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Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production

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ABSTRACT

Sulfur content of diesel fuel has been cut down to ultra low levels by environmental regulation in many countries with the aim of reducing diesel engine's harmful emissions and improving air quality. As a result, research on the production of ultra low sulfur diesel (ULSD) has gained enormous interest in the scientific community worldwide. The renewed interest in ULSD research is driven by the need, to have a comprehensive understanding of the various factors influencing deep desulfurization of diesel to the ultra low level as well as to find cost-effective ways for ULSD production. This review discusses the recent advancement on ULSD production from both scientific and applied point of view. The key fundamentals and the factors influencing the removal of the least reactive sterically hindered sulfur species from diesel feedstocks are reviewed and discussed in detail. Latest development in deep HDS catalyst and the scientific basis for the improvements in the activity of the new generation HDS catalyst are presented. Advancement in the deep HDS process technologies is reviewed and various options available for revamping and modifying the existing low sulfur diesel HDS units for ULSD production are described highlighting the importance of catalyst selection and hydrogen consumption issues. Special attention has been paid to the progress in the alternative (non-hydrogenation) process concepts and technologies that are being developed for ULSD production.

Abbreviations: AC, Activated Carbon; ACF, Activated Carbon Fiber; ACMB, Activated carbon; ADS, Adsorptive Desulfurization; AED, Atomic Emission Detector; API, American Petroleum Institute; ASA, Amorphous Silica Alumina; ASTM, American Society for Testing Materials; atm, atmospheres; BDS, Biodesulfurization; BNT, Benzonaphthothiophene; B.P., Boiling Point; BP, Biphenyl; BPD, Barrels Per Day; BT, Benzothiophene; CAA, Clean Air Act; CED, Conversion Extraction Desulfurization; CFI, Cold-Flow Improvement; CGO, Coker Gas Oil; CHB, Cyclohexylbenzene; CSTR, Continuous Stirred Tank Reactor; CTC, Charge Transfer Complex; CUS, Coordinatively Unsaturated Sites; CVD, Chemical Vapor Deposition; DBT, Dibenzothiophene; DBTO, Dibenzothiophene sulfone (oxide); DDS, Direct desulfurization; DFT, Density Functional Theory; 2,3-DHT, 2,3-dihydrothiophene; 2,5-DHT, 2,5-dihydrothiophene; 3,3′-DMBP, 3,3′-dimethylbiphenyl; 3,3′-DMBCH, 3,3′-dimethylbicyclohexane; 2,8-DMDBT, 2,8-dimethyldibenzothiophene; 4,6-DMDBT, 4,6-dimethyldibenzothiophene; 4H-DMDBT, 4,6-dimethyl-tetrahydrodibenzothiophene; 6H-DMDBT, 4,6-dimethyl-hexahydrodibenzothiophene; 12H-DMDBT, 4,6-dimethyl-dodecahydrodibenzothiophene; 1,4-DMCARB, 1,4-dimethyl dicarbazole; DMF, Dimethyl Formamide; DMSO, Dimethyl Sulfoxide; DOC, Diesel Oxidation Catalyst; DOE, Department of Energy; E2, Bimolecular Elimination; EBC, Energy Bio-systems Company; 4-EDBT, 4-Ethyl Dihydrothiophene; CED, Conversion/Extraction Desulfurization; EDTA, Ethylene Diamine Tetraacetic Acid; EOR, End-Of-Run; EPA, Environmental Protection Agency; EPEFE, European Programs on Emissions, Fuels and Engine Technologies; EXAFS, Extended X-ray Absorption Fine Structure; FBP, Final Boiling Point; FBR, Fixed Bed Reactor; FID, Flame Ionization Detector; FPD, Flame Photometric Detector; FR-LB-GO, Full Range and Low-Boiling Gas Oil; FT-ICR-MS, Fourier Transform Ion Cyclotron Resonance Mass Spectrometer; FTIR, Fourier Transform Infrared; GC–MS, Gas Chromatography–Mass Spectrometer; GC-SCD, Gas Chromatography-Sulfur Chemiluminescence Detector; GC-FPD, Gas Chromatography Flame Photometric Detection; GC-PFPD, Gas Chromatography-Pulsed Flame Photometric Detector; GO-KEC, Gas Oil Kuwait Export Crude; GO-LF, Gas Oil Lower Fars; HAADF, High-Angle Annular Dark-Field; HC, Hydrocarbons; HCK, Hydrocracking; HCO, Heavy Cycle Oil; HCGO, Heavy Coker Gas Oil; HDAr, Hydrodearomatization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; HDS, Hydrodesulfurization; HDSCS, HDS of Concentrated Sulfur; HDT, Hydrotreating; HO, Heavy Oil; HOMO, Highest Occupied Molecular Orbital; hp, Horsepower; HRTEM, High-resolution Transmission Electron Microscopy; HYD, Hydrogenation; HDHDC, Mild Hydrocracking of Heavy Distillate; IBP, Initial Boiling Point; IFP, Institute Francais de Petrole; ILs, Ionic Liquids; KCC, Kuwait Catalyst Company; LBPP, Linde BOC Process Plants; LCO, Light Cycle Oil; LGO, Light Gas Oil; LHSV, liquid hourly space velocity; LM, Locomotive; LSD, Low Sulfur Diesel; MCM-41, Mesoporous Catalytic Material-41; 4-MDBT, 4-Methyl Dibenzothiophene; MDUF, Middle Distillate Unit Feed; MIDW, Dewaxing by hydroisomerization of paraffin; MJF, Model Jet Fuel; 2-MPiper, 2-methylpiperidine; 2-MPy, 2-Methylpyridine; MECA, Manufacturers of Emission Controls Association; MPHC, Moderate Pressure Hydrocracking; MR, Membered Ring; MTBE, Methyl Tertiary Butyl Ether; NPC, Nitrogen-Based Polar Compounds; NR, Non-Road; NTA, Nitriloacetic acid; ODS, Oxidative Desulfurization; OICA, Organization Internationale des Constructeurs d'Automobiles; OFG, Oxygen Functional Groups; OHA, Octahydroacridine; PFPD, Pulse Flame Photometric Detector; PFR, Plug Flow Reactor; Pip, Piperidine; PM, Particulate Matter; PNA, Poly-Nuclear Aromatics; POLF, Presaturated One Liquid Flow; SARS, Selective Adsorption for Removing Sulfur; SCD, Sulfur Chemiluminescence Detector; SCF/B, Standard Cubic Feet per Barrel; SFPAs, Sulfur Free Poly-Aromatic; SMART, Sulfur Minimization by ART; SN2, Nucleophilic Bimolecular Substitution; SOR, Start Of Run; SPA, Substituted Poly-Aromatic; SRGO, Straight-Run Gas Oil; SR-LGO, Straight-Run Light Gas Oil; SR VGO, Straight-Run Vacuum Gas Oil; STM, Scanning Tunnelling Microscopy; STEM, Scanning Tunnelling Electron Microscopy; TBN, Total Basic Nitrogen; TBP, True Boiling Point; t-BuOCl, t-Butyl hypochlorite; TBHP, t-Butyl Hydroperoxide; TGA, thermogravimetric analysis; TGR, Treat Gas Rate; THDT, Tetrahydrodibenzothiophene; TPR, Temperature Programmed Reduction; TPS, Temperature Programmed Sulfidation; UAOD, Ultrasound-Assisted Oxidative Desulfurization; UDHDS, Ultra deep hydrodesulfurization; ULSD, Ultra Low-Sulfur Diesel; USEPA, United States Environmental Protection Agency; USY, Ultra-Stable Y-zeolite; VGO, Vacuum Gas Oil; WHSV, Weight-Hourly Space Velocity; WABT, Weighted Average Bed Temperature; wppm, Weight Parts-Per-Million; WWFC, Worldwide Fuel Charter; XANES, X-ray Absorption Near Edge Structure; XRF, X-ray fluorescence; XRD, X-ray Diffraction.

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1. Introduction

Diesel is extensively used as a fuel both in high way transportation vehicles (e.g. cars, buses and trucks) and non-highway transportation systems (e.g. locomotives, marine vessels, farm equipments, etc.). Diesel engines are 25–40% more fuel-efficient than comparable gasoline engines. Nevertheless, they suffer from associated particulate, NO_x and SO_x emissions that are harmful to human health. Sulfur, a natural part of the crude oil from which diesel fuel is derived, is one of the key causes of particulates or soot in diesel [1–5]. Soot is the main culprit of diesel engine's noxious black exhaust fumes, and is among the prime contributors to air pollution [6]. Traces of sulfur present in the diesel fuels also poison the oxidation catalysts in the emission control system and reduce their effectiveness for the oxidation of harmful carbon monoxide, hydrocarbons and volatile organic matter [7,8]. Environmental regulations have been introduced in many countries around the world to reduce the sulfur content of diesel fuel to ultra low levels (10–15 ppm) with the intention of lowering diesel engine's harmful exhaust emissions and improving air quality. The environmental issues related to sulfur in diesel, current and future diesel fuel sulfur specifications in various countries around the world, air quality standards, and ULSD market demand are presented in more detail in a separate section (Section 2), since the need for ULSD is driven by these environmental issues.

Although the new environmental regulations that limit the sulfur levels of diesel and other transportation fuels to very low levels are beneficial from environmental point of view, meeting the required stringent specifications represent a major operational and economic challenge for the petroleum refining industry [9–13]. The tightening of sulfur specifications of diesel fuel to very low levels requires ultra deep desulfurization of diesel feed stream. The shift from normal to ultra deep desulfurization is very complicated technical problem. Many factors such as the catalysts [14–22], process parameters [9,21–23], feedstock source and quality [9,24–28], reactivities of sulfur compounds [27–30], inhibition effects of H_2S [31–35], nitrogen compounds [36–39] and aromatics [40–43] present in the feed, etc. can have significant influences on the degree of desulfurization of diesel feeds. Some sulfur compounds that contain alkyl side chains in the 4- and 6-positions in the dibenzothiophene molecule close to the sulfur atom (e.g. 4,6-dimethyl dibenzothiophene; 4-methyl,6-ethyl dibenzothiophene) are difficult to desulfurize under conventional desulfurization conditions. The removal of such refractory sulfur species from the diesel by HDS is a tough challenge [44a,b]. The conventional hydrotreaters have to be modified and revamped for ultra low sulfur diesel (ULSD) production.

Another problem faced by the refiners is the difficulty in meeting the increasing market demand for ULSD. Global market for middle distillates is increasing steadily and this trend is expected to continue for the next few years. At the same time, the quality of crude and diesel feed streams available to the refiners is declining. The refiners are, thus, required to produce a high quality diesel product such as ULSD from lower quality feedstocks, which is a tough challenge. Flexibility to process heavy gas oils and low grade streams such as light cycle oil (LCO) from the FCC units into ULSD will be needed in the refineries to produce and supply the additional volume of ULSD.

Extensive research studies have been carried out during the past two decades on the development of improved hydrotreating catalysts and processes as well as on finding alternative routes for deep desulfurization of diesel fuel. Earlier studies on the subject were reported in some general reviews on deep desulfurizations that were published in the mid-nineties [45–47]. The work done on the subject up to year 2002 was summarized and discussed in three review papers published in the year 2003 [11,12a,b]. Since then, a large number of articles addressing the various aspects of ultra deep desulfurization of diesel have appeared in the scientific literature. Most of these studies have focused on finding effective ways for the desulfurization of least reactive sterically hindered alkyl DBTs. The role of catalysts and other key factors, such as feed quality, inhibition effects, process variables, kinetic and thermodynamic effects, reactor internals and feed distribution effects, influencing the desulfurization of the least reactive sulfur species have received increasing attention in recent years.

Various options for cost-effective revamping of the existing hydrotreaters for ULSD production have been investigated. In addition, enormous amount of research studies have been carried out during the last 7 years on the development of highly active HDS catalysts, new hydrotreating process concepts and technologies, and alternative (non-hydrogenation) routes such as oxidative desulfurization, bio-desulfurization, extractive desulfurization and adsorptive desulfurization for removing sulfur from diesel streams to ultra low levels.

The purpose of this article is to review the recent advances in ULSD production from both fundamental and applied points of view. Information available in the literature on the subject up to 2009 are covered in this review. The key fundamentals and the factors influencing ultra deep HDS of diesel fuel are updated and discussed on a scientific basis. Particular emphasis is given to the inhibitory effects of H_2S, N-compounds and aromatic molecules on the HDS of sterically hindered alkyl DBTs. Latest developments in hydrotreating catalysts, nature of the hydrogenation and hydrogenolysis sites, and the scientific basis for the improvements in the activity of new generation HDS catalysts are presented and discussed in detail. The various options available for revamping and modifying the existing low-sulfur diesel HDS units for ULSD production are described highlighting the importance of catalyst selection and hydrogen consumption issues. New hydrotreating process concepts and technologies introduced in recent years for ULSD production are also critically reviewed. Finally, the progress in alternative process concepts and emerging technologies for ULSD production are reviewed in detail and their advantages and limitations are indicated.

2. Drivers of ULSD production

The main drivers of ULSD production in the petroleum refineries are the environmental problems and health hazards caused by exhaust emissions from the diesel powered vehicles, the strong influence of sulfur in enhancing the formation of harmful components of the emission (e.g. particulate matter (PM), NO_x, SO_x and CO), and the environmental legislations on diesel fuel sulfur level and air quality standard. Another important driver that encourages refiners to favor ULSD production over gasoline is the continued increase in the demand of ULSD.

2.1. Environmental problems and health hazards caused by sulfur in diesel fuel

Diesel fuels contain a complex mixture of hydrocarbons having different molecular weights and boiling points composed of mainly paraffins and aromatics together with small amounts of organic sulfur and nitrogen compounds. The sulfur present in the diesel fuel is a major source of air pollution. During combustion in the diesel engines, the sulfur compounds burn to form harmful sulfur oxides (SO_x) and sulfate particulates. The nitrogen compounds are oxidized to nitrogen oxides (NO_x).

The exhaust emissions contain SO_x, NO_x, CO, CO_2, PM and unburned hydrocarbons (HC). Several studies have shown that the amount of SO_x emissions is directly proportional to the amount

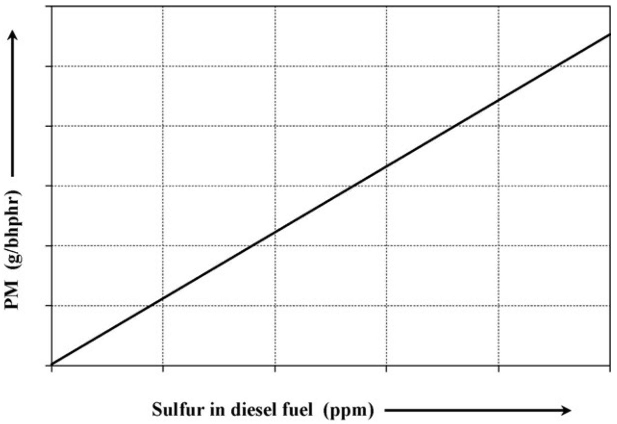


Fig. 1. Direct particulate material (PM) emissions as a function of diesel fuel sulfur level.

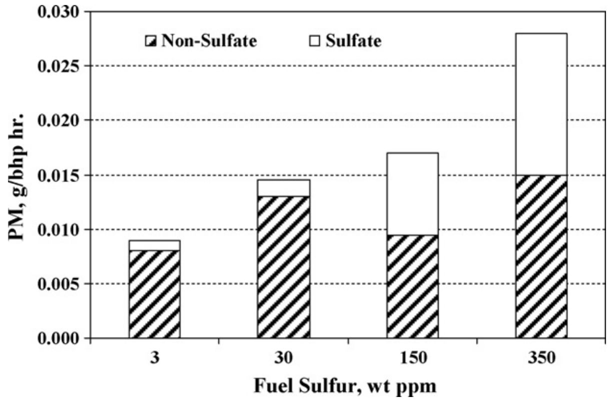


Fig. 2. Particulate material (PM) emissions after diesel oxidation catalyst (DOC) as a function of diesel fuel sulfur level [7].

of sulfur contained in the fuel. In addition, total particulate matter (PM) emissions are proportional to the amount of sulfur in the diesel fuel [5,7,48–50]. In the oxygen rich exhaust of diesel vehicles, the organic "S" is converted into SO_x, consisting mainly SO_3 which dissolves in the water vapor present to form sulfuric acid (H_2SO_4) vapor. H_2SO_4 forms very small (so called ultrafine) particles in diesel exhaust which are considered especially hazardous because of their ability to penetrate deeply into the lungs. The influence of sulfur content of diesel fuel on direct PM emissions is illustrated in Fig. 1.

According to the US EPA, approximately 2% of the sulfur in the diesel fuel is converted to direct PM emissions. The oxides of S and N (i.e. SO_x and NO_x) and the PM present in the diesel engine exhaust emission can deteriorate the air quality and cause adverse effects on human health [6]. The particulate matter (PM) emitted from diesel engine consists of three primary constituents: a carbonaceous core, a soluble organic fraction (SOF) and a mixture of SO_x and water, and it has been found to be a human carcinogen.

Emission control devices such as Diesel Oxidation Catalysts (DOC), NO_x absorbers, PM filters and selective catalyst reduction (SCR) systems are commonly used in diesel vehicles to control and minimize the hazardous effects of diesel engine exhaust emissions. Oxidation catalysts work by oxidizing CO, HC and the soluble organic fraction of the PM to CO_2 and H_2O in the oxygen rich exhaust stream of the diesel engine. When sulfur is present in the fuel, DOCs also increase the oxidation rate of SO_2, and produce high level of hazardous sulfate in the emission (Fig. 2) [7,8]. In addition, sulfur poisons the oxidation catalysts and reduces their effectiveness for the oxidation of harmful SOF, CO and HC in the exhaust stream. The PM filter performance and NO_x absorber/control efficiencies are also impaired by higher levels of sulfur.

Reducing sulfur levels in fuels can reduce harmful emissions in three general ways: (i) by directly reducing sulfur dioxide (SO_2) and sulfate PM, (ii) by achieving better performance from the emissions control systems, especially catalysts, and (iii) by enabling the use of new emission control technologies such as diesel PM filters, NO_x absorbers and SCR systems.

A study of fuel sulfur effects completed by the U.S. Department of Energy (DOE) found that engine PM emissions decreased with lower sulfur fuels [7]. Baseline PM emissions measured over the Organization Internationale des Constructeurs d'Automobiles (OICA) drive cycle indicated that diesel engine PM emissions decreased by about 29% when going from a 350 wppm sulfur diesel to a 3 wppm sulfur diesel. A 1999 study completed by the Manufacturers of Emission Controls Association (MECA) also looked at fuel sulfur effects. MECA noted a 14% decrease in PM emissions for a 1998 Detroit Diesel Corporation Series 60 engine when operating on 54 wppm sulfur fuel versus 368 wppm sulfur fuel [51]. In California, ARCO developed an ultra low sulfur fuel marketed under the name ECD. When compared against a CARB diesel blend fuel containing 120 wppm sulfur, the ECD fuel lowered diesel PM emissions by 13% on average [52]. New York City Transit test results reported PM emission reductions of 23% when using ULSD fuels without any after treatment [53]. While lower PM emissions will result from the use of low-sulfur diesel alone, the primary emission benefit is achieved when exhaust after treatment is used [7,54].

The effects of other properties of diesel such as cetane number, aromatics content, density and distillation temperature (T_{90} or T_{95}) on emissions have also been studied by many investigators [55–64]. A study by Shell [57] revealed that the ignition qua1ity, as measured by cetane number, influenced both gaseous and particulate emissions – higher cetane numbers giving lower emissions. It was also shown that the effect on gaseous emissions was true for any engine type while the effect on particulates was different between light-duty and heavy-duty engines. Moreover, the size of the effect was engine-dependent. CONCAWE [58] reported that for light duty vehicles, reductions of carbon monoxide and particulate emissions were observed with increasing cetane number. The study suggested that benefits appear to be true for higher cetane number achieved either naturally or by use of additives.

A comprehensive study of fuel composition impacts on light-duty diesel emissions was performed, as part of the European Programs on Emissions, Fuels and Engine Technologies (EPEFE) [65]. This study investigated the impact of the density, cetane number, T_{95}, and polycyclic aromatic content of diesel fuels on emissions

Table 1

Impact of fuel composition changes on emission of current light duty diesel vehicles [65a,65b].

Change	NO_x		PM	
	Indirect injection	Direct injection	Indirect injection	Direct injection
Increase cetane (50–58)	Very small increase	Very small decrease	No effect	Small increase
Decrease density (0.855–0.828 g/cm^3)	No effect	Small increase	Large decrease	Large decrease
Decrease T_{95} (371–326 °C)	Very small increase	Small increase	No effect	Small decrease
Decrease polycyclics (8–1 vol.%)	Very small decrease	Very small decrease	Very small decrease	Small decrease

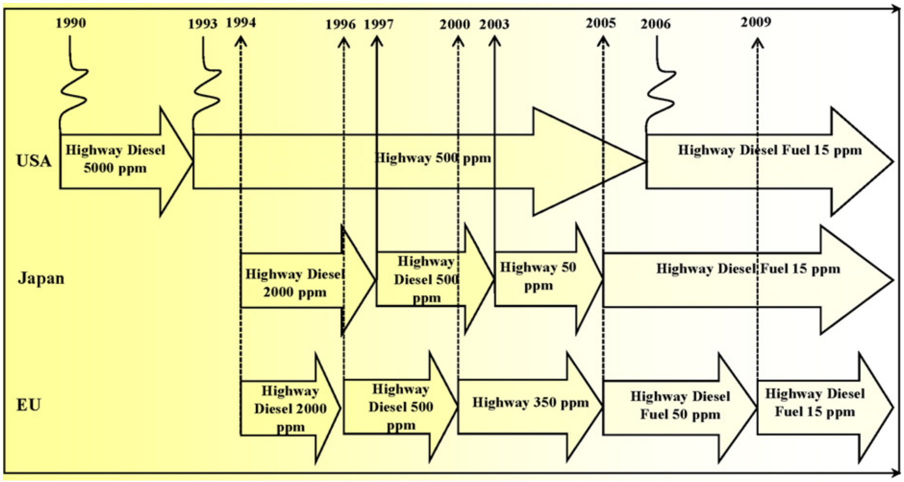


Fig. 3. Trends in diesel sulfur fuel specification for high way transportation vehicles.

from light-duty vehicles sold in Europe. The program involved 19 vehicles, 14 of which had indirect-injection engines.

The generalized results of this study are presented in Table 1.

A decrease in the poly-nuclear aromatics content of diesel fuel leads to a small reduction in the amount of both NO_x and PM in the emission. Density reduction results in a large decrease of PM, but slightly increases the NO_x emissions from direct injection engines. A decrease in the T_{95} temperature increases the NO_x emissions slightly from both direct and indirect injection engines. In general, unlike sulfur, the changes in the other diesel properties do not have noticeable benefits in reducing harmful NO_x and PM emissions from current light-duty diesel vehicles.

2.2. Environmental legislation on diesel fuel specification

The linear relationship observed between sulfur level in the diesel fuel and the particulates and other harmful pollutants in the emissions are the main reasons for targeting sulfur content in diesel fuel specifications and reducing it to lower and lower levels in many countries worldwide. Studies have shown that a combination of

Table 2
Sulfur standards for diesel in some countries other than USA, Japan and Europe [72,73].

Region	Country	Sulfur (wppm)	Year of implementation
South (central) America	Argentina	50	2008[a]
	Brazil	500	2008[a]
		50	2009[b]
	Chile	350	2007
		50	2010
	Mexico	500	2005
		15	2009[a]
	Peru	50	2010[a]
	Uruguay	50	2009
Asia pacific	China	2000	2000
		500	2005[a]
		50	2012[b]
	Hong Kong	50	2007
	India	350	2005[a]
		350	2010[b]
		50	2010[a]
	Singapore	50	2005
	Taiwan	50	2007
	Australia	500	2002
		10	2009
Middle East	Kuwait	2000	2008
		50	2010[b]
	Saudi Arabia	800	2008[a]
		10	2013[b]
	Bahrain, Lebnon, Oman, Qatar, UAE	50	2008
	Qatar, UAE	10	2010
	Bahrain	10	2013
	Iran	50	2008[a]
	Jordon	10,000	2008
		350	2012
	Russia	500	2008[a]
		50	2010[b]
EU	Germany, France, Denmark, Sweden	<10	Pushing hard for Euro 5/6

[a] Majority of city (selected cities).
[b] Expected to limit (national-wide).

Table 3
Worldwide fuel charter diesel fuel category 4 specifications.

Source fuel specification	Worldwide fuel charter category 4
Density, max (g/cm^3)	0.840
S (ppm)	5–10
Cetane index (min)	≥52
Cetane number	≥55
Aromatics	<15 vol.%
PNA	<2 vol.%
T_{90} (max °C)	320
T_{95} (max °C)	340

very low sulfur fuel and particulate filters can bring about approximately 90% reductions in PM and further substantial reductions in CO and HC from existing diesel vehicles, even after 400,000 miles of operation [7]. Significant reduction of sulfur induced corrosion and slower acidification of engine lubricating oil, which lead to longer maintenance intervals and lower maintenance costs, are additional benefits of using ultra low sulfur diesel in diesel powered vehicles.

In the USA, the acceptable level of sulfur in the high way diesel was first reduced from 2000 ppm to 500 ppm by the Clean Air Act (CAA) amendments in the nineties, then to 350 ppm, 50 ppm and 15 ppm, respectively, in the years 2000, 2005, and 2006 [66,67] (Fig. 3). In Europe, Germany introduced 10 ppm sulfur limit for diesel from January 2003. Other European Union countries and Japan introduced diesel fuel with 10 ppm to the market from the year 2008 (Fig. 3) [68–71]. Similar ultra low sulfur specifications are also targeted in many other countries, and will be predominant worldwide during the next decade (Table 2) [72,73].

The specifications proposed for clean diesel by Worldwide Fuel Charter (WWFC), which reflects the view of the automobile/engine manufactures concerning the fuel qualities required for engines in use and for those yet to be developed, require increased cetane index, significant reduction of poly-nuclear aromatics (PNA), and lower T_{95} distillation temperature in addition to ultra low sulfur levels (Table 3). Automotive manufactures have concluded that substantial reductions in both gasoline and diesel fuel sulfur levels to quasi sulfur-free levels are essential to enable future vehicle technologies to meet the stringent vehicle emissions control requirements and reduce fuel consumption.

Similar tighter sulfur specifications (Fig. 4) have also been introduced for non-road diesel [74]. In 2004, the USEPA issued the clean air-non-road-Tier 4 final rule which mandates that starting in 2007, fuel sulfur levels in non-road diesel fuel should be reduced to 500 ppm from its current 3000 ppm level. This includes fuels used in locomotive and marine applications (except marine residual fuel used by very large engines on ocean-going vessels). In 2010, fuel sulfur levels in most non-road diesel fuel will be reduced to 15 ppm, making it possible for engine manufacturers to use advanced emissions control systems that significantly reduce harmful emission, in accordance with the emission standards presented in Table 4.

Table 4
Non-road final emission standards [74].

Rated power	First year that standards apply	Grams per horsepower hour (g/hp h)	
		PM	NO_x
Hp < 25	2008	0.30	–
25 < hp < 75	2013	0.02	3.5
75 < hp < 175	2012–2013	0.01	0.3
175 < hp < 750	2011–2013	0.01	0.3
Hp > 750	2011–2014	0.075	2.6/0.50

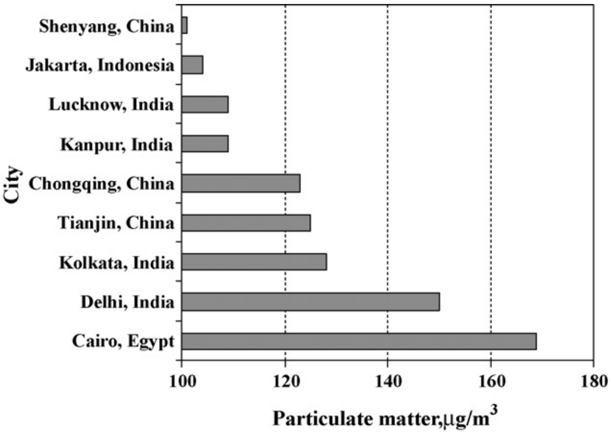


Fig. 5. Particulate matter present in the atmosphere of some highly populated cities.

To meet these emission standards, engine manufactures will be required to produce new engines with advanced emission control technologies similar to those already expected for on-road (highway) heavy trucks and buses. Refiners will be producing and supplying ultra low sulfur diesel for both highway and non-highway diesel vehicles and equipments.

Many countries do not have standards to control pollution adequately. An example of particulate matter present in the atmosphere of different cities is shown in Fig. 5. The beneficial effects of switching over to more and more stringent specification in accordance with Euro 1 to Euro 5 on the major pollutants (PM and NO_x) in the emissions from diesel vehicles are illustrated in Fig. 6 [75].

2.3. Market demand for ULSD fuel

The demand for middle distillates is growing steadily as shown in Fig. 7. According to a recent estimate by the International Energy Agency (IEA), distillates (jet fuel, kerosene, diesel and other gas oils) will continue to remain as the main growth drivers of world oil demand for the next few years [76]. A major contributor to the growth in the world distillate demand is increased consumption in

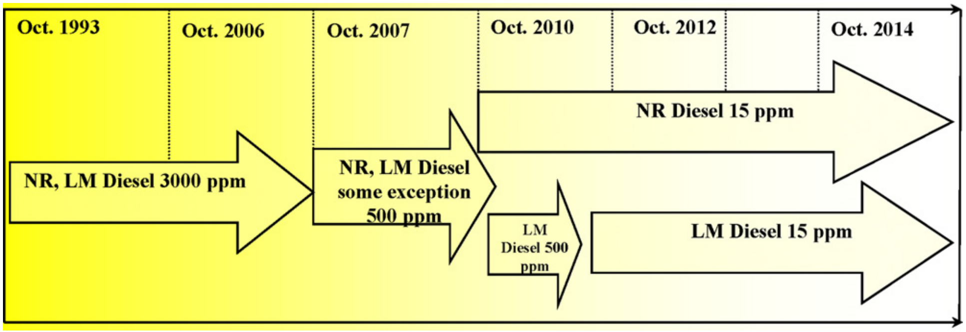


Fig. 4. Trends in sulfur specification for non-road diesel (NR, non-road and LM, locomotive and marine diesel).

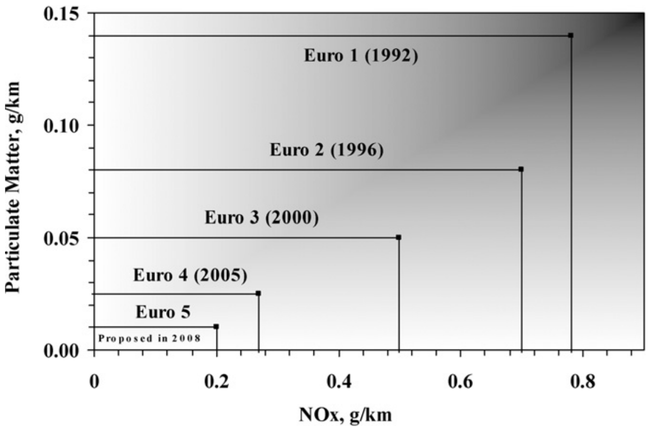


Fig. 6. Influence of diesel fuel specifications on NO_x and particulate matter (PM) emission [75].

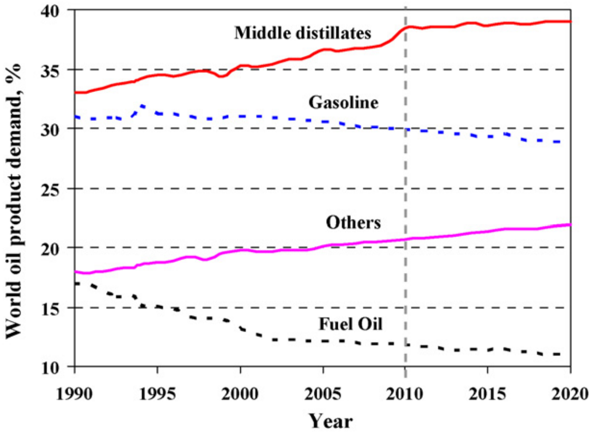


Fig. 7. Variation in petroleum fuels demand in recent years.

developing nations. According to IEA projection, about 48% of global product demand growth over the next 5 years will be concentrated in middle distillate fuels, dominated by diesel. This trend is likely to continue for many more years. The main sources of increased diesel fuel consumption are: (i) transportation and (ii) power generation.

In diesel-hungry China and India the demand is growing at a fast pace irrespective of the global economic crisis. Traditional demand for diesel in truck is increasingly supplemented by a growing share in the light passenger vehicle market, especially, in Europe and Asia. Now, with the tightening of the sulfur specifications of both high-way and non-road diesel fuels to ultra low levels, refiners will face tough challenges in meeting the increasing demand for ULSD. Supplies of ULSD are likely to remain tight for some more time. Refiners worldwide are investing heavily in middle distillates producing conversion units, such as cokers and hydrocrackers, and in the necessary hydrotreating capacity to produce ultra low sulfur diesel.

3. Deep HDS chemistry and kinetics

Diesel fuels contain a complex mixture of a large variety of sulfur compounds with different reactivities. To achieve ultra deep desulfurization diesel fuels, a clear understanding of the types of sulfur compounds present in diesel feeds, their reactivity, reaction pathways, deep HDS kinetics and mechanism, and the factors that influence the reactivity of the sulfur compounds in diesel feeds including inhibition effects is very important. These issues are discussed in detail in this section.

3.1. Sulfur compounds in diesel feeds

Recent developments in the separation and analytical techniques have facilitated the separation and quantitative analysis of individual sulfur compounds present in diesel feeds. A combination of high resolution gas chromatography and sulfur selective detectors such as flame photometric detector (FPD) and sulfur chemiluminescence detector (SCD), pulse flame photometric detector (PFPD), atomic emission detector (AED), FT-ICR-MS, etc. have been currently used for detailed analysis of different types of sulfur species present in diesel blending streams [12,21,22,46,77–81]. Fig. 8 shows the various types of sulfur containing compounds present in a typical Kuwait straight-run light gas oil analyzed by GC-SCD [82]. The results clearly indicate that diesel feeds contain a large number of individual sulfur compounds which can be divided into two groups. The first group includes benzothiophenes (BTs) with alkyl substituents containing 1–7 carbon atoms, and the second class comprises dibenzothiophene (DBT) with alkyl substituents containing 1–5 carbon atoms. Distribution of the alkyl BTs and alkyl DBTs are found to be in accordance

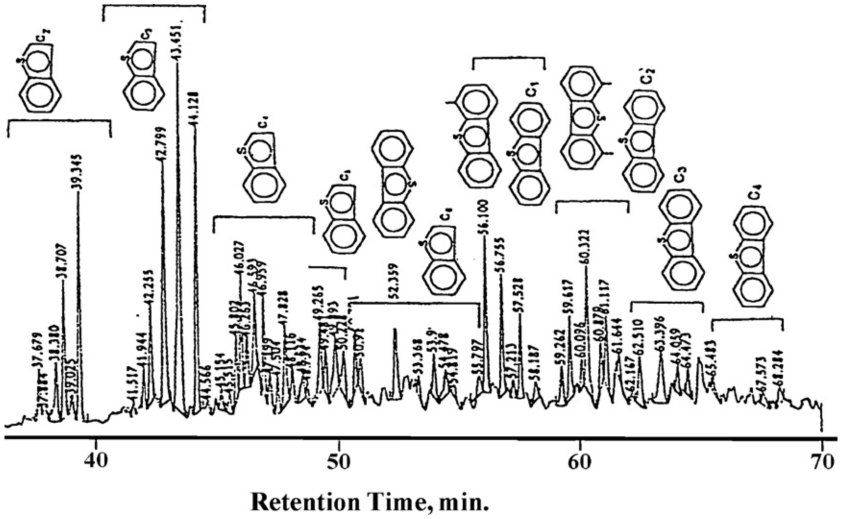


Fig. 8. GC–SCD chromatograms of sulfur compounds distribution in Kuwait atmospheric gas oil [82].

with their boiling points. Cx-BTs are mainly concentrated in fractions having boiling points <300 °C and Cx-DBTs in fraction boiling above 300 °C. The 300–340 °C fraction contains high concentration of C1–C2 DBTs together with C5 and C6-BTs.

The same two groups of sulfur compounds are usually present in a different gas oils (SRGO, LCO, CGO), but the distribution among these compounds is somewhat different in cracked and straight-run feeds [77,83–85]. The distribution of sulfur compounds mainly depends on the origin of the petroleum. The types and volume of different streams feeding into the diesel fuel will also have a strong influence on the concentrations of different types of sulfur compounds in the diesel feedstocks.

3.2. Reactivities of sulfur compounds

Several studies have shown that the relative reactivities of different thiophenic sulfur compounds are significantly different [21,22,29,86–88]. Fig. 9 shows various sulfur compounds and their relative reaction rates as a function of boiling point. It is evident that benzothiophenes and their alkyl derivatives can be desulfurized at a faster rate than DBT and alkyl DBTs. Among the various isomers of alkyl DBTs, the ones which contain alkyl groups close to the sulfur atom known as β-DBTs, (e.g. 4-MDBT, 4,6-DMDBT, 4,6-MEDBT) are less reactive and more difficult to desulfurize [27,29,30]. Over conventional alumina-supported CoMo and NiMo catalysts, 4,6-DMDBT is 4–10 times less reactive than DBT [22,29,47,88–94]. The size of the alkyl group in the position (4 and 6) close to the sulfur atom in the DBT molecule was found to have a large effect on the reactivity of alkyl DBTs [95]. Thus, the conversion of 4,6-DiPrDBT was found 7 times smaller than that of 4,6-DMDBT. The resistance of this alkyl substituted DBTs to desulfurization has been suggested to be due to steric hindrance preventing the interaction between the sulfur atom and the catalytic active site.

The nature of the steric hindrance in β-DBTs has been a subject of debate. One view is that it retards the adsorption of β-DBTs on the catalyst surface [22,29,30,46,96]. This implies that the rate-limiting step lies in adsorption suggesting an end-on adsorption mode involving interactions between the sulfur atom and active sites. Simulation of the geometry of such molecules showed that the sulfur atom in the DBT molecule is screened by bulky alkyl groups in the 4- and 6-positions adjacent to it. An alternate view is that the steric hindrance slows down the surface C–S bond scission [92,94,97]. Here, the rate-limiting step lies not in sulfur-centered adsorption, suggesting a side-on adsorption mode involving the π-electrons of the aromatic ring.

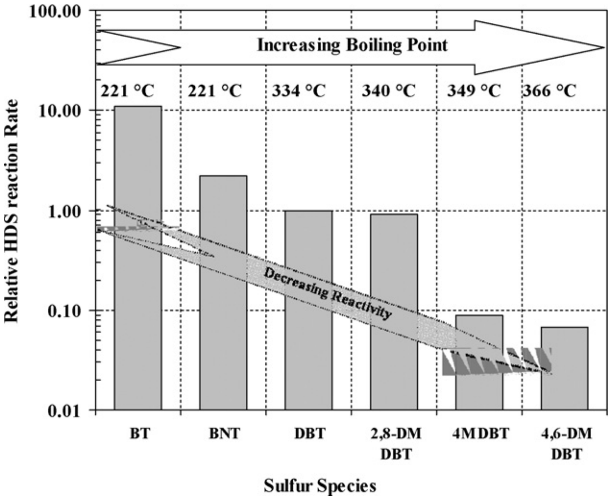


Fig. 9. Reactivities of different sulfur compounds and their boiling points as a function of diesel sulfur species [29]. (Catalyst: $CoMo/Al_2O_3$; $T = 350$ °C; $P = 10$ MPa.)

The adsorption equilibrium constants of DBT, 4-methyldibenzothiophene, 4,6-DMDBT and 2,8-DMDBT were almost the same on a sulfided NiMo catalyst [94]. Kabe et al. reported that the adsorption equilibrium constants of 4-methyldibenzothiophene and 4,6-DMDBT were even higher than that of DBT on a $CoMo/Al_2O_3$ catalyst [88]. Heats of adsorption of DBT, 4-MDBT and 4,6-DMDBT were 12, 20 and 21 kcal/mole,

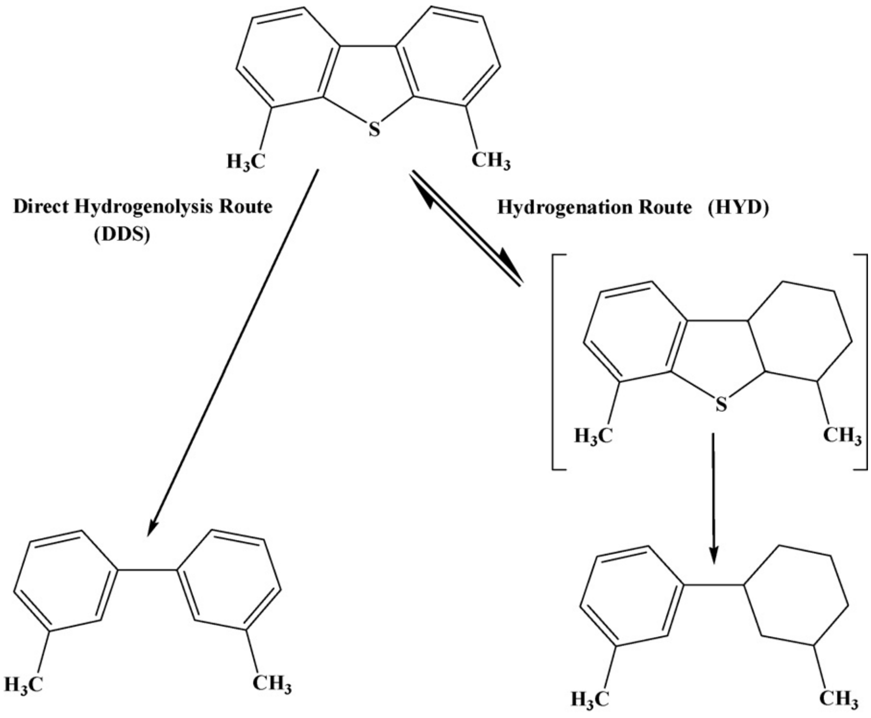


Fig. 10. Reaction pathways for HDS of alkyl DBTs.

