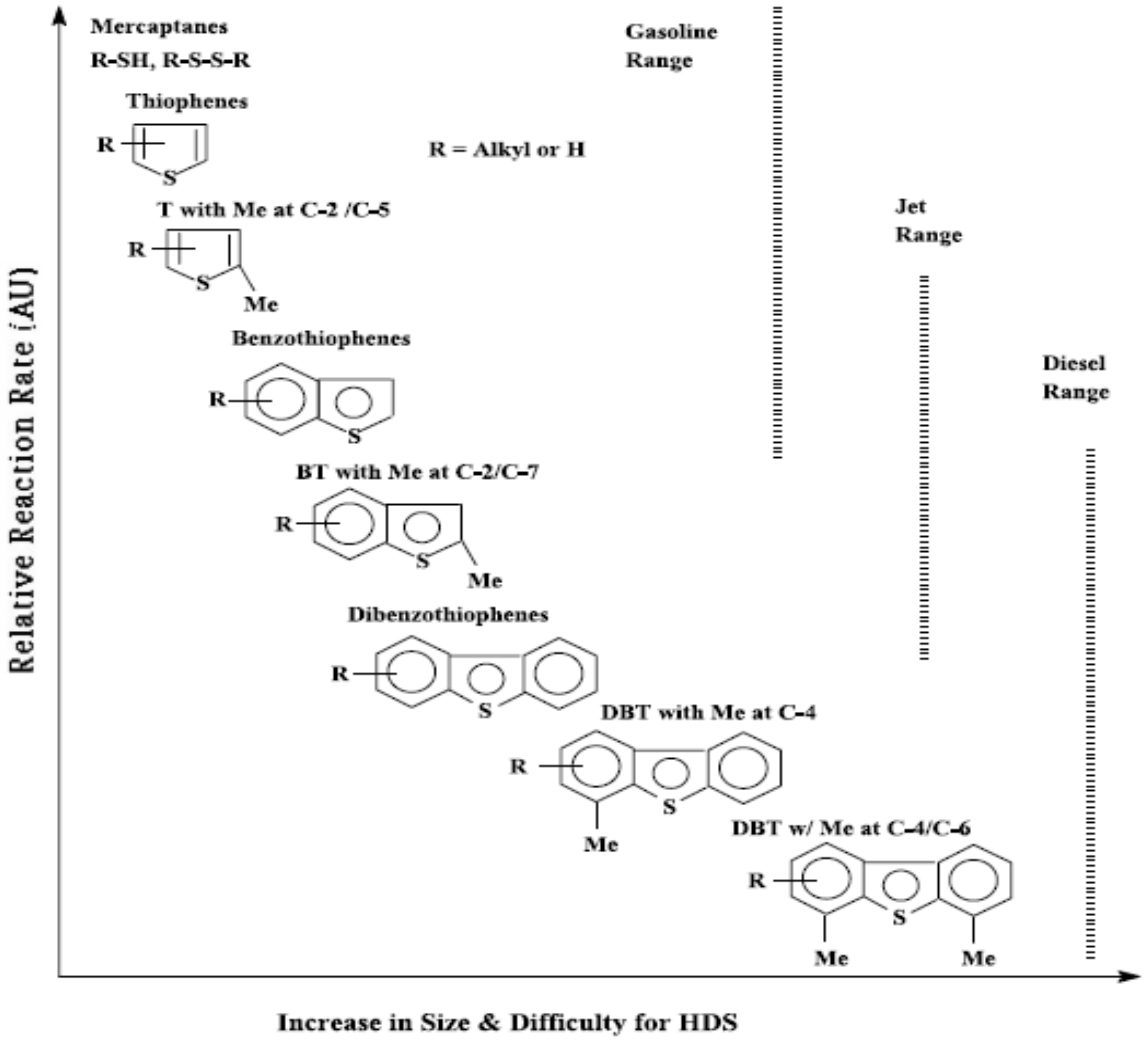
Petroleum cuts	Distillation range (°C)	Sulfur content (%wt)	Sulfur compounds (%wt total S)			
			Mercaptans	sulfides	thiophenes	Benzo-thiophenes and heavy sulfides
Naphtha	70-180	0.02	50	50	traces	--
Kerosene	160-240	0.2	25	25	35	15
Gas oil	230-350	0.9	15	15	35	35
Vacuum gas oil	350-550	1.8	5	5	30	55
Vacuum residue	550^{+}	2.9	Traces	traces	10	90

Sulfur and nitrogen species in full range diesel cuts





Reactivity of S compounds in HDS



Pseudo-1st order rate k (L/g cat)