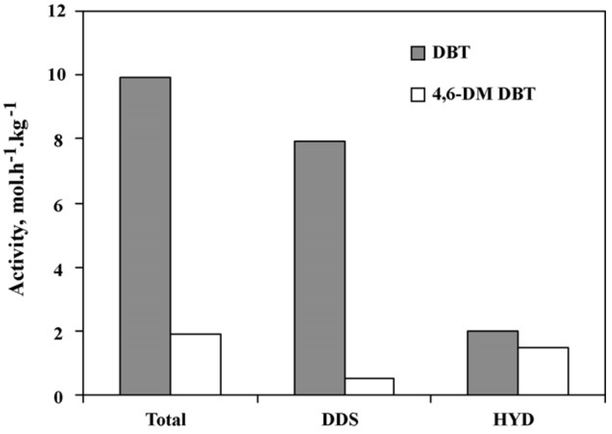


Fig. 11. HDS of DBT and 4,6-DMDBT over sulfided NiMo/Al_2O_3 (fixed bed reactor, 340 °C, 4.0 MPa). DDS pathway; HYD [93,101].

respectively. Methyl groups present in aromatic rings are strong electron donors. Kabe et al. [88], therefore, proposed that 4-MDBT and 4,6-DMDBT can be adsorbed strongly than DBT on the catalyst surface through π-electrons in the aromatic ring, and that the C–S bond cleavage of the adsorbed DBTs is disturbed by steric hindrance of the methyl group.

When the sulfur content of the diesel fuel has to be reduced to ultra low levels by catalytic hydrotreating, even the very refractory sulfur compounds like 4,6-DMDBT must be removed. Kinetic studies with DBT and 4,6-DMDBT have demonstrated that the alkyl substituent in the 4- and 6-positions not only reduce the overall HDS reactivity, but also strongly effect the rates of different pathways in the HDS of 4,6-DMDBT. It will be useful to discuss the reaction pathways and mechanism of HDS of DBT and 4,6-DMDBT to have clear understanding of the various factors influencing the HDS reactivity of the sterically hindered alkyl DBTs through different pathways.

3.3. *HDS reaction pathways and mechanism*

It is now well established that HDS of DBT and alkyl DBT molecules proceed mainly via two parallel routes as shown in Fig. 10. The first route involves direct desulfurization (DDS) leading to the formation of biphenyl while the second route involves hydrogenation (HYD) of one of the benzene rings of the DBT producing tetrahydrodibenzothiophene in the first step which is further desulfurized to cyclohexyl benzene [87,98,99]. Model compound tests have shown that the HDS reaction of un-substituted DBT preferentially progresses via the direct sulfur extraction (DDS) route. The alkyl substituents affect the HDS of DBT in two ways: (i) they reduce their HDS reactivity and (ii) they change the ratio between rates of the two routes. The HYD route becomes dominant with the introduction of alkyl substituents in the 4 and/or, 6-positions of the DBT molecules [22,46,99,100]. It has been reported [88,92] that the partial saturation changes the spatial configuration of the molecule, making the previously sterically hindered sulfur more accessible for effective adsorption on the active site and subsequent reaction.

DDS pathway is severely inhibited while the HYD pathway is hardly affected by the presence of alkyl groups in the 4- and 6-positions of DBT as shown in Fig. 11. It has been suggested that the alkyl groups in the 4,6-DMDBT do not play a significant role in the reactivity of 4,6-DMDBT along the HYD pathway, and the difference in reactivity between DBT and 4,6-DMDBT originates essentially in the selective promoting effect on the DDS pathway [94,101]. Studies on the HDS of DBT on unpromoted and cobalt promoted MoS_2/Al_2O_3 catalysts have shown that the DDS pathway is more selectively enhanced than the HYD pathway by the cobalt promoter [101]. In the case of HDS of 4,6-DMDBT, the promoting effect of Co on the DDS route is significantly small while the HYD pathway is about the same as that of DBT.

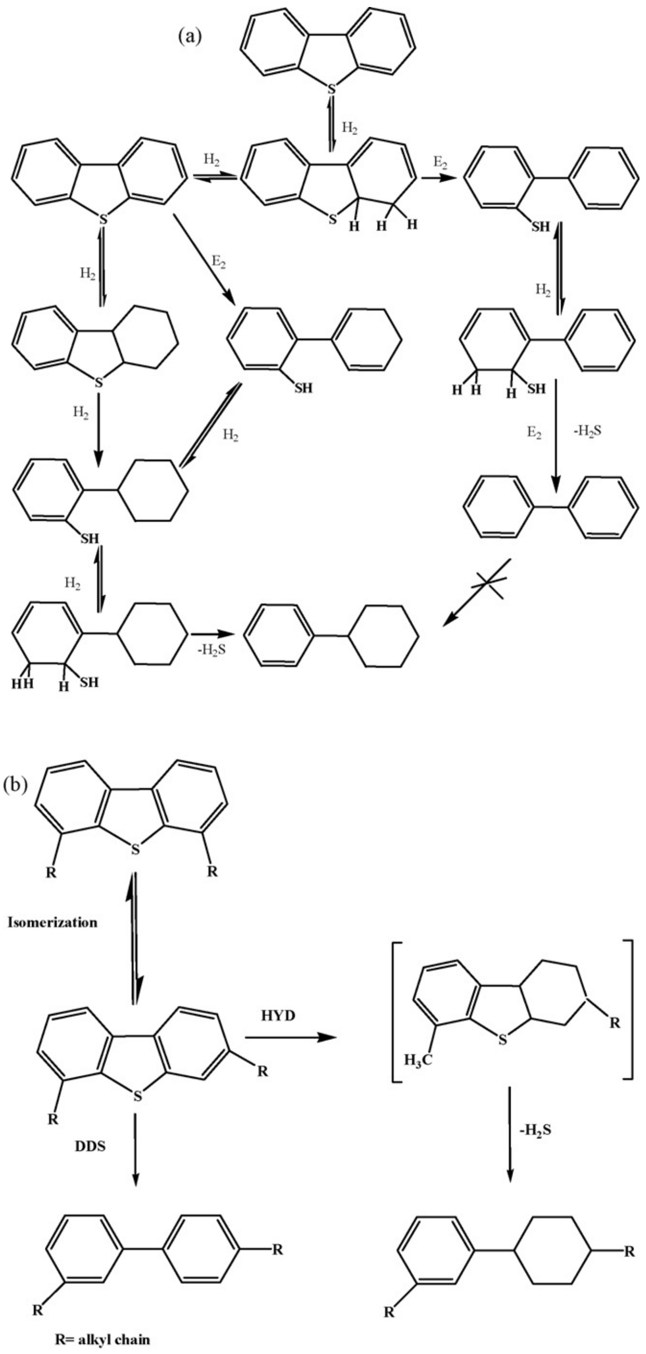


Fig. 12. (a) The various steps of the HDS of DBT through the HYD and DDS pathways. E2: C–S bond cleavage through an elimination process involving sulfur anions as basic sites [101]. (b) Transformation of 4,6-DMDBT through isomerization route over acid containing hydrotreating catalysts.

A common dihydro-dibenzothiophene intermediate as shown in Fig. 12a was suggested for the DDS and HYD reaction routes to explain these results [101]. The orientation of the reaction toward one or the other of the two possible pathways is the consequence of the difference in reactivity of the common dihydro-intermediate in further hydrogenation or in C–S bond cleavage through elimination. It was supposed that by increasing the basic character of the sulfur anions, which is in accordance with accepted theories, the promoter enhances the rate of C–S bond cleavage through the elimination (E_2) mechanism. Consequently, this step which in the case of DBT is rate-limiting on MoS_2/Al_2O_3 becomes fast on promoted catalysts so that the DDS route becomes prominent. With 4,6-DMDBT, C–S bond cleavage in the common dihydro-intermediate remains relatively slow because of steric hindrance, which annihilates to a large extent the effect of the promoter on the HDS. The hindrance of the C–S bond cleavage in the partially hydrogenated intermediate could thus be the most likely reason for low reactivity of alkyl DBTs with alkyl substituent in the 4 and 6 positions.

The proposal of a common dihyro-dibenzothiophene intermediate for both DDS and HYD reaction pathways, which is based on the assumption that elimination is the only reaction responsible for C–S bond breaking is not accepted by some authors [31], who suggest that hydrogenolysis of the two C–S bonds in DBT is a clear alternative to elimination. It has been proposed by these authors that the two HDS pathways do not have a common intermediate and are determined by the conformation of the adsorbed DBT molecule. DDS occurs through σ adsorption of the DBT molecule via the sulfur atom, and HYD proceeds through π adsorption of the reactant via the aromatic system. This would require different sites and different adsorption constants for the DDS and HYD pathways. DFT calculations of different adsorption conformations of DBT derivatives indicated that the adsorption properties of the refractory DBT and 4,6-DMDBT molecules are very different from those of smaller model compounds such as thiophene and benzothiophene. The main reason for this difference is the aromaticity of the DBT structure, making π adsorption more likely than σ adsorption. It was shown that the methyl groups do indeed hinder the perpendicular σ adsorption of DBT but hardly affect the flat adsorption via the aromatic π system. It is suggested that in the HYD route, 1,2,3,4-tetrahydrothiophene is formed as a partially hydrogenated intermediate and the final removal of the sulfur from the tetrahydrothiophene could occur by hydrogenolysis (through σ adsorption). Thus, a similar mechanism of sulfur removal is involved in the DDS pathway and in the final step of HYD pathway. This is further supported by the finding that the final desulfurization of the hindered 4,6-DMDBT via HYD is substantially slower than that of DBT [31]. Therefore, the methyl groups suppress not only the σ adsorption of the reactant, but also of the partially hydrogenated intermediate. The DDS pathway is retarded to a great extent by the presence of the methyl groups than the sulfur removal via HYD pathway. This may be due to the lower flexibility in DBT and 4,6-DMDBT than in their partly hydrogenated intermediates, making adsorption easier for the latter molecules.

The hydrogenation pathway is, however; inhibited by organic nitrogen compounds present in the feed and by H_2S produced from desulfurization of sulfur compounds [25,36–38,104–106]. 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 the catalyst surface than sulfur species, they inhibit the HDS of the refractory sulfur compound via the hydrogenation route. Details of the inhibition effects on ultra deep HDS of diesel fuel are presented and discussed in Section 3.4.

Isomerization of the alkyl group present in the 4- and 6-positions of the DBT molecules to other positions away from the sulfur atom can reduce the steric hindrance and improve the reactivity of the refractory sulfur species through DDS route (Fig. 12b). Catalyst with acid function (e.g. zeolite) has been found to promote HDS of sterically hindered alkyl DBTs (4,6-DMDBT) through the isomerization route [93,101–103]. However, a careful balance between the acid and the hydrogenation/hydrogenolysis functions is important to obtain the optimum conversion of sulfur compound and stability of the catalyst.

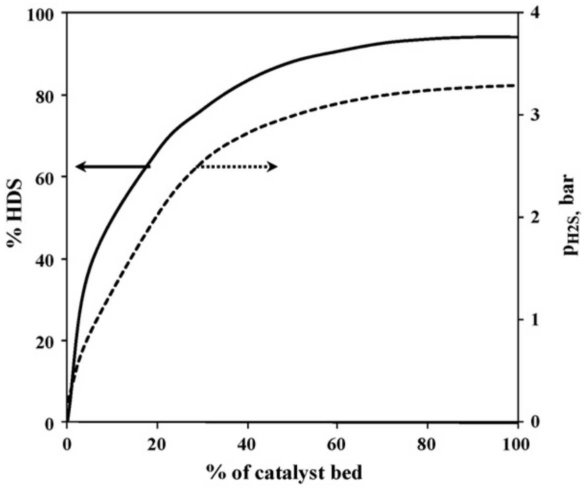


Fig. 13. HDS conversion and H_2S partial pressure profiles along with catalyst bed in the integral reactor [123a,123b].

3.4. Inhibition effects

For the production of ultra low sulfur diesel fuel (<10 ppm S) more than 99% of the sulfur compounds, including the traces of least reactive alkyl DBTs present in the feedstock should be removed during catalytic hydrotreating. The main problem in the HDS of the sterically hindered alkyl DBTs is the inhibiting effects of different poisons such as H_2S, N-containing compounds and aromatic molecules on their reactivity under deep desulfurization conditions. As discussed earlier (in Section 3.3) sulfur removal from DBT and alkyl substituted DBTs can take place along two distinct routes. The first route involves direct sulfur extraction while the second route involves two steps, hydrogenation of one of the aromatic rings in the first step followed by sulfur removal as H_2S in the second step. The poisoning effects of the inhibitors (H_2S, nitrogen compounds and aromatics) have been found to be different for the two routes in many studies [10,14,29,31,36,94,98,99,107–117]. Therefore a clear understanding of the influence of different inhibiting species on deep HDS of these substituted dibenzothiophenes is important for ULSD production. In general, the inhibition order is as follows: nitrogen compounds > organic sulfur compounds > polyaromatics ≈ oxygen compounds ≈ H_2S > monoaromatics. The inhibition is not only for HDS but also between inter- and intra-molecular reactions as well as its intermediate reaction products. Individual account of different inhibitors is given in the following sections.

3.4.1. Effect of H_2S

The effect of hydrogen disulfide (H_2S) on three different catalytic functionalities, namely, hydrogenolysis (HDS), hydrogenation (HYD) and acidity of the catalyst (isomerization and cracking function) has been investigated [10,118–122]. It is reported that these functionalities are not affected at similar magnitude with added H_2S or along the trickle bed integrated reactor. Usually in such reactor the organic sulfur is converted to H_2S, which generate high H_2S partial pressure along the reactor [123,124] as shown in Fig. 13. Having such amount of H_2S, it is expected that the coordinately unsaturated sites (CUS) (sulfur vacancy sites) in Mo are converted into saturated sites (sulfhydryl groups, –SH) [125–127]. Indeed H_2S is competitively adsorbed on the active sites that decreases the total number of available CUS sites, and convert CUS into –SH. Thus, sulfided catalysts are possessing two different kind of sites, in which one is CUS and other one is sulfhydryl groups, which enhance the hydrogenation activity along with the crack-

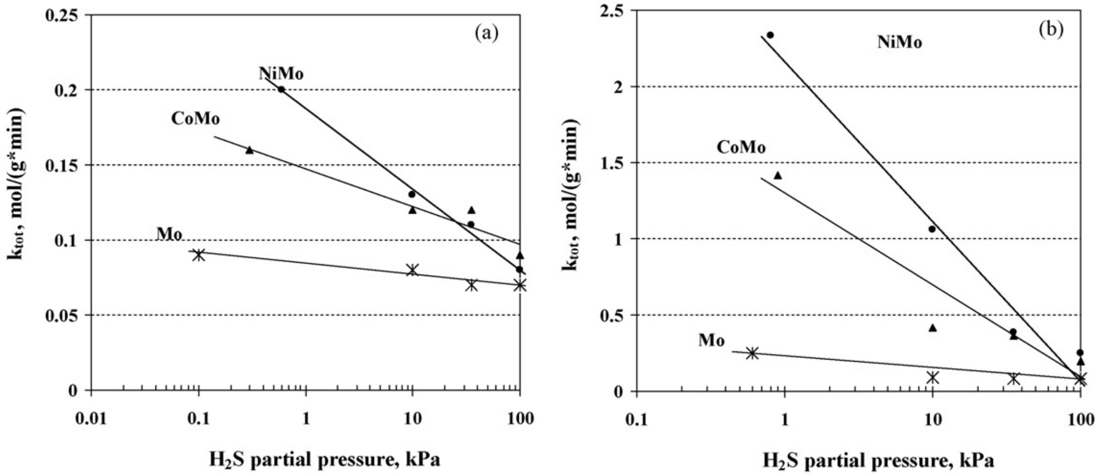


Fig. 14. Rate constants of the total conversion of 4,6-DMDBT (a) and DBT (b) over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts as function of H_2S partial pressures [31] (T = 340 °C; P = 4.8 MPa).

ing function by the presence of Brønsted acid sites. However, the acidic (Brønsted) nature of SH groups will depend on the electron affinity of a H^+ and metal–sulfide bond strength [128]. Thus, the sulfhydryl groups could act as Brønsted acid sites if the metal–sulfur bond strength is strong, while it acts as nucleophilic center if the metal–sulfur bond strength is weak. But the contribution of both has been suggested to be involved in the hydrotreating reactions, e.g., as a source of hydrogen or as an acid site [129–134].

Since H_2S is the byproduct of HDS reaction, its presence in a hydrotreating reactor is unavoidable. Moreover, at low partial pressures, H_2S also plays a beneficial role in maintaining the sulfided state of the CoMo and NiMo type hydrotreating catalysts used in the hydrotreating process. H_2S may in some cases (i.e. under specific conditions) enhance hydrogenation. This has been observed with HDS of DBT on MoS_2 and CoMo/Al_2O_3 catalysts [32,33]; and in the HDS of 4,6-DMDBT over NiMo/C [43,135]. This could result from an increase in the surface SH groups formed by H_2S dissociation on the CUS sites.

The inhibiting effect of H_2S on the HDS of DBT and alkyl DBTs (e.g. 4,6-DMDBT) have been investigated in many studies using different types of catalysts. The important observations made in these studies are the following:

- The inhibition effect of H_2S on the two main desulfurization routes of DBT type compounds is not the same. H_2S is a strong inhibitor for sulfur removal via DDS route, but only has a minor effect on HYD route [31,47,92,94,98,136–142].
- Sensitivities to H_2S poisoning are different for different types of catalysts. NiMo/Al_2O_3 catalyst is more susceptible to H_2S inhibition than CoMo/Al_2O_3 catalyst [22,31,135,142–145]. An example of this observation reported in a recent study by Egorova and Prins [31] is shown in Fig. 14a and b.
- The inhibiting effect of H_2S is less pronounced in the HDS of sterically hindered alkyl DBTs such as 4,6-DMDBT than the HDS of DBT as shown in Fig. 15. This has been confirmed by many other studies [43,47,94,98,137,139,146].
- H_2S partial pressure has a strong influence on the sensitivities of NiMo and CoMo catalysts to H_2S poisoning [139]. However, at very low partial pressure, H_2S has a promotional effect on HDS [147,148a] (Fig. 16).

Several theories have been proposed and discussed in the literature to explain the above results. Adsorption of H_2S in competition with the reactants on the active sites of the catalyst is generally suggested to be the reason for inhibition of HDS reaction by H_2S [147,148a,b,c]. The inhibition can be explained considering H_2 as

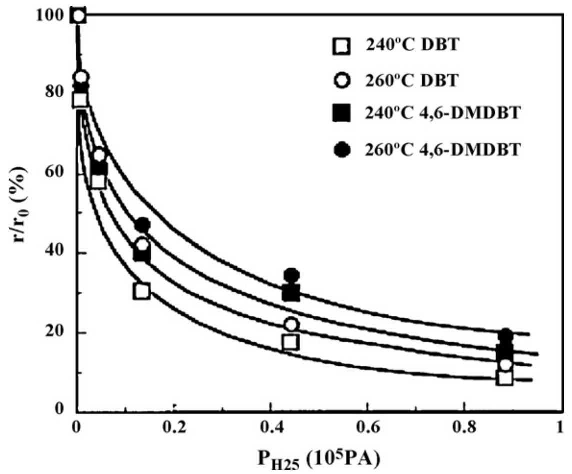


Fig. 15. Effects of H_2S partial pressure on HDS activities of DBTs on NiMo/Al_2O_3 [139] (P = 5 MPa).

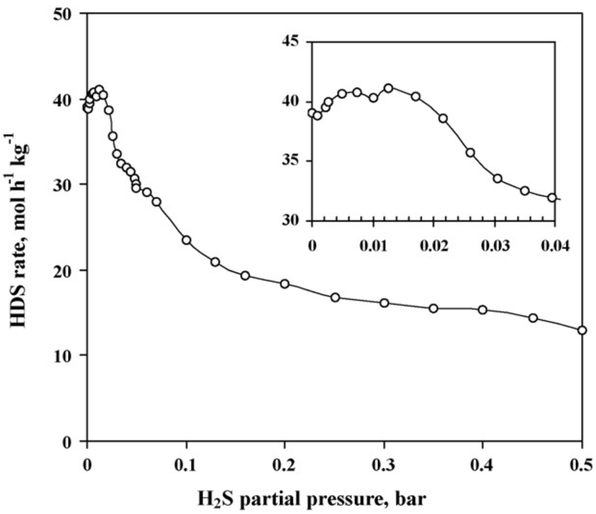


Fig. 16. Influence of H_2S on thiophene reaction (P_T = 0.08 bar) and HDS rate as a function of added H_2S over CoMo/Al_2O_3 at 400 °C and 1 bar [147].

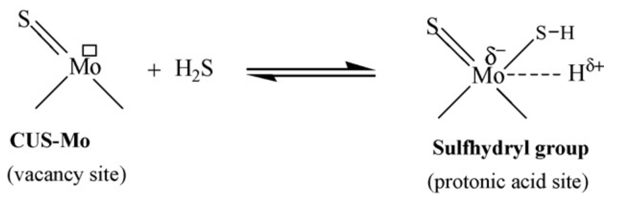


Fig. 17. Transformation in surface catalytic sites by the adsorption of H_2S [100].

well as H_2S heterolytic dissociation on sulfided catalyst surface, the dissociative species are $H^{\delta+}$, $H^{\delta-}$ and $SH^{\delta-}$ issued from H_2 and H_2S, which are competitively adsorbed with sulfur molecule on the surface of catalyst. Indeed, without H_2S, only H^+ and H^- species are formed by heterolytic dissociation of H_2 on catalyst surface, while in presence of H_2S the $H^{\delta+}$ to $H^{\delta-}$ ratio increases due to simultaneous heterolytic dissociation of H_2S into H^+ and SH^-. Therefore, evidently the inhibition mechanism depends on the H_2S and H_2 concentrations. Various authors [128,149,150] have suggested that hydrogenation sites on the catalyst surface is transformed into hydrogenolysis centers by the adsorption of H_2S as shown in Fig. 17, where anion vacancies are located at the edges of MoS_2 while weak acid protonic sites are generated due to dissociative adsorption of H_2S on the anionic vacancy sites.

The differences in the degree of inhibition observed between different catalysts (e.g. $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$), different types of sulfur compounds (e.g. DBT and 4,6-DMDBT), and between DDS and HYD pathways have been explained on the basis of different catalytic sites involved in DDS and HYD reactions, as well as based on the mode of adsorption of the reactants. Kabe et al. [139] suggested that H_2S was more strongly adsorbed on the DDS site than on the HYD site to explain the larger inhibition effect of H_2S on DBT than on 4,6-DMDBT. The mode of adsorption of the DBT and 4,6-DMDBT on the DDS and HYD sites has also been suggested to be different to explain the difference in the HDS reactivities. The DDS sites would adsorb the thiophenic sulfur compounds (e.g. DBT) vertically by σ-bonding through the sulfur atom [95,140], while the hydrogenation sites would adsorb such molecules horizontally by π-bonding through one of the aromatic rings [31,140].

While it is widely accepted that sulfur vacancies (CUS) in the sulfided CoMo and NiMo type hydrotreating catalyst are involved in DDS, the specific nature of the HYD sites is still a matter of debate. Some authors [12,151] have proposed that HYD sites are multiple vacancy sites on Mo edges capable of π-bonding the large molecules. The rim-edge model proposed by Daage and Chianelli [152] suggests that C–S bond cleavage (DDS) could occur both on the rim and edge sites of MoS_2 slabs while hydrogenation would occur exclusively on the rim sites where more room is available for flat adsorption. However, since the multiple vacancies will readily react with H_2S, the reactions involving such sites can be expected to be strongly inhibited by H_2S. Because, H_2S is not a significant poison for HYD, some other sites should be responsible for HYD. Recently, Moses et al. [153a] reported that the brim sites in MoS_2 slabs are involved in the hydrogenation reactions. The brim sites are fully sulfur coordinated Mo (1 0 1 0) edges of MoS_2 slabs with a metallic character. Since the Mo edge brim sites is a very open site, unlike the vacancy site it can adsorb DBT and other large sulfur containing molecules with aromatic structure (e.g. 4,6-DMDBT) horizontally through π-bonding without any steric constraint. The adsorption of H_2S will be negligibly weak at these sites which explain the week inhibition of the HYD pathway by H_2S. Interplay between the Mo edge brim site [HYD site] and the S edge vacancy site [DDS site] is considered to be important in this mechanism. The HYD pathway would be initiated by the hydrogenation of the DBT or 4,6-DMDBT, molecule at the Mo edge without steric hindrance, and the final removal of S from the hydrogenated intermediate would occur at the DDS site. This is consistent with the inhibition of the final steps of desulfurization by H_2S observed by Egorova and Prins [31].

In apparent contradiction with the above two-site mechanism, Rabarihoela-Rakotovao et al. [34] argue that the catalytic centers would be the same for both pathways but that the rate limiting steps of the latter would be different and therefore, their sensitivities to H_2S could be different. It is suggested that the rate-limiting step would be the addition of a hydrogen species for the HYD pathway and the beta-elimination of H_2S in the dihydrodimethyldibenzothiophene intermediate for the DDS pathway. This is consistent with the fact that the order with respect to hydrogen of the DDS pathway decreases significantly when the partial pressure of H_2S increases. The rate of the HYD pathway is expected to depend on the acidity of the SH group connected to the centre while the rate of the DDS pathway is expected to depend both on the basicity of the S^{2-} anion and on the Lewis acidity of the coordinatively unsaturated Mo atom. Consequently, the effect of H_2S could be different. For C–S bond cleavage where the sulfur anion is supposed to be directly involved through its basic properties, the effect of adsorbed H_2S is expected to be more significant.

3.4.2. *Effect of nitrogen compounds*

Several studies have shown that catalytic hydrodesulfurization reaction is significantly inhibited by organic nitrogen compounds [22,36,38,39,154–167]. It is generally suggested that there is competitive adsorption between nitrogen-containing compounds and sulfur containing compounds on catalyst's active sites, and nitrogen compounds inhibited HDS reactions because of their strong adsorptive strength. The extent of inhibition, however, depends on the type and concentration of organic nitrogen compounds. In straight run light gas oil feeds, typical nitrogen content is in the range 100–300 ppm. Cracked distillate feeds (e.g. LCO, CGO), usually contain higher nitrogen levels (>500 ppm). Reducing the nitrogen content of diesel feeds has been found to increase their HDS reactivity significantly [168,169].

Three types of nitrogen compounds are mainly present: non-heterocycles, heterocycles of 6 membered ring (6MR), and heterocycles of five membered ring (5MR). The non-heterocyclic nitrogen compounds such as anilines and aliphatic amines are not important as they undergo HDN quickly. Among the heterocyclic nitrogen compounds, 6MR pyridinic species (e.g. quinoline, acridine) are basic and 5MR pyrrole species (e.g. carbazole, indole) are non-basic or even acidic. Generally, the inhibiting effect of basic nitrogen compounds is the strongest [36,38,170–173]. Koltai et al. [171] compared the reaction rate of 4,6-DMDBT in the presence of acridine or carbazole on NiMo catalysts, using an autoclave. They found that the inhibiting effect on initial HDS activity by acridine was higher than by carbazole, due to its stronger adsorption.

Van Looij et al. [116] found that the HDS rate during deep desulfurization of SRGO feed was markedly reduced by trace amounts of basic nitrogen compounds (0–30 ppm) (Fig. 18). They did not study the effect of non-basic nitrogen compounds on the HDS rate. Knudsen et al. [105] found that although the non-basic nitrogen compounds (e.g. indole, carbazole) were the most abundant nitrogen-containing species in the diesel fuel, they were not major inhibiting species. Basic nitrogen compounds appeared to be the strongest inhibitors in the overall HDS process, affecting both hydrogenolysis and hydrogenation routes. Rabarihoela-Rakotovao et al. [174] investigated the effect of a basic nitrogen compound (acridine) and its main hydrogenated product, octahydroacridine (OHA), on the hydrodesulfurization of 4,6-DMDBT over a commercial $NiMoP/Al_2O_3$ catalyst under the conditions commonly used in the deep hydrotreating of diesel fuels. Their results showed that both pathways (HYD and DDS) involved in the HDS of 4,6-DMDBT were strongly inhibited as soon as a low concentration of acridine was introduced. However, a significant change in the relative con-

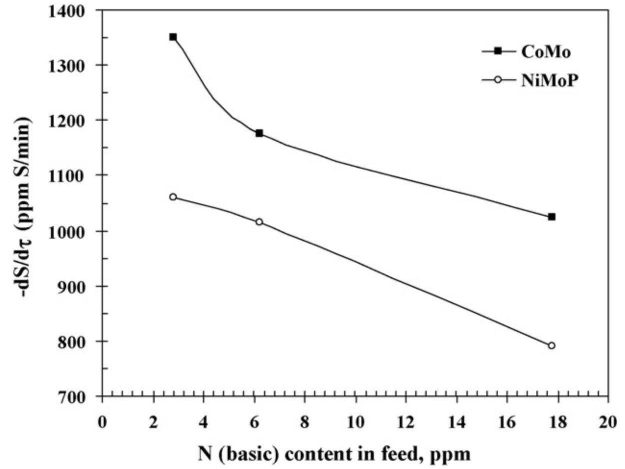


Fig. 18. The hydrodesulfurization rate of dibenzothiophene in a gas oil matrix as a function of the content of basic organo-nitrogen compounds [116].

tributions of the two pathways was found at higher concentrations of acridine. After reaching a minimum, the activity through the DDS pathway increased with increasing acridine concentration and with increasing total pressure while the activity through the HYD pathway remained constant at its low level. It was suggested that this promotion effect on the DDS pathway was due to a co-catalytic contribution of the nitrogen compound or of its hydrogenation products to the elimination process leading to C–S bond cleavage.

In another related study, these authors reported recently [39] that the effect of acridine was much more significant than the effect of 1,4-dimethyl dicarbazole (1,4-DMCARB) on the HDS of 4,6-DMDBT. The HDN of 1,4-DMCARB was found to be inhibited by acridine. In contrast to this, Ho [104,162] reported recently that non-basic nitrogen compounds such as carbazole and alkyl carbazoles are strong poisons to the HDS of refractory sulfur compounds over commercial HDS catalysts. The non-basic nitrogen compounds are transformed to strong basic nitrogen compounds by hydrogenation in a hydrotreating reactor, and play a dominant role, in the HDS of prehydrotreated distillates. They are also the predominant nitrogen species in cracked distillate diesel feeds (e.g. LCO) [175–178].

Egorova and Prins [112,179] examined the influence of 2-methyl pyridine (2-MPy) and 2-methyl piperidine (2-MPiper) on the HDS of DBT and 4,6-DMDBT. Both N-containing compounds strongly suppressed the HYD pathway of DBT than the DDS pathway. The inhibitory effect on the DDS pathway was larger for 2-MPy (Fig. 19). In the HDS of 4,6-DMDBT, both N-compounds had a strong inhibitory effect on both pathways and the effect of 2-MPiper was slightly stronger than that of 2-MPy (Fig. 20). The desulfurization of 4,6-dimethyl tetra-hydrodibenzothiophene, an intermediate in the hydrogenation pathway, was extremely difficult in the presence of N-containing molecules.

The susceptibility of different types of catalysts to poisoning by nitrogen compounds has been investigated in some studies. Sumbogo Murti et al. [172] compared the inhibition effect of nitrogen species in gas oil on staged hydrodesulfurization over Ni–Mo–S and Co–Mo–S/Al_2O_3 catalysts of variable activity and found significant differences in their propensity to poisoning by nitrogen species. Catalysts with strong acid sites suffered more HDS inhibition by nitrogen compounds. HDS of reactive sulfur species suffered less inhibition by nitrogen species than the HDS of refractory sulfur compounds. Satterfield and Cocchetto [180] studied the mutual influences of the HDS of thiophene and HDN of pyridine in the presence of sulfided CoMo/Al_2O_3, NiMo/Al_2O_3, NiW/Al_2O_3, and NiW/SiO_2–Al_2O_3 catalysts. Over all four catalysts pyridine inhibited the HDS reaction, whereas thiophene had a dual effect on HDN. At low temperatures thiophene inhibited the HDN reaction by competing with pyridine for hydrogenation sites and at high temperatures the dominant effect was an improvement of C–N bond cleavage by H_2S, the product of the HDS reaction. The enhancement of the HDN by H_2S was ascribed to the conservation of the catalyst in a completely sulfided state, in which it has a better HDN activity. Simultaneous hydrodesulfurization (HDS) of dibenzothiophene (DBT) and hydrodenitrogenation (HDN) of carbazole was carried out by Kagami et al. [173] in order to evaluate mutual inhibiting effects on NiMo catalysts in comparison to CoMo catalyst. Carbazole significantly inhibited not only both the direct desulfurization (DDS) and the hydrogenation (HYD) pathways in HDS of DBT, but also the HDN reaction itself. For HDS of DBT the HYD (pathway) was more strongly inhibited by carbazole than the DDS pathway. Tetrahydrocarbazole was added in order to evaluate the influence of the hydrogenation of carbazole that occurs simultaneously with HDS. Compared to carbazole, tetrahydrocarbazole retarded HDS of DBT more significantly, probably because of its stronger basicity. The NiMo type II high metal loading catalyst was inhibited the most by carbazole, probably related to its high HYD activity.

Egorova and Prins [181] compared the susceptibility of Mo/Al_2O_3, CoMo/Al_2O_3 and NiMo/Al_2O_3 to inhibition by basic nitrogen compounds such as 2-methyl pyridine and 2-methyl piperidine during HDS of DBT. The results showed that the NiMo catalyst is much less sensitive to poisoning by these nitrogen compounds than the Mo and CoMo catalysts (Fig. 21). At low

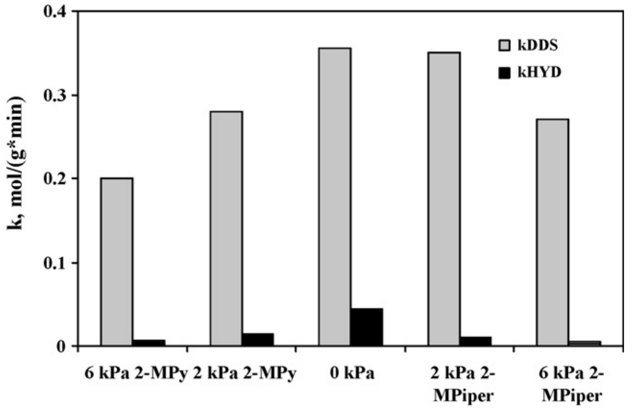


Fig. 19. Rate constants of the DDS and HYD pathways in the HDS of DBT in the presence of 2-MPy and 2-MPiper [179] ($T = 340\,^{\circ}C$; $P = 5$ MPa).

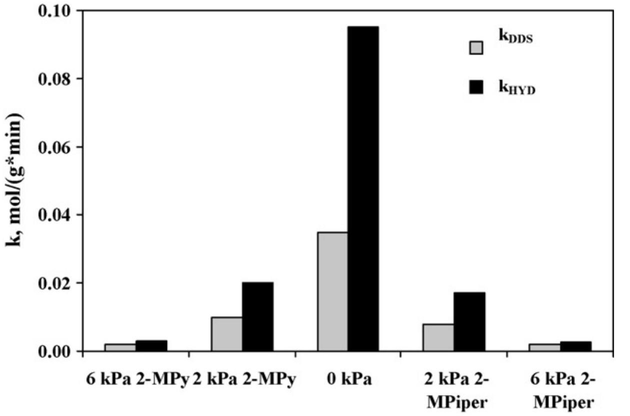


Fig. 20. Rate constants of the DDS and HYD pathways in the HDS of 4,6-DMDBT in the presence of 2-MPy and 2-MPiper [179] ($T = 340\,^{\circ}C$; $P = 5$ MPa).

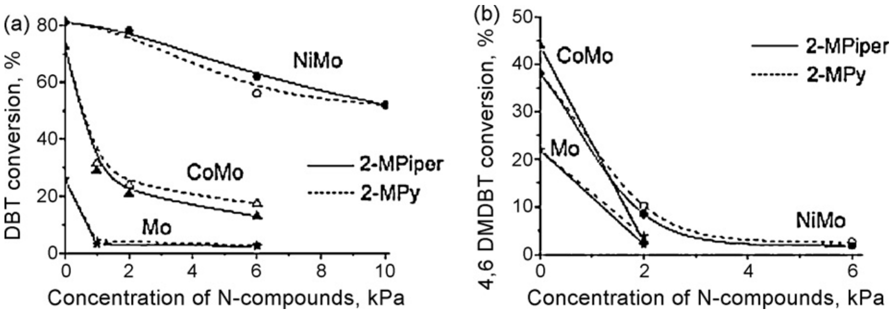


Fig. 21. Conversion of DBT (a) and 4,6-DMDBT (b) in the presence of 2-methylpyridine and 2-methylpiperidine over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 at $\tau = 4$ g min/mol; $T = 340$ °C; $P = 5$ MPa; $p_{H_2S} = 35$ kPa [181].

concentrations the nitrogen compounds even promoted the DDS pathway in the HDS of DBT over the NiMo catalysts.

Detailed studies by many research groups on the inhibition effect of model nitrogen compounds on DDS and HYD pathways of DBT HDS have clearly indicated that the HYD pathway is strong suppressed, whereas the DDS route is only moderately affected [36,104,112,179,182–185]. In some cases, the DDS route is enhanced even though the overall HDS decreased [182,183,186]. Studies of nitrogen inhibition with real feed also support this conclusion [36]. These results indicate that different sites are involved in HYD and DDS, and the HYD sites of the catalyst which convert the least reactive sterically hindered alkyl DBTs suffer more by poisoning by nitrogen compounds.

According to Egorova and Prins [181], geometric factors are held responsible for this inhibition. Amines adsorb in the σ mode through an interaction of their lone electron pair on the nitrogen atom with the catalyst surface. In their standing-up configuration, they hinder the flat π adsorption of the DBT and 4,6-DMDBT aromatic molecules and thus their hydrogenation. It is suggested that hydrogenation can occur over the whole edge surface on sites with and without sulfur vacancies. DDS sites, on the other hand, need vacancies. Consequently, vacancy sites are able to do hydrogenation as well as direct desulfurization, whereas fully covered sites can do only hydrogenation.

Topsøe and his coworkers [109,153] have suggested that the preferential binding of the nitrogen-containing compounds to the Mo edge brim sites (HYD sites) is responsible for the inhibition of the HYD pathway more than that of the DDS pathway. At these sites the basic nitrogen compounds such as pyridine can not only adsorb like aromatics but also can react with H^+ ions from neighboring –SH groups resulting in the formation of a pyridinium ion which adsorbs more strongly than pyridine. Thus, the inhibition of hydrogenation reaction by nitrogen compounds results not only from the blocking of the HYD site, but also from the decrease in the number of H atoms available for hydrogenation.

3.4.3. *Effect of aromatics content*

The middle distillate petroleum fraction (diesel stream) contains large amount of aromatic hydrocarbons, condensed naphtheno-aromatics and aromatic olefins along with sulfur- and nitrogen-containing compounds. The aromatic hydrocarbons consist of mono-, di-, and poly-nuclear aromatics. Depending on the origin of the feedstock, the total aromatics content of the diesel feed streams could vary in the range 25–75% [187]. For example, straight run gas oils usually contain 25–30% total aromatics, whereas the cracked distillates (e.g. LCO, CGO) contain significantly high concentrations of aromatics in the range 50–75%.

The influence of aromatic compounds on the hydrodesulfurization of diesel fuel has been investigated by many researchers [40,42,43,84,116,188–193]. Conflicting results have been reported in the literature regarding the inhibiting effect of aromatics on HDS. van Looij et al. [116] studied the effects of naphthalene, tetraline, crysene and pyrene on deep HDS of diesel and found that these poly-nuclear aromatics had negligible inhibitory effect on HDS. Koltai et al. [171] found a strong inhibiting effect of polycondensed aromatics on the HDS of 4,6-DMDBT. Aromatics were found to be much stronger inhibitors than H_2S in a study on the desulfurization of light gas oil (LGO) by Kabe et al. [193].

Inhibition effects of some model aromatic compounds on the HDS of 4,6-DMDBT were found to be in the following order: naphthalene > tetralin > isobutyl benzene as shown in Fig. 22. In a recent study on the influence of aromatics on deep HDS of DBT and 4,6-DMDBT over a NiMo/Al_2O_3 catalyst, Song et al. [41] reported that aromatics with 2 or more rings were stronger inhibitors of HDS than mono-aromatics. This adverse effect was more pronounced for 4,6-DMDBT than for DBT. The competitive adsorption between the sulfur compounds and aromatics on the catalyst surface was the main reason for the decreased HDS efficiency as quantitatively verified by the heat of adsorption. Poly-nuclear aromatics showed stronger inhibition effect compared to 1-methyl naphthalene. Isoda et al. [190] reported that 10% naphthalene severely retarded the HDS of 4,6-DMDBT on NiMo catalysts. Hydrogenation of naphthalene to tetralin was preferred to HDS of 4,6-DMDBT on this catalyst.

The inhibiting effect of aromatic compounds on different routes of HDS of DBT and 4,6-DMDBT has been examined in some studies [10,43,112,144,194]. Whitehurst observed that naphthalene inhibited all hydrogenation reactions, but had only a small effect on direct desulfurization [194]. In a study on the effect of naphthalene on HDS of 4,6-DMDBT, Lecrenay et al. [144] found that the

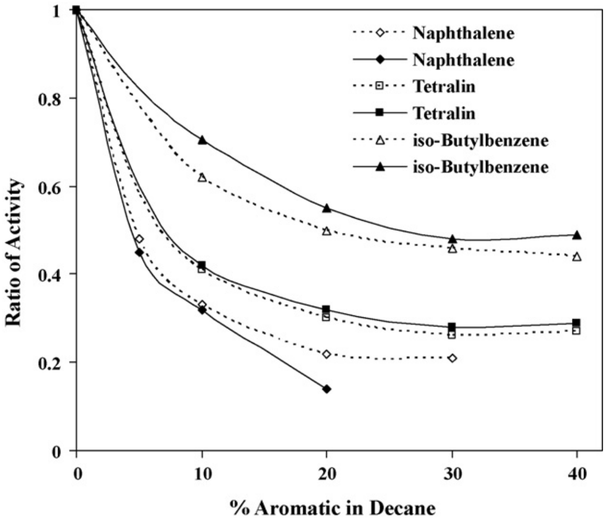


Fig. 22. Ratio of activity for HDS of 4,6-DMDBT in decane as a function of aromatic content over NiMo (solid line) CoMo (doted line) ($T = 270$–360 °C; $P = 2.4$–5 MPa) [192].

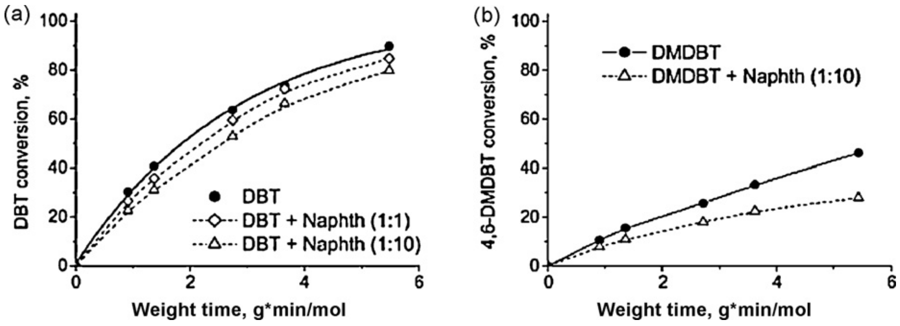


Fig. 23. Inhibition of the HDS of DBT (a) and 4,6-DMDBT (b) in the presence of naphthalene at 340 °C; P = 5 MPa [179].

hydrogenation route was more affected than the direct desulfurization route. On the other hand, only a slight decrease in the hydrogenation selectivity was observed by Farag et al. [43] during the HDS of 4,6-DMDBT in the presence of naphthalene. Steiner [42] found that naphthalene is a strong inhibitor of both DDS and HYD reaction pathways in DBT HDS, but the inhibition of the DDS route was much larger than that of the HYD route. Hydrogenation of naphthalene to tetralin was also observed in this study indicating the competition between DBT and naphthalene for the hydrogenation sites, which contradicts the observed increase in the selectivity for the hydrogenation route. In a recent study, Egorova and Prins [112] observed that the inhibitory effect of naphthalene was much larger in the HDS of 4,6-DMDBT than in the HDS of DBT (Fig. 23a and b). Both DDS and HYD pathways of the HDS of DBT and 4,6-DMDBT were affected to the same extent in the presence of naphthalene, and the hydrogenation of naphthalene was equally suppressed by DBT of 4,6-DMDBT. It was concluded that the hydrogenation of naphthalene takes place at both the DDS and the HYD sites. Moreover, it was assumed that the DDS and the HYD sites were the same and that the only factor, which determines the HDS pathway, is the adsorption conformation of the S-containing molecule. This conclusion however, contradicts with many other studies which indicate that HYD and DDS reactions occur on different sites [10,100,109,153,195]. Suppression of the hydrogenation route more than the DDS route by aromatic hydrocarbons has been reported in many studies [100,109,150], which indicates that the hydrogenation sites are different from the hydrogenolysis sites.

Preferential adsorption of the aromatic compounds on the HYD sites (Mo-edge brim sites) could be responsible for the selective inhibition of the HYD route in the HDS of DBT and alkyl DBTs. The π electrons in the aromatics ring can be polarized to be negatively charged, and adsorb strongly on the electron deficient sites of the catalyst. The differences in the observed inhibiting effects of different aromatic hydrocarbons could be related to the differences in their adsorption strength. The π electron density has been found to correlate well with hydrogenation rate [187]. The strong inhibition is due to the high electron density of aromatic species which leads to a strong adsorption on active sites. The inhibiting effect of aromatics on HDS is however, weaker than that of basic nitrogen compounds because of their lower adsorption coefficients compared to that of nitrogen species. The adsorption coefficient of organo-nitrogen species are usually several orders of magnitude higher compared to those of aromatic compounds [114,139].

3.5. Deep HDS kinetics

The kinetics of many individual sulfur compounds such as thiophene, benzothiophenes, dibenzothiophene and alkyl dibenzothiophenes have been studied in detail by many researchers. Langmuir–Hinshelwood type mechanistic kinetic equations, which assume various forms of competitive and non-competitive adsorption, have been developed for the HDS of these pure sulfur compounds. Vrinat [196] and Girgis and Gates [98] have reviewed the HDS kinetic expressions reported in the literature for various individual sulfur compounds. Some important kinetic equations reported [47,98,114,138,170,196–206] in the literature for the HDS of DBT are presented in Table 5.

Broderick and Gates [138] proposed separate Langmuir–Hinshelwood type rate equation for the hydrogenolysis and hydrogenation of DBT as shown in the following equations.

(i) Dibenzothiophene hydrogenolysis:

$$r = \frac{kK_{\mathrm{DBT}}K_{\mathrm{H_2}}C_{\mathrm{DBT}}C_{\mathrm{H_2}}}{(1 + K_{\mathrm{DBT}}C_{\mathrm{DBT}} + K_{\mathrm{H_2S}}C_{\mathrm{H_2S}})^2(1 + K_{\mathrm{H_2}}C_{\mathrm{H_2}})}$$

Table 5
Kinetic expression for middle distillate range of sulfur compounds [196–206].

Catalysts	Conditions	Ref.	Reaction expression
CoMo/alumina		[203]	$r_{\mathrm{HDS}} = k\frac{K_{\mathrm{DBT}}P_{\mathrm{DBT}}}{(1+K_{\mathrm{DBT}}P_{\mathrm{DBT}}+K_{\mathrm{PROD}}P_{\mathrm{PROD}})}\cdot\frac{K_{\mathrm{H_2}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{H_2}}P_{\mathrm{H_2}})}$
		[196a,196b,201]	$r_{\mathrm{HDS}} = \frac{k_{\mathrm{HDS}}K_{\mathrm{DBT}}K_{\mathrm{H_2}}P_{\mathrm{DBT}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{DBT}}P_{\mathrm{DBT}}+K_{\mathrm{H_2S}}P_{\mathrm{H_2S}})(1+K_{\mathrm{H_2}}P_{\mathrm{H_2}})}$
CoMo/alumina	200–240 °C	[202]	$r_{\mathrm{HDS}} = k\frac{K_{\mathrm{DBT}}P_{\mathrm{DBT}}}{(1+K_{\mathrm{DBT}}P_{\mathrm{DBT}}+K_{\mathrm{H_2S}}P_{\mathrm{H_2S}})^2}\cdot\frac{K_{\mathrm{H_2}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{H_2}}P_{\mathrm{H_2}})}$
CoMo/alumina	275–325 °C, 7–26 bar	[138]	$r_{\mathrm{HDS}} = k\frac{K_{\mathrm{DBT}}P_{\mathrm{DBT}}}{(1+K_{\mathrm{DBT}}P_{\mathrm{DBT}}+K_{\mathrm{H_2S}}P_{\mathrm{H_2S}})^2}\cdot\frac{K_{\mathrm{H_2}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{H_2}}P_{\mathrm{H_2}})}$
NiMo type II	350 °C, 50 bar	[98,204]	$r_{\mathrm{HDS}} = \frac{k'_{\mathrm{DDS}}C_{DBT}}{(1+K'_{\mathrm{DDS,N}}C_{\mathrm{CZ}}+K'_{\mathrm{DDS,N}}C_{\mathrm{TC}})} + \frac{k'_{\mathrm{HG}}C_{\mathrm{DBT}}}{(1+k'_{\mathrm{HG,N}}C_{\mathrm{CZ}}+K'_{\mathrm{HG,N}}C_{\mathrm{TC}})}$
CoMo/alumina (monolith)	270–300 °C, 60–80 bar	[197]	$-r_{\mathrm{DBT}} = \frac{kK_{\mathrm{DBT}}K_{\mathrm{H_2}}C_{\mathrm{DBT}}C_{\mathrm{H_2}}}{(1+K_{\mathrm{DBT}}C_{\mathrm{DBT}}+K_{\mathrm{H_2}}C_{\mathrm{H_2}}+K_{\mathrm{H_2S}}C_{\mathrm{H_2S}})^2}$
CoMo/alumina	240–30 °C, 50–80 bar	[198,199]	$-r_{\mathrm{DBT}} = \frac{kK_{\mathrm{DBT}}K_{\mathrm{H_2}}C_{\mathrm{DBT}}C_{\mathrm{H_2}}}{(1+K_{\mathrm{DBT}}C_{\mathrm{DBT}}+K_{\mathrm{H_2S}}C_{\mathrm{H_2S}}(1+K_{\mathrm{H_2}}C_{\mathrm{H_2}})^{0.5})^3}$
CoMo/alumina	Hexadecane, 280–320 °C, 53 bar	[114,170]	$r_{\mathrm{HDS}} = \frac{K_{\mathrm{DBT}}C_{\mathrm{DBT}}}{1+\Sigma(K_iC_i)^{ni}}$

(ii) Dibenzothiophene hydrogenation:

$$r = \frac{k' K'_{\mathrm{DBT}} K'_{\mathrm{H_2}} C_{\mathrm{DBT}} C_{\mathrm{H_2}}}{1 + K'_{\mathrm{DBT}} C_{\mathrm{DBT}}}$$

where DBT represents dibenzothiophene, k the rate constant for dibenzothiophene hydrogenolysis (mol/(g of catalyst s^{-1})), K_{DBT} the adsorption parameter for DBT (atm^{-1}), C_{DBT} the coverage of DBT on catalyst surface, $C_{\mathrm{H_2}}$ the coverage of H_2 on catalyst surface, $K_{\mathrm{H_2S}}$ the adsorption parameter for H_2S (atm^{-1}), $C_{\mathrm{H_2S}}$ the coverage of H_2S on the catalyst surface, k' the rate constant for DBT hydrogenation (mol/(g of catalyst s^{-1})), K'_{DBT} the adsorption parameter for DBT in DBT hydrogenation (atm^{-1}), and $K'_{\mathrm{H_2}}$ the adsorption parameter for H_2 in DBT hydrogenation (atm^{-1}).

It has been suggested that kinetic expression for the overall HDS rate of alkyl DBTs should be expressed by as a sum of two rate equations as shown below.

$$\gamma_{\mathrm{HDS}} = k \frac{K_{\mathrm{DBT}} P_{\mathrm{DBT}}}{1 + K_{\mathrm{DBT}} P_{\mathrm{DBT}} + K_{\mathrm{H_2S}} P_{\mathrm{H_2S}}} \cdot \frac{K_{\mathrm{H_2}} P_{\mathrm{H_2}}}{1 + K_{\mathrm{H_2}} P_{\mathrm{H_2}}} + k_2 \frac{P_{\mathrm{DBT}} P_{\mathrm{H_2}}}{1 + K_{\mathrm{DBT}} P_{\mathrm{DBT}}}$$

The first term in the above equation represents the rate of direct HDS and the second term represents the rate of HDS through the hydrogenation route, k_1 and k_2 are the HDS rate constants for the two routes, respectively. In a recent study by Chen et al. [207], the two-route kinetic model was found to describe satisfactorily the HDS of refractory alkyl DBTs present in LCO, particularly at high temperatures.

A dual site Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic model (molecular based kinetic model) shown in the following rate equation was proposed by Hou and Klein [199b] to take into account the inhibition of various compounds in the process stream (especially the H_2S inhibition at the σ site for direct desulfurization). The surface reaction step between adsorbed reactants and two competitively adsorbed hydrogen atoms is the rate determining step for both types of reactions.

$$r = \frac{f k K_{A,\sigma} K_{H,\sigma} [A][\mathrm{H_2}]}{\left(1 + \sum_i K_{i,\sigma}[I] + \sqrt{K_{H,\sigma}[\mathrm{H_2}]}\right)^n} + \frac{f_\tau k_\tau K_{A,\tau} K_{H,\tau} ([A][\mathrm{H_2}] - [B]/K)}{\left(1 + \sum_i K_{i,\tau}[I] + \sqrt{K_{H,\tau}[\mathrm{H_2}]}\right)^n}$$

where r is reaction rate, $[I]$ is concentration of component, k is the rate constant, K_i is adsorption constant of component, K is equilibrium constant and n is the exponent of inhibition term. The two global factors (f_σ and f_τ) are introduced to account for the total steric and electronic effects of substituents on thiophenic compounds at both σ (DDS) and τ (HYD) sites.

From practical point of view, when a model compound feed is used, the value of kinetic data is limited because mutual effects of various components of real feeds cannot be identified. Kinetic data on the HDS of real industrial diesel feedstocks under deep HDS conditions is important to have a clear understanding of the mechanism of HDS reactions occurring through different pathways, and to develop suitable kinetic expressions that can be used to predict the effect of process variables such as LHSV, temperature, hydrogen partial pressure, H_2S partial pressure, etc., on catalyst activity.

HDS kinetics of industrial diesel feeds is, however, very complex. The HDS kinetics of various aromatic sulfur compounds were modeled by a structural contribution approach in some studies [199,205,208]. This approach is highly complex because of the need for estimation of a large number of kinetics parameters, even after model simplification. The use of LHHW type of mechanistic rate equations to describe the HDS kinetics of diesel feeds is very difficult and impractical due to the presence of a wide variety of sulfur compounds with different reactivities. For industrial diesel feeds, a simple power-form equation of the type as given below, which relates total sulfur concentration of the feed to the HDS reaction rate, is frequently used to fit kinetic data and obtain kinetic parameters.

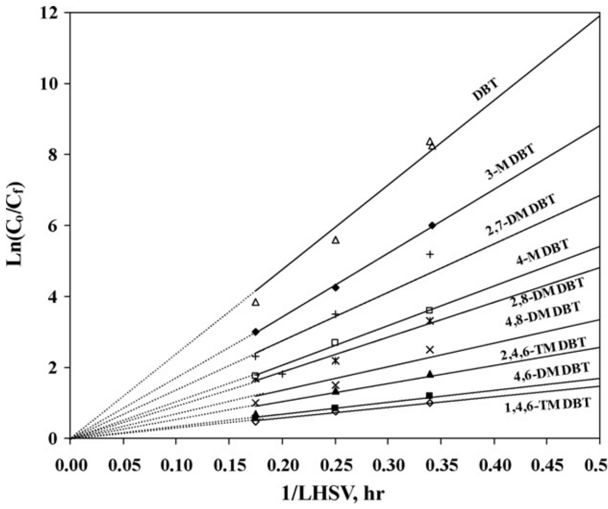


Fig. 24. First-order plot for some important alkyl-substituted dibenzothiophenes in the HDS process [21]. (Catalyst: $CoMo/Al_2O_3$; $T = 340\,^\circ C$; $P = 3$ MPa; $H_2/HC = 200$ mL/mL.)

$$\gamma_{\mathrm{HDS}} = k c_s^n$$

where k is the reaction rate constant, c_s is the initial concentration of total sulfur in the feed, and n is the order of the reaction. Fractional reaction orders in the range 1.4–1.7 have been reported by many researchers for conventional desulfurization of gas oils [209–212]. Conflicting reports have been found in the literature on the apparent reaction order and activation energy for the HDS of diesel streams under the deep desulfurization conditions. Thus, for example, Reinhoudt et al. [213] found second order kinetics for deep desulfurization of SRGO over a NiMo/γ-Al_2O_3 catalyst to reduce the total sulfur content of the product well below 150 wppm. On the other hand, Bacaud et al. [214] reported a kinetic order of 1.61 for deep desulfurization of a SRGO to less than 300 wppm sulfur in the product over a $CoMo/Al_2O_3$ catalyst. These researchers also determined the apparent kinetic order for the HDS of different groups of sulfur compounds such as alkyl benzothiophenes (e.g. C3-BTs; C4-BTs) and alkyl dibenzothiophenes (e.g. C1-DBTs; C2-DBTs; C3+-DBTs) in the SRGO and found a higher order ($n = 1.57$) for the C3+-DBTs than the other groups, which all showed $n = 1.2$.

Andari et al. [21] used a commercial $CoMo/Al_2O_3$ catalyst and fixed bed reactor (300–380 °C; 2–6 MPa; LHSV of 2–6 h^{-1}) to study kinetics of the deep HDS of a diesel feed. The HDS of the individual S-containing compounds identified in the feed exhibited first order kinetics as it is shown in Fig. 24. In this case, the first order kinetic expression, i.e.,

$$\ln\left(\frac{C_0}{C}\right) = \frac{k}{\mathrm{LHSV}}$$

was applied. In this expression, Co and C were the initial sulfur concentration and concentration at a given LHSV (or contact time), respectively. It is evident that dimethyl substitution in 4,6-positions of DBT had the most adverse effect on the overall HDS. In the same study [21], the conventional nth order kinetic expression

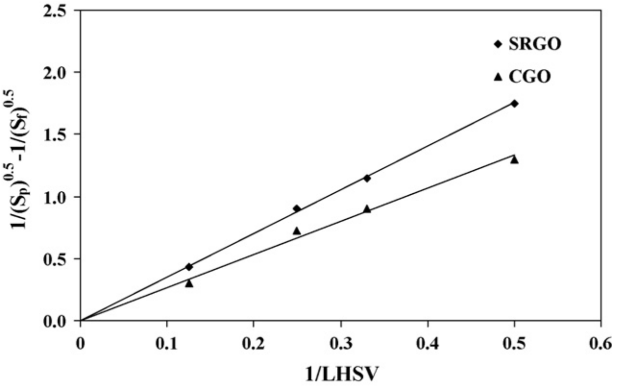


Fig. 25. 1.5-order plot of kinetic data for HDS of SRGO and CGO at 340 °C [446]. (Catalyst: $CoMo/Al_2O_3$; $T = 340$ °C; $P = 3$ MPa; $H_2/HC = 200$ mL/mL.)

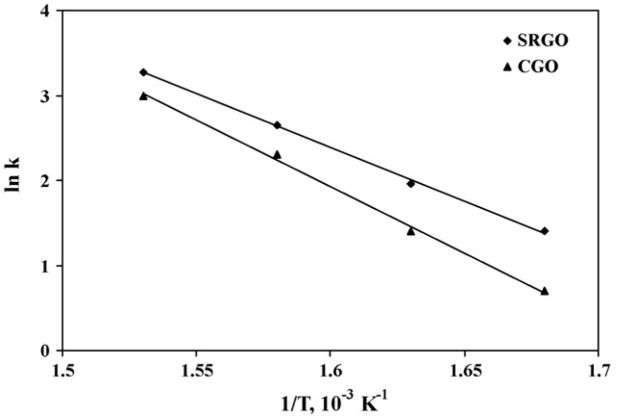


Fig. 26. Arrhenius plot for sulfur removal from straight run gas oil (SRGO) and coker gas oil (CGO) [446]. (Catalyst: $CoMo/Al_2O_3$; $P = 3$ MPa; $H_2/HC = 200$ mL/mL.)

such as:

$$K = \frac{\text{LHSV}}{(n-1)}\left\{\frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}}\right\}$$

was used to fit the experimental data for the overall HDS. Besides usual terms, S_p and S_f represent sulfur concentrations in products and feed, respectively. The best fit of data was obtained for 1.5 order kinetics. Under identical conditions, two feeds such as SRGO and CGO were compared by Al-Barood and Stanislaus [83]. For both feeds 1.5 order kinetics gave the best fit of experimental data (Fig. 25). Ancheyta [209,210] observed that the order increased from 1.7 to almost 2.0 with the increasing content of sulfur and average molecular weight of the feed. The apparent overall reaction orders higher than 1 observed for real industrial diesel feeds corresponds to the summation of several first order reactions with different rates related to the reactivity of individual sulfur compounds in each family of sulfur compounds. The overall reaction order will be expected to be close to 1 after a relatively deep desulfurization. Since the feedstock will contain only the least reactive sterically hindered alkyl DBTs. However, Sie [215a] found that even at total sulfur concentrations well below 150 wppm, the overall HDS reaction can still be described by a second order rate equation. This indicates clearly that the differences in the HDS reaction rates of the remaining individual sulfur compounds are still sufficiently large enough to result in second order kinetics. It is also likely that the inhibitors play an increasing role in the HDS kinetics under deep HDS conditions.

Some discrepancies in reported values of activation energies for HDS have been noted. Apparent activation energy values reported in the literature for sulfur removal from diesel feeds vary from 14 to 41 kcal/mole, depending on the nature of feedstock, catalyst type, and reaction order [210]. Lower apparent activation energies were observed for HDS of SRGO-LCO blends compared to that of pure SRGO [209]. Al-Barood and Stanislaus [83] reported a higher activation energy (30 kcal/mole) for the HDS of coker gas oil compared to that of pure SRGO (24 kcal/mole). There might be other parameters (e.g. inhibiting effects) which contribute to the observed differences. The effect of feed origin is evident in Fig. 26.

Ho [215b] compared kinetics of hydroprocessing using a plug-flow reactor (PFR) with CSTR system. The total concentration of all reactants (e.g. total sulfur) could be approximated by the following expressions:

$$C(t) = \int_0^\infty c_f(k)\exp(-kt)dk \quad \text{for PFR}$$

where $C(t)$ and c_f are the total concentration and the concentration of individual S-containing components at time t, respectively, whereas $c_f(k)dk$ is the concentration of compounds with rate constants between k and $k + dk$. Then, $c_f(k)$ represents the distribution of individual species in the feed which approaches zero at $k \to \infty$. To distinguish among reactivities of components, Ho [215b] introduced a gamma function, i.e., $\Gamma(\gamma)$. Thus, for $\gamma = 1$, $c_f(k)$ has an exponential distribution meaning that feed consists predominantly of unreactive components. On the other hand, for $\gamma > 1$ the function is monomodal and the feed comprises very reactive components. For PFR, an overall aggregated kinetics $R(C)$ of a mixture can be expressed by the power low with overall order n higher than 1, i.e.,

$$\frac{dC}{dt} = R(C) = -k'Cn$$

where k' is rate constant for overall kinetics, while k for kinetics of individual species in the feed. The $C(t)$ expression for CSTR system differs from that for PFR system, e.g.

$$C(t) = \int_0^\infty \frac{c_f(k)dk}{1+kt} \quad \text{for CSTR}$$

For the former system, $R(C)$ cannot be found for γ feeds. This problem may be overcome by assuming an asymptotic kinetics $R_a(C)$ in which C is governed by the most refractory S-compounds. Table 6 compares $R_a(C)$ concentration dependencies in PFR with those in CSTR for different γ values. It is evident that the order for PFR systems is higher than that in CSTR systems. For the same feeds, the performance of PFR can be predicted from CSTR data and vice versa.

The above examples show that kinetics of the hydroprocessing reactions of distillate feeds exhibit many peculiarities. For HDS reactions, these peculiarities were summarized by Ho [215b] as follows:

1. The reaction order for overall HDS of a distillate feed is higher than that of the individual S-containing compounds present in the feeds.
2. High-activity catalysts show lower overall order than low-activity catalysts.
3. Difficult feed show a higher order than easy feeds.
4. The overall HDS order decreases with increasing temperature.
5. The overall order depends on reactor type.

Table 6
Asymptotic kinetic expression for PFR and CSTR [215b].

PFR		CSTR		
	$\gamma > 0$	$\gamma > 1$	$\gamma < 1$	$\gamma = 1$
R_a α	$C^{1+1/\gamma}$	C	$C^{1/\gamma}$	$C/\lvert\ln C\rvert$

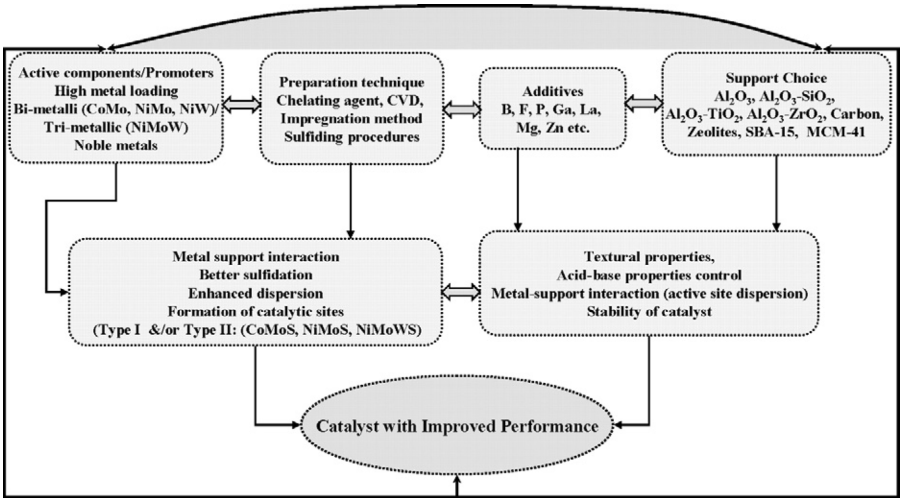


Fig. 27. Catalyst components and their key role to the hydroprocessing catalyst: a concept of acid–base supported catalyst.

Knudsen et al. [22] found that the following kinetic expression could be used to describe the deep desulfurization kinetics of diesel over CoMo and NiMo catalysts.

$$\frac{-dC_s}{dt} = \frac{K_D C_S^n P_{\mathrm{H_2}}^{\alpha}}{(1 + K_{\mathrm{H_2S}}.P_{\mathrm{H_2S}})} + \frac{k_H.C_S^m.P_{\mathrm{H_2}}^{\beta}}{(1 + K_F.C_F)}$$

In this expression for the rate of desulfurization ($-dC_s/dt$), the first term represents the direct desulfurization route, which is enhanced by an increase of the hydrogen partial pressure and inhibited by the presence of H_2S. The second term represents the hydrogenation route, which is also enhanced by an increase of the hydrogen partial pressure and inhibited by the presence of aromatic compounds, and in particular heterocyclic compounds (denoted by F in the equation).

For CoMo catalysts, which favors direct desulfurization route, the second term can to a good approximation be neglected, and the rate constant, k, can be determined by integration of the expression. The partial pressure of hydrogen sulfide, $P_{\mathrm{H_2S}}$, can be expressed in terms of the sulfur concentration, C_s, which means that an explicit expression can be obtained for k. The rate constant is a function of catalyst type, temperature and feedstock. For NiMo catalysts both terms are important, and the removal of the inhibitors has to be solved simultaneously in the rate equation. A plot of the measured product sulfur concentration obtained under different operating conditions versus the predicted product sulfur based on the above kinetic model showed reasonably good agreement between the measured and predicted values of sulfur concentrations down to low levels.

4. Catalyst development for deep HDS

Catalysts play an important role in the purification of various petroleum streams including diesel feedstocks by hydrotreatment to produce clean fuels. Catalysts consisting of molybdenum supported on γ-alumina and promoted with cobalt or nickel are traditionally used in the hydrotreating processes. The role of the catalyst is to enhance the removal of sulfur, nitrogen and other undesirable contaminants present in the refinery streams by promoting hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD) reactions. Conventional CoMo and NiMo based catalysts, however, do not have sufficient activity to desulfurize diesel feed streams to ultra low sulfur levels under normal operating conditions. They require severe operating conditions such as high temperature, low space velocity and high hydrogen partial pressure. Such severe processing conditions generally lead to rapid catalyst deactivation, shorter cycle lengths and reduced throughput. The development and application of more active and stable catalysts are among the most desired options for reducing the sulfur content of diesel to ultra low levels by deep desulfurization [22,216–220].

Studies have been shown that about 4 times more active catalysts are required to reduce the sulfur content of diesel fuel from 500 to 50 ppm [22]. Further improvement in catalyst activity is necessary when the sulfur content is to be reduced to ultra low levels (<15 ppm). Intensive efforts have been devoted by catalyst scientists worldwide to develop highly active hydrotreating catalysts for deep desulfurization of diesel to ultralow sulfur levels [14,18,22,221–238], and new generation catalysts with very high HDS activity are being continuously developed and introduced in the market by major catalyst companies [239–247].

Development of improved hydrotreating catalysts has been possible through a clear understanding of the key properties, namely, nature of the active sites and their structure, support effects and the textural characteristics of supports, that have significant influence on the catalysts performance [16,17,20,100,225,248–254]. The scientific basis for the high activity of the new generation hydrotreating catalysts is presented and discussed in detail in the following sections.

4.1. Catalyst components

Hydroprocessing catalysts have mainly two components, namely, support and active metals. Alumina is the most widely used support for hydroprocessing catalysts, but many other supports based on mixed oxides and zeolites have been developed in recent years [20,100,101,255,256]. A general classification of a hydroprocessing catalyst component and their key parameters is shown in Fig. 27.

4.2. Nature of active phase

The nature of active sites (or active phases) in unpromoted and promoted MoS_2 catalysts have been widely studied and reported in several reviews [16,100,251–261]. For unpromoted molybdenum sulfide catalysts, it has been proposed that the coordinatively unsaturated (CUS) sites or exposed Mo ions with sulfur vacancies at the edges and corners of MoS_2 structures are active in hydrogenation and hydrogenolysis reactions. Basal planes are inactive in adsorption of molecules and are probably unimportant in hydrotreating reactions. For Co- or Ni-promoted catalysts, several different structural models such as monolayer model, intercalation model, contact synergy model, Co–Mo–S (or Ni–Mo–S) phase model, and catalytic Co site model have been proposed to explain the role of the promoter and its location in the catalyst. Among these, the Co–Mo–S (or Ni–Mo–S) phase model proposed by Topsøe et al. [100,248,258] has been widely accepted at present.

The building blocks of Co–Mo–S (or Ni–Mo–S) structures are small MoS_2 nano-crystals with the Co (or Ni) promoter atoms located at the edges of the MoS_2 layers in the same plane of Mo atoms. The relative amount of Co atom present as Co–Mo–S phase was found to correlate linearly with HDS activity. Further studies on the structure–activity correlation of these catalyst systems led to the identification of two types of Co–Mo–S structures, one type exhibiting substantially higher activity than the other. The high and low activity forms of Co–Mo–S were termed types II and I Co–Mo–S, respectively. The type I Co–Mo–S structures were proposed to be incompletely sulfided and have some remaining Mo–O–Al linkages to the support. The presence of such linkages was related to the interaction which occurs in the calcined state between Mo and surface alumina OH groups leading to oxygen bridged monolayer type structures that are difficult to sulfide completely. Several subsequent studies have provided evidence for the existence of Mo–O–Al linkages in type I structures.

In type II Co–Mo–S or (Ni–Mo–S) phases, the support interactions are weaker and they are fully sulfided (i.e. have higher sulfur coordination of Mo and Co or Ni). The underlying MoS_2 in Type II Co–Mo–S phases are less disperse, consisting of multiple slabs not linked with the support. Further studies have shown that the degree of staking in MoS_2 and Co–Mo–S structures can be controlled by carefully controlling support properties and preparation parameters and the formation of small stable single slabs of MoS_2 on alumina supports have been achieved [262,263]. These will have a high MoS_2 edge dispersion which can accommodate more Co atoms to form higher active single slab type II Co–Mo–S structures. More recently Okamoto et al. [264,265] reported the formation of a third type of Co–Mo–S phase (Co–Mo–S Type III) with high intrinsic HDS activity when a SiO_2-supported CoMo catalyst was sulfided with 10% H_2/He. The structure of this phase (Co–Mo–S type III) was suggested to consist of dinuclear Co sulfide cluster with S-dimer between two Co atoms and situated on the Mo-edge of MoS_2 particles.

4.2.1. *Origin of synergy between Co(Ni) and Mo*

Daage and Chianelli [152] initially developed a model correlating stacking degree, and selectivity properties for non-promoted and non-supported MoS_2 catalysts. Two types of sites were distinguished based on their location on the layers: the "rim" sites on the top and bottom layers able to hydrogenate and to cleave C–S bonds, and the "edge" sites located at the outer edges of interior layers able only to cleave C–S bonds. The specific location of "rim" sites on exterior layers is responsible for their hydrogenating character by making possible the η^6 flat adsorption of dibenzothiophene (DBT), a requirement for the hydrogenation step [266].

In a recent study by Berhault et al. [267], it was shown that cobalt promoter strongly enhanced the stacking height of MoS_2 layers, and however, this effect was counter balanced by hydrodesulfurization conditions leading to the formation of single slabs. Single slab morphology suggests that the vast majority of the sites on MoS_2 layers are "rim" sites able to perform both hydrogenation and C–S bond cleavage steps. Regarding the HYD and DDS pathways of the hydrodesulfurization of DBT, it was shown that cobalt promotion enhances strongly the quality of the sites involved in C–S bond cleavage steps. Only, a very moderate effect of the promoter was observed for hydrogenation sites.

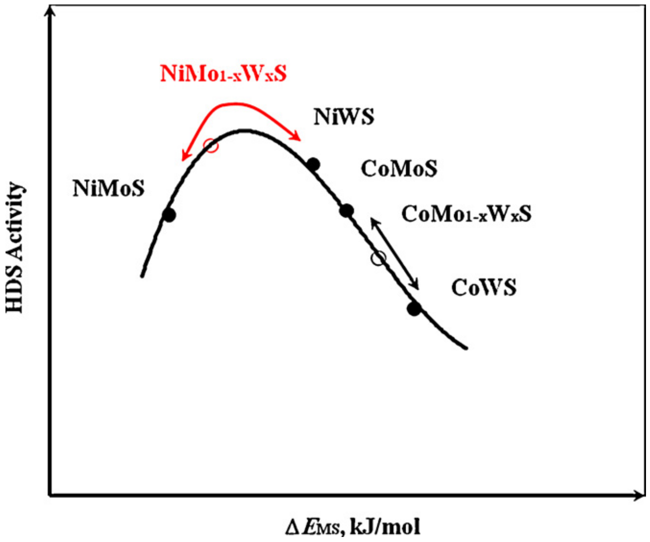


Fig. 28. Schematic representation of the relative positions of the Co(Ni)MoWS systems on the volcano curve and explanation of the new synergy effects for NiMoWS systems (DE_{MS}, energy variation associated to a catalytic system) [225].

Following the identification of Co–Mo–S phase structures as the catalytically active phase by Topsøe et al. [14,100,248], many theories were proposed to explain the electronic origin of synergy between Co and Mo in the Co–Mo–S phase in enhancing HDS reaction. Norskov et al., approached the problem using *ab-initio* calculations [268]. Their basic idea was that the binding energy of a sulfur atom was the important variable in explaining the periodic trends and the promoted systems. They found a monotonic relation between sulfur bond strength per sulfur atom and the catalytic specific activity of the sulfides using literature data. The weaker the metal sulfur bond strength, the higher the HDS activity. Consequently, the HDS rate would be proportional to the number of active sites (i.e. sulfur vacancies) at the catalyst surface, which in turn will be inversely proportional to the metal–sulfur bond strength. Harris and Chianelli [269] proposed that the specific and unique activity of the cobalt (or nickel) promoted MoS_2 phase is related to an electron donation from Co to Mo decreasing the Mo-S bond strength to an optimum range for HDS activity. This explanation was based on previous results obtained by Pecoraro and Chianelli [270] using the Sabatier principle. These electron donations will increase the number of electrons in the highest occupied molecular orbital (HOMO) of Mo, occupying antibonding orbitals and then somewhat weakening the Mo–S bond energy. It should be underlined that this electron transfer will also decrease the occupancy of anti-bonding orbitals for Co, strengthening the Co–S bond. A sulfur atom shared between Co and Mo will then present intermediate metal–sulfur bond strength. It was then assumed that this intermediate strength would be at optimum range for HDS activity according to the Sabatier principle interpretation of periodic trends.

This weakening effect of the cobalt promotion on the metal–sulfur bond strength is now well accepted and was confirmed using theoretical calculations as well as experimental techniques [271–276]. For example, Thomazeau et al. [225] demonstrated both by DFT-volcano curve predication based on sulfur bond energy calculation and experimental work that Ni promoted MoW sulfide (NiMoWS) catalysts are better than conventional Ni–W–S, Ni–Mo–S and Co–Mo–S catalysts as shown in Fig. 28.

Further insight into atomic structure, morphology of MoS_2, Co–Mo–S, and Ni–Mo–S phases were obtained by Topsøe and coworkers using a combination of advanced experimental and theoretical techniques like scanning tunnelling microscopy (STM), high-angle annular dark-field scanning transmission electron

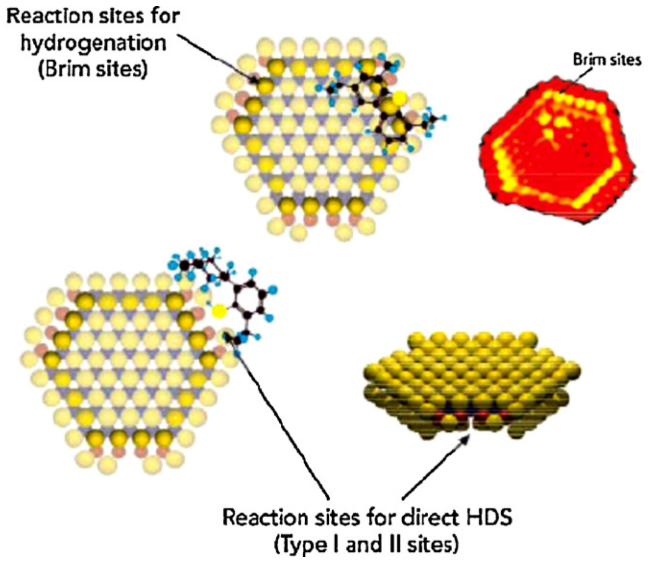


Fig. 29. Hydrogenation of the refractive S compound takes place on the BRIM sites, and the extraction of sulfur atom takes place at the edge of the Co–Mo–S slab [14,428].

microscopy (HAADF-STEM) and density functional theory (DFT). STEM showed atom-resolved images of the catalytically active edges of MoS_2, Co–Mo–S, and Ni–Mo–S nano-clusters [277–282]. The Mo edge was found to exhibit a special electronic edge state identified as brim sites (Fig. 29). Detailed analysis using DFT revealed the brim sites have metallic character. It was proposed that brim sites due to their metallic character may bind the sulfur containing molecules, and when hydrogen is available at the neighboring edge sites in the form of SH groups hydrogen transfer and hydrogenation reactions can take place. The brim sites are, thus, catalytically active for hydrogenation reactions. The brim sites are not co-ordinatively unsaturated sites.

The new "brim site" model proposed by Topsøe and coworkers [14,153a,b] is consistent with many aspects such as inhibitions, steric and poisoning effects which have been difficult to interpret using a "vacancy model". DFT calculations have been useful in gaining detailed insight into the HDS of thiophene under industrial conditions, and it is suggested that the hydrogenation reactions take place on the brim sites whereas the direct sulfur removal can take place at both edges. The mechanism involving the brim sites in hydrogenation allows the understanding of many observations which were difficult to explain in previous models. Since the brim sites are fully co-ordinated sites, they do not adsorb H_2S. The brim site model also explains the lack of steric hindrance of alkyl substituents in the hydrogenation pathway of molecules such as 4,6-DMDBT. The brim sites are very open sites and, therefore, allow the adsorption of the refractory sterically hindered molecules, which need to be removed in ULSD production. The brim sites and their neighboring acidic protons can interact strongly with basic N-containing molecules. This interaction is stronger than the interaction with simple aromatic compounds like benzene. Thus, the observed strong inhibition of the HYD pathway by basic nitrogen compounds could be explained.