1.38×10^{-3}

8.11×10^{-4}

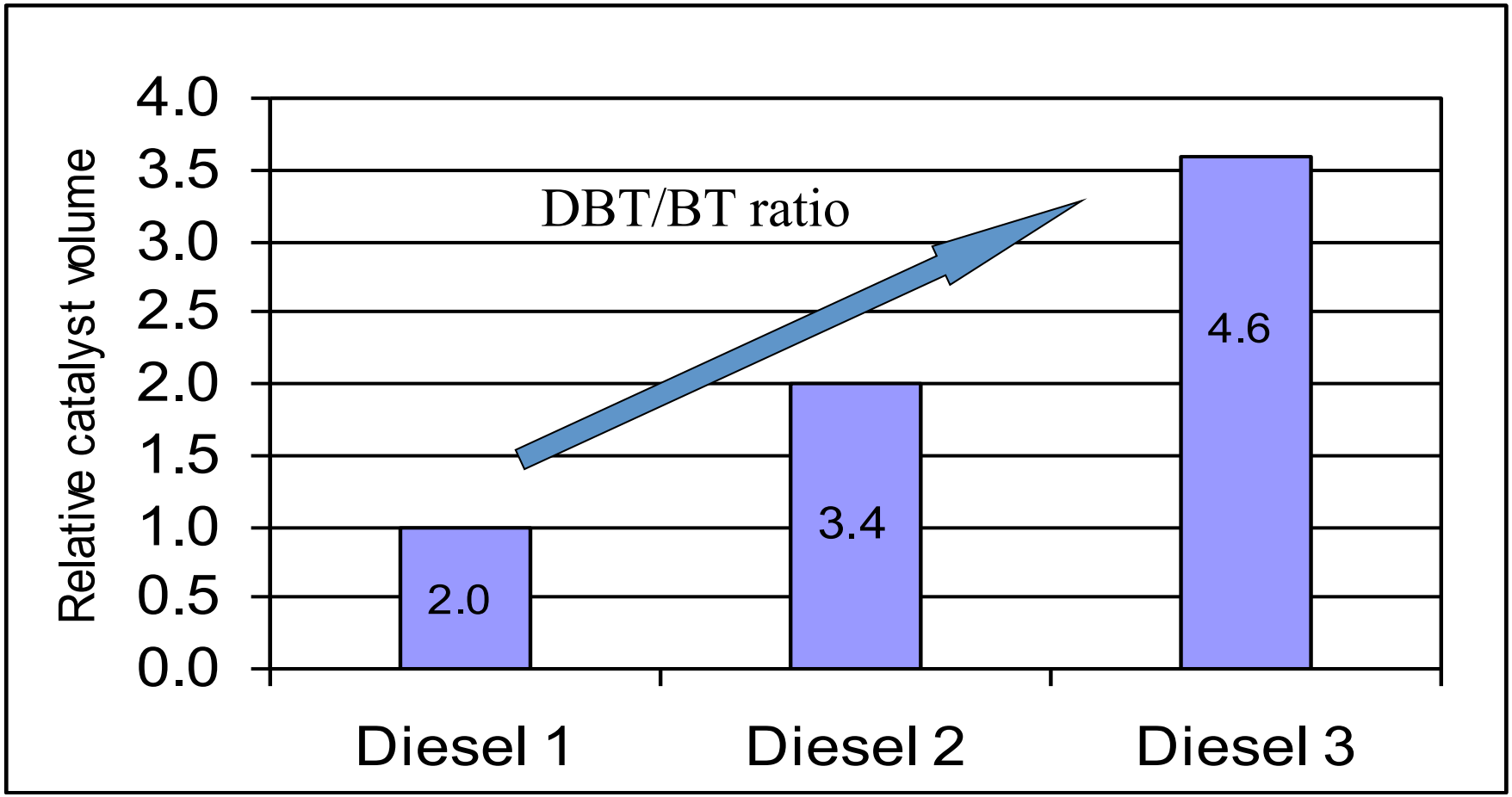
7.38×10^{-5}

6.64×10^{-6}

4.92×10^{-6}

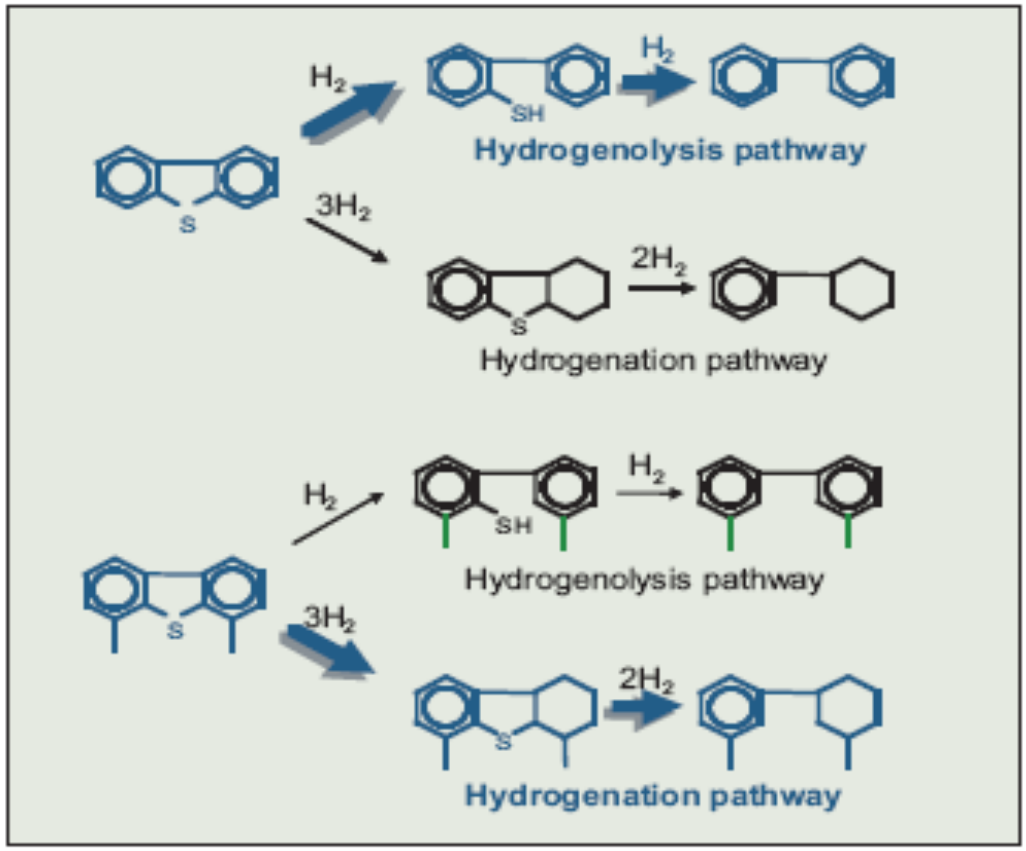
Source: C. Song, Catalysis Today 86 (2003) 211

Effect of feedstock sulfur distribution on diesel HDS (from 50 to 10ppm S)



HDS / HDN mechanisms

- Direct extraction of sulfur or hydrogenolysis (i.e. C-S bond breaking)
  - $CoMo/Al_2O_3$, moderate reactor pressure, high T & low H_2 consumption
  - CoMo less active for HDN & HYD of aromatics
- Hydrogenation route
  - $NiMo/Al_2O_3$, high reactor P , lower T & high H_2 consumption
  - NiMo & NiW good HDN and HYD catalyst, hence used for unsaturated feeds



Typical process conditions

T: 315 – 425; P: 35 – 100 bar; LHSV: 0.5 – 3.0 h^{-1}

- The key to produce ULSD fuel with 10ppm sulfur, is the removal of refractory sulfur compounds such as 4,6-DMDBT.
- To meet the ULS fuel specification (50 and 10ppm S), catalyst activity improvement alone is not enough, process optimization, etc., are required.
- Refiners have to address other issues such as handling, storage, transporatation and distribution which are equally challenging while implementing ULS fuel specifications

Approaches to deep desulfurization of diesel

- Improving HDS catalyst activity by new catalyst formulations and improved methods of production, etc.
- Optimization of process conditions such as temperature, H2 partial pressure, minimization of reaction inhibition by H2S and NH3, minimization of feed vaporization, vapor-liquid distribution, etc.
- Designing solutions such as counter-current flow of H2 and feed diesel, Inter-bed separation/dilution of H2S and NH3, Two step desulphurization, Feed splitting followed by diesel hydrotreating
- Alternate processes, e.g., adsorptive and oxidative desulfurization
- Technology available for the production of ULS fuels, but each refinery has to find unique solution based on its present configuration, type of feed processed, etc.

Challenges to be addressed by refineries/OMCs

- Increasing crude price and other factors forcing refiners to process tougher crude oils to improve GRMs
- For India to move to Euro IV/V fuls (50 ppm and 10 ppm S), hydroprocessing capacity has to be increased to 50 – 65% depending on refinery configuration, type of crude processed, etc. This necessitates further investment.
- Problems of contamination while processing, handling, storing, transportation and distribution, e.g. Pipeline transport – interface issues
- Refineries already under strain, have to find ways to recover the large investment required to further upgrade technology for the production of ULS fuels.