4.3. *Preparation of ultra deep HDS catalysts*

It is widely accepted now that in the CoMo and NiMo based hydrotreating catalysts type II Co–Mo–S and Ni–Mo–S sites are highly active for HDS. Therefore, during the past decade intensive efforts have been made to improve the HDS activity of alumina supported CoMo and NiMo catalysts by maximizing the concentration of the type II sites by a variety of methods. These include: (i) the use of modified supports [255,256,283–285], (ii) development of new carriers [286–288], (iii) improvements in catalyst impregnation and preparation techniques [19,286,289,290], and (iv) the use of some additives [291–294] or modifiers in the catalyst formulation. As mentioned before, deep hydrodesulfurization of sterically hindered sulfur compounds in diesel fuel will require enhancement of hydrogenation activity to hydrogenate the aromatic rings of the sulfur compounds. The use of supports with high acidity can also improve the HDS of refractory sulfur compounds by promoting the isomerization and dealkylation reactions [101–103,288,295].

4.3.1. *Support effects*

In hydrotreating catalysts, the active components (mixed sulfides of Mo and Co or Ni as Co–Mo–S or Ni–Mo–S phases) are supported on a carrier. The carrier or support material usually provides high surface area to maximize active phase dispersion. The support also provides mechanical strength to the catalyst. γ-Al_2O_3 is the most widely used support material in hydrotreating catalysts. This is largely because it combines virtually most of the above characteristics. It is highly stable, contains acidic and basic sites, has reasonably high surface area and porosity, can be easily formed into desired shapes, and is relatively inexpensive. There has been immense interest in new supports for HDS catalysts due to the need to develop better catalysts [255,256,287,295–299]. A large number of new materials with high surface area and other properties suitable for support applications have been developed and tested. These include TiO_2, ZrO_2, MgO, carbon, SiO_2, zeolites, etc. [250,300–310]. Attempts have also been made to modify the alumina by mixing with zeolites and other metal oxides such as SiO_2, TiO_2, ZrO_2, etc. to take advantages of the favorable characteristics of both systems. The mixed oxides have reasonably high surface areas and exhibit acid–base properties that are favorable for promoting desulfurization of alkyl DBTs [255,256,299,311].

Differences in catalytic activities due to changes in support may arise as a result of variations in metal–support interactions which, in turn, may influence the dispersion and morphology of active components. The formation of the active phases of the catalyst (e.g. Co–Mo–S and Ni–Mo–S phases) and their dispersion on the support surface is strongly influenced by the interaction between the support and the impregnated metals or metal salts. Strong interaction of the deposited molybdate and nickel or cobalt ions with the support will retard their reducibility and sulfidability and lead to the formation low active species [312,313]. Studies have been shown the strong interactions between the molybdate and support in the catalyst lead to the formation of low-active type I Co–Mo–S structures which are incompletely sulfided and have some remaining Mo–O–Al linkages [312–317].

Support interaction also plays a key role on the degree of staking of MoS_2 and Co–Mo–S structures. The application of high-resolution electron microscopy has provided valuable information on the degree of staking in MoS_2 and Co–Mo–S structures prepared with different supports [318,319]. Very weak support interaction resulted in the formation of multi-staking of type II Co–Mo–S phases. Recent studies have shown that the degree of stacking in MoS_2 and Co–Mo–S structures can be controlled by carefully controlling support properties. Formation of small stable, single slab MoS_2 on alumina supports have been observed. These will have a high MoS_2-edge dispersion which can accommodate more Co atoms to form higher active single slab type II Co–Mo–S structures.

A few studies have been concentrated on the acidic and basic natures of the support and its effect on the nature of interaction with the active metal. TiO_2 mixed oxide received relatively higher attention because it shows higher activity. A detailed account of characterization of hydrotreating catalysts supported on TiO_2–Al_2O_3 binary oxides was given by Ramirez et al. [298]

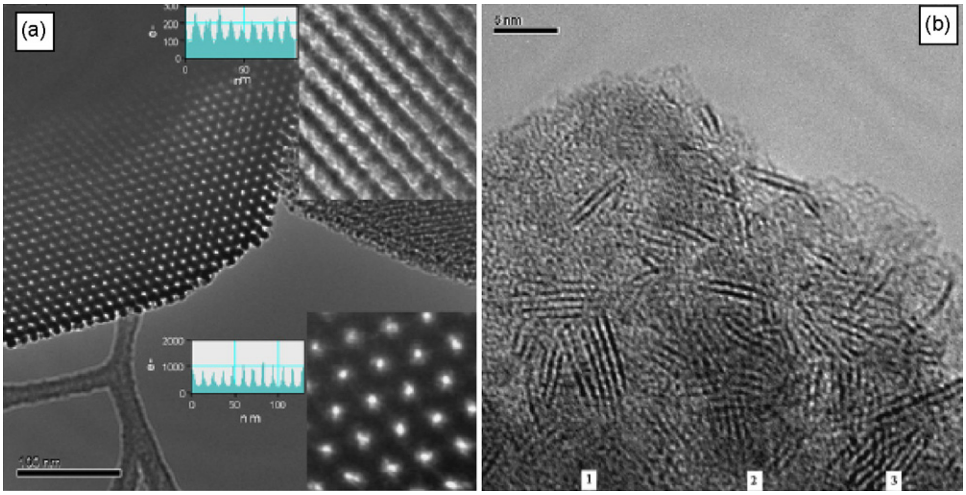


Fig. 30. Effect of meso-porous material on the catalyst properties: HRTEM micrographs of: (a) SBA-15; and (b) supported NiMo SBA-15 [286].

indicating electronic structural changes during the sulfidation of TiO_2–Al_2O_3 supported catalysts compared to Al_2O_3 supported catalysts. The catalytic behavior over the TiO_2–Al_2O_3 supported Mo catalysts, in particular for the 4,6-dimethyl-DBT, was much higher than that obtained over Al_2O_3 supported Mo catalyst. The ratio of the corresponding cyclohexylbenzene (CHB)/biphenyl (BP) derivatives was increased over the Mo/TiO_2–Al_2O_3. This indicated that the pre-hydrogenation of an aromatic ring played an important role on the HDS of DBT derivatives over TiO_2–Al_2O_3 supported catalysts. HDS activities over NiMo/TiO_2–Al_2O_3 catalysts were more active than NiMo/Al_2O_3 catalysts for the model compound HDS of DBT, 4-MDBT and 4,6-DMDBT [258]. The industrial HDS tests of straight run distillate gas oil showed that sulfide catalysts supported on TiO_2–Al_2O_3 composite (11 mol%) could reduce the sulfur level of diesel fuel from 500 to 50 ppm under conventional hydrodesulfurization conditions [255,256]. TiO_2 mixed oxide support not only enhanced light molecule HDS but also showed clear promotion for crude oil hydrodesulfurization [320–324].

The use of zeolites and amorphous silica-alumina as supports for HDS active phases (e.g. Mo, CoMo, NiMo, etc) have been the subject of many studies. Zeolites are highly acidic and contain Brønsted acidity that can improve the HDS activity for refractory sulfur compounds such as 4,6-DMDBT. The Brønsted acidity of the support can promote isomerization of the alkyl groups in the alkyl DBTs and suppress their steric hindrance [101]. The main problem in using zeolites as supports for hydrotreating catalysts is the difficulty in the impregnation and dispersion of the active phase (e.g. MoS_2, Co–Mo–S or Ni–Mo–S) on the support surface. The size of the zeolites pores is too small (<1 nm) to accommodate the active phase and to ensure the access of bulky reactants like 4,6-DMDBT. In the case of amorphous SiO_2–Al_2O_3 (ASA) the Brønsted acidity is milder compared to zeolites, but strong enough to modify the electronic properties of the active phase [16,325] as well as to promote isomerization of alkyl groups. Michaud et al. [93] observed a 2.5-fold increase in the 4,6-DMDBT HDS when amorphous silica alumina (ASA) was mixed with a NiMo alumina catalyst, and concluded that the isomerization of 4,6-DMDBT to 3,6-DMDBT on the Bronsted acid sites of the ASA was responsible for this increase. Unlike zeolites, pore size of amorphous SiO_2–Al_2O_3 is not a limiting factor for active phase dispersion and for the diffusion of the reactant molecules to the active sites within the pores.

Recently, nano-porous alumino-silicate based materials such as MCM-41, Al-MCM-41, SBA-15 have received considerable attention as supports for Co and Ni promoted MoS_2 catalysts [326–334]. The high surface area of these nanopore materials (pore size 5–l0 nm) permits to achieve high CoMo or NiMo loading without the restricted access of the zeolite structure to bulky molecules. Thus, the catalytic properties of these materials are expected to be high due to its defined textural properties (pore size 5–30 nm, wall thickness 3–7 nm) and high dispersion of nano-sized MoS_2 as shown in Fig. 30. Substantially more active catalysts than alumina-supported ones can be obtained by using these materials as support. The surface acidity of these materials can be modified by the incorporation of additives such as Al, Ti, Zr, etc. into the silica framework [250,330,335–339].

Carbon-supported catalysts have also been found to show high HDS activity with reduced deactivation by coke deposition due to a lower acidity of the carbon support [340,341]. Rapid sintering of the active phase under reaction conditions and its unsuitability for regeneration (after deactivation) are major disadvantages in using this support.

4.3.2. *Effects of additives*

Improvements in hydrotreating catalyst performance have also been achieved by the use of some additives to the γ-alumina support. The additives used as modifiers include P, F, B, Si, Mg, Zn, La, V, Ga, etc. The acidic and basic properties of the alumina support are modified by the additives [100,255,294,297,342a,b,343], which in turn can influence the interaction between the impregnation solution and the support, the dispersion of the active phase, and the reducibility and sulfidability of the Mo and Co. Modification of the isoelectric point of the carrier surface by the additive can influence the amount and distribution of the active phase inside the pellet [284,286]. It has been suggested that sodium enhances the reducibility and sulfidability of Co and Mo and increases the ratio of tetrahedral to octahedral cobalt species. In lanthanum-modified hydrotreating catalysts, it has been suggested that La inhibited the lateral growth of MoS_2 layers to form stacked MoS2 layers. Essentially monolayer slabs of MoS_2 after sulfiding. The La loading influences the surface concentration of active components, and causes a decrease in surface Ni concentration of the sulfided catalysts. La also has been reported to increase the thermal stability of Al_2O_3 support [344,345]. Addition of noble metals such as Ru, Pd, Pt to CoMo, NiMo catalysts has been reported to improve the HDS activity [346,347].

The modifier used most often in recent years is phosphorus which has been reported to improve the performance of hydroprocessing catalysts and especially the HDN activity of NiMo/Al_2O_3 system [100]. Several explanations have appeared in the literature to explain this beneficial effect of phosphorus [294,348–352].

Improved dispersion of the active metal sulfide phase, reduced coking due to modified acidic properties, reduced interaction between the oxidic precursors of Mo and Ni with the alumina support, increase in the MoS_2 stacking and formation of larger MoS_2 slabs with phosphorus addition have been reported. Besides the above suggestions, it has been proposed that the main role of phosphorus is to inhibit the formation of tetrahedrally co-ordinated cobalt and nickel ions. Studies have also shown that phosphorus interacts with the active Ni and Mo components forming a P–Ni–Mo type heteropoly compound. Nitric oxide (NO) adsorption studies using IR spectroscopy have clearly indicated that phosphorus not only changes the number of adsorption sites, but also interacts with the active phase resulting in a change in the properties of the co-ordinatively unsaturated Mo and Co (or Ni) edge sites.

Incorporation of fluoride into the catalysts has been found to have a beneficial effect on HDS, HDN and hydrogenation activities, depending on the fluoride loading and catalyst preparation procedures [293,294,353,354]. This effect has been attributed primarily to changes in the dispersion and distribution of active phases as well as to the increase in acidity. Fluoride addition is also reported to be more effective in the conversion of type I into type II Ni–Mo–S in Ni-Mo-Al_2O_3 catalysts. Boron is another additive currently used to enhance the performance of hydrotreating catalysts [349,355–363]. It has been widely reported that the increased acidity of boron-modified alumina improves catalyst performance. Saih and Segawa [355] reported that the addition of boron to alumina carrier reduced the formation of inactive bulk C_9S_8 phase and facilitated the formation of more active Co–Mo–S phases. The activity of a $CoMo/Al_2O_3$ catalyst containing 3 wt.% B was found to be 36% higher than that of a conventional $CoMo/Al_2O_3$ for HDS of 4,6-DMDBT.

4.3.3. Improvements in catalyst impregnation techniques

Since the active components (i.e. Mo, Co and Ni) of a hydrotreating catalyst are deposited on the support surface by impregnation of molybdate and cobalt or nickel ions from aqueous solutions, the impregnation step plays an important role in influencing the structure of the active phase and its dispersion. Different methods have been described in the literature for the impregnation of Mo and Co or Ni promoters on the support surface [257,364–370]. Among these, the incipient wetness and the equilibrium adsorption methods are widely used [371–376]. The former involves contacting the support with a solution containing the precursor salt (e.g. ammonium heptamolybdate) in a predetermined volume of water sufficient to fill the pores. The equilibrium adsorption method consists of adsorbing Mo from an aqueous solution of ammonium heptamolybdate over an extended period of time until equilibrium is attained, followed by the filtration of the leftover liquid.

The use of modified impregnation procedures for the preparation of highly active HDS catalysts by maximizing the formation of well dispersed type II Co–Mo–S and Ni–Mo–S with strong synergies between Co(Ni) and Mo sulfides have been reported in many recent studies. Remarkable improvements in HDS activity of CoMo and NiMo catalysts can be achieved by the addition of some chelating compounds such as citric acid, urea, glycol, nitriloacetic acid (NTA) and ethylene diamine tetraacetic acid (EDTA) to the impregnation solution [221,291,294,306,377–385]. These complexing agents have been found to be very effective in the formation the highly active Co–Mo–S(II) sites with extremely high selectivity.

One important effect of complexing agents is to delay the sulfidation of Co or Ni [386–389]. Studies have shown that, in CoMo catalysts prepared without complexing agents, the sulfidation of Co starts at 50 °C and are completed at 150 °C, whereas Mo is fully sulfided above 175 °C. Thus, the sulfidation of the promoter metals (Co or Ni) is complete before that of Mo on the CoMo catalyst precursors prepared without chelating agents. On the other hand, in the catalysts prepared with NTA or EDTA, sulfidation of Co starts at around 150 °C and is complete at 225 °C. The complexing agent, thus, delays the sulfidation of the cobalt promoter. Thus, the strong interaction between chelating ligands and Co ions leads to the sulfidation of these promoter metals at a higher temperature than that of Mo. Consequently, sulfided Co atoms could be formed at the edges of the already formed MoS_2 crystallites (slabs) and create the highly active Co–Mo–S and Ni–Mo–S type II structures.

Okamoto and his coworkers investigated the sulfidation degrees of Co(Ni) and W oxides to the corresponding sulfides as a function of sulfidation temperature for a Co(Ni–WS_2/Al_2O_3 impregnation catalyst, as measured by XAFS [390]. Actually, the addition of a chelating agent, NTA (nitrilotriacetic acid), increased the sulfidation temperature of Co(Ni) by 150 K and the HDS activity was almost doubled. In another study, Co coverage on the edges of MoS_2 particles was found to increase in the $CoMo/Al_2O_3$ catalyst prepared with NTA [391].

Another mechanism by which chelating agents improve the catalytic activity of CoMo-type HDS catalysts is by enhancing the formation of highly active type II Co–Mo–S sites through preventing strong interactions between the metals (Mo and Co) and support [294,392]. In the absence of chelating agents, a strong interaction between the support surface and molybdate species may occur, and polymolybdates may be dissociated to monomolybdates through such strong interactions. Extended X-ray absorption fine structure (EXAFS) spectrum of a $CoMo/Al_2O_3$ catalyst precursor prepared with chelating agents showed a strong Mo–Mo peak at 3.7 Å, indicating that most of the Mo is present as polymolybdate. In the case of the catalyst prepared without a chelating agent, this peak was considerably smaller, indicating that polymolybdates decomposed to monomolybdate by the interaction with the support.

Chemical vapor deposition (CVD) of the Co promoter on the surface of the sulfided Mo/Al_2O_3 catalyst is another method that would lead to the selective formation of Co–Mo–S phases completely [358a,b,393–395]. In the CVD technique reported by Okamoto [358a], supported Mo oxide precursor was first sulfided at 673 K to prepare MoS_2, and the MoS_2 catalyst was then exposed to a vapor of $Co(CO)_3NO$ at room temperature for 5 min, followed by evacuation at room temperature for 10 min to remove physisorbed $Co(CO)_3NO$ molecules. The $Co(CO)_3NO/MoS_2$ sample was sulfided again at 673 K for 1.5 h. The Co coverage of MoS_2 edge sites was found to be extremely high in the CoMo catalysts prepared by the CVD technique, and the HDS activities were substantially higher than the activities of CoMo catalysts prepared by conventional impregnation method. When Co was added by CVD to a conventionally prepared Co–Mo–S_2/Al_2O_3 catalyst the HDS activity increased significantly as shown in Fig. 31.

4.4. Unsupported catalysts

Unsupported transition metal sulfides, have also attracted a great deal of attention in recent years as potential new catalysts for promoting hydrotreating reactions [20,27,259,396,397]. The materials tested include RuS_2, V_2S_3, Rh_2S_3, NbS_3, mixed sulfides of Co–Mo, Ni–Mo, Ni–W, Ni–Mo–W, Fe–W, Fe–Mo, Ni–Ru, etc. RuS_2, Rh_2S_3 and NbS_3 were found to exhibit improved HDS performance over the traditional Co–Ni and Mo–W metal sulfides [398]. Bulk (unsupported) $Ni_{0.5}$, $Mn_{0.5}$ Mo sulfide was found to be a superior catalyst than NiMo for the HDS of both DBT and 4-EDBT in a study by Ho (Fig. 32). Unsupported tri-metallic Ni–Mo–W sulfide exhibited at least 3 times higher activity than the alumina supported NiMo and CoMo catalysts [399–402]. Unsupported Ni–Mo–W sulfide composition is commercially used for deep HDS of diesel under the commercial trade name NEBuLA [403a,b,c]. Apart from the unsupported transition metal sulfides, the hydrotreating activities of carbides and nitrides of Mo and W have also been investigated.

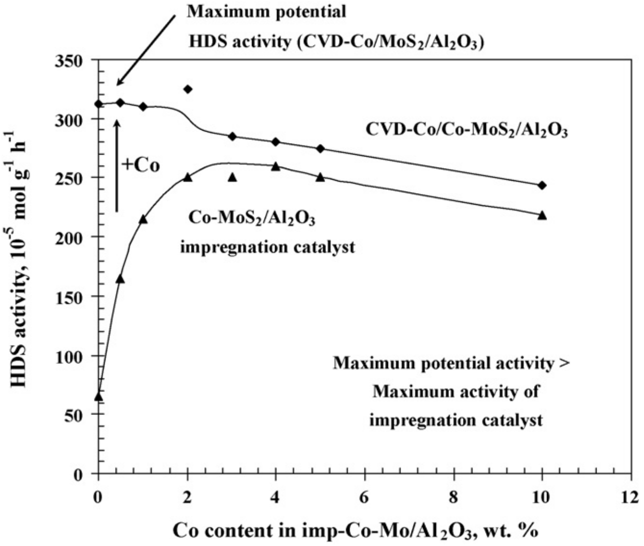


Fig. 31. HDS activity of Co–MoS_2/Al_2O_3 impregnation catalysts before and after the Co-addition by the CVD technique [358]. (Reactant: thiophene; $T = 350\,^{\circ}C$; $P = 20$ kPa; $p_{thiophene} = 2.6$ kPa.)

The materials tested include Mo carbide [404,405], W–Mo carbide [406], W carbide [407], Mo nitride [408–410], Co nitride [410] CoMo nitride [410] and Ni nitride [411]. These materials are stable under the hydroprocessing reaction conditions, which form surface sulfide and remain active in HDS reactions with time-on-stream, i.e. the surface of these materials gets sulfided under the reaction conditions [404]. Moreover, spectroscopic evidence confirms the presence of hydrogen in the form of sulfhydryl groups (–SH), whereas the presence of a hydride form is less convincing [131].

Unsupported metal phosphides have also received much attention due to their high activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum feedstocks [20,412–415]. It has been shown that MoP, and WP have moderate activity and Ni_2P has excellent activity in hydroprocessing [416–418]. The overall activity was found to be in the order: $Fe_2P < CoP < MoP < WP < Ni_2P$ in the simultaneous HDS of dibenzothiophene and HDN of quinoline are reported [417–419].

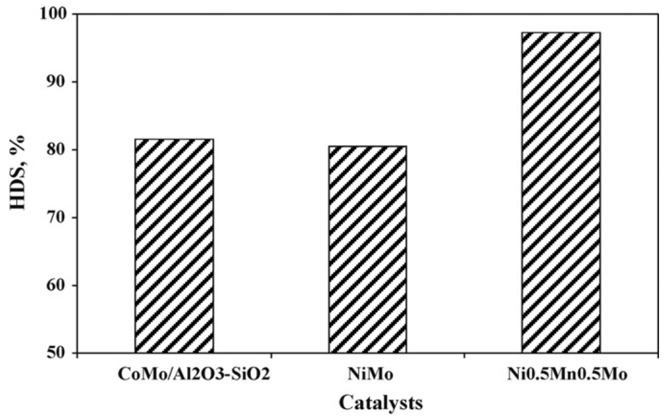


Fig. 32. HDS of 4EDBT at 285 °C, 3.21 MPa, 5 WHSV, of unsupported (bulk) Ni0.5Mn0.5Mo and NiMo sulfide catalysts [27].

4.5. Improved commercial deep HDS catalysts

Based on the scientific principles discussed in Sections 4.1–4.4 many improved HDS catalysts (Table 7) have been developed and introduced in the market by major catalyst companies [420–431]. A new highly active HDS catalyst (C-606A) with 3 times higher HDS activity compared to the conventional $CoMoP/Al_2O_3$ catalyst has been developed recently by Cosmo Oil Co. Ltd. [221]. The new catalyst was prepared by co-impregnation using an aqueous solution containing Co, Mo, orthophosphoric acid and carboxylic acid on a support consisting of HY–Al_2O_3. After impregnation, the catalysts were air-dried only without calcinations. The new catalyst preparation method could increase the formation of the active Co–Mo–S phase and provide more highly active Co–Mo–S Type II, in which Co is located at the edges of the MoS_2 multilayers. The performance of this new catalyst in the production ultra low sulfur (10 ppm) diesel compared with that of a conventional $CoMo/Al_2O_3$ catalyst is shown in Fig. 33a which demonstrates the excellent activity of

Table 7
Commercial new generation high active catalyst for deep HDS and aromatic hydrogenation.

Company	Ref.	CoMo type	NiMo type	Tri-metallic (NiCoMo/NiMoW)	Precious metal type
Akzo (Albemarle)	[240,241,244,420–423]	KF757, KF767, KF752, KF756, KF770STAR, KF760STAR	KF-848, KF 857, KF-901, KF-902	KF905STAR, NEBuLA-20	KF-200
Criterion	[242,243,424,425]	DC-160, DC-185, DC-200DHT, CENTINEL™DC-2118, CENTINEL GOLD DC2318, ACENT DC2531	DN200, SENTRYMax-Trap[As], CENTINEL™DN-3110, CENTINEL GOLD DN3330,		
Topsøe	[14,427,428]	TK554, TK574, TK558BRIM™, TK576BRIM™	TK-573, TK-525, TK-555, TK575BRIM™, TK605BRIM™		TK907, TK908, TK911, TK915
Axen (IFP)	[429,430]	HR426, HR-416, HR506, HR515, HR526, HR626,	HR448, HR538, HR548,	HR568	Platinum type
KCC catalyst	[431]	HOP-467	HOP-414		

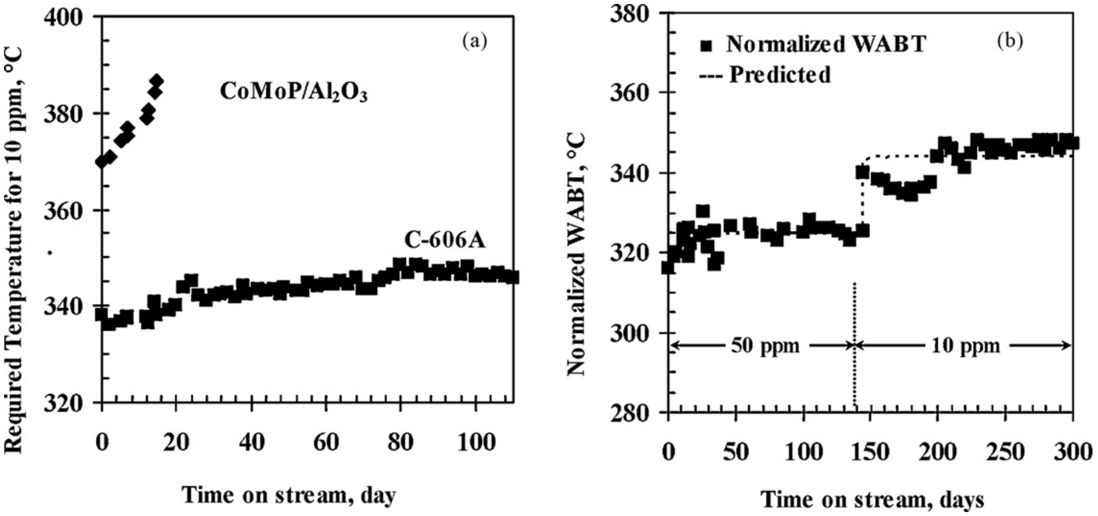


Fig. 33. (a) Temperature required to maintain 10 ppm sulfur in the product using conventional CoMoP/Al_2O_3 and C-606A catalysts for HDS of SRLGO. (b) Commercial operation with C-606A for production of 50 ppm sulfur and 10 ppm sulfur diesel fuels in the hydrotreater at Cosmo Oil Chiba Refinery [221]. (LHSV = 1.3 h^{-1}; P_{H_2} = 4.9 MPa; H_2/oil = 200 Nm^3/kl.)

the catalyst. Long-term stability tests on deep HDS of straight-run gas oils demonstrate the excellent stability of this catalyst for the production of 10 ppm sulfur diesel fuel (Fig. 33b).

Akzo Nobel (now Albemarle) came up with the STARS (Table 7) KF-757, KF-767, KF-848, KF-770, etc. catalyst series [241,244], which almost doubled the HDS activity. More recently the company started to market a new catalyst, the NEBuLA, which is considered a breakthrough in hydrotreating catalysts [240,403]. The new catalyst which contains unsupported bulk sulfides of group VIII and group VI metals is almost 4 times as active as classical gas oil hydrotreating catalysts (Fig. 34). AXENS has also introduced HR-448, HR-548. HR-526 and HR-568, which have superior HDS activities over their conventional middle distillate HDS catalysts [429,430], Kuwait Catalyst Company has introduced two new catalysts, HOP-414 and HOP-467, which as a combination can achieve the target low sulfur levels using existing diesel hydrotreating facilities [431]. Criterion has introduced the CENTINEL Ascent and CENTINEL Gold series of catalyst, which are designed to meet the ultralow sulfur specifications for diesel [424,425]. ART has introduced the sulfur minimization by ART (SMART) catalyst system, with a remarkably high activity than predecessor hydrotreating catalysts [426].

Topsøe has introduced a number of catalysts such as TK-573, TK-574, TK-911 and TK-915, which not only significantly improved desulfurization activity, but also tackled density and aromatics reduction. Recently, Topsøe has developed a new catalyst preparation technology, giving highly active hydroprocessing catalysts. This new proprietary BRIM technology not only optimizes the brim site hydrogenation functionally, but also increases the type II activity sites for direct desulfurization [14,427,428]. The first two commercial catalysts based on the brim technology were Topsøe's TK-558 BRIM (CoMo) and TK-559 BRIM (NiMo) for FCC pretreatment service. This was followed by a new series of high performance TK-576 BRIM (CoMo), TK-575 BRIM (NiMo) and TK-605 BRIM catalysts for ultra low sulfur diesel production and for hydrocracker feed pretreatment.

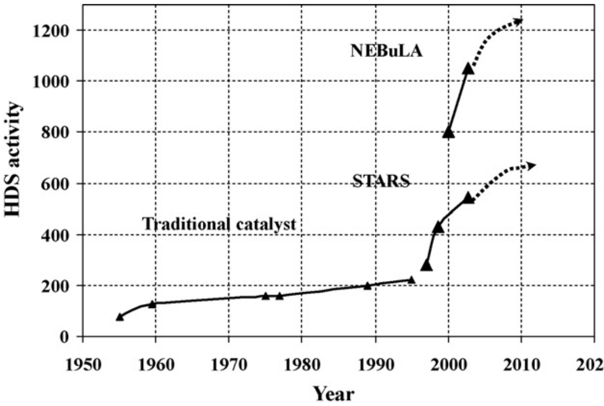


Fig. 34. Relative activity of the new NEBuLA and STARS catalysts compared to conventional CoMo/Al_2O_3 developed over the last 50 years [403].

5. Feed quality effect

Feedstock quality plays an important role on the performance of a diesel hydrotreater used for the production of ULSD. Industrial feedstocks used for diesel fuel production in different refineries are usually different in their characteristics with regard to sulfur, nitrogen, and aromatic contents which may affect the degree of desulfurization during hydrotreating. Diesel fuel feedstocks mainly consist of middle distillates in the boiling range 220–360 °C with plus or minus some front or back ends. Depending on refinery complexity, the deep HDS unit feed components may comprise a variety of distillate sources including straight-run gasoil (SRGO), coker gas oil (CGO) thermally cracked distillates, and FCC light cycle oil (LCO).

Most refiners process a wide variety of crudes and routinely adjust the operating conditions of major processing units according to the changing feeds and overall product needs. Additionally, the types and volume of streams feeding into the diesel pool may change due to seasonal swing in the product demand and changes in upstream operations. These changes in upstream operations as well as the blending of CGO and LCO with SRGO will cause the type and concentrations of sulfur and nitrogen and aromatic compounds and their distributions in the diesel feedstock to vary.

5.1. Properties of diesel feeds

The properties and reactivities of diesel feeds are strongly dependent on their source [25,26,432,433]. In a recent study Marafi et al. [434] compared the total sulfur content and other characteristics of two Kuwaiti crudes and their straight run gas oils (diesel cuts). The results presented in Table 8 indicate significant differ-

Table 8
Characteristics of various straight run gas oil (SRGO) feedstocks derived from two different Kuwait crudes [434].

Feed properties	GO-KEC	GO-LF
Density @ 15 °C (g/cm^3)	0.8508	0.8962
Sulfur (wt.%)	1.52	3.22
Nitrogen (ppm)	50	187
TBN (mg/mg KOC)	0.179	0.457
Total aromatics (wt.%)	30.45	44.73
Mono aromatics (wt.%)	15.09	19.47
Polyaromatics (wt.%)	14.92	26.21
Kinematic viscosity @ 40 °C (cSt)	4.32	5.635
Cetane index	50.2	38.2
Distillation (°C)		
IBP	220	236
10 vol.%	245	261
30 vol.%	264	288
50 vol.%	305	314
70 vol.%	334	340
90 vol.%	370	366
95 vol.%	370	375

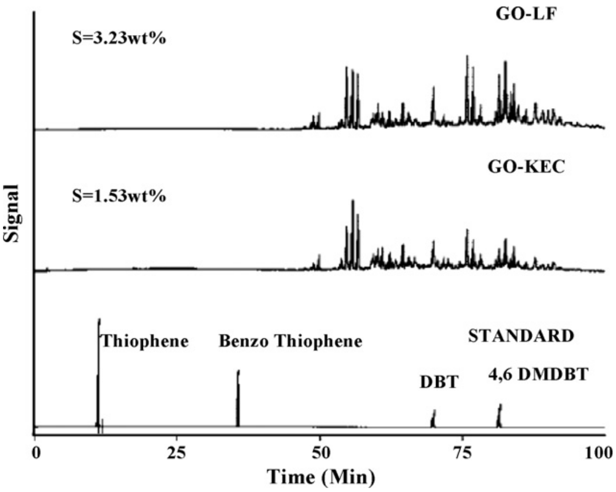


Fig. 35. GC–FPD analysis for sulfur compounds of GO-KEC and GO-LF [24].

ences in the key properties of the two crudes and their diesel cuts. The gas oil from the heavy Lower Fars crude (GO-LF) contains substantially higher sulfur nitrogen and aromatic contents than that from light Kuwait export crude (GO-KEC). Furthermore, the concentrations of the low-reactive sterically hindered alkyl DBTs are significantly higher in the GO-LF than in the GO-KEC (Fig. 35). Another example of the effect of crude source on diesel stream sulfur species distribution is presented in Fig. 36. It is seen that the diesel cut from North Sea crude (feed A) contains predominantly sterically hindered alkyl DBTs even though its total sulfur content is significantly low while other two feeds B (SRGO/LCO, from an Arabian crude) and C (SRGO/cracked blend derived from Nigerian crudes) with higher sulfur level contain relatively lower amount of refractory sulfur compounds.

Cracked distillates such as LCO and CGO are poor quality diesel feeds [25,435–437]. In a recent study, Ho [25] examined the key properties of thirteen middle distillates including SRGO, CGO and LCO. A comparison between the properties of these feedstocks presented in Table 9 clearly indicates that LCO and CGO are substantially more aromatic compared to straight run distillates. The aromatic content of LCO can be as high as 78%. The nitrogen content of the cracked distillates is also considerably higher than straight run gas oils [178,438,439]. A significant portion of the sulfur in LCO is found in refractory alkyl DBTs [440]. Similar results have been reported in many other studies [40,77,89,168,171]. The cracked distillates have a significantly lower cetane value than straight run distillate. LCO cetane ranges from 15 to 25 compared to 40 to 60 for the straight run distillates.

Blending of LCO with SRGO has been reported to deteriorate the feed quality [9,437,441–443] (Fig. 37). For a blended feedstock, aromatic content as a function of cetane number is shown in Fig. 38. The amount of refractory sulfur species and the nitrogen and aromatic contents of the feedstock have been found to increase significantly when LCO is blended with SRGO [9,84,86,444].

Besides the feedstock source, the distillation temperature also plays an important role on the feedstock properties and HDS reactivity [24,119]. Particularly, the distributions of different types of sulfur compounds are strongly influenced by the boiling point of the feedstock. Several studies have shown that benzothiophenes and its alkyl derivatives are concentrated mainly in the fractions boiling below 300 °C and DBT and alkyl DBTs are present mainly in the fraction boiling above 300 °C. As the boiling point of the feed-

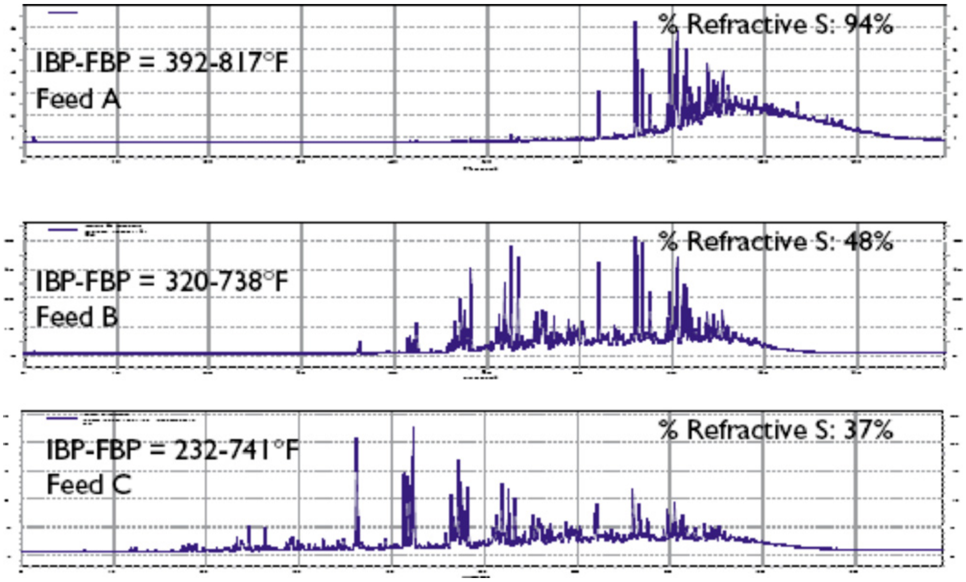


Fig. 36. Sulfur distribution depends upon crude source and upstream processing (feed A: North Sea SRGO, S = 0.196 wt.%; feeds B: SRGO/LCO, from an Arabian crude, S = 1.29 wt.%; feed C: SRGO/cracked blend derived from Nigerian crude, S = 0.517 wt.%) [86].

Table 9
Middle distillates tested and some of their properties [25].

	Feed description	S (wt.%)	N (ppm)	Aromatic (wt.%)	95% B.P. (F)	S as β-DBTs
1	Light cycle oil A	2.31	610	59.8	807	16.6
2	620+ Arab medium virgin	1.919	134	37.8	696	21.1
3	Gas oil	1.444	61	35.5	671	8.2
4	450–580 F fraction	2.715	591	28.4	600	0.1
5	Virgin	0.938	67	18.2	656	6.7
6	620– Arab medium virgin	1.284	30	21.7	641	5.4
7	Full Arab medium	1.294	61	25	679	12.1
8	Light Cycle Oil B	1.328	265	78.6	656	10.6
9	580–700 F fraction	3.171	2061	30	720	6.4
10	Light coker gas oil	2.735	1674	44.5	732	4.2
11	Heavy gas oil	0.297	306	24.5	738	26
12	570– Arab medium virgin	0.953	12	21.5	598	0.4
13	570+ Arab medium virgin	1.551	69	22.1	682	13.5

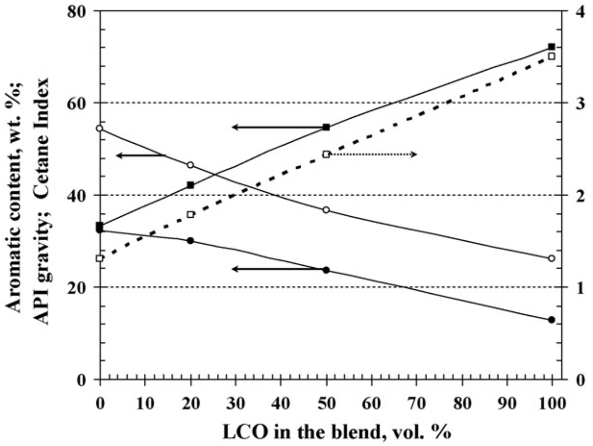


Fig. 37. Variation in feedstock quality as a function of LCO content in straight run gas oil (SRGO) blend: (○) cetane index; (●) API gravity; (□) sulfur content, wt.%; (■) aromatics content, wt.% [209].

Table 10
Characteristics of full range and low-boiling diesel feed streams distilled from Kuwait Lower Fars (LF) crude [24].

Feed properties	GO-LF	
	Low-boiling range	Full range
Density at 15 °C (g/cm^3)	0.8705	0.8962
Sulfur (wt.%)	2.29	3.22
Nitrogen (ppm)	100	187
Total aromatics (wt.%)	0.168	0.457
Monoaromatic (wt.%)	39.32	44.72
Polyaromatics (wt.%)	18.53	19.47
Kinematics viscosity @ 40 °C (cSt)	3.258	5.635
Cetane index	41.1	38.2
Distillation (°C)		
IBP	222	236
10 vol.%	226	261
30 vol.%	255	288
50 vol.%	277	314
70 vol.%	299	340
90 vol.%	321	366
95 vol.%	338	375
FBP	343	393

stock increased, the concentration of the sterically hindered alkyl DBT type sulfur compounds increased [24,25,83].

Characteristics of the full range and low-boiling diesel feeds (FR-LF-GO and LB-LF-GO) obtained from the Kuwait LF crude are shown in Table 10. The full range gas oil feed has a higher density and contains higher concentrations of sulfur, nitrogen and aromatics than the low-boiling cut. The sulfur compounds distribution in the two gas oils are also significantly different (Fig. 39). It is seen that the LF-GO feed with low cut-point contains predominantly alkyl BTs, whereas, the full range gas oil contains a larger amount of alkyl DBTs in addition to alkyl BTs. The concentration of alkyl DBTs with two or more alkyl carbon atoms is remarkably high in the full range LF-GO. The sulfur compounds in petroleum fractions are usually distributed in the order of their boiling points. Since the alkyl DBTs

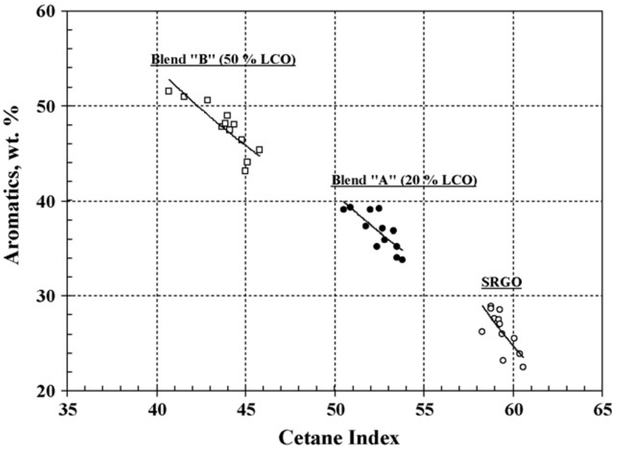


Fig. 38. Effect of feed blend on the relationship between aromatics content and cetane index: (○) SRGO; (●) "A" blend; (□) "B" blend [209]. (Catalyst: CoMo/Al_2O_3; T = 360–380 °C; P = 5.4–9 MPa; LHSV = 1–2 h^{-1}; H_2/HC = 2000 ft^3/bbl.)