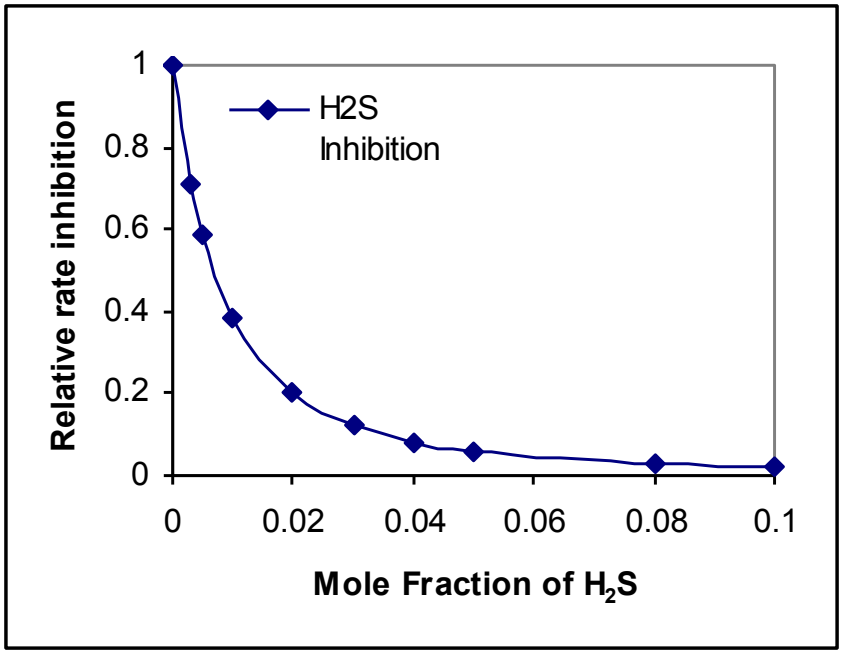
Summary

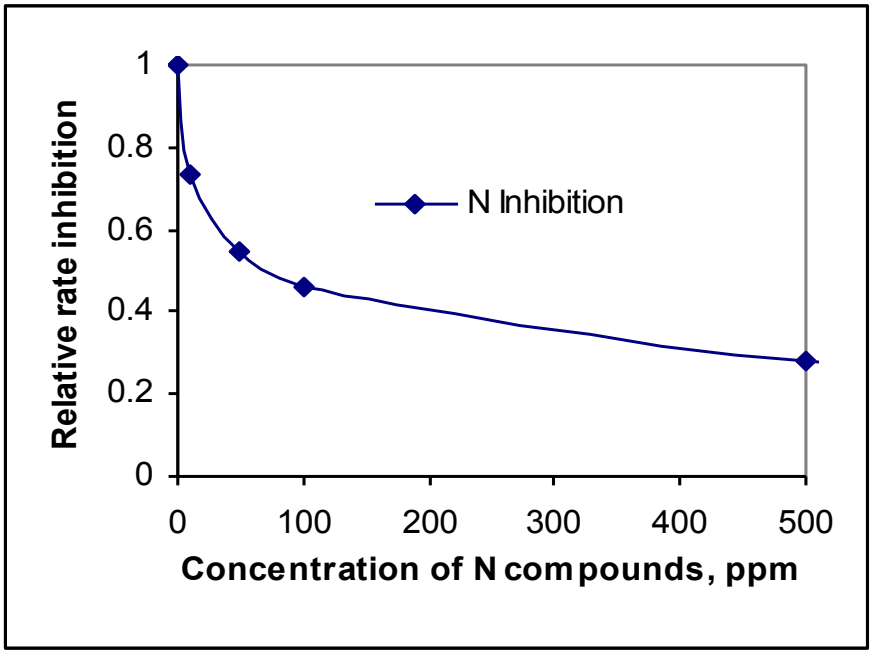
- Indian refiners have made huge investment to upgrade technology for producing Euro III/IV fuels
- Technology is available for upgrading fuel quality to next level, however, large investment is required
- Oil companies already under strain with decreasing GRMs and under recoveries need to find ways to recover huge investment for producing ULS fuels and sustain
- To produce Euro IV/V fuels with 50/10 ppm S, refineries have to overcome not only production issues, but also issues related to handling, storing, transportation and distribution


Thank you

Reaction inhibition due to H2S and NH3

- Presence of H_2S & NH_3 inhibits the desulfurization and hydrogenation reactions





PK Rakshit, P George, V Ravikumar, N V Choudary, Proceedings of 6th ISFL held in New Delhi during March 9-12, 2008.