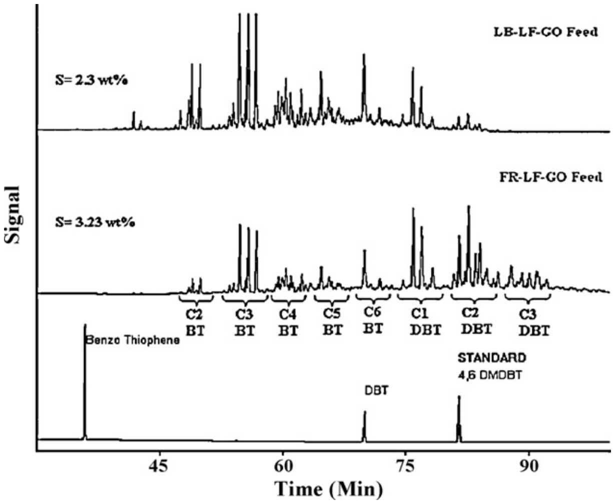


Fig. 39. GC–FPD analysis for sulfur compounds in full range and low-boiling diesel cuts derived from the LF crude. [24].

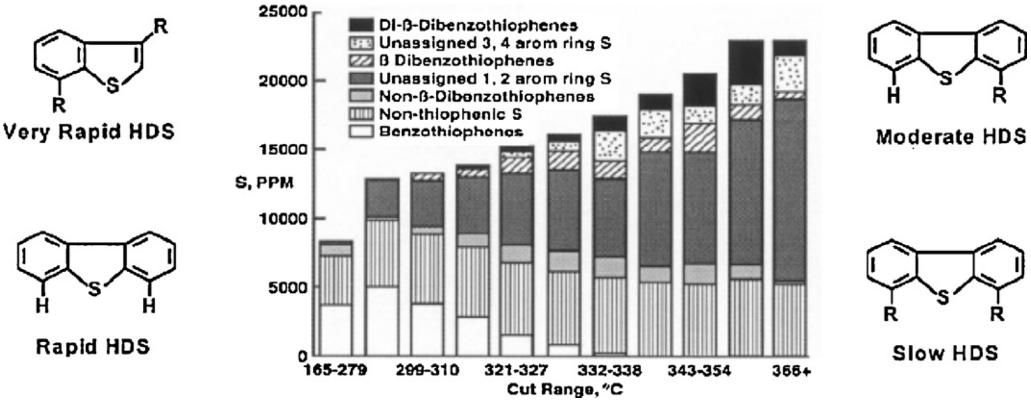


Fig. 40. An example of sulfur types distribution as a function of distillation temperature (fraction) in Arab Medium distillate [85].

have higher boiling points (>330 °C), they are mostly excluded during distillation and their concentrations in the low-boiling cut are relatively low.

Another example of sulfur types distribution in LCO as a function of distillation temperature is presented in Fig. 40 [85]. Here again, it is seen that the lighter cuts contain easy reactive sulfur types (e.g. benzothiophenes, non-beta substituted DBTs, etc.), which undergo rapid hydrodesulfurization. The heavier cuts contain relatively higher concentrations of least reactive sterically hindered alkyl DBTs.

5.2. *Feed quality effect on HDS reactivity*

In the deep desulfurization of diesel to ultra low sulfur levels, the quality of the feedstock plays a major role [25,86,432,434,436,445]. The degree of desulfurization of two diesel feeds (Table 11) derived from two different crudes was examined by Marafi et al. [434] in a recent study. Hydrotreating experiments were conducted using the feeds under identical conditions in the temperature range 320–380 °C. The results (Fig. 41a) showed that the degree of desulfurization of the diesel cut (GO-LF) from the heavy crude was remarkably lower than that of the light crude diesel cut (GO-KEC).

The variation in feedstock quality with distillation temperature (T_{90}) also leads to large differences in the hydrotreating reactivity as shown in Fig. 41b, which clearly provides the relationship between the reactor temperature and product sulfur content for diesel feedstocks having different cut temperatures. Marafi et al. [24] studied the deep desulfurization of full range and low-boiling diesel streams obtained from Kuwait Lower Fars heavy crudes, and concluded that the full range diesel feed stream produced from the LF crude was very difficult to desulfurize due to its low quality caused by high aromatics content (low feed saturation) together with the presence of high concentrations of organic nitrogen compounds and sterically hindered alkyl DBTs. Similar results were also obtained by Al-Barood and Stanislaus [83] in a comparative study on the deep HDS of a full range and low-boiling straight un diesel cuts of Kuwait export crude (Fig. 42).

Table 11
Quality of diesel product obtained by hydrotreating of GO-KEC and GO-LF at 350 °C [434].

Product properties	Diesel from GO-KEC	Diesel from GO-LF
Density @ 15 °C (g/cm^3)	0.8307	0.8609
Sulfur (wppm)	65	689
Nitrogen (wppm)	6	17
Total aromatics (wppm)	24.96	37.91
Monoaromatics (wppm)	20.32	29.45
Polyaromatics (wppm)	4.64	8.45
Cetane index	62	51

Light cycle oil (LCO) from fluid catalytic cracking (FCC) units and thermally processed distillates from Visbreaker, thermal cracker and coker units are generally more difficult to desulfurize. These streams contain high concentrations of aromatics and nitrogen compounds which inhibit deep HDS of the alkyl DBTs through the hydrogenation route. Studies have shown that LCO is typically 2–4 times harder to desulfurize than the average straight run feed [26]. These low reactive diesel feed streams are usually blended with straight run gas oils (diesel cuts) in order to improve the feedstock quality.

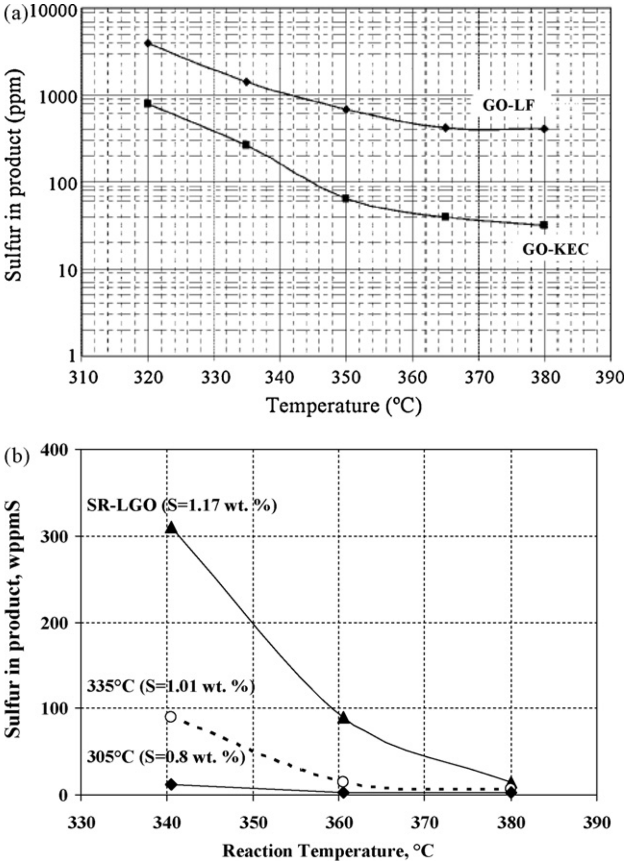


Fig. 41. (a) Temperature effect on desulfurization of diesel cuts derived from two different crudes (GO-LF and GO-KEC) [434]. (Catalyst: CoMo/Al_2O_3; P = 4 MPa; LHSV = 1.3 h^{-1}; H_2/HC = 200 mL/mL.) (b) Effect of feedstock cut temperature as a function of reaction temperature on product sulfur content [475b]. (P = 5 MPa; LHSV = 2 h^{-1}.)

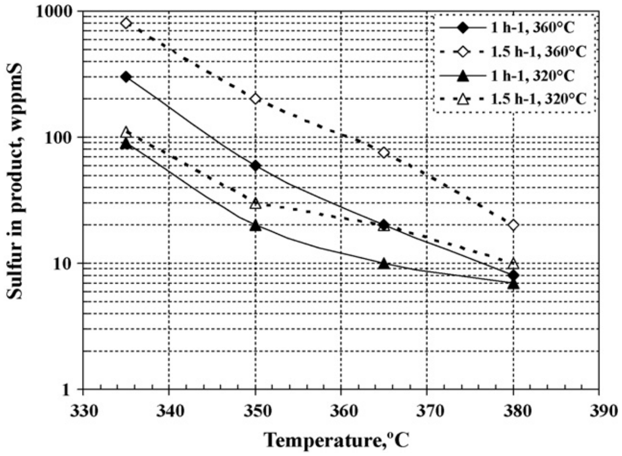


Fig. 42. Effect of lowering T_{95} (320 °C and 360 °C) of SRGO on deep HDS as a function of reaction temperature and with variation liquid hour space velocity (1 h^{-1} and 1.5 h^{-1}) [83]. (Catalyst: CoMo/Al_2O_3; P = 5 MPa; H_2/HC = 200 mL/mL.)

Ancheyta et al. [441] carried out hydrotreating studies for SRGO/LCO blends and concluded that in order to get lower sulfur and nitrogen content in the diesel product, higher temperatures and pressures and lower space velocities are required for SRGO/LCO blends than for SRGO alone. Additionally, aromatics and cetane numbers were always lower for SRGO/LCO blends than for SRGO and did not show a significant improvement at the experimental conditions studied. Optimum conditions were found to be 370 °C, LHSV of 1.0 h^{-1} and 8.7 MPa. Therefore, these studies showed that optimum conditions for LCO and SRGO/LCO blends HDT are far beyond the capacity of conventional hydrotreaters. Detailed characterization of sulfur compounds distribution along the distillation curves of SRGO and LCO feedstock and hydrotreated products [10,77,432,445] have shown that under deep HDT conditions, certain alkyldibenzothiophenes (i.e. 4-methyldibenzothiophene and 4,6-dimehtyldibenzothiophene) with boiling points above 316 °C, exhibit the lowest reaction rates, making it difficult to obtain very low sulfur levels in the hydrotreated product.

Al-Barood and Stanislaus [446] compared the degree of desulfurization of CGO, SRGO and their blends under identical reaction conditions. The results revealed that SRGO, in spite of having a significantly larger amount of total sulfur, desulfurized more easily and produced diesel fuel with low sulfur levels in the desired range at lower temperatures compared with CGO. More severe operating conditions were found necessary to bring about deep desulfurization of CGO and its blends with SRGO to the same sulfur level as that obtained with SRGO alone. The CGO contained 17 times higher nitrogen content than that of SRGO. The aromatics content of the CGO was also substantially higher than that of SRGO. The low reactivities of LCO and thermally cracked distillates (e.g. CGO) and their blends with SRGO have been attributed to the inhibition effects of nitrogen and aromatic compounds present in these feeds in large concentrations.

Desulfurization of the refractory cracked distillates such as LCO to produce 10 wppm ULSD could be achieved via a combination of catalysts and process solutions [9,447,448]. Lowering the boiling point of the feedstock is another approach for achieving ULSD from cracked distillates. Choi et al. [84] reported that lowering of the boiling point of LCO feed to <340 °C can lead to easy desulfurization to reach <10 ppm sulfur level under conventional conditions (Fig. 43). In a similar study, Al-Barood and Stanislaus [83] found easy desulfurization of CGO to <10 ppm sulfur by reducing the T_{95} distillation temperature from 370 to 300 °C (Fig. 44).

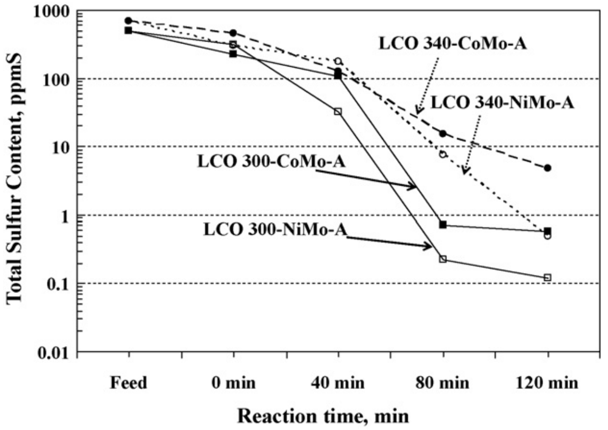


Fig. 43. Remaining amount of sulfur in HDS product from LCO 300- and 340-over CoMo-A and NiMo-A [84]. (T = 340 °C; P = 7 MPa; LHSV = 1.3 h^{-1}; H_2/HC = 200 mL/mL.)

5.3. Correlation between feedstock properties and HDS reactivity

To obtain a better understanding of feedstock effects on hydrodesulfurization of middle distillates, it is important to develop some form of correlations to relate feed property to reactivity. A number of such correlations are available in the open literature.

A simple empirical correlation was developed by Shih et al. [432] to describe the temperature required for desulfurization of distillates to 0.05 wt.% sulfur. A total of eight feedstock components were employed in the correlation, covering straight-run gas oil (GO), coker gas oil (CGO), and FCC light cycle oil (LCO). The temperature required to achieve 500 wppm product sulfur (T_{500}) was found to be correlated with the concentration of 600 °F (315.5 °C) sulfur and total nitrogen in the feed, but independent of the feedstock source. The reactivity, T_{500}, was expressed as a function of S_{600F+} (sulfur content in wt % of the 600 °F^{+} (315.5 °C) fraction of the feed) and N_f (feed nitrogen content) as,

$$T_{500} = (454\ ^{\circ}\mathrm{F}) + (31\ ^{\circ}\mathrm{F})\exp(S_{600\ ^{\circ}\mathrm{F}}) + (25\ ^{\circ}\mathrm{F})\ln(N_{\mathrm{f}}) \qquad (1)$$

However, the correlation does not include the overall feed quality such as the API gravity. This property–reactivity correlation was later modified in the form of HDS reactivity. The T_{5oo} reactivity data

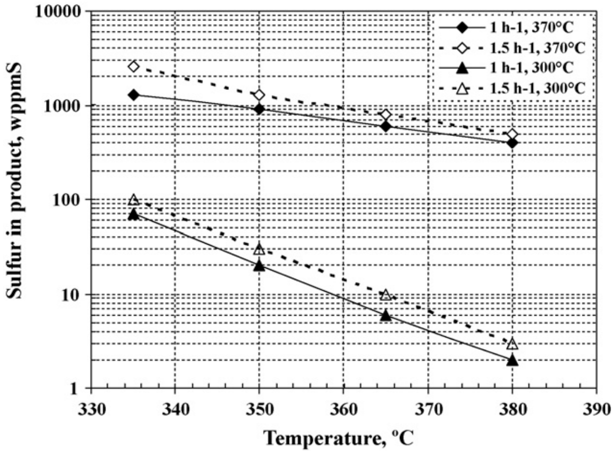


Fig. 44. Effect of lowering T_{95} of CGO on deep HDS as a function of reaction temperature and with variation liquid hour space velocity (1 h^{-1} and 1.5 h^{-1}) [83]. (Catalyst: CoMo/Al_2O_3; P = 5 MPa; H_2/HC = 200 mL/mL.)

was resealed through an Arrhenius expression of

$$R_{\text{HDS}} = 0.0008 \exp\left(\frac{5398}{T_{500}}\right)$$

where T_{500} was now in K instead of °F. And the modified correlation became:

$$R_{\text{HDS}} = (S_{600\,^\circ\text{F}})^{-0.33}(N_\text{f})^{-0.2} \tag{2}$$

Ho [25] also developed a property–reactivity correlation based on 13 high-sulfur (0.9–3.2 wt.%) distillates, each of which was characterized by 24 physicochemical properties. According to the analysis, the HDS reactivity, which was found to be 1.5-order volumetric rate constant, was dominated by three properties in the order of decreasing importance: degree of feed saturation (API gravity) ≫ DBTs (DBT = [β-DBTs) self-inhibition ≫ organonitrogen (N_f) poisoning. The property–reactivity correlation was formulated in the following expression:

$$\text{HDS activity},\ R_{\text{HDS}} = (^\circ\text{API})^{2.18}(\text{DBTs})^{-0.31} + (N_\text{f})^{-0.2} \tag{3}$$

Eq. (2) is very similar to Eq. (3). The only difference was an additional term of °API in the later correlation. Hence Ho [25] considered Eq. (2) is a special form of Eq. (3), which had included the degree of feed saturation and hence Eq. (3) should be more comprehensive and reliable.

In hydrodesulfurizing low sulfur, pre-hydrotreated distillates, Ho and Markley [449] had developed a more compact correlation using fewer adjustable parameters. In this development, 13 low-sulfur (250–1567 wppm) feedstocks of different sources and processing histories were tested with 10 property characteristics. They concluded that for the HDS of low-sulfur, pre-hydrotreated distillates, the feed nitrogen content should be used as an overall, approximate indicator of the HDS reactivity. The corresponding correlation was expressed as,

$$R_{\text{HDS}} = k_{\text{HDS}}(1 - \lambda K_\text{N} N_\text{f}) \tag{4}$$

where λ is a dimensionless parameter which characterizes the extent of HDN reaction, and K_N is the adsorption constant of feed nitrogen.

In a recent study, Choudary et al. [433] demonstrated that for heavy gas oil feeds the desulfurization chemistry is essentially controlled by the strong inhibitory effect of large 3+ ring aromatic hydrocarbon content as shown in the following correlation.

$$S_{\text{Product}} = \left[S^f \exp\left(\frac{-k}{(K)(3+R)}\,\frac{P_{H2}\alpha}{\text{LHSV}}\right)\right]$$

where S^f = feed sulfur, K = 3+ ring, aromatic inhibition constant = 0.0663, 3+R = 3+ ring core aromatic content, α = pressure dependence term, LHSV = liquid hourly space velocity, $K_{\text{group}(x)} = A_{\text{group}(x)} \exp(-E_{\text{group}(x)}/RT)$, k = rate constant, A = pre-exponential factor = 84,370 1/h, and E = activation energy = 56.5 kJ/mol. An excellent correlation was observed between the sulfur conversion (644 K and 6.9 MPa) for the eight different heavy oil feeds and 3 + ring aromatic content (Fig. 45).

Kagami et al. [450] applied a data-mining method to analyze data generated from their ultra deep hydrodesulfurization of straight-run LGO to determine the effective factor of the feed properties to HDS reaction rate. The range of S in the five SRLGO was between 1.18 and 1.36 wt.% and each feed was characterized by 25 properties. The weighted average temperature was used as the reactivity indicator for HDS of SRLGO, and the correlation was expressed as,

$$\ln(A') = \ln(A) + a\ \ln\left(\frac{\text{SpGr}'}{\text{SpGr}}\right) + b\ \ln\left(\frac{N_{\text{f}'}}{N_\text{f}}\right) + c\ \ln\left(\frac{T_{90'}}{T_{90}}\right) \tag{5}$$

where SpGr is the specific gravity, T_{90} is the temperature of 90% distillation, and a, b and c are coefficients. However, for feedstocks of blending SRLGO with LCO, which may contains olefin, the following correlation, including the total aromatics, Sa, was recommended,

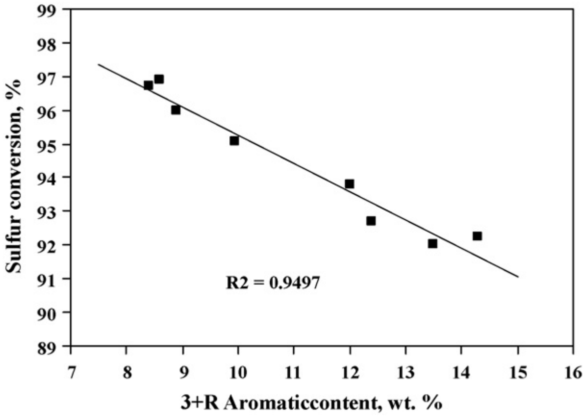


Fig. 45. Relationship between three + ring aromatic content of eight heavy oils and the corresponding sulfur conversion (reaction conditions: temperature = 644 K; LHSV = 1 h^{-1}; pressure = 6.9 MPa; H_2/HO ratio = 356 m^3/m^3) [433].

$$\ln(A') = \ln(A) + a\ \ln\left(\frac{\text{SpGr}'}{\text{SpGr}}\right) + b\ \ln\left(\frac{N_{\text{f}'}}{N_\text{f}}\right) + c\ \ln\left(\frac{T_{90'}}{T_{90}}\right) + d\ \ln\left(\frac{100-\text{Sa}'}{100-\text{Sa}}\right) \tag{6}$$

From these published correlations, the selection of the right feedstock properties is very important to correlate a reliable reactivity indicator.

6. Effect of process variables and thermodynamic limitation

The performances of gas oil hydrotreaters is affected by operating conditions such as reactor temperature, liquid hourly space velocity (LHSV), hydrogen partial pressure and recycle gas to oil ratio. Kinetics studies [21] have shown that the rate of HDS can be increased and the sulfur content can be reduced to lower levels with increase of temperature, increase of hydrogen partial pressure and decrease of space velocity (Fig. 46). Similar results have also been reported in many other studies [9,22,23,46,451,452]. The use of higher operating severity for lowering sulfur levels to ultra low levels in conventional diesel hydrotreaters have practical limitations related to cycle length, throughput, design pressure, hydrogen availability, thermodynamic equilibrium, etc.

The optimum operating conditions for the ultra low sulfur hydrotreater operations will vary depending on the feedstock quality, catalyst type, and thermodynamic limitations. The beneficial effects and limitations of the key process variables in ultra deep desulfurization of diesel are discussed in detail in the next section (Section 7) dealing with the revamping of existing conventional hydrotreaters for ULSD production. The thermodynamic constraint on ultra deep HDS of diesel is discussed in more detail in the following paragraphs.

Since most of the sterically hindered refractory sulfur molecules are present as polyaromatic sulfur compounds, thermodynamic constraint can easily play a role in ultra deep desulfurization of diesel. The increase in reactor temperature does not result in the HDS rate increase expected on the basis of the traditional activation energy. Actually, the removal of sulfur itself is not limited by thermodynamics, but the pre-hydrogenation of one of the aromatic rings before sulfur removal will be strongly influenced by thermodynamics. Aromatics hydrogenation reactions are highly exothermic and reversible. Hydrogenation is promoted by a decrease in temperature and by an increase in hydrogen pres-

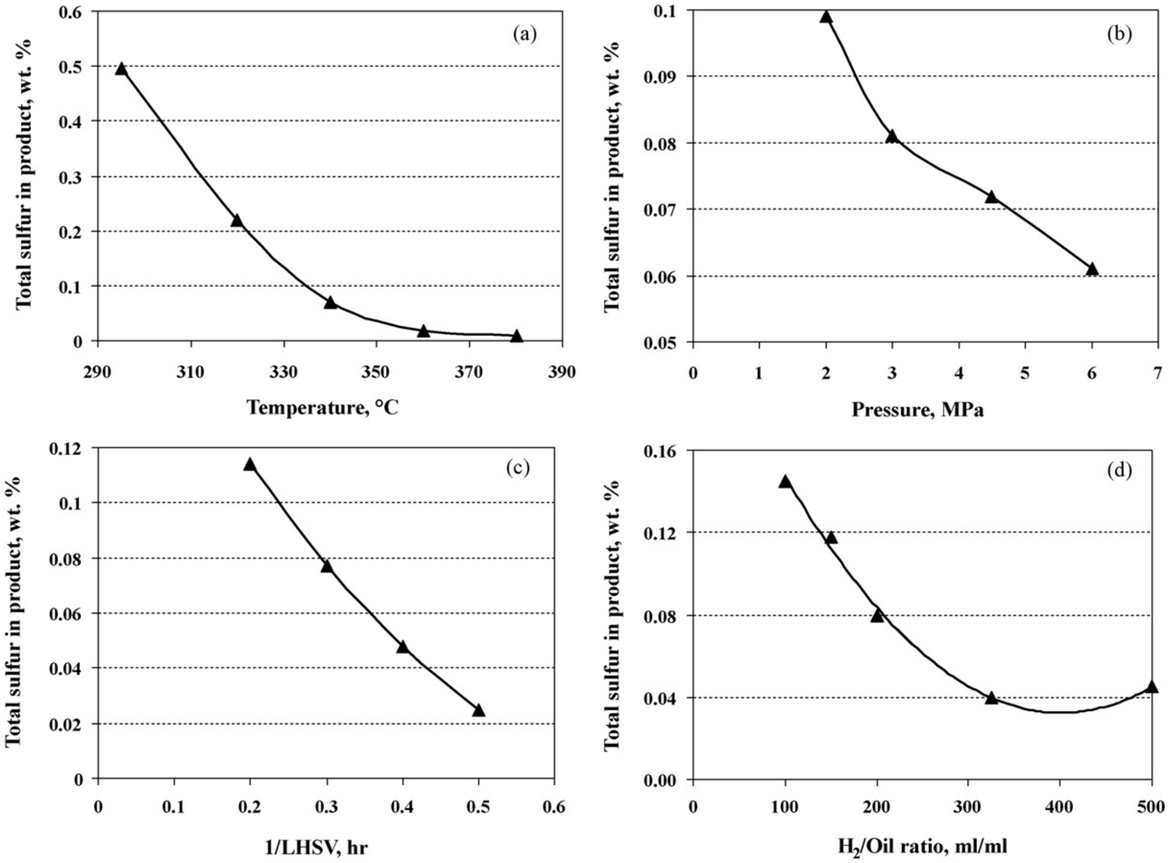


Fig. 46. Effect of temperature (a), pressure (b), LHSV (c) and H_2/HC ratio (d) on the total sulfur removal from gas oil [21]. (Catalyst: CoMo/Al_2O_3; for temperature effect: $P = 3$ MPa; H_2/HC = 200 mL/mL; LHSV = 4 h^{-1}; for pressure effect: $T = 340\,^\circ C$; H_2/HC = 200 mL/mL; LHSV = 4 h^{-1}; for LHSV effect: $T = 340\,^\circ C$; $P = 3$ MPa; H_2/HC = 200 mL/mL; for H_2/HC effect: $T = 340\,^\circ C$; $P = 3$ MPa; LHSV = 4 h^{-1}.)

sure [44b,187,447,453]. At lower hydrogen pressure, increasing reactor temperature to very high levels will have a negative effect on the desulfurization of the polyaromatic sulfur containing compounds (e.g. DBT and alkyl DBT) (Fig. 47). This limitation will be particularly problematic at temperatures close to the end-of the run temperature and in the downstream zone of a commercial hydrotreater where hydrogen partial pressure is low. Farag et al. [454] studied the effect of temperature on the HDS of 4,6-DMDBT at 2.9 MPa hydrogen pressure over two CoMo catalysts, one supported on Al_2O_3 and the other supported on carbon. The results are presented in Fig. 47b, which shows the effect of temperature (as Arrhenius plots) on the rates of direct desulfurization (DDS) and hydrogenation (HYD) reactions of 4,6-DMDBT over the two catalysts. It is seen that at low temperatures [$T < 340\,^\circ C$ (613 K)], the HYD route is predominant while at higher temperatures [e.g. 380 °C (653 K)], the DDS route becomes significant. For both catalysts, the HYD route passes through a maximum as the reactor temperature is increased from 300 °C (573 K) to 380 °C (653 K) and becomes unflavored at higher temperatures. This could be attributed to the thermodynamic limitation of the hydrogenation of 4,6-DMDBT to 4,6-dimethyl tetrahydrodibenzothiophene (H4–4,6-DMDBT). In another related study, Whitehurst et al. [194] experimentally demonstrated that the preferred mode of sulfur removal from 4,6-DMDBT was about 90% by the hydrogenation (HYD) route at 300 °C while at 380 °C the preferred route was about 90% by the direct desulfurization (DDS) route. This dramatic shift in reaction pathway in this temperature range was due to a marked shift in the thermodynamic equilibrium limit imposed on the tetrahydro-4,6-DMDBT (THDMDBT) intermediate at the higher temperature

At higher pressures the thermodynamic equilibrium limitation for polyaromatics saturation is reduced and pure kinetic plays a major role in deep HDS. In addition to deep HDS, cetane improvement by aromatics hydrogenation will also be favored at lower temperatures and higher pressures.

7. Revamping of hydrotreaters for ULSD production

It has been widely reported by hydrotreating catalyst manufacturers and process licensors that most of hydrotreaters that were installed to meet the 1993 low sulfur requirement (500 wppm) can be revamped and modified for ultra low sulfur diesel (10 wppm) production with a modest increase in capital and operational cost [9,23,455–465]. The feedstock properties, its source (straight run, thermally cracked, catalytically cracked, hydrotreated, etc.), limitations in pressure and hydrogen availability in the existing unit should be thoroughly examined before considering the revamping options.

The important options to be considered for the revamp design are:

- Use of highly active catalysts.
- Increase of operating severity (e.g. increased temperature, increase in hydrogen pressure, lower LHSV).
- Increase catalyst volume (by using additional reactor, dense loading, etc.).
- Removal of H_2S from recycle gas.
- Improve feed distribution in the reactor by using high efficiency vapor/liquid distribution trays.
- Use of easier feeds; reduce feedstock end boiling point.

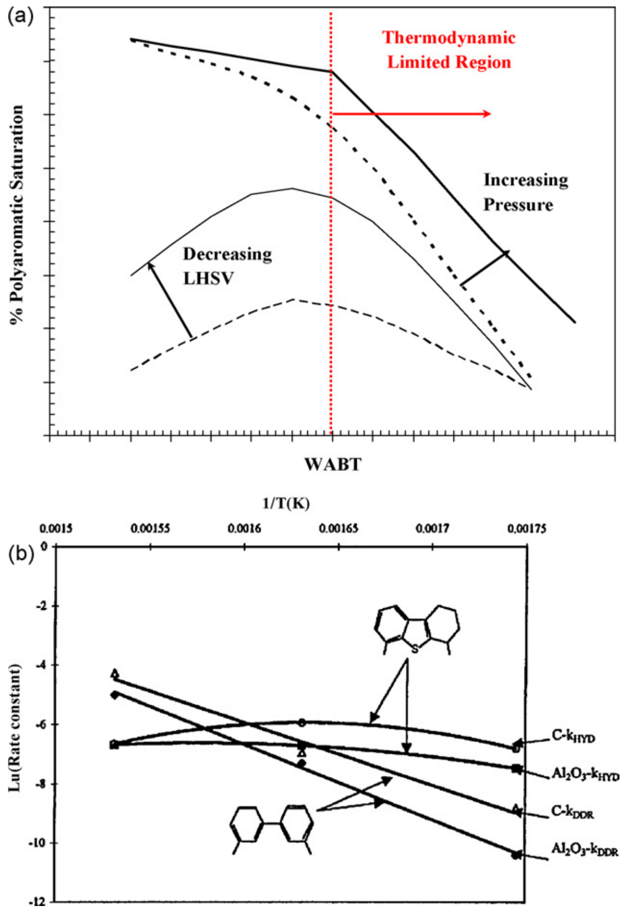


Fig. 47. (a) Reaction rate for removal of substituted polyaromatic (SPA) sulfur and sulfur free polyaromatic (SFPA) compounds is limited at high temperature due to thermodynamics [44b]. (b) Arrhenius plot of individual steps in HDS of 4,6-DMDBT (CoMo/Al_2O_3 and CoMo/C (Carbon), 2.9 MPa H_2; batch reactor) [454].

A combination of the above options may be necessary to achieve the target sulfur level cost effectively. Selection of the most appropriate option or a combination of those is specific for each refinery depending on its configuration, existing hydrotreater design parameters, feedstock quality, product slate, hydrogen availability, etc. Details of various revamping options are presented in the following sections.

7.1. *Use of improved catalysts*

Application of improved hydrotreating catalysts with high activity can improve considerably the desulfurization performance of the existing hydrotreating units. As mentioned earlier, there is information that new generation hydrotreating catalysts developed by various catalyst manufacturing companies such as Albemarle (STARS Series KF-757, KF-760, KF-848, KF-770), Criterion (Centinel Ascent and Centinel Gold Series), Haldor Topsøe (BRIM series TK-558, TK-559, TK-575, TK-576), and Axens (HR-548, HR-526, HR-568) have 40–100% higher HDS activity compared with the ones used in the early 1990s. Selection of the appropriate catalyst or catalyst combinations depending on the feedstock quality, hydrogen availability other design parameters is important for optimum performance as discussed below.

7.1.1. *Catalyst selection for ultra deep desulfurization of diesel feeds*

Both CoMo and NiMo type catalysts with remarkable improvements in HDS activities have been developed and marketed by major catalyst companies for ULSD production (see Table 7, in Section 4). The choice between them is not easy and straight forward, but depends on many factors. The main factors that should be considered in the selection of appropriate catalysts for the production of ultra low sulfur diesel (ULSD) in gas oil hydrotreaters are the following [216–219,466–468].

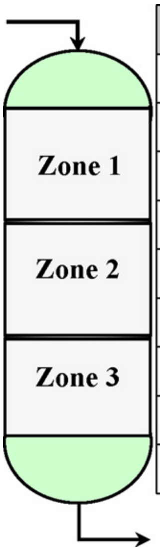
- The activity or performance of the catalyst in desulfurizing the least reactive sterically hindered alkyl DBTs.
- Feedstock quality, especially the concentration of inhibiting compounds (e.g. nitrogen and aromatic compounds) in the feedstock, feed blend components, distillation range, etc.).
- Operating variables, especially, the hydrogen partial pressure.

Studies with model DBT and alkyl DBT compounds have shown that CoMo catalyst desulfurize primarily via the direct desulfurization (DDS) route, whereas, NiMo catalysts exhibit a relatively high activity for the removal of sulfur via the hydrogenation (HYD) route. CoMo catalysts become less effective for desulfurization of the alkyl DBTs containing alkyl groups in the 4 and 6 position due to steric hindrance. NiMo catalysts, on the other hand, are more effective for the desulfurization of such sterically hindered alkyl DBTs through the hydrogenation route. But the hydrogenation route becomes less effective in the presence of inhibitors such as organic nitrogen compounds present in the feedstock.

The differences that CoMo and NiMo catalysts exhibit with respect to the desulfurization routes of the least reactive compounds have a great significance on the choice of the best catalyst for a given feedstock at a given set of conditions. Studies have shown that the hydrogen partial pressure dependency is different for the two different reaction routes. The direct extraction route (for which the CoMo catalyst has the highest activity) has a relatively low hydrogen pressure dependency, whereas the hydrogenation route (for which the NiMo catalyst has the highest activity) exhibits a high hydrogen partial pressure dependency.

A CoMo catalyst would be the best choice in the case where the operating pressure is low, and the feed is a straight run distillate with very little nitrogen. The use of CoMo catalysts also has the added benefit of lower hydrogen consumption compared to the NiMo catalysts. On the other hand, if the feed has a high percentage of cracked feed that contains a lot of nitrogen and the operating pressure is high, a NiMo catalyst would be preferred. Organic nitrogen compounds are strong inhibitors of HDS of the sterically hindered alkyl DBTs via the HYD route. Catalysts with high hydrogenation activity can be beneficial in removing the organic nitrogen by enhancing HDN reaction. This will allow the remaining catalyst volume to desulfurize the refractory sulfur species more effectively through the hydrogenation route. NiMo catalyst is also reported to perform better than CoMo for heavier feeds and exhibit better flexibility [457]. At low pressures and high temperatures, removal of the sterically hindered alkyl DBTs through the hydrogenation route will be less effective over NiMo catalysts due to thermodynamic equilibrium limitations on the hydrogenation step. Under these conditions, a CoMo catalyst may be a better choice than a NiMo catalyst even for feedstocks containing cracked distillates [9,217]. NiMo catalysts are also better choice for aromatics saturation and cetane improvement. Aromatics hydrogenation reaction also proceeds via the hydrogenation route and is inhibited by nitrogen compounds [187].

Thus, at moderate to high pressures, NiMo catalyst will outperform CoMo catalyst significantly for deep HDS of feeds with high nitrogen content, high percentage of cracked distillates or high end point due to their superior HDN and hydrogenation functionality. However, the hydrogen consumption is high for NiMo catalysts. Because of the limitations in the available hydrogen supply and reactor design pressure, many refineries will not be able to



	Zone 1	Zone 2	Zone 3
Sulfur content	High	Medium	Low
Nitrogen content	High	Medium-Low	Very Low
Poly aromatic	High	Medium-Low	Zero
H_2S in gas	0-Medium	High	Highest
NH_3 in gas	0-Medium	Medium	High
H_2 in gas	High	Medium	Medium-Low
Main HDS reaction	Direct	Mainly Direct	Hydrogenation
Main HDS inhibitor	H_2S	Organic Nitrogen	-
HDS reaction rate	Fast	Slow	Fast

Fig. 48. A three zone reactor example [469].

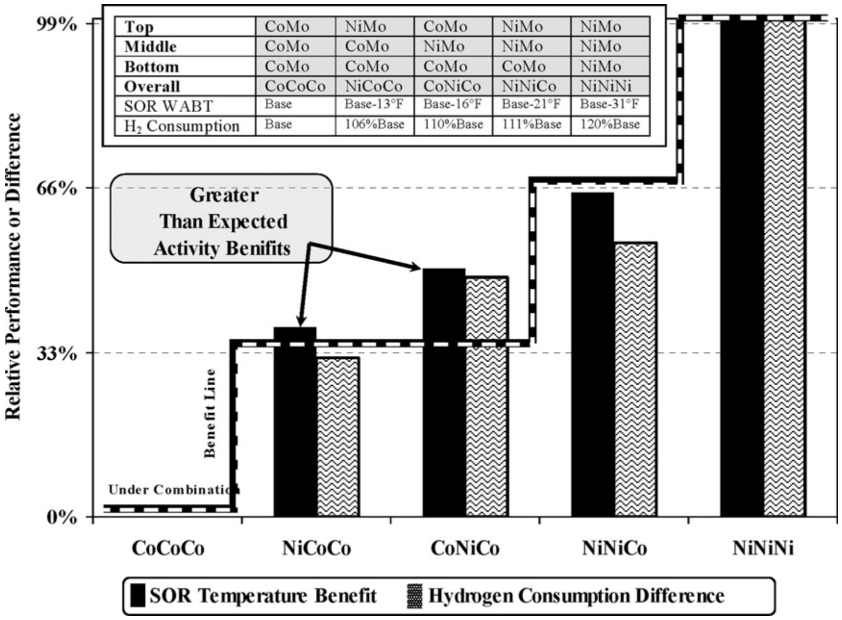
operate at pressures high enough for NiMo catalysts. A trimetallic NiCoMo catalyst (HR468) developed marketed by Axens is claimed to have an improved (optimum) hydrogenation activity without affecting hydrogen consumption [457]. It has been reported that this catalyst combines the good HDS activity of CoMo catalysts with the hydrogenation activity of Ni required for ultra deep HDS activity. Albemarle's Stars CoMo catalyst (KF-760) has been reported to possess higher HDN activity. Where the nitrogen content is inhibiting HDS of diesel fuel, this catalyst can have 15–20% higher HDS activity with only a moderate increase in hydrogen consumption.

The use of stacked CoMo and NiMo catalyst beds is also possible for some feeds (e.g. cracked feeds) to achieve the optimal balance of activity and selectivity for ULSD production [188]. Loading of the reactor with multiple catalysts in various stacking configurations has been reported by some catalyst companies to enhance overall ULSD performance with small increase in hydrogen demand [469,470]. Catalyst selection for stacked catalyst bed design is usually based on a clear understanding of the reaction chemistry of sulfur compounds in different parts of the reactor.

In a recent report, Albemarle claims that its STAX® technology that uses a multi-catalyst system can achieve the following targets in ULSD operation [469].

- Maximum HDS with constrained hydrogen consumption.
- Maximum cetane uplift up to unit hydrogen limit.
- Maximum cycle length at specific sulfur target.
- Simultaneous sulfur and volume gain target.

The scientific basis for their approach in the selection of the best catalyst for optimum system performance is explained with a three-zone reactor example as shown in Fig. 48. Each of the three



Top	CoMo	NiMo	CoMo	NiMo	NiMo
Middle	CoMo	CoMo	NiMo	NiMo	NiMo
Bottom	CoMo	CoMo	CoMo	CoMo	NiMo
Overall	CoCoCo	NiCoCo	CoNiCo	NiNiCo	NiNiNi
SOR WABT	Base	Base-13°F	Base-16°F	Base-21°F	Base-31°F
H_2 Consumption	Base	106%Base	110%Base	111%Base	120%Base

Fig. 49. Strategic placement of CoMo and NiMo catalysts generate greater than expected performance benefits [470].

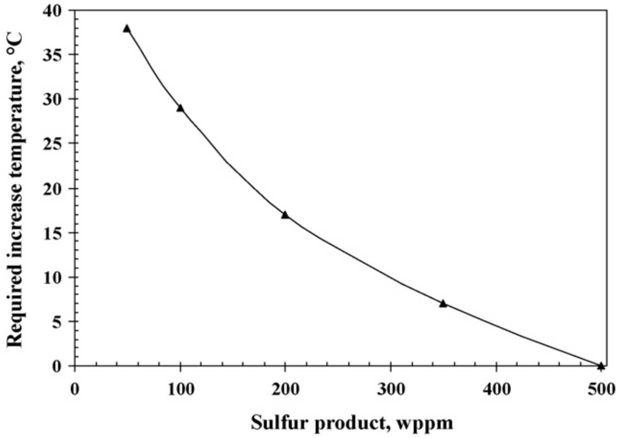


Fig. 50. Required increase in reactor temperature (or bed temperature) to achieve different reductions in the sulfur content of the diesel products (500 wppm is chosen as the base case and LHSV and pressure is kept constant over CoMo catalyst) [22].

zones in this example has dramatically different reaction conditions which affect catalyst performance. In zone 1, the primary reaction occurring is direct route HDS. The rate of desulfurization is fast and sulfur content drops rapidly. At the same time, hydrogen is consumed so ppH_2 is reduced and ppH_2S increases, the latter creating some inhibition.

As the rate of direct route HDS slows, the feedstock moves into zone 2, where the focus shifts from removal of sulfur to removal of nitrogen, organic nitrogen being the main inhibitor to increased HDS reaction rate. Zone 2 ends when organic nitrogen has been almost completely removed. As the, feedstock enters zone 3, hydrogenation route HDS picks up speed. Even though ppH_2 is at its lowest in zone 3, the catalyst is operating in a nitrogen free environment, where the rate of hydrogenation of aromatics – including the aromatic rings of sterically hindered dibenzothiophene molecules – increases. Finally the feedstock exits the reactor as ULSD.

Criterion Catalysts and Technologies have also applied multiple catalysts in various stacking configurations for ULSD production [470]. An example of their approach showing the strategic placement of CoMo and NiMo catalysts in various configurations that can improve ULSD performance (with moderate increase of SOR H_2 consumption) is presented in Fig. 49.

7.2. Increase of SOR temperature

Reactor temperature is an important variable that has a significant influence on HDS and other reactions which occur during hydrotreating. The start of the run (SOR) temperature is normally selected based on the required sulfur reduction which usually depends on the other operating conditions (e.g. LHSV, pH_2), the type of feedstock and catalyst used in the process. Fig. 50 shows the required increase in the catalyst bed temperature to achieve different reductions in the sulfur content of the diesel product over a conventional CoMo catalyst when the other process parameters (e.g. LHSV and pressure) are kept constant [22]. It is seen that a 38 °C increase in reactor temperature is required to reduce the sulfur content of diesel from 500 to 50 ppm. Further large increases in temperature will be required to reduce the sulfur level to 10 ppm. Hydrotreating reactors are usually operated at constant performance to achieve the desired product specifications. During the course of a run, the temperature of the reactor is gradually raised to maintain the catalyst performance to achieve the target sulfur level by compensating a drop in activity due to coke deposits until the maximum permissible end-of-run (EOR) temperature limit for the HDS catalyst is reached.

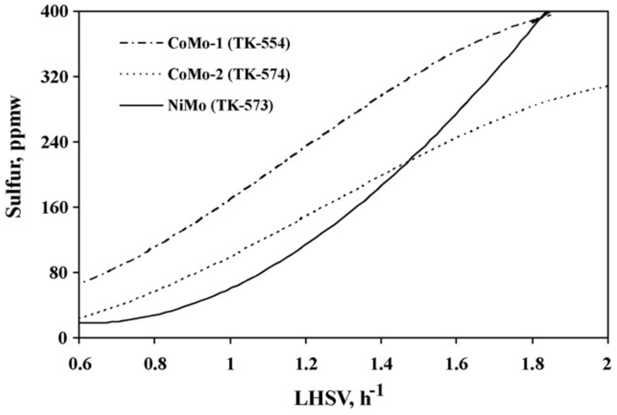


Fig. 51. Product sulfur vs. LHSV (feed SRGO; $P = 3$ MPa; $H_2/HC = 250$ Nl/l) [22].

Most diesel hydrotreating units producing 350–500 wppm product sulfur levels achieved cycle lengths of 2–3 years. A higher SOR will reduce the overall operating window for the ULSD unit. High operating temperature will also increase the rate of catalyst deactivation by coke formation and reduce run length. Another disadvantage of the high temperature operation is its influence on the thermodynamic limitation for desulfurization of alkyl DBTs by the hydrogenation route. The EOR reactor temperature may be reduced by 10–20 °F in ULSD mode compared with current operations due to the thermodynamic equilibrium limitations. Thus, the available temperature window for operation could be reduced from both SOR and EOR resulting in unacceptably short cycle lengths. However, these problems can be eliminated by reducing the SOR temperature to the optimum low levels (320–340 °C) and by using increased hydrogen partial pressure, low LHSV or increased reactor volume and highly active catalyst. A combination of these factors expands the overall operating temperature window for the ULSD unit. A balance between reactor temperature which affects both reaction rate and the aromatic equilibrium in sterically hindered alkyl DBTs and other operating conditions such as hydrogen partial pressure, residence time in the reactor (LHSV), hydrogen availability, etc. must be taken into account in the revamping existing units.

7.3. Reduction of liquid hourly space velocity (LHSV) or increase of catalyst volume

LHSV is the flow rate of the feed oil into the reactor relative to the catalyst, and it is expressed in m^3 of fresh feed per m^3 of catalyst per hour. The inverse of LHSV is generally called residence time. Decreasing LHSV usually increases the degree of desulfurization and reduces product sulfur content (Fig. 51) due to an increase in the contact time between the liquid feed and the catalyst. The LHSV be used in an ULSD unit mainly depends on the catalyst activity, the type of feed and the hydrogen partial pressure. The LHSV is used to define the amount of catalyst needed to get a specified performance. The use of low space velocities will, however, decrease throughput, which implies, that less gas oil can be hydrotreated. Increase of catalyst volume (or additional reactor) is required if the throughput has to be maintained at lower LHSVs. Although the addition of reactor volume appears like a big change relative to some of the other options, it has many benefits and is significantly less expensive compared with a grassroots investment.

An important benefit of increasing catalyst volume (or reducing LHSV) is that the reactor can be operated at much lower temperature. Studies have shown that reducing the LHSV by half by doubling the catalyst volume results in 20 °C decrease in average reactor temperature to achieve the same specific performance when all other operating conditions are unchanged [22]. The removal of the sterically hindered alkyl DBTs through the hydrogenation route will be favored both kinetically and thermodynamically under these conditions (i.e. low LHSV and low temperature). Lower deactivation rate of the catalyst as a result of the decrease in SOR temperature is an additional benefit of reducing LHSV or increasing catalyst volume. Furthermore, because the start of run temperature is lowered more operating temperature span is available. The second reactor can be located either in parallel or in series connection with the existing one [471]. A number of process configurations are possible which includes: (i) series placement without inter reactor separator, (ii) series placement with inter reactor separator and H_2S scrubber, (iii) series placement with intermediate light-end fractionators, (iv) simple parallel placement, and (v) parallel placement with fractionator. Capital investment, operating cost and desulfurization efficiency would differ significantly for different process configuration. Limitations of the existing facilities and cost consideration will largely dictate the location of the second reactor. The main problem to be considered in adding another reactor is hydraulic resistance of the system, space availability, and additional piping and instrumentation. Other factors affecting the choice of series and parallel placement are the capacity of the recycle compressor, catalyst volume in the new reactor, and reactor temperature control requirement. Dense loading of catalyst is another option for increasing the quantity of catalyst in the reactor. The dense catalyst charging can lead to increase of the quantity in the same volume by 15% but this can cause pressure drop in the reactor. The required additional reactor volume generally depends on operating conditions and feedstock properties [22,455].

7.4. Increase of hydrogen pressure

An increase in partial pressure of hydrogen increases the HDS rate and diminishes the coke deposits on the catalyst, thereby reducing the catalyst fouling rate with time-on-stream, and increasing the catalyst life. Changes in hydrogen partial pressure also lead to variation in reaction mechanism for the two different HDS reaction routes. For example, direct desulfurization may occur at relatively low hydrogen pressure, whereas the hydrogenation route is favored at a high hydrogen partial pressure.

At higher hydrogen pressures, desulfurization of the sterically hindered alkyl DBTs through the hydrogenation route is enhanced. Another important benefit of increasing hydrogen partial pressure in the hydrotreater is in removing the thermodynamic equilibrium limits associated with polyaromatics saturation reactions. If the hydrogen partial pressure is high, the thermodynamic equilibrium constraints on the desulfurization of sterically hindered alkyl DBTs are removed and deeper HDS is reported via the hydrogenation. The inhibiting effects of nitrogen compounds and H_2S on HDS reaction will also be reduced significantly at higher hydrogen partial pressures.

Reactor total operating pressure has the most influence on hydrogen partial pressure, but recycle gas hydrogen purity, recycle gas rate, and hydrogen consumption are also important operating variables that affect the hydrogen partial pressure throughout the reactor. Studies have shown that increasing the reactor hydrogen partial pressure by purging recycle gas or by increasing the hydrogen concentration in the make-up gas reduces the reactor start of run temperature and increase cycle length significantly [22].

ULSD operations can be grouped into three reactor pressure severities [26]: low, medium and high (Table 12). Low pressure units are typically best suited to produce ULSD from feeds that are easy to desulfurize, such as SRGO using CoMo catalysts to promote the direct extraction desulfurization reaction. Medium-pressure units can handle some cracked feeds and can operate with CoMo or NiMo catalysts, depending on the desulfurization and denitrogenation requirements and the amount of hydrogen available. High pressure units are effective for dealing with refractory feeds, such as cracked feedstocks (e.g. LCO, CGO, etc.) that contain high concentrations of sterically hindered alkyl DBT sulfur compounds, poly-nuclear aromatics and nitrogen species. Nickel–molybdenum catalyst are preferred in this case to facilitate the removal of sterically hindered alkyl DBT sulfur compounds via the HYD route and to more effectively remove nitrogen species that can inhibit the desulfurization reaction. High pressure operation has, thus, many benefits in the desulfurization of diesel feeds to ultra low sulfur levels. However, it increases the hydrogen consumption and operational cost substantially which has limited its uses.

Table 12
Reactor hydrogen pressure and catalyst type requirements for different type of feeds.

	Severity		
	Low	Medium	High
Pressure (MPa)	2.7–4.1	3.4–5.5	4.8–8.9
H_2 pressure (MPa)	1.4–3.1	2.7–4.5	4.5–6.5
LHSV (h^{-1})	0.5–1.5	0.5–1.5	0.5–1.0
TGR, SCF/B	<1000	1000–3000	2500–6000
H2 cons, SCF/B	<250	200–500	>500
Catalyst	CoMo	CoMo/NiMo/CoNiMo	NiMo

7.5. Removal of H_2S from recycle gas

The sulfur removed from the sulfur compounds present in the feed oil by hydrotreating is in the form of H_2S and it mixes with hydrogen in the hydrotreating reactor. It is well known that H_2S has an inhibitory effect on catalytic HDS reaction. Increasing sulfur removal in the deep HDS process increases the H_2S concentration, especially in the lower catalyst layers. Kinetic studies have shown that hydrogen sulfide inhibits the desulfurization by direct extraction route. Increase of the SOR reactor temperature becomes necessary to maintain the target sulfur level of the product in accordance with the required specifications if the recycle gas H_2S concentration is increased as shown in Fig. 52.

Since the recycle gas hydrogen concentration decreases when the hydrogen sulfide concentration increases, there is an additional effect of the lower hydrogen partial pressure on deactivation rate. Increase of H_2S from 0% to 5% in the recycle gas is equivalent to a required increase in average reactor temperature of about 17 °C at 30 bar and 22 °C at 60 bar [22].

Removal of H_2S from the recycle gas by the installation of H_2S scrubber (amine scrubbing) is important in hydrotreater revamps for ULSD production. This will have two advantages, namely, increase in the partial pressure of H_2, and improvement in catalyst's

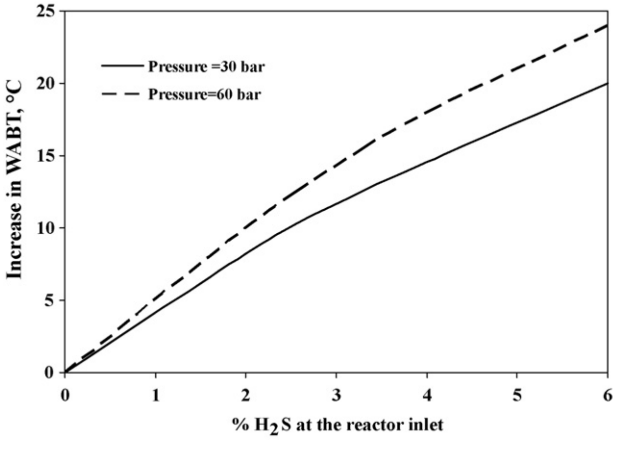


Fig. 52. Impact of recycling gas scrubbing [22].

Table 13
Distribution tray effectiveness [475].

	Simple chimney tray	Topsøe dense pattern flexible distribution tray
Average reaction temperature (°C)	346	321
Feedstock sulfur content (wt.%)	0.7	0.9
Product sulfur content (wt.%)	0.05	0.035
Relative desulfurization activity	1	2.5

HDS activity, since the inhibition effect of H_2S on HDS reaction by direct sulfur extraction route is reduced. The SOR temperature of the reactor could be significantly reduced because of these benefits.

7.6. Improve feed distribution in the reactor

Liquid feed flow distribution in the reactor plays an important role on the performance of hydrotreating units, particularly, when the sulfur content of the products has to be reduced to ultra low levels. Maximum catalyst utilization can only be achieved if the gas and liquid reactants are uniformly distributed both volumetrically and thermally before they are introduced into the top of each catalyst bed. Poor selection and design of reactor internals can lead not only to a significant and unnecessary loss of reactor volume, but also significant under-utilization of the installed catalyst volume.

Many types of vapor/liquid distributor trays have been designed and commercialized in recent years. Some examples from these are Haldor Topsøe's “Dense Pattern Flexible Distribution Tray” and “Vapor-Lift Distribution Tray”; Axens “EquiFlow Reactor Internals”; AKZO Nobel's “Duplex vapor/liquid distribution tray”; Shell Global Solutions “High Dispersion” and “Ultra Flat Quench” trays. Table 13 shows an industrial example from the Philips Petroleum Company of the benefit gained by replacing a chimney type distributor with a Topsøe Dense Pattern Flexible Distribution Tray. The relative HDS activity achieved with the dense pattern flexible tray is 2.5 times higher than that with a simple chimney tray.

7.7. Use less problematic feeds

Feedstock quality is an important issue that should be taken into account in the revamping of an existing HDS unit for ULSD production. Selecting the right feeds matching with the existing unit's capabilities is important for cost effective revamping. Most straight-run distillates contain relatively low levels of the sterically hindered compounds. The concentrations of nitrogen and PNA compounds which inhibit deep HDS reactions are also relatively low in straight run gas oil (SRGO) feeds. LCO contains the greatest concentration of sterically hindered compounds, while other cracked distillate streams from the coker and the visbreaker contains sterically hindered compounds in concentrations between SRGO and LCO. Thus, LCO is generally more difficult to desulfurize than coker distillate, which is in turn more difficult to treat than straight-run distillate. In addition, cracked stocks have high levels of nitrogen and PNA compounds.

Since, the cracked distillates (i.e. LCO and CGO) are more difficult to desulfurize than SRGO, they should be avoided if the existing reactor operates at low pressures. If the existing units are capable of high pressure operation feed blends containing SRGO and LCO or CGO could be used.

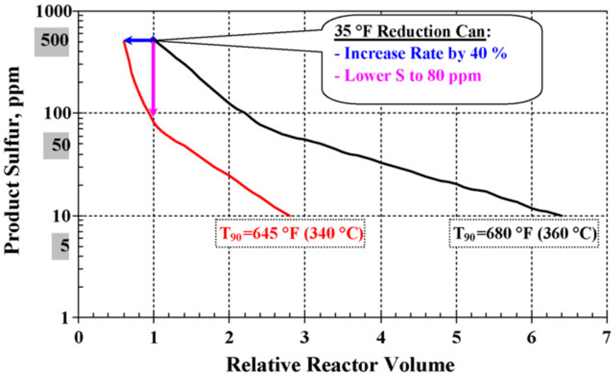


Fig. 53. Relative reactor volume vs. feed T_{90} [86].

Lowering the cut-point of the diesel streams is an attractive option for improving the units capability for ULSD production without major revamping. The refractory sulfur and nitrogen species that boil above 335 °C will be excluded from the feed if the cut-point is reduced to 330–340 °C. The remaining sulfur species will be much easier to process. It is reported [86] that by lowering the T_{90} distillation temperature of a feed from 360 °C to 340 °C sulfur reduction to 50–100 wppm levels could achieved in a unit producing 500 ppm as shown in Fig. 53.

Although undercutting can effectively increase HDS reactivity of the feedstock significantly, about 10–20% of the oil in the high value diesel streams will have to be downgraded to low value heavy gas oil products, which may affect the refinery economics. However, if a refinery has hydrocracking units, the hydrocracker would be an ideal place for processing or these streams. Another disadvantage is that the energy content of the ULSD will decline because undercutting will result in a lighter diesel stream.

7.8. Hydrogen consumption

The hydrogen requirement for the ULSD unit is significantly higher compared to that is needed to make diesel meeting the 500 wppm sulfur specification (Fig. 54). Increase in hydrogen consumption from 40 to 100% has been reported in some studies [9,472,473]. The required increase in hydrogen consumption depends on several factors such as, feedstock quality, the amount of cracked material blended in the feed, catalyst type, unit pressure, LHSV, and the level of aromatics saturation.

Feedstock type used for ULSD production can have a large influence on the amount of hydrogen consumption. Increase in hydrogen consumption could be as little as 5–10% for a feed with little heavy material and with no cracked stocks. For feeds containing a large amount of heavy cracked distillates, the hydrogen

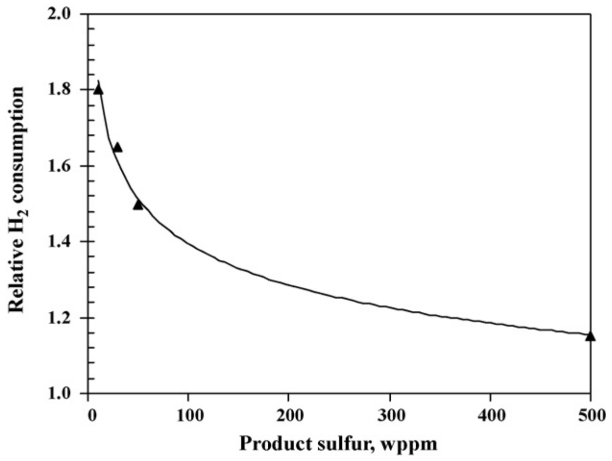


Fig. 54. Hydrogen consumption as a function of sulfur content in the product [9].

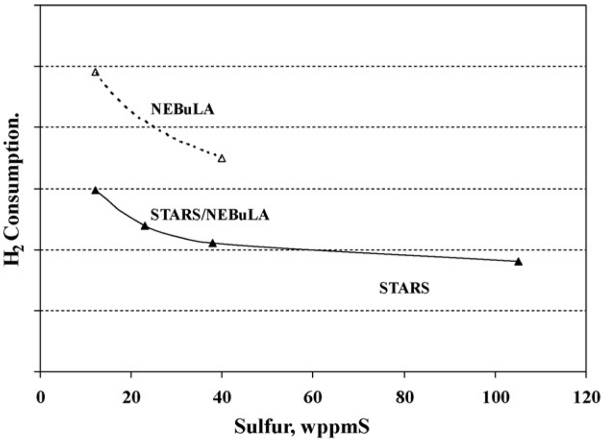


Fig. 55. H_2 consumption comparison between NEBuLA/STARS system and NEBuLA [474].

consumption may increase significantly. The hydrogenation activity of the catalyst also plays a key role on hydrogen consumption in ULSD units. CoMo catalyst which removes sulfur more selectively by direct hydrodesulfurization route with less organic nitrogen inhibition consume less hydrogen compared to the NiMo catalysts.

Refiners with feed that contains a large amount of high boiling cracked material currently using Co/Mo catalyst will experience a large increase in hydrogen consumption when switching to Ni/Mo catalysts for ULSD production. The amount of hydrogen required to remove the last 500 ppm sulfur is small, even considering the hydrogenation route to desulfurizing the substituted dibenzothiophenes with saturation followed by desulfurization. However, the other aromatics in the feed will be saturated along with the target molecules resulting in a large increase in hydrogen consumption [474]. The hydrogen consumption for two different commercial catalysts as a function of sulfur content of the product is shown in Fig. 55.

Higher hydrogen consumption requires more make up gas and higher treat gas rate. Typical recommended treat gas rates are 3–4 times chemical hydrogen consumption. Hydrogen consumption is the largest operating cost in diesel hydrotreaters. Increased hydrogen consumption in the ULSD production will, therefore, increase the operating cost significantly. To meet the increase in hydrogen demand, additional hydrogen producing equipment and compressors with related piping and instrumentation will be required for revamping. Another important point to be considered is additional quench system for the reactor. The higher hydrogen consumption results in a significant increase in reaction heat for all cases and, thus, quench has to be added to limit the temperature rise in the reactor.

7.9. Summary of revamping options

In summary, a combination of several factors such as increase of catalyst volume (with an additional reactor), replacement of the old generation catalyst with highly active new generation hydrotreating catalysts, increased hydrogen partial pressure, removal of H_2S from the recycle gas by scrubbing and the use of high efficiency feed distributors in the reactor, and the use of feedstocks that are easy to desulfurize could be considered in hydrotreater revamps for ULSD production. Simple catalyst change with moderate adjustments in operating conditions would be the best desirable options for revamping existing gas oil hydrotreating units to produce ULSD with minimum capital expenses. This could be possible with catalysts showing extremely high HDS activity such as Nebula. However, the catalyst cost, hydrogen consumption and other operating costs are substantially high for such catalyst, which would partly offset the savings in capital expenses. Since increase in hydrogen consumption increases the operating cost and related capital investment, minimizing hydrogen consumption should be given importance in the selection of revamping options for diesel hydrotreaters.

The preferred combination of options proposed by five major companies for modifications of existing diesel hydrotreating units for reducing the product sulfur content from the current 500 ppm level to 30 and 10 ppm levels are summarized in Table 14. The modifications were estimated based on the use of a feedstock with a sulfur content of 0.9 wt.%, a specific gravity of 0.86, and a T_{90} value of 321 °C. It can be seen that for 30 ppm sulfur level all of them recommended the installation of amine scrubber. 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. For reducing sulfur to 10 ppm level they require the significant sacrifice of LHSV. In addition, IFP says that a sulfur content level of 10 ppm cannot 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 [475].

Table 14
Modifications for reducing the sulfur content from 500 ppm to 30 ppm and 10 ppm [475].

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

	Current	UOP	IFP	Akzo	Criterion	Topsøe
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

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

	UOP	IFP	Akzo	Criterion	Topsøe
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

Table 15
Important catalytic reactor technologies and commercial processes for middle distillate ultra deep HDS and hydrogenation.

Licensor (year of introduction)	Process name	Process objective	Ref.
Shell	Shell middle distillate hydrogenation process	Deep desulfurization and aromatic saturation of gas oil to produce low S and low aromatics in diesel	[476,477]
Topsøe	Two stage process for improving diesel quality	Deep HDS and aromatic hydrogenation of diesel blends	[478,479,480]
	Ultra deep HDS process (UD HDS)	The process is a two stage process for producing low-sulfur and low-aromatic diesel fuel	
IFP/Axen	IFP deep HDS and HDA	Diesel deep HDS and aromatic hydrogenation	[481,482,483,484,485]
	Axen (IFP) Prime-D process	Producing diesel fuel with ultra-low sulfur content, reduced polycyclic aromatic compounds, and a boosted cetane rating	
	Moderate pressure hydrocracking (MPHC) and deep HDS	10 ppm S diesel through hydrocracking under medium to high pressure at relatively high conversion level	
Nippon Oil	Two stage deep HDS	Diesel deep HDS	[486]
Texaco	T-star	Light and middle distillate HDS HYD Heavy distillate hydrocracking	[487,488]
Exxon	DODD	Middle distillate deep HDS	[489,490]
Akzo Nobel-Fina	Akzo-Fina CFI	Diesel quality improvement by dewaxing, hydrotreating and hydrocracking	[491]
Japan Energy	Gas oil deep HDS process (two step)	Middle distillate deep HDS	[492]
Mobil, Akzo, Kellogg, Fina	MAK Fining	To match the current diesel fuel standards as well as the upgraded standards in years ahead	[493,494,495]
Process Dynamics and and Linde BOC	Isotherming	Pretreatment before conventional HDS for ULSD	[496,497,498]
UOP	MQD Unionfining	High-quality, low-sulfur diesel fuel by combining base metals and noble metal catalyst in the first and second stages, respectively	[499,500]
SK corporation, Korea	SK HDS pretreatment technology	ULDS production with pretreatment of middle distillate by adsorption	[501,502a,502b]
POLF	POLF Technology	Presaturated one liquid flow technology for ULDS	[503,504,505]
Criterion, ABB Lummus	SynSAT	Diesel HDS and hydrogenation to improve diesel quality	[506,507,508,509,510]
	SynHDS	Ultra deep HDS	
	SynShift	Ultra deep HDS, density reduction, cetane, increase, distillation shift, polyaromatics, saturation	
	SynSat	Ultra deep HDS, poly and mono-aromatics saturation, cetane increase and density reduction	
	SynFlow	Ultra deep HDS and cold flow improvement	

It should be noted that the revamp design options discussed here for reducing sulfur in diesel to ultra low levels may not be sufficient to improve the other important properties of diesel with high cetane number, lower poly-nuclear aromatics content, lower total aromatics content and lower density. If improvements in these properties are also required to meet future changes in specifications, the refiner may choose to build new grassroots facility which might involve more costly investments.

8. Deep HDS process technology developments

Many new concepts and technologies have been developed during the last 20 years to desulfurize the least reactive sulfur species from the diesel feed that make reaching the near zero sulfur requirements attainable cost effectively. Some important new catalytic hydrotreating reactor technologies and processes [476–509] that have been developed and commercialized for ultra deep HDS and dearomatization of diesel are presented in Table 15 and discussed in the following sections.

8.1. Two-stage processes

Two-stage processes using fixed bed reactors in each stage have been developed and commercialized by some process licensors. The two-stage processes are very effective in reducing both sulfur and aromatics in diesel fuel to very low levels. A schematic flow diagram of the two-stage diesel hydrotreating process licensed by Shell [476,477a,b] is shown in Fig. 56. In the first stage, gas oil is hydrotreated over a conventional $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ type catalyst and after the interstage stripping to remove H_2S and NH_3, the first stage product gas oil is further treated in the second stage over a sulfur resistant noble metal/zeolite catalyst. Reduction of H_2S and increase of H_2 partial pressure are primarily responsible for ultra deep HDS and aromatics hydrogenation in the second stage reactor. The properties of the diesel in terms of sulfur and aromatics level can be fine-tuned with the temperature of the second stage reactor as variable.

Similar two-stage processes have been developed by Topsøe, UOP and IFP. The two-stage ultra deep HDS process developed by Topsøe (Fig. 57) consists of a first stage reactor, an intermediate stripper, a second stage reactor and second stage stripper [478–480]. NiMo type catalysts are used in the first stage reactor. The second stage reactor employs a precious metal catalyst (e.g. TK-907). Both sulfur and aromatic contents of diesel is reduced to ultra low levels in this process as shown in Table 16.

UOP's MQD uniting process [499,500] is also a two-stage process designed to achieve the highest quality diesel by using a base metal catalyst in the first stage and a noble metal catalyst in the

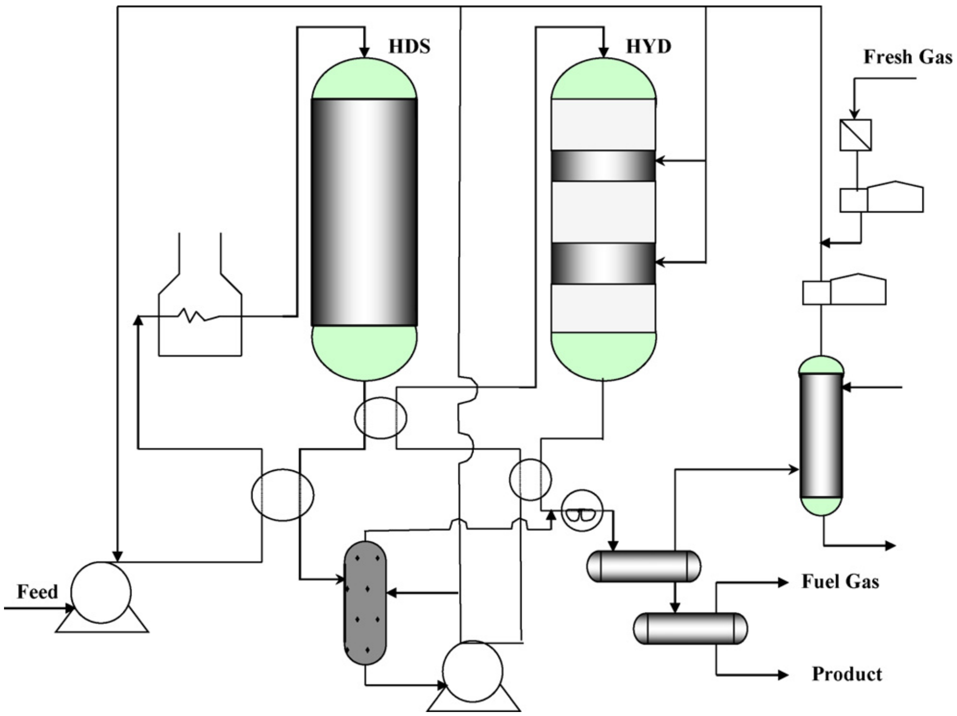


Fig. 56. Gas oil hydrotreating, decoupling HDS and aromatic hydrogenation: shell middle distillate hydrotreating process [477a,477b].

second stage. UOP recommends using AS-250^{TM} catalyst for aromatics saturation because it exhibits high activity and shows much lower sensitivity to feedstock sulfur and nitrogen levels than other diesel aromatics saturation catalysts.

In IFP's Prime-D30 process diesel fuel with ultra low sulfur content, reduced polycyclic aromatics and high cetane index is produced by two-stage hydrotreating/hydrogenation operations [475,481–483]. In the first stage a NiMo catalyst at comparatively high pressure (6–8 MPa) is used to reduce the sulfur content of cracked diesel fuel to 50 wppm or less. After fractional distillation of the reaction products, the diesel fuel fraction containing virtually no sulfur and hydrogen sulphide 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 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

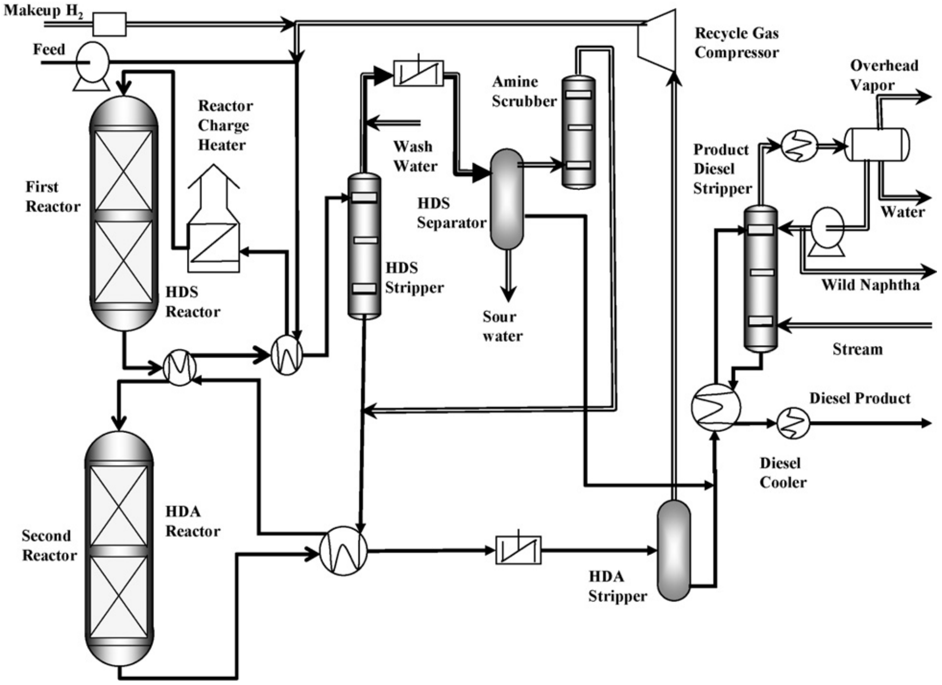


Fig. 57. Diesel upgrading-Topsøe's two stage process [480b].

Table 16
Performance of Topsøe two stage HDS/HDA unit [480b].

	Feed	1st stage product	2nd stage product
Catalysts	–	TK-555	TK-907
Density @ 15 °C (g/cm^3)	0.91	0.88	0.87
Sulfur (wppm)	6515	9	1
Nitrogen (wppm)	775	3	<1
Cetane index	39	46	49
Total aromatics (wt.%)	33	24	3.5
TBP distillation (°C)			
10%	255	–	–
50%	315	–	–
95%	370	–	–
Operating conditions			
H_2 pressure (kg/cm^2)		71	70
Temperature (°C)		367	287
LHSV (h^{-1})		Base	Base × 3

content is reduced to 1.4% in the second stage as shown in Table 17.

8.2. *Syn Technologies*

Syn Technologies which include SynHDS, SynShift and SynSat were developed by the SynAlliance, consisting of Shell Global Solutions, ABB Lummus Global, and Criterion Catalyst Company. SynHDS technology is primarily focused on producing ultra low sulfur diesel and is capable of meeting sulfur specifications of <10 wppm. SynShift is a selective ring opening technology for processing even the most difficult-to-treat feedstocks for the purpose of density reduction, T_{95} reduction (shift), cetane improvement and aromatics (poly-nuclear and total) reduction. SynSat is specifically focused on aromatics saturation, providing added density reduction and cetane improvement. SynShift and SynSat can be combined for deep HDA and T_{95} reduction, along with deep HDS.

A combination of different catalysts and reactor configurations are used in the SynTechnologies [506–509]. Typical reactor configurations are shown in Fig. 58. The number of catalyst beds in each reactor stage can vary depending on feedstock type and targeted diesel product specifications. A general guide to applying the right reactor system and associated SynTechnology is shown in Table 18. For example, the SynSat technology uses multiple catalyst beds and a reactor design that uses both co-current and counter current liquid/vapor contacting in separate catalyst beds (Fig. 58D). Hydrogen and oil are processed in co-current flow to achieve deep desulfurization in the first reactor. Desulfurized oil is stripped with hydrogen to remove H_2S and then is processed in countercurrent flow over a noble metal-based hydrogenation catalyst in the second reactor. This enables a relatively high hydrogen partial pressure in this part of the reactor and, therefore, improved hydrotreating performance for deep HDS and deep HDA to produce ultra low sulfur diesel with low aromatics content and high cetane index.

8.3. *Multicatalyst bed—catalytic distillation combined reactor technology*

This reactor technology was designed by Mochida et al. [117] to achieve deep HDS of diesel by hydrotreating the light and heavy fractions of the diesel feed in separate catalyst beds. Fig. 59 shows a schematic diagram of the reactor system. This reactor combines catalytic distillation and the characteristics of low H_2S partial pressure in the final stage hydrotreating with counter-current operation. Fresh gas oil is introduced at about two thirds reactor height in between the top bed of sulfided CoMo/alumina catalyst and a middle bed of sulfided NiMo/alumina catalyst. Hydrogen is fed at the bottom of the reactor below the bottom bed of sulfided NiMo/alumina catalyst. The reactive light S-containing molecules are hydrodesulfurized in the small top CoMo catalyst bed at high H_2S partial pressures. The less reactive and heavier S-containing molecules are deeply desulfurized over a sulfided NiMo/alumina catalyst in the main catalyst bed in gas/liquid counter current operation. In the virtually H_2S free bottom part of the reactor, where fresh and relatively cold H_2 is introduced, deep HDS and hydrogenation of the aromatics is accomplished at a relatively low operating temperature.

8.4. *MAK Fining process [493–495]*

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 hydrodesulfurization (CoMo catalyst); (2) HDHDC: mild hydrocracking of heavy distillate (NiMo 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.

A combination of UDHDS and HDHDC with a zeolites containing catalyst could be used to produce high quality diesel fuel with lower PNA content, lower density, lower T_{95} and higher cetane number. UDHDS and MIDW could be combined to produce ultra low sulfur diesel fuel (<10 ppm sulfur) with significant improvement in cloud point.

Table 17
IFP Prime-D30 process reaction example].

	T_{95} (°C)	Sulfur (ppm)	Nitrogen (ppm)	Aromatic (wt.%)	Cetane index
LCO feedstock	319	15,800	1,100	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

Table 18
General guideline to apply the right reactor system to SynTechnology [507].

Objective					Reactor system			SynTechnology		
Deep HDS	Deep HDA	PNA reduction	Cetane increase	API gain	CO	CO/CO	CO/CTR	SynHDS	SynShift	SynShift/SynSat
x					x			x		
x			x	x	x				x	
x		x	x	x		x	or x		x	x
x	x	x	x	x			x			x

CO, cocurrent only; CO/CO, cocurrent/cocurrent with or without integrated interstage stripper; CO/CTR, cocurrent/countercurrent with integrated interstage stripper.

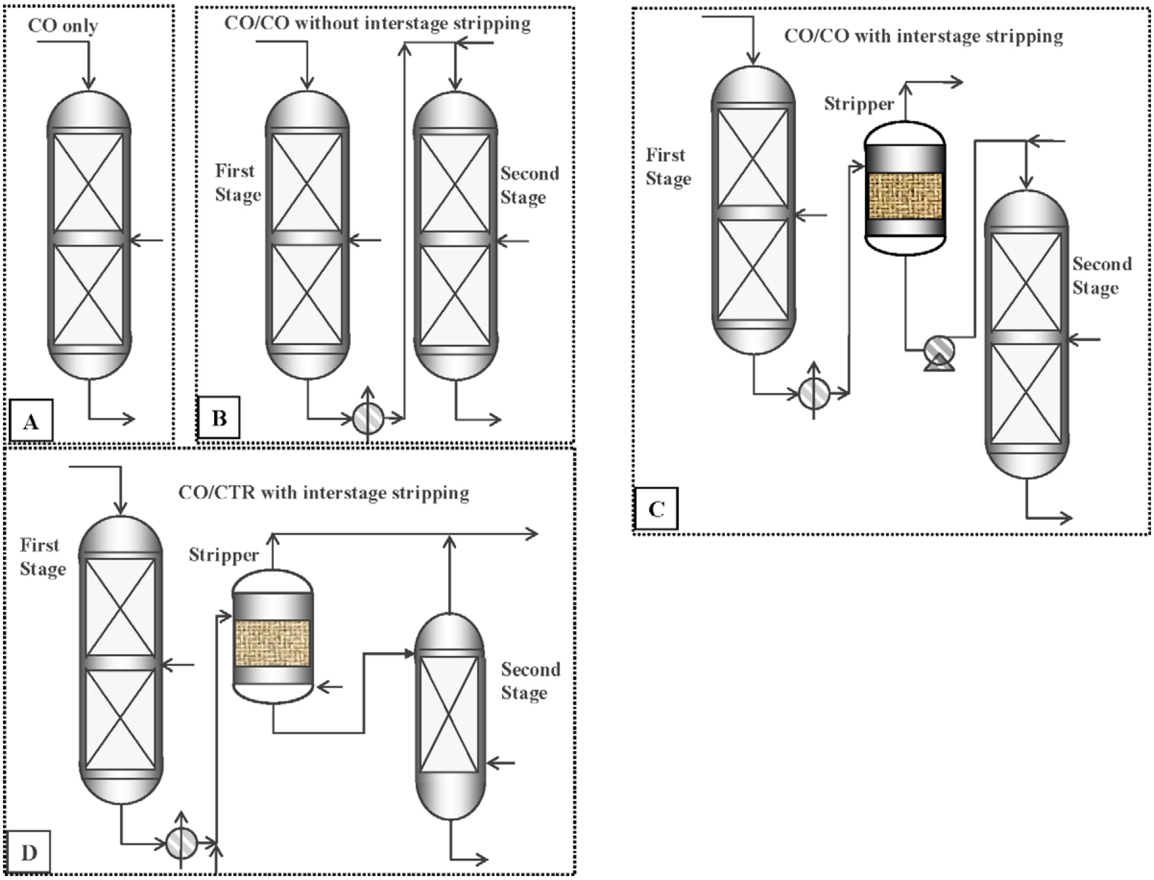


Fig. 58. Combinations of different reactors and their configurations used in SynTecnology [507].

8.5. *IsoTherming technology [496–498]*

The IsoTherming process design and technology for ultra deep desulfurization of diesel was developed by Process Dynamics and Linde BOC Process Plants (LBPP). A schematic diagram of the process is shown in Fig. 60. The basic principle of this process is to enrich the liquid feed with hydrogen (i.e. by pre-saturation) in a pretreating reactor before it enters the catalyst bed. The pretreat

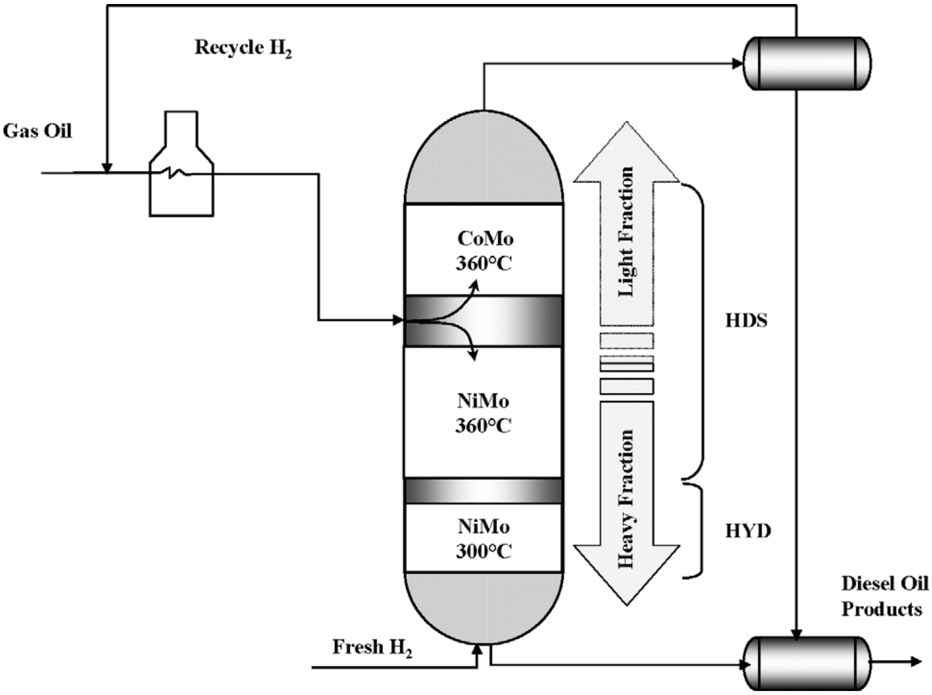


Fig. 59. Alternative gas oil hydrotreating concept: separating light and heavier S-containing molecules [117].

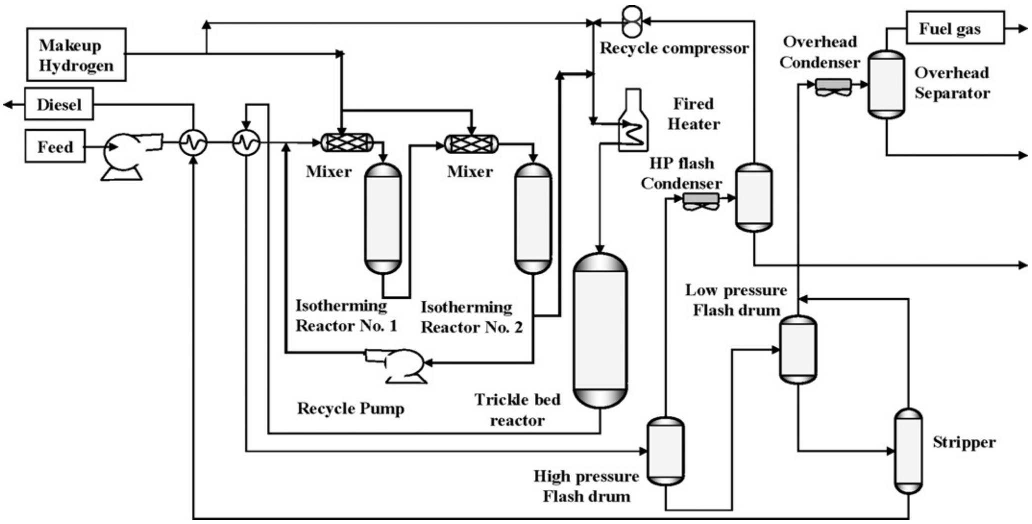


Fig. 60. IsoTherming: pilot plant process flow configuration [496].

reactor is positioned before the main reactor. The fresh feed is mixed with a part of the recycle stream of previously hydrotreated liquid in the pretreater and saturated with hydrogen. With all the necessary hydrogen in the liquid, the combined feed and recycle enters the catalyst bed where the reactions occur. The overall reaction is controlled by the intrinsic reaction rate (the product of the effectiveness factor of the catalyst and the actual reaction rate). An added benefit to the recycled product is its ability to control the heat of reaction, hence the name IsoTherming. Installed in the pretreat position in an ultra low sulfur diesel application, the IsoTherming unit will account for 90–98% of the sulfur removal and 70–90% of the hydrogen consumption while containing only 15–30% of the total catalyst volume. The intermediate product is then sent to the main HDS reactor, which produces the final ultra low sulfur product. The pretreater is claimed to desulfurize a gas-oil feed to low sulfur and nitrogen levels such that the main HDS reactor can bring the feed to <10 wppm sulfur levels in a hydro-finishing or polishing step.

Since the IsoTherming unit is not contained within the existing hydrogen recycle system, the pretreat IsoTherming unit can be operated at higher pressure than the existing unit. The pretreat IsoTherming configuration allows refiners with low-pressure units to add the enhanced performance of a high-pressure unit without having to upgrade the entire hydroprocessing unit to a higher pressure. The total cost of an isoTherming revamp is reported to be 60% of a conventional revamp [498]. Hydrogen consumption, nitrogen removal and heat removal are all accomplished by carrying out the reactions in a kinetically limited liquid full reactor scheme.

The first commercial IsoTherming hydrotreater was completed in 2003 at Giant Industries refinery (now Western Refining Incorporation) in Ciniza, New Mexico, USA. It was one of the first refineries in the USA to begin production of EPA-mandated ultra low sulfur diesel. Process Dynamics has now licensed a total of nine IsoTherming technology packages to U.S. refiners.

8.6. *POLF (presaturated one liquid flow) technology [503–505]*

In this process, the oil is externally saturated with H_2 in a presaturator and only the H_2 saturated liquid oil (without any gaseous H_2) is passed over the catalyst (e.g. CoMo) in a fixed bed reactor (Fig. 61). Thus, a two-phase reactor with a presaturator is used in this process. The process concept is based on the principle that the hydrogen consumption is small compared to the amount of dissolved H_2 in the oil. So, the amount of dissolved hydrogen entering the two-phase reactor clearly exceeds the demand for HDS and would be adequate for desulfurization of the oil to ultra low sulfur levels.

The two-phase process is reported to be more economical than the conventional three phase trickle bed HDS technology because of the following reasons. (i) gas–liquid and liquid–solid mass transfer enhanced; (ii) H_2-recirculation is not needed; (iii) hydrodynamics are simplified, e.g. a proper gas–liquid-distribution or a high degree of wetting of the catalyst as demanded for trickle beds

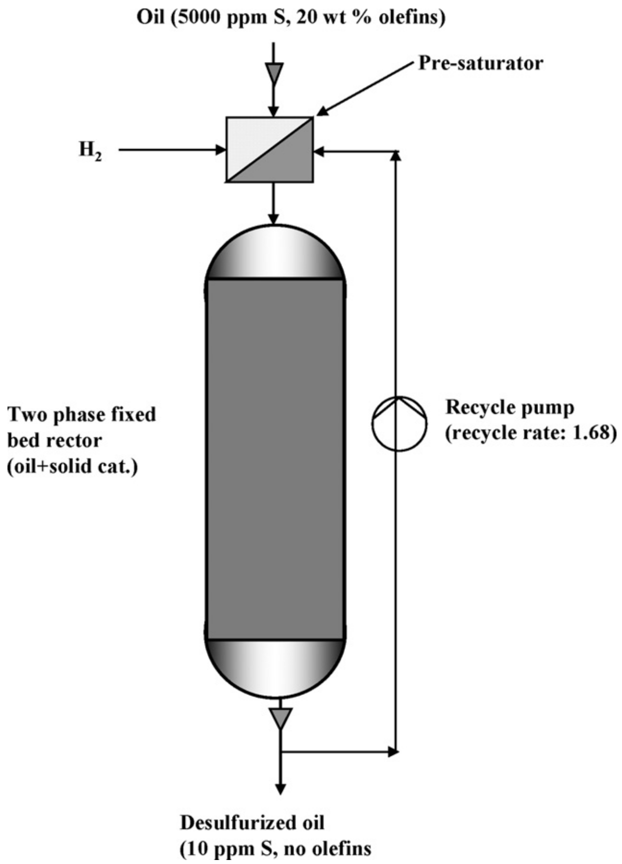


Fig. 61. HDS of a diesel oil rich in sulfur and olefins in a two phase reactor with H_2-pre-saturation [505].

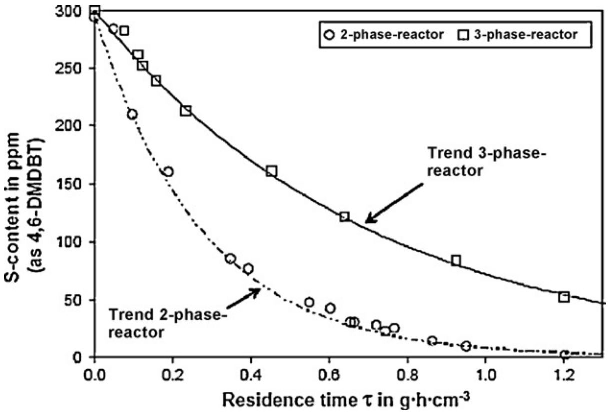


Fig. 62. HDS in a conventional trickle bed reactor and in a reactor with H_2-pre-saturation of oil (model oil with 4,6-DMDBT in n-dodecane, 360 °C, 3 MPa, Siud-Chemie CoMo-catalyst) [505].

are not needed, which probably reduces the reactor size; and (iv) scale-up problems practically cease to exist, as the reactor with pre-saturator can be regarded as a simple tubular plug flow reactor. Comparative deep HDS experiments of 2,4-DMDBT in conventional trickle bed reactor and in the two-phase reactor with a presaturator have shown 2.5 times higher HDS in the two-phase reactor than in the trickle bed reactor (Fig. 62).

8.7. SK hydrodesulfurization (HDS) pretreatment technology [501,502a,b]

This technology was developed by SK Corporation Korea. It involves adsorptive removal of nitrogen-based polar compounds (NPC) from the diesel feed followed by catalytic hydrotreating to produce ultra low sulfur diesel. Dramatic improvement in deep HDS efficiency is observed with the removal of NPC from the feedstock. SK HDS pretreatment process consists of multiple adsorbers, two stripping columns for desorbent recovery, associated pumps, and overhead system. Middle distillate feed is pretreated prior to HDS process in the adsorbent vessels followed by stripping to remove a small amount of desorbent. The pretreated feed is then sent to the downstream HDS unit for sulfur removal. The rejected stream with high nitrogen content, about 2 vol.%, can be either used as a blending stock for heavy petroleum products or processed in other refining units. This technology has been successfully demonstrated through a 1000 barrel/day plant.

8.8. Integrated moderate pressure hydrocracking (MPHC)/hydrotreating process

The process is a recent approach to produce clean diesel fuel from heavy gas oils such as SRGO, HCO, HCGO, and VGO [484a,b,485]. A schematic diagram of the process is shown in Fig. 63, where a fresh VGO feed is mixed with recycled hydrogen and sent to the MPHC reactor. The reactor effluent is cooled, stripped and fractionated in a distillation section. The hydrotreated VGO cut is sent to either in FCC unit or to storage. The diesel cut is mixed with fresh hydrogen and sent to a once through polishing reactor. All make-up hydrogen needed for both the reaction sections enter the finishing reactor first. The hydrogen pressure in the polishing reactor ensures that the converted diesel undergoes the maximum possible hydrofinishing. This approach ensures a steady diesel product quality throughout the cycle regardless of operating variations in the MPHC section. By dissociating diesel quality improvement by hydrofinishing from the MPHC operation, it is possible to achieve other quality specifications such as reduced density or poly-aromatic content. Compared to two separate units, this process reduces process equipment investment and operating costs, and eliminates two compressors and an air cooler while offering flexibility for better heat integration. About 35% conversion with the production of 10 wppm sulfur diesel from a SR VGO and heavy coker gas oil feed has been reported in this process [485].

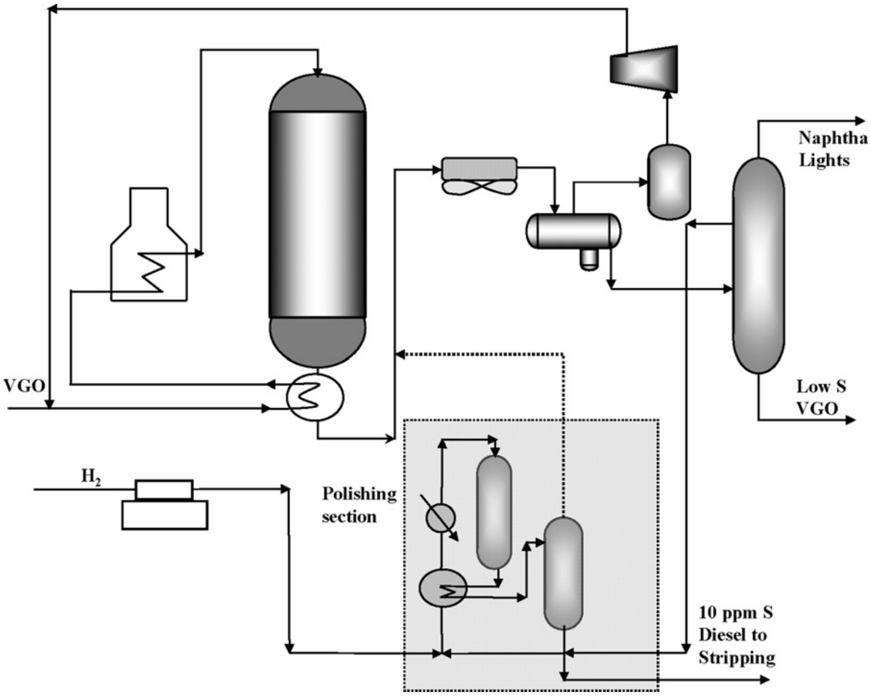


Fig. 63. Simplified process scheme that adapts the core of the mild hydrocracking (MHC) unit into a fully integrated scheme [484].

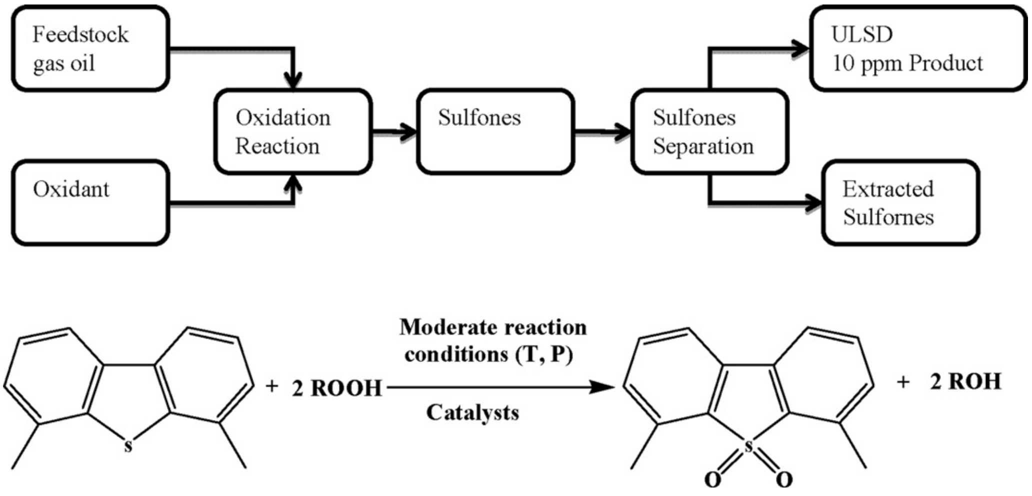


Fig. 64. General flow diagram of 4,6-DMDBT oxidation by hydroperoxides at mild conditions in presence of a solid catalyst.

9. Progress in the development of alternative (non-hydrogenation) processes for deep desulfurization of diesel

Significant advances have been made in recent years on the development of processes alternative to the conventional catalytic hydrodesulfurization process for removing sulfur from diesel streams to ultra low levels. In the conventional hydrodesulfurization process, some alkyl dibenzothiophene compounds (e.g. 4,6-DMDBT) that have alkyl groups adjacent to the sulfur atom resist desulfurization because of steric hindrance, and the use of higher temperatures and pressures, more active catalysts, longer residence times, large volume of catalysts or additional reactors are needed to increase the effectiveness of the HDS process to reduce the product sulfur to ultra low levels. These changes would require additional facility investments and lead to significant economic penalties. In view of this, efforts have been devoted to develop alternative processes for desulfurization, particularly to remove those highly refractory sterically hindered sulfur compounds under mild, less severe operating conditions [511].

A variety of alternative routes such as oxidative desulfurization (ODS) [512–521], biodesulfurization (BDS) [522–525], adsorptive desulfurization [526–536], extractive desulfurization of sulfur compounds using solvents and ionic liquids [537–542], have been investigated to remove sulfur from diesel streams. Details of these methods together with their advantages and limitation are presented in the following sections.

9.1. Oxidative desulfurization

In the oxidative desulfurization process (Fig. 64), the organic sulfur compounds are oxidized to their corresponding sulfones, which can be subsequently removed by extractions, adsorption, distillation or decomposition methods [512,513–521]. Different oxidizing agents such as H_2O_2, ozone, t-butyl hydroperoxide, t-butyl hypochlorite (t-BuOCl) have been used in various studies on the oxidative desulfurization process [512]. H_2O_2 is a rather slow oxidizing agent in the absence of a catalyst, but it becomes highly effective in the presence of a catalyst. The use of both homogenous catalysts (e.g. organic acids, polyoxometallic acids and their salts in aqueous solution) and heterogeneous catalysts (e.g. transition metal compounds, supported-transition metal oxides, etc.) have been used as catalysts in the oxidation of organic sulfur compounds to sulfones by H_2O_2 [512,513,515,543–545].

The reactivity of organosulfur compounds to oxidation varies widely depending on their structure and local environment of the sulfur atom. The following order of reactivity has been reported for the oxidation of some model sulfur compounds with the homogeneous H_2O_2–formic acid system [512,546].

Methyl phenyl sulfide > thiophenol > diphenyl sulfide > 4,6-DMDBT > 4-MDBT > DBT > BT.

It is interesting that the oxidative reactivity of the 4,6-DBT molecule is higher than that of DBT and BT which is inverse to their reactivity in hydrodesulfurization. This has been explained on the basis of an electrophilic addition mechanism for the oxidation of sulfur. A sulfur atom with higher electron density has been found to exhibit higher reactivity for oxidation (Fig. 65). The electrophilic attack on the sulfur atom is promoted with the increase of electron density at the sulfur atom by attached electron rich aromatic rings. In addition, alkyl groups attached to the aromatic rings will further increase the electron density at the sulfur atom. Thus, the intrinsic reactivity of molecules like 4,6-dimethyl DBT is substantially higher than that of DBT. The higher reactivity of the alkyl DBTs under mild reaction conditions in oxidative desulfurization compared to hydrodesulfurization offers an important advantage to this process. Another advantage is that expensive hydrogen is not used in the process.

The potential application of the ODS process for deep desulfurization of industrial and model diesel feeds have been investigated in many studies. Otsuki et al. [547a] studied the oxidation of

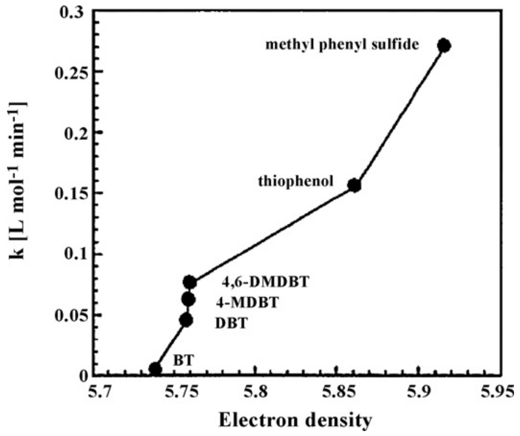


Fig. 65. Relationship between the rate constant, *k* of model sulfur compounds and electron densities on the sulfur atom of various sulfur compounds [512,546].

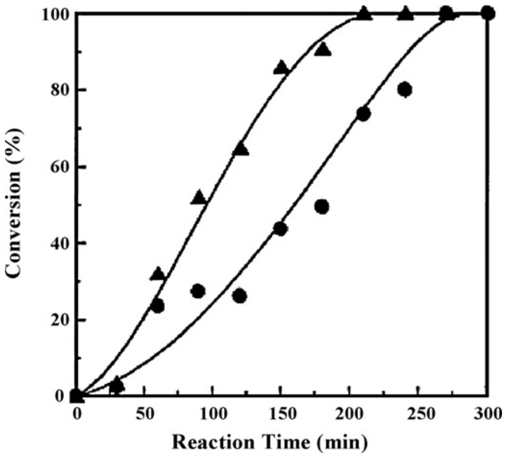


Fig. 66. Changes in conversion of DBTs in light gas oil (reaction temperature 50 °C, O_3/O_2 gas flow rate; 20 Nl/h; O_3 concentration: 1.83 vol.%; initial DBT concentration, DBT (●): 150 ppm; 4,6-DMDBT (▲): 145 ppm) [512].

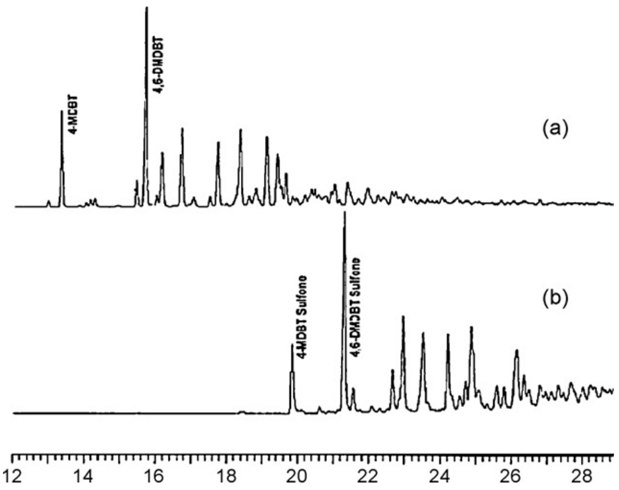


Fig. 67. GC–SCD chromatograms of (a) diesel feed and (b) oxidixed diesel [548b].

DBT and 4,6-DMDBT present in a hydrotreated light gas oil that contained 150 ppm DBT and 145 ppm 4,6-DMDBT using ozone as oxidant. Their results showed that 4,6-DMDBT was more readily oxidized than DBT (Fig. 66). In another study, these authors used H_2O_2–formic acid as oxidant for ODS of straight-run light gas oil (SR-LGO). The sulfur content of the gas oil feed was reduced from 1.35 wt.% to 0.65 wt.% in this study [546].

Wang et al. [548a] reported complete conversion of traces of the refractory sulfur compounds present in a hydrotreated diesel feed (total sulfur content = 39 ppm) to sulfones by oxidation with t-butyl hydroperoxide in the presence of MoO_3/Al_2O_3 catalyst. More recently, Nanoti et al. [548b] used H_2O_2–formic acid reagent for the oxidation of sulfur compounds presents in diesel fuel (total S content 500 ppm) and found complete conversion of sulfur to sulfones. The SCD chromatograms of the light gas oil obtained before and after this oxidation are shown in Fig. 67. It can be seen that after the sulfur-containing feed is oxidized with H_2O_2–formic acid, the peaks of the sulfur compounds are shifted to higher retention times, i.e., heavier molecular weights. The peaks of the DBTs almost completely disappeared, whereas the peaks of the corresponding DBT sulfones appeared after oxidation, confirming that the oxidation of DBTs led to the formation of DBT sulfones which can be removed by adsorption or extraction. Chica et al. [544] carried out ODS of a partially hydrotreated LCO containing 330 ppm total sulfur formed by mainly mono-, di-, and trimethyl DBTs in a continuous fixed bed reactor using Ti–MCM-41C (calcined) and Ti–MCM-41S (sililated) catalyst in the presence of t-butyl hydroperoxide. The results presented in Fig. 68 show complete conversions of the sulfur compounds to sulfones by the Ti–MCM-41S catalyst.

Mei et al. [549] observed a significant enhancement on the rate of the oxidation of sulfur compounds to sulfones when ultrasound was applied during the oxidation process (Fig. 69). The use of molecular oxygen or air as oxidizing agent instead of peroxides or peroxyacids in the ODS process have been reported in some studies. Sampanthar et al. [550] demonstrated the reduction of sulfur content of a diesel fuel from 430 ppm to 40–60 ppm by oxidation using molecular oxygen in air in the presence of Mn- and Co-containing oxide catalysts supported on γ-Al_2O_3 followed by extraction by a polar solvent.

The second step in the ODS process is the removal of the sulfones from the oxidized fuels. Extraction of the sulfones with solvents has been widely studied [547–556]. Table 19 shows concentrations of DBT and alkyl DBTs in diesel (SR-LGO) before

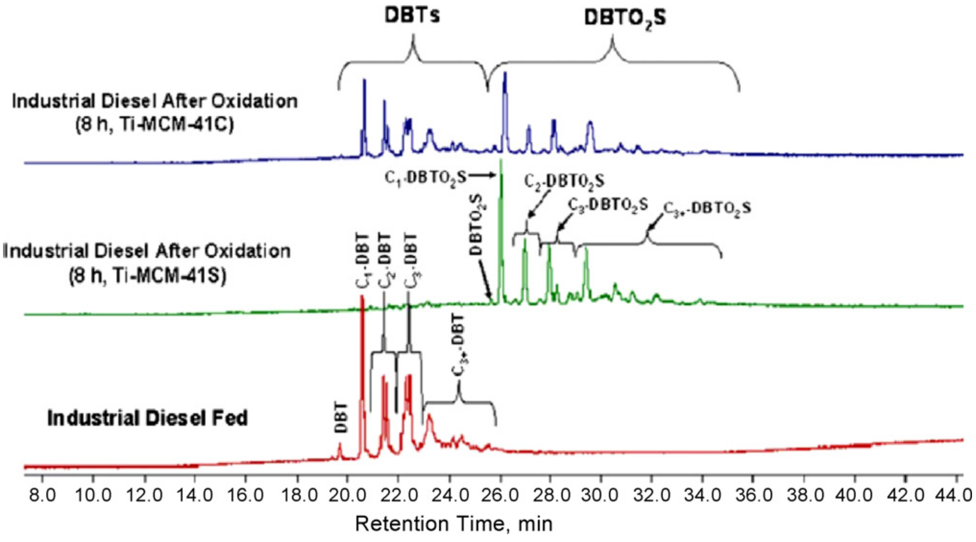


Fig. 68. Sulfur-specific GC–PFPD chromatograms of industrial diesel fed and industrial diesel in the reactor outlet after 8 h of reaction time with Ti–MCM-41C (calcined) and Ti–MCM-41S (silylated) catalysts. Reaction conditions: industrial diesel, 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51.5 h^{-1}, and oxidant/S ratio of 6 mol mol^{-1} [544].

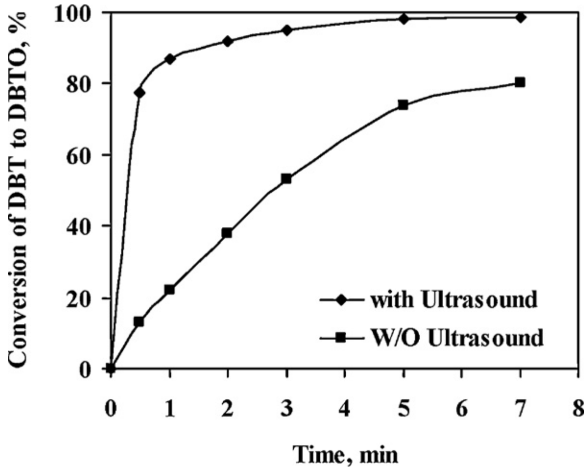


Fig. 69. Conversion of DBT to DBTO with and without the use of ultra sound [549].

and after oxidation and after extraction with five different solvents namely, dimethyl formamide (DMF), acetonitrile, methanol, dimethyl sulfoxide (DMSO), and sulfolone. The results show that the concentrations of DBT and its alkyl derivatives can be reduced to less than 1 ppm level by oxidation/solvent extraction treatments. The polarity of the solvent plays a key role in the extent of extraction of sulfones. Therefore, the removal of sulfones can be improved by using a solvent with higher polarity [557]. The presence of a sulfones extracting agent like acetonitrile in the oxidation phase has been found to enhance sulfur oxidation [516,519,557]. Recently, Garcia-Gutierrez et al. [515] evaluated a $Mo/Al_2O_3–H_2O_2$ system for ultra deep desulfurization of diesel fuel. The sulfur content of the diesel was reduced from 320 wppm to less than 10 wppm at 60 °C and atmospheric pressure. The activity of the catalyst was found to depend on the support acidity and the presence of a polar aprotic solvent.

The removal of the sulfones from the oxidized fuels by adsorption has also been reported in some studies [548b,558–560]. The results of a study conducted by Otsuki [559] showed that silica–alumina and silica gel are more effective for the adsorption of sulfur compounds (sulfones) from an oxidized diesel feed (LGO) than many other adsorbents such as activated carbon, molecular sieves, γ-Al_2O_3, zeolites and ZSM-5. The sulfur content of the diesel fuel was reduced by adsorption after oxidation using $SiO_2–Al_2O_3$ or SiO_2 from 730 ppm to less than 10 ppm.

Recently, Ma et al. [561], developed a ODS process that combines the oxidation of the sulfur compounds with molecular oxygen in the presence of Fe(III) salts at ambient conditions, and the adsorptive removal of the oxidized sulfur compounds by activated carbon. The result presented in Fig. 70 show that the sulfur content of a model jet fuel (MJF) is reduced from 412 ppm to 2 ppm by this combined approach. Loading of Fe(III) salts on the activated carbon (ACMB) increased the oxidation activity of the Fe(III) salts. The use of molecular oxygen in the ODS process at ambient conditions might have several advantages compared to other ODS processes, which use costly oxidants such as H_2O_2 t-butyl peroxide, etc. with respect to cost-effectiveness, energy efficiency and environmental and safety aspects.

Many well known companies have been actively engaged in ODS process developments because of its attractive cost benefits as an alternative to conventional HDS process. During the past 20 years alone more than 30 process patents [562–593] have been issued to these companies (Table 20). Currently, five processes involving the ODS route for deep desulfurization of diesel to ultra low sulfur levels have reached commercialization stage. These include (i) Sulphco process, (ii) Lyondell chemicals process (iii) Enichem/UOP process, (iv) Unipure process, and (v) PetroStar Process. The reactor technology, oxidizing agents and sulfones separation method used in these processes and their advantages and disadvantages are discussed below.

9.1.1. SulphCo process [590,594–596]

This process utilizes sonocracking technology for oxidative desulfurization (ODS). Ultrasound energy is applied to increase the oxidation reaction rate of sulfur compounds present in the diesel feeds. H_2O_2 is used as the oxidizing agent in the presence of a tungsten phosphoric acid catalyst. The ultrasound helps inducing cavitation in a water/oil stream, which when combined with the oxidizing agent (H_2O_2), allows oxidation reactions to occur (Fig. 71). As cavitations bubbles grow, they become unstable and collapse generating excess heat and pressure in and around every nanometer-sized bubble, resulting in intense shear and mixing, as well as high localized temperatures and pressures. This combination permits the reactions to occur within milliseconds, yet at relatively low temperatures and pressures. Ultrasound can also create more molecular surface area, so there are more opportunities for molecules to rapidly react. The residence time for the ultrasonic reactor is reported to be 1 min.

The first ultrasonic desulfurization unit has been installed at the IPLOM petroleum refinery near Genoa in Italy. It showed continuous and successful desulfurization of diesel fuel at a rate of up to 350 bbl per day. For light diesel fuels, the proposed technology meets the 10 ppm S requirement. The SulphCo process is reported to be economically feasible. In accordance with the preliminary estimation of Betchel Corp, Scientists, the SulphCo unit will cost about 50% of what an equivalent hydrotreater would cost. The application of SulphCo's technology for crude oil upgrading has also been studied. Sulfur reduction in crude oil up to 50%, API gravity increase up to 3 points and viscosity reduction up to 15% have been reported [596].

Table 19
Concentrations of dibenzothiophenes and their derivatives in oil layers of diesel feed before oxidation and after oxidative extraction [512].

	Dipole moment, μ	Dielectric constant, ε	Unoxidized SR-LOO				Oxidized SR-LGO			
			DBT (ppm)[a]	4-MDBT (ppm)[a]	4,6-DMDBT (ppm)[a]	Total S (wt.%)[b]	$DBTO_2$ (ppm)[a]	$4\text{-}MDBTO_2$ (ppm)[a]	$4,6\text{-}DMDBTO_2$ (ppm)[a]	Total S (wt.%)[b]
Feed			1620	3350	525	1.35	19	67	19	0.65
DMF	3.24	36.71	26	71	16	0.57	<1	<1	<1	0.11
Acetonitrile	3.53	35.94	165	567	101	1.13	1	<1	<1	0.10
Methanol	2.87	32.66	315	769	112	1.13	<1	<1	<1	0.18
DMSO	4.06	46.45	28	169	48	1.06	<1	1	<1	0.11
Sulfolane	4.81	43.26	34	163	40	1.08	<1	<1	<1	0.12

[a] Determined by GC–FPD analysis.
[b] Determined by XRF (X-ray fluorescence) analysis.

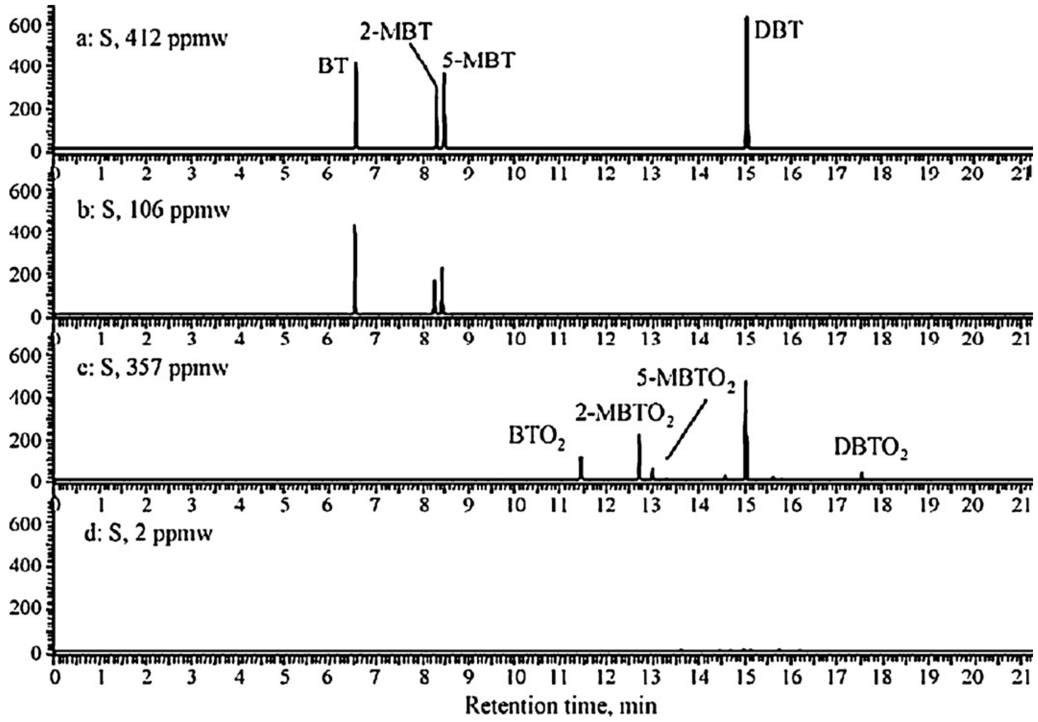


Fig. 70. PFPD chromatograms of MJF and the treated MJF samples: (a) MJF (feed); (b) the adsorption-treated MJF (A) over ACMB at 25 °C, for 3 h; (c) the oxidized MJF over Fe–Fe at 25 °C, 2 h; (d) the adsorption-treated c over ACMB at 25 °C, 3 h. [561].

9.1.2. Lyondell Chemicals Process [571,597,598]

In this process t-butyl hydroperoxide (TBHP) is used for the oxidation of the sulfur species present in the diesel feed to sulfones. A schematic diagram of the process is shown in Fig. 72. The fuel (diesel feed) and TBHP are co-fed over a fixed bed catalyst at mild temperatures (less than 200 °F) and pressures (<100 psig). The oxidation takes place in less than 10 min with near quantitative conversion of the thiophenic sulfur compounds to sulfones. Removal of sulfones is accomplished by solvent extraction. The extraction solvent is recovered by distillation and reused. Any unreacted TBHP is decomposed in a separate reactor or in a separate zone in the oxidation reactor. The t-butyl alcohol is produced as a coproduct from the oxidation and it is easily removed from the fuel during post processing. The t-butyl alcohol can be converted to MTBE is used as fuel within the refinery. It is estimated that for a typical 30,000 BPD unit processing diesel fuel with a sulfur level of 350–500 ppm the sulfones stream will amount to approximately 50–100 BPD. The sulfones stream could be sent to a coker or to a bio-processor. As a result of the mild process conditions with no hydrogen requirements, it is estimated that the capital and operating costs of the process will be substantially low and the economics will be more favorable compared to competitive options. The nature of the process makes it well suited as a finishing process for desulfurizing moderately hydrotreated low sulfur diesel fuels having sulfur content around 500 ppm to ultra low sulfur fuels (<10 ppm). The process is still not available for licensing.

9.1.3. ENI–UOP Process [581,599,600]

ENI–UOP oxidative desulfurization process is illustrated schematically in Fig. 73. The process consists of three process steps; an oxidant supply section, a sulfur reaction section, and finally a sulfone separation section. The UOP/ENI technology uses organic peroxide as an oxidant. The oxidant supply section can consist either of the handling equipment associated with purchased organic peroxide such as t-butyl-hydroperoxide, or the facility for

Table 20
Recently issued patents for ODS process development.

Company[a]	Country	Oxidant	Patent nos.	Ref.
BP Corp., Amoco	USA	H_2O_2	3	[562,563,564]
DS2 Tech., Inc.	USA	H_2O_2	2	[565,566]
Carnegie Mellon Univ.	USA	H_2O_2	2	[567,568]
Exxon Corp.	USA	H_2O_2	2	[569,570]
Lyondell Chem. Comp.	USA	TBHP	2	[571,572]
Petrobras	Brazil	H_2O_2	2	[573,574]
Petro Star Inc.	USA	H_2O_2	3	[575,576,577]
UOP	USA	HCHP	4	[578,579,580,581]
Ministry of Natural Resources, Ottawa, CA	USA	H_2O_2	2	[582,583]
Unipure Energy Corp.	USA	H_2O_2	4	[584,585,586,587]
Saudi Arabian Oil Comp.	SA	H_2O_2	1	[588]
SulfCo	USA	H_2O_2	3	[589,590,591]
Gulf Oil Corp. R&D	USA	HNO_3	1	[592]
General Electric Company	USA		1	[593]

[a] Companies engaged during the last 25 years; none are in commercial operation.

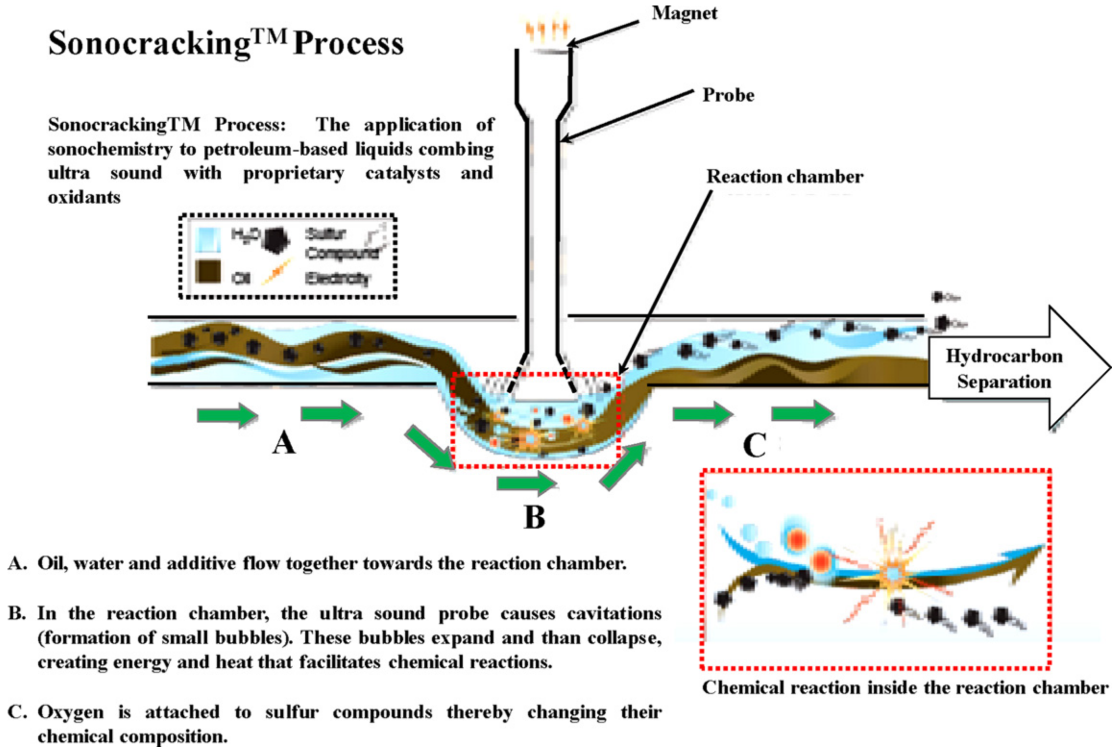


Fig. 71. Effect of sonocracking (SulphCo process) on oxidative desulfurization [596].

generating peroxide (oxidant) internally via direct oxidation of a hydrocarbon with air.

In the process, the first step is a circulating reaction loop in which the gas oil (diesel) feed is mixed with air to produce a hydroperoxide-containing stream. This is performed in the presence of an organic initiator, at 130 °C and 70 atm; no catalyst is necessary in this step. The stream-containing approximately 2000 wppm O as the peroxide, and where a fraction of S has already been oxidized to sulfone, is then fed to the sulfur oxidation section. The sulfur oxidation reaction section operates at low temperature and pressure, less than 200 °F and less than 100 psig. The reaction occurs in the presence of a proprietary heterogeneous catalyst in a conventional fixed bed reactor. The use of an organic peroxide as the oxidant avoids the need to recycle corrosive organic acid catalysts that are needed when hydrogen peroxide is used. Very high conversion is obtained in the sulfur oxidation reaction section, in excess of 98% conversion of organic sulfur compounds.

The final step is the sulfone separation section. The sulfones are polar molecules so they are easily separated by either extraction or adsorption. UOP and ENI have evaluated both routes, and have concluded that the adsorption route is more cost-effective. The adsorption section also serves to remove any trace by-products

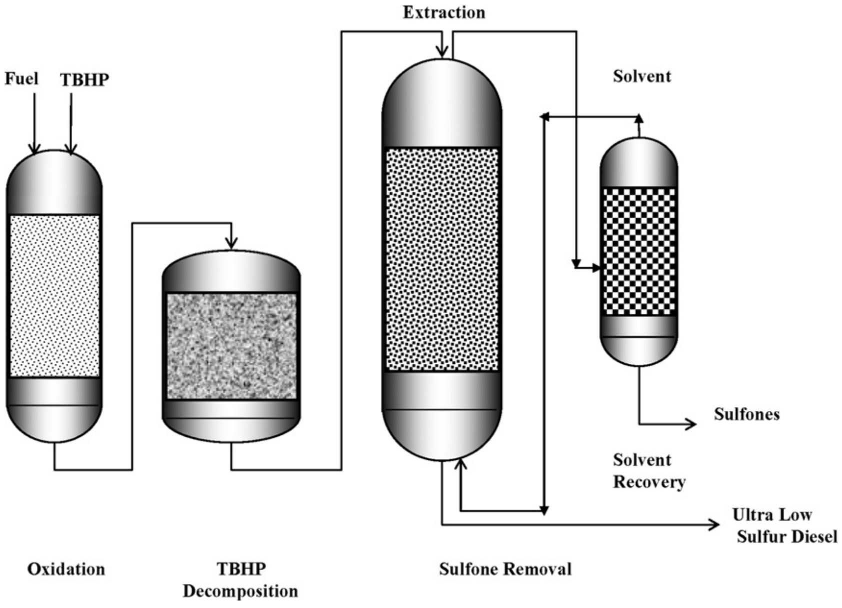


Fig. 72. Schematic illustration of Lyondell chemicals oxidation process [597].

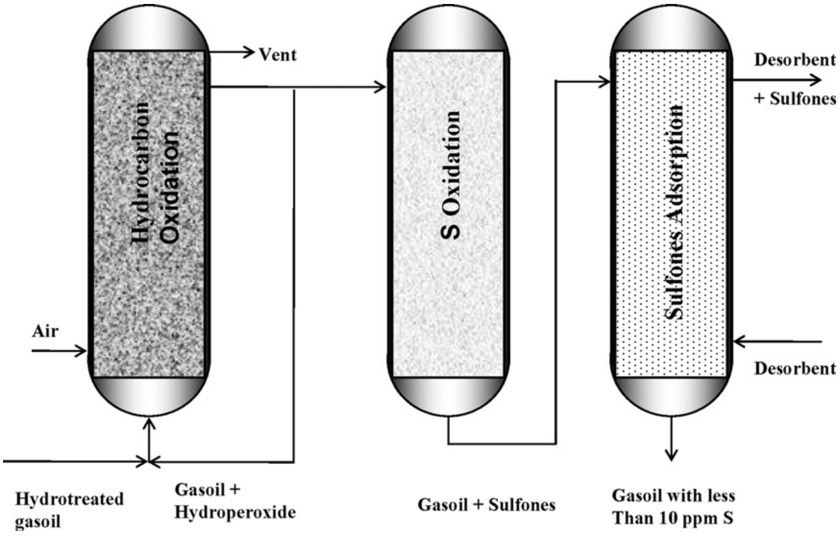


Fig. 73. Simplified flow-sheet of the ENI-UOP ODS process [599].

formed during the oxidation and reaction steps. The sulfones that are separated can either be processed in a coker or can be blended directly into the heavy fuel oil pool in some locations. One innovative aspect of this process involves the in situ production of the alkylhydroperoxide. This considerably limits the costs of the storage, handling and use of the oxidant.

9.1.4. Unipure ASR-2 process [601–603]

This process was developed jointly by Unipure and Texaco. A schematic diagram of the Unipure ASR-2 process is shown in Fig. 74. In this process, the sulfur species present in the diesel feed are oxidized into sulfones using H_2O_2–formic acid as the oxidizing agent. The oxidized diesel is first separated in a phase separator then washed and dried, and passed over an alumina bed to separate the sulfones by adsorption. The sulfone loaded-alumina bed is regenerated by washing with methanol. The oxidation reactions occur at mild temperatures (<250 °C) and at atmospheric pressure. It is suggested that the recovered sulfones can be disposed of in the refinery coker. A demonstration plant of Unipure's ASR-2 process for the production of diesel with less than 8 ppm sulfur content from a feed with 500 ppm is in operation at Valero Energy Corp's Krotz Spring, LA, refinery.

The major advantages of this new technology include low cost, lower reactor temperatures and pressures, short residence time, no emissions and no hydrogen requirement. Because the process removes the molecules containing sulfur as sulfones, higher volume losses can occur when high sulfur content diesel feeds are desulfurized by ODS technology. Hence, integrating the ODS units with existing low pressure or moderate pressure hydrotreating units will offer many advantages for ultra deep desulfurization of diesel fuels. It is claimed that Unipure's ASR-2 process can produce diesel fuel and gasoline having $\leq$5 ppm sulfur, from feeds having up to 1500 ppm sulfur at a cost <50% the cost of a grass roots hydrotreater. Large stand-alone ASR-2 plants will be able to produce ultra low sulfur products from low sulfur fuels having sulfur in the range of 50–1500 ppm. Unipure is developing an extension to its ASR-2 pro-

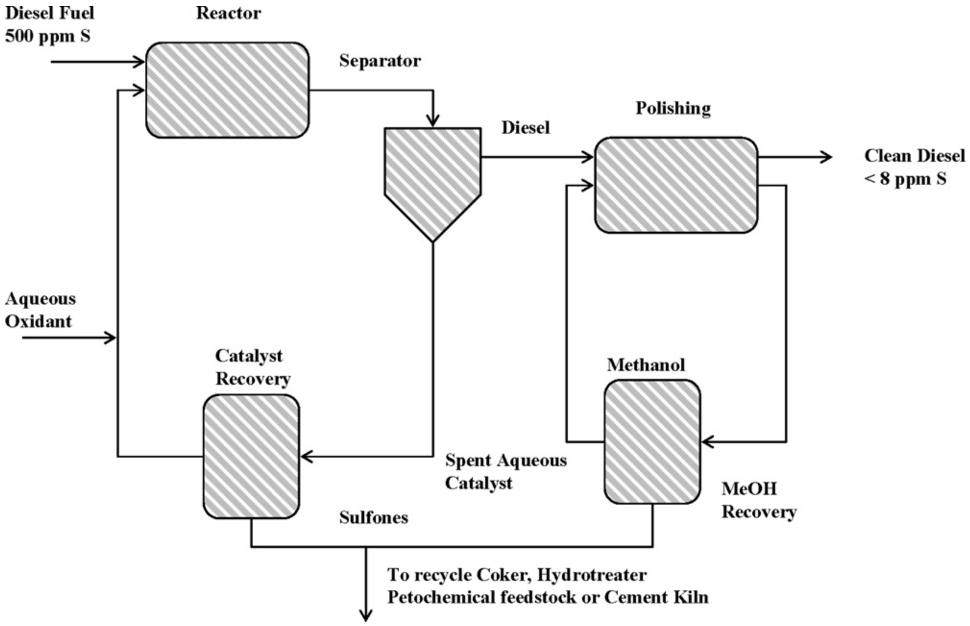


Fig. 74. Schematic illustration of Unipure process.

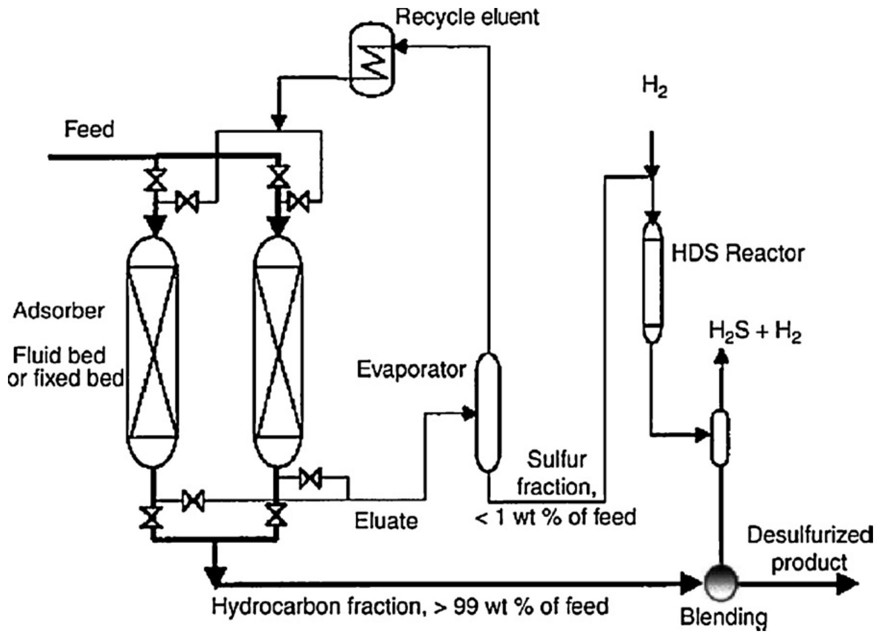


Fig. 75. The proposed integrated PSU-SARS-HDSCS processed based on adsorption for deep desulfurization [533].

cess that, under certain circumstances, can cost effectively handle feeds with sulfur levels up to >1 wt.%.

9.1.5. PetroStar's conversion/extraction desulfurization (CED) process [604–606]

This is essentially on oxidative desulfurization process, which utilizes a peroxyacid (peroxo acetic acid) for the oxidation of the sulfur compounds followed by the extraction of the sulfones. The oxidation proceeds at temperatures below 100 °C at atmospheric pressure. Desulfurization of a diesel from 3500 ppm to <20 ppm has been demonstrated in a bench scale pilot plant unit. Other fuel specifications like cetane number and API gravity were also improved. The CED process of PetroStar was developed in co-operation with US Department of Energy and Degussa [606]. The process needs further development before licensing and commercialization.

9.2. Desulfurization by adsorption

Desulfurization by adsorption (ADS) is based on the ability of a solid sorbent to selectively adsorb organosulfur compounds from refinery streams. Based on the mechanism of the sulfur compound interaction with the sorbent, ADS can be divided into two groups: desulfurization by physical adsorption and reactive adsorption desulfurization.

9.2.1. Desulfurization by physical adsorption

In this method, the sulfur molecules present in the diesel feed are selectively removed by adsorption on a solid adsorbent without conversion. Development of adsorbents with high sorption capacity, selectivity and regenerability is the key to an efficient adsorptive desulfurization process.

Song and his coworkers [529,533,607,608] tested a wide variety of adsorbents based on transition metal complex supported on porous materials, zeolites, supported transition metals, mixed metal oxides, activated carbon, etc., for adsorptive desulfurization of gasoline, diesel and jet fuel at ambient conditions. Based on these studies, these authors identified some adsorbents with high sulfur adsorption capacities and then proposed a new integrated process concept (Fig. 75) that combined selective adsorption for removing sulfur (SARS), recovery of concentrated sulfur compounds and HDS of concentrated sulfur (HDSCS) fraction. Recently, carbon based adsorbent have been tested for selective adsorption of nitrogen compounds from liquid hydrocarbon stream [609,610]. Ni phosphides supported on high surface area silica have also been tested for adsorptive desulfurization of diesel fuel to ultra low sulfur level [611].

Hernandez-Maldonado and Yang have investigated the efficiencies of many Π complexation adsorbents for selective adsorption of

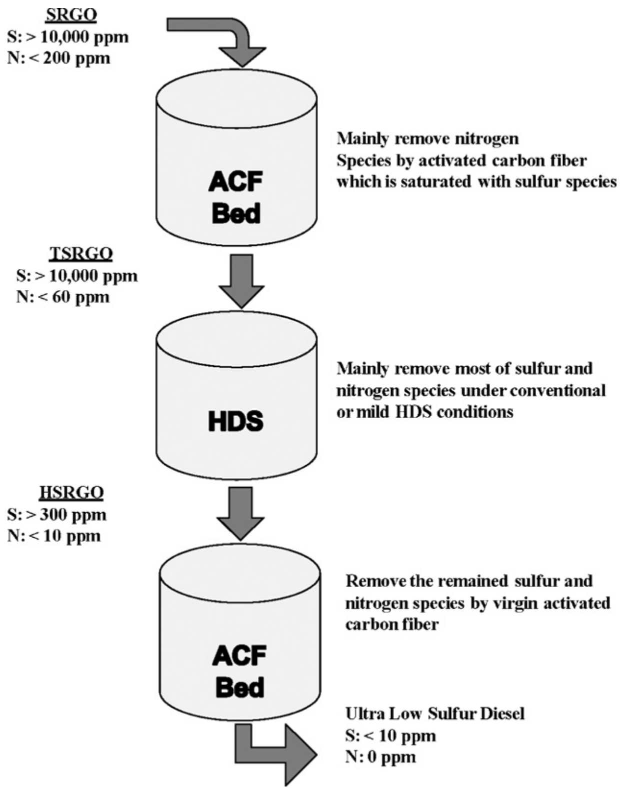


Fig. 76. Concept of the two step adsorption process [526].

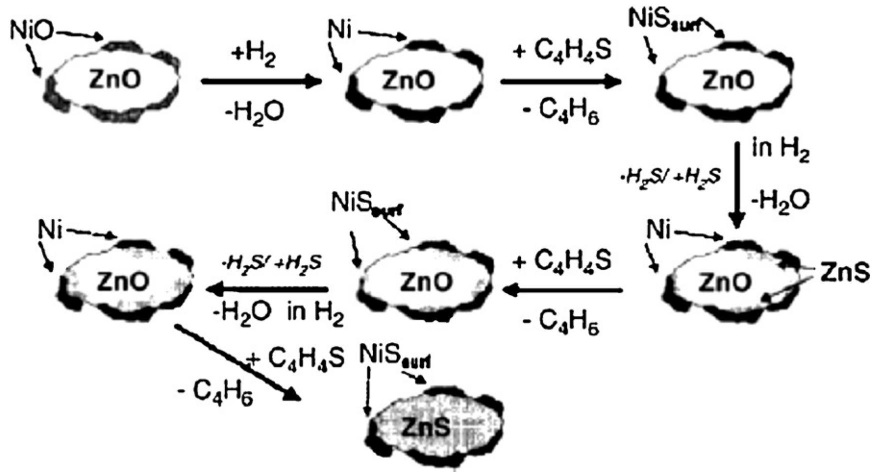


Fig. 77. Mechanism of reactive adsorption desulfurization [11].

sulfur compounds from fuels [612–619]. These authors showed that vapor phase ion exchanged Cu(1)-Y zeolites possessed improved absorption capacity for sulfur compounds than the liquid phase exchanged zeolites. Using the Π complexation sorbents in layered beds further improved the desulfurization capacity. Metal exchanged zeolites such as Ag-Y, Cu(I)-Y, Ni(II)-Y, and Ni(II)-X were found to be superior adsorbents for removal of all sulfur compounds from commercial fuels [534]. These Π complexation sorbents were capable of producing fuels with sulfur content of 0.20 wppm or less, which is desired for fuel cell based applications. Copper (I)-, nickel-, and silver-exchanged zeolites interact via Π-complexation with thiophenic aromatic rings instead of attacking sulfur atoms directly like HDS catalysts. The Cu(I)-Y zeolites could be regenerated in a two-step process after treating fuels for deep desulfurization at room temperature: (1) calcination in air at 350 °C followed by (2) reduction of Cu^{2+} to Cu^{+}. For the nickel-exchanged zeolites, complete regeneration required only the first step calcination because of the Ni (II) ion stability.

Mochida and his coworkers conducted extensive research on the removal of sulfur and nitrogen compounds from gas oil (diesel) feeds by adsorption [526,536,620]. It was found that activated carbon materials removed nitrogen species and refractory sulfur species simultaneously. Adsorption capacity was estimated to be 0.098 g-sulfur and 0.039 g-nitrogen per 1 g of activated carbon at 30 °C. The performance of activated carbon fiber (ACF) in the adsorptive removal of nitrogen and sulfur species from conventional gas oils was strongly dependent on the surface properties, such as surface area and the amount of surface oxygen groups. They proposed a two-step adsorption process concept illustrated in Fig. 76 for ultra deep desulfurization diesel. Nitrogen and refractory sulfur species present in the feed are removed by adsorption using activated carbon in the first stage adsorption. The pretreated feed with very low-nitrogen content is then hydrotreated under conventional or mild HDS conditions. The unreacted sulfur and nitrogen species remaining in the hydrotreated gas oil are removed in the second stage activated carbon adsorption bed to produce ultra low sulfur diesel (S: <10 ppm and N: 0 ppm). Regeneration of used activated carbon fiber with a conventional solvent such as toluene was very effective in restoring the adsorption capacity.

Selective adsorption of dibenzothiophenes from diesel feeds by formation of charge transfer complexes with immobilized Π-acceptor molecules has been explored by the group of Lemaire in France [621–625]. In a recent study [625], they used a Π-acceptor compound, 4,5-dicyano-2,7-dinitro fluorenone immobilized on a polystyrene resin for deep desulfurization of a partially hydrotreated diesel fuel that contained 390 ppm sulfur. As shown in Table 21, sulfur content of the diesel fuel was reduced from 390 ppm to 40 ppm in four steps at ambient temperature. For a pretreated feed with 60 ppm initial sulfur, the sulfur content was reduced to <10 ppm. The sulfur loaded resin can be regenerated and reused in many cycles without loss of activity.

9.2.2. Reactive adsorption

In the reactive adsorption desulfurization process, the sulfur molecules present in the feed are converted to H_2S and hydrocarbons, and the H_2S is subsequently adsorbed by the

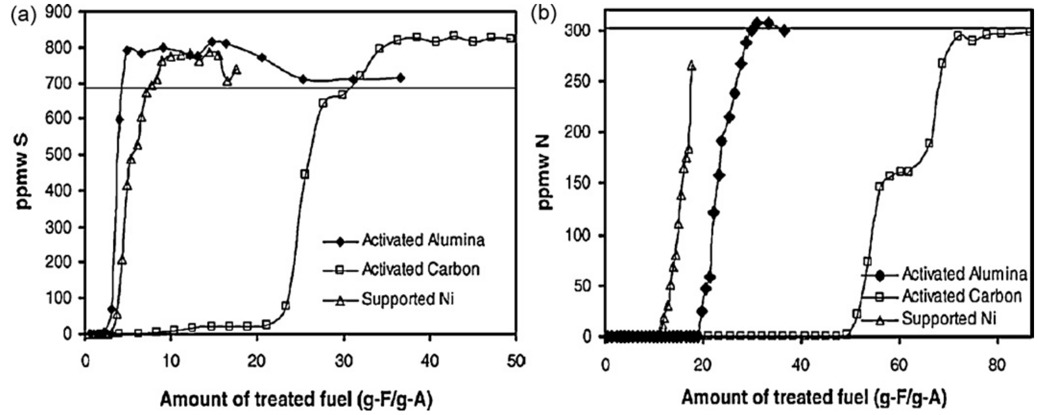


Fig. 78. Breakthrough curves for (a) total sulfur and (b) total nitrogen over the three different adsorbents [529].

Table 21
Multistage desulfurization at ambient conditions and with 4 h contact time of diesel oil via charge transfer complex [625].

Stage	Sulfur content (ppm)	
	SR oil after classical HDS (fuel/polymer = 2)	SR oil after classical deep HDS (fuel/polymer = 10)
Initial	390	60
1	175	40
2	80	27
3	40	17
4	–	9

adsorbent [527,626–630]. Materials containing a combination of transition metal catalyst and sorbent, are usually used for reactive adsorption of sulfur compounds. For diesel, the reaction occurs in the presence of hydrogen at temperatures in the range 300–400 °C and pressures in the range 275–500 psig. Several types of adsorbent–catalyst combinations such as Cu–ZnO, Ni–Al_2O_3, Ni–ZnO, Ni/Al–SiO_2, NiP/SiO_2, Ni–SiO_2, Ni–SBA-15 have been tested, but the best performance has been observed for Ni–ZnO system. The overall mechanism which involves the participation of both Ni and ZnO for sulfur removal from the sulfur compounds by Ni–ZnO system by reactive adsorption is illustrated in Fig. 77. Nickel reacts with sulfur under hydrogen to form NiS which then passes the S to ZnO to form ZnS and regenerates Ni.

Phillips Petroleum Company (now Conoco-phillips) has developed a technology, named S-Zorb SRT for deep desulfurization of diesel by reactive adsorption [629–631]. In this process, the diesel stream is contacted with a solid proprietary sorbent in a fluid bed reactor in the presence of hydrogen. The sulfur is retained on the adsorbent while the hydrocarbon desorbs. The sulfur-loaded sorbent is regenerated in a separate regeneration vessel and reused. Sulfur is typically reduced to about 5 ppm from feedstock of 500 ppm sulfur. Feedstocks containing greater than 2000 ppm could also be deeply desulfurized to ultra low sulfur levels by this process. The process responds well to feed sulfur changes. Depending upon the feedstock, the process operating conditions can vary in the range: pressure = 275–500 psig; temperature about 700–800 °F. H_2S is not released. Critical diesel fuel properties are unchanged. Due to very low hydrogen consumption, the process potentially produces relatively lower CO_2 and NO_x refinery emissions. The technology is expected to help minimizing capital costs and operating expenses while achieving targeted product quality. Recently, Park et al. [527] evaluated the effectiveness of nickel nanoparticles supported on mesoporous silica materials such as SBA-15 and KIT-6 for desulfurization by reactive adsorption. The sulfur content of a diesel fuel was reduced from 240 to <10 ppm by reactive adsorption on 30% Ni/SBA-15.

9.2.3. *Removal of nitrogen compounds by adsorption*

In view of the fact that nitrogen-containing compounds are strong inhibitors of desulfurization of DBT and alkyl DBTs through the HYD route, intensive efforts have been made to develop pretreatment processes for selective removal of nitrogen from diesel feed streams. Both basic (aniline, pyridine, acridine and quinoline and their alkyl substituent derivatives) and neutral (pyrrole, indole, carbazole and their alkyl substituent derivatives) are present in diesel feeds. Laredo et al. [178] distinguished different nitrogen compounds in SRGO and LCO derived from Mexican crude oil using gas chromatography with a mass spectrometer (GC–MS). They found that the most abundant nitrogen compounds in the SRGO sample were quinoline, indole, carbazole, and their alkyl substituent derivatives, whereas aniline, indole, carbazole, and their alkyl substituent derivatives were the predominant nitrogen compounds in the LCO sample. Studies have shown that the reduction of nitrogen species in the feed oil improves the desulfurization of refractory sulfur compounds very significantly [25,36,169,526,632–634].

Several alternative methods such as solvent extraction [634–637], ion-exchange [638,639], extraction with ionic liquids [637,640,641], extraction by complex formation [642], membrane [643] and adsorption [169,526,529,609,644,645] have been studied for nitrogen removal from diesel feeds. Using physical adsorption method for the selective removal of nitrogen compounds is an attractive approach as the adsorption can be carried out at ambient temperatures without using hydrogen. Several types of adsorbents such as zeolite [646,647], activated carbon [526,609,648,649], activated alumina [526,529], SiO_2-Al_2O_3 [650], and silica gel [105,501,651,652], mesoporous silica [653], have been reported to be effective for adsorptive denitrogenation of diesel fuel.

Kim et al. [529] studied the adsorptive desulfurization and denitrogenation of a model diesel feed that contained nitrogen, sulfur and aromatic compounds over three different adsorbents, namely activated carbon, activated alumina and supported nickel adsorbent in a fixed bed adsorption system. Activated carbon exhibited higher capacity for the adsorption of nitrogen and sulfur compounds than the other two adsorbents (Fig. 78). Activated carbon also showed higher selectivity for the adsorption of sulfur compounds with methyl groups, such as 4,6-DMDBT. The activated alumina was very effective for selective separation of nitrogen compounds, especially for basic nitrogen compounds, but not very successful for separating the sulfur compounds from hydrocarbon streams.

The effectiveness of activated carbon materials for adsorptive denitrogenation of gas oil feeds has been examined by Mochida and his coworkers in many studies [526,620,654–655]. They found that a particular activated carbon, namely MAXSORB-II, prepared from petroleum coke through KOH activation with an apparent surface area of 3000 m^2/g, was effective for adsorptive denitrogenation of gas oil at ambient temperature. These authors also modified the chemical nature of conventional activated carbon surface by treatment with oxidizing agents such as HNO_3, H_2SO_4 and H_2O_2 followed by heat treatment [620]. The adsorption capacity of the treated activated carbon material for the removal of nitrogen species improved significantly. It was suggested that some specific oxygen functional groups that release CO in the temperature range 600–800 °C were formed in the activated carbon surface during the oxidative pretreatment, and these oxygen functional groups were responsible for the enhancement of adsorption capacity.

Yang and his coworkers found that Cu(I)-Y zeolite is a good Π-complexation adsorbent for the sulfur and nitrogen compounds with higher selectivity and high capacity [534,646,656]. In a recent study, the adsorption configurations of quinoline, acridine, indole and carbazole over Cu(I)Y zeolite were studied by Liu et al. [644] using the density functional theory method. The η^2 adsorption mode was found to be energetically preferred for neutral nitrogen compounds, i.e., indole and carbazole; while for basic ones, (e.g. quinoline and acridine) the η^1N adsorption mode was the most preferential one. The adsorption energies of the adsorbate over Cu(I)Y zeolite decreased as follows: basic heterocyclic nitrogen compounds > neutral heterocyclic nitrogen compounds > thiophenic compounds. This suggests that when deep denitrogenation and desulfurization is carried out simultaneously over Cu(I)Y zeolite under ambient temperature, the adsorption of nitrogen compounds is preferable to that of sulfur compounds, and good selectivity will be shown for the basic nitrogen compounds during denitrogenation. When the adsorbent is used for selective deep desulfurization, the presence of nitrogen compounds can greatly retard sulfur removal.

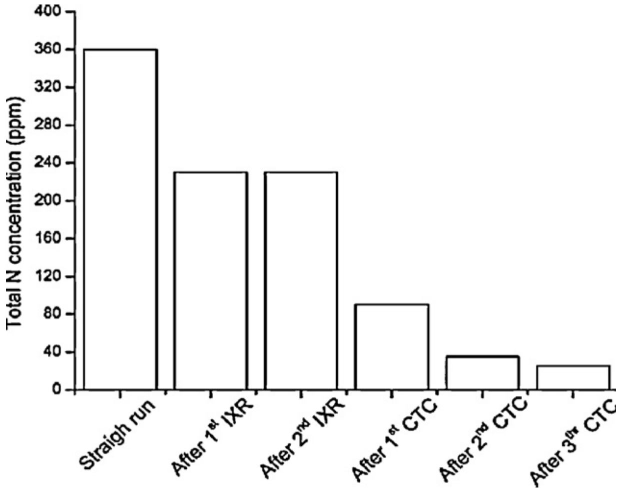


Fig. 79. Batch removal of N-compounds from straight run (13,600 ppm S, 360 ppm N), 1 h of mechanical stirring at 400 rpm and at room temperature. Ion-exchange (IXR) process: straight run/Amberlite IR 120 is 17/1; charge transfer (CTC) process: straight run/polymer 6 is 3/1 [169].

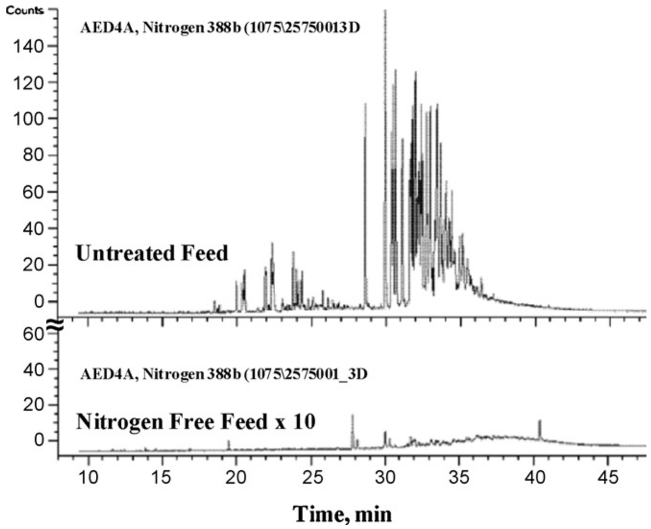


Fig. 80. GC/AED analysis of untreated feed and nitrogen free feed (10×) [9].

Macaud et al. [169] used a two-step process for selectively removing both basic and non-basic nitrogen compounds from diesel feed. The basic nitrogen compounds were effectively removed using strongly acidic ion-exchange resins, and the non-basic nitrogen compounds were selectively adsorbed by the formation charge transfer complexes with π-acceptor molecules immobilized on a polar polymer. The total nitrogen content of the diesel feed was reduced from 360 ppm to less than 30 ppm in this combined process as shown in Fig. 79. Regeneration of the N-loaded polymer was easily achieved by washing with toluene.

Knudsen et al. [9,105] used silica gel as adsorbent and achieved selective removal of N-compounds, leaving all sulfur compounds unaltered. The total nitrogen content of a diesel feed was reduced from 300 wppm to 5wppm in this study (Fig. 80). In a related study, Whitehurst et al. [657] reported that spent FCC catalyst is an effective and economical adsorbent for nitrogen compounds. SK Corporation in South Korea has developed a pretreatment adsorption process that removes over 90% of nitrogen based polar compounds from diesel feeds using silica gel as adsorbent [501,652]. Details of this process are presented in Section 8.7.

In a recent study, Al-Marri et al. [609] compared the adsorption performance of seven representative activated carbon samples and three activated alumina samples in a batch adsorption system and a fixed-bed flow adsorption system for removing quinoline and indole from a model diesel fuel in the coexistence of sulfur compounds and aromatics. Different adsorbents showed quite different selectivity toward basic and nonbasic nitrogen compounds (quinoline and indole) and sulfur compounds (dibenzothiophene and 4,6-dimethyldibenzothiophene). The activated carbons generally showed higher capacity than activated alumina samples for removing the nitrogen compounds. The adsorption capacity and selectivity of the activated carbons for nitrogen compounds were further correlated with their textural properties and oxygen content. It was found that the micro-porous surface area and micro-pore volume are not key factors for removal of the nitrogen compounds in the tested activated carbon. The oxygen functionality of the activated carbons was suggested to play a more prominent role in determining the adsorption capacity and selectivity: In a subsequent study [610], these authors characterized the chemical properties in terms of the type and concentration of the oxygen-containing functional groups on the surface of the adsorbents by using TPD on the basis of CO_2 and CO evolution profiles and correlated with the adsorption performance. The results showed that both the type and the amount of oxygen functional groups on the surface played an important role in determining the performance of the AC samples for the adsorption of nitrogen compounds (Fig. 81). The acidic functional groups, especially the stronger acidic ones such as carboxyl and anhydride, contributed more for adsorption of the basic nitrogen compound (quinoline), whereas the basic

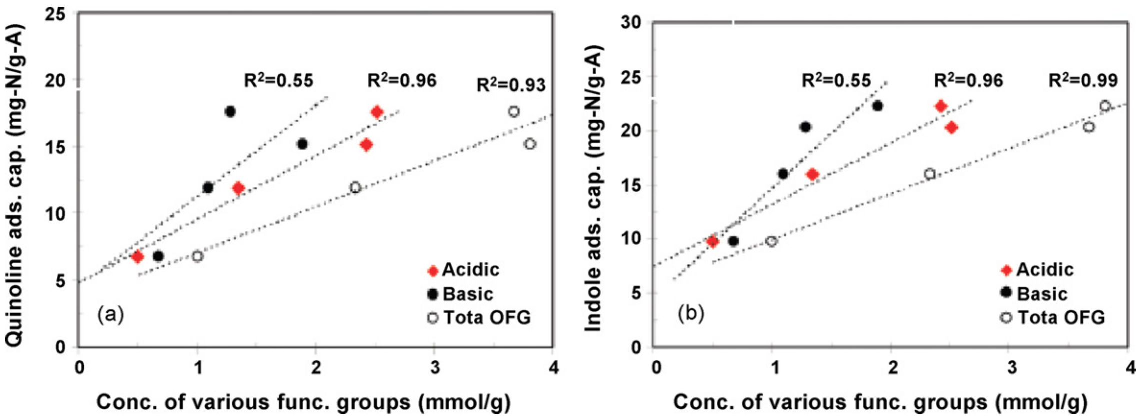


Fig. 81. Correlation between the maximum adsorption capacity (*q*m) of the activated carbon (AC) samples for quinoline (a) and indole (b) to the concentration of the functional groups. Acidic: total acidic groups; basic: total basic groups; total oxygen functional groups (OFG) [610].

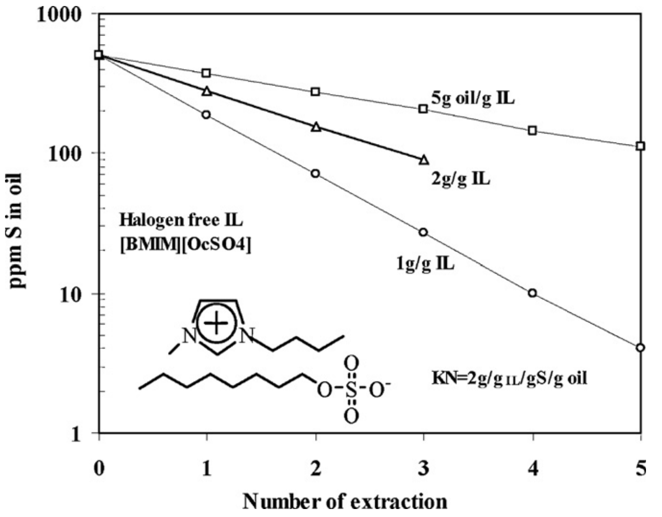


Fig. 82. Influence of the oil to IL mass ratio for cross current extraction of a model oil (500 ppm S as DBT in n-dodecane; IL: [BMIM][OcSO4], room temperature) [537].

oxygen-containing groups such as carbonyl and quinine showed greater contributions to adsorption of the neutral nitrogen compound (indole).

9.3. *Extractive desulfurization*

Removal of sulfur containing compounds from diesel feedstocks to produce ultra low sulfur diesel fuel by extraction with selective solvents has received increasing attention in recent years. This is because, the sulfur extraction technologies could reduce the cost of desulfurization substantially since they do not demand hydrogen, and are carried out at atmospheric pressure and temperatures. Another advantage is that the process can be applied to all types of middle distillates including cracked feeds which will widen the raw material pool for diesel fuel production.

9.3.1. *Extraction with conventional solvents*

Since extractive desulfurization is based on the fact that organosulfur compounds are more soluble than hydrocarbons in an appropriate solvent, the selection of extractants and optimization of the conditions for maximum extraction of the sulfur compounds with high selectivity is very important to make the process efficient. Solvents such as acetone, ethanol [631], polyethylene glycol [658–660], and nitrogen-containing solvents [660,661] have been tested and sulfur removal in the range 50–90% has been achieved with these solvents. Bailes [662] studied the extractability of the sulfur compounds and aromatic hydrocarbons from light oil by mixing the light oil with organic solvents such as acetonitrile, dimethyl sulfoxide (DMSO) and tetramethylene sulfone at room temperature. He found that the extraction equilibrium between light oil and organic solvents was achieved in five minutes or less and that the phase separation was achieved in about 10 s. The light oil was washed once with an equal volume of water to remove the dissolved polar solvents. From this experiment he concluded that acetonitrile is a suitable solvent for light distillates to achieve deep desulfurization.

Petkov et al. [663] showed that the sulfur content of a hydrotreated middle distillate can be reduced 7-fold (from 0.2% to 0.029%) and the aromatics content 3-fold (from 27.1% to 8%) by extraction with solvents such as methanol, furfural and ethylene glycol. Other solvents commonly used for sulfur extraction are acetonitrile, lactones like gamma butyrolactone, DMF, N-containing solvents like amines and pyrrolidones, or sulfur containing solvents like DMSO and sulpholane. Recently, Toteva and Topalova [541] reported the reduction in the sulfur content of a diesel cut from 2.0% to 0.33 wt.% by two-stage extraction using dimethylformamide as solvent. The aromatics content of the feedstock was found to be reduced by 5 times in this study. The reduction of the sulfur level to ultra low levels (e.g. 10 wppm) is not achieved by these solvents. Another disadvantage of this method is the co-extraction of large amount of aromatics hydrocarbon molecules leading to a high loss of diesel product.

The polarity of the sulfur compounds present in diesel feeds can be increased and their solubility in the solvents can be enhanced if the sulfur compounds are oxidized to sulfones prior to solvent extraction. This approach was discussed in detail earlier in Section 9.1. Another approach that is growing rapidly in recent years is based on the use of ionic liquids. Recent developments on the use of ionic liquids for selective extraction of sulfur compounds from diesel feeds are reviewed in the following section.

9.3.2. *Extraction with ionic liquids*

Ionic liquids (ILs) are ionic, salt-like materials that are liquid below 100 °C or even at room temperature. They are non-volatile and have no measurable vapor pressure. The application of ionic liquids as media for liquid–liquid extractions is growing rapidly, since their hydrophobic or hydrophilic nature can be modulated by modifications in both cation and anion [664–667]. They have been used in the separation of variety substances such as metallic ions, organic molecules, fuel desulfurization and gas separation [668,669]. Various ILs have been tested for the, extraction of sulfur compounds from model and commercial diesel oils [537,538,670–676].

Chloroaluminate, hexafluorophosphate and tetrafluoroborate type ILs were found to show good selectivity for the extraction of sulfur compounds from model diesel oil that contained DBT derivatives [672]. Holbrey et al. [539] tested a range of ionic liquids with varying cation classes [imidazolium, pyridinium and pyrrolidinium] and a range of anion types for liquid–liquid extraction of dibenzothiophene from dodecane. The partition ratio of dibenzothiophene to the ionic liquids showed a clear variation with cation class (dimethylpyridinium > methylpyridinium > pyridinium imidazolium pyrrolidinium), and much less significant variation with anion type. Polyaromatic quinolinium-based ionic liquids showed even greater extraction potential, but were compromised by higher melting points. For example, l-butyl-6-methylquinolinium bis (trifluoromethyl) sulfonylamide (mp 47 °C) extracted 90% of the available dibenzothiophene from dodecane at 60 °C.

Recently, Gaon et al. [677a] demonstrated that 3-methylpyridinium-based ionic liquids (ILs) were highly effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature. The results indicated that the extractive performance using 3-methylpyridinium-based ILs followed the order: 1-octyl-3-methylpyridinium tetrafluoroborate ($[C_8{}^3MPy][BF_4]$) > 1-hexyl-3-methylpyridinium tetrafluoroborate ($[C_6{}^3MPy], [BF_4]$) > 1-butyl-3-methylpyridinium tetrafluoroborate ($[C_4{}^3MPy][BF_4]$). For a given IL, the sulfur removal selectivity of sulfur compounds followed the order of dibenzothiophene (DBT) > benzothiophene (BT) > thiophene (TS) > 4,6-dibenzothiophene (4,6-DMDBT) under the same conditions, except for $[C_8{}^3MPy][BF_4]$ IL, which followed the order of DBT > BT > 4,6-DMDBT > TS. Reduction of the sulfur content of a diesel fuel from 97 ppm to 38.4 ppm was achieved in this study.

A detailed study of the extraction of sulfur and N-compounds present in oil refinery streams using halogen free ILs was carried out by Eber et al. [537]. In the first step, suitable ILs as extracting agents were identified by screening experiments with model diesel oil. Selected ILs was then used to study the influence of different S-compounds, the IL to oil ratio, and of the level of S-concentration (multi-step extraction). The possible extension of extractive IL desulfurization to other refinery streams was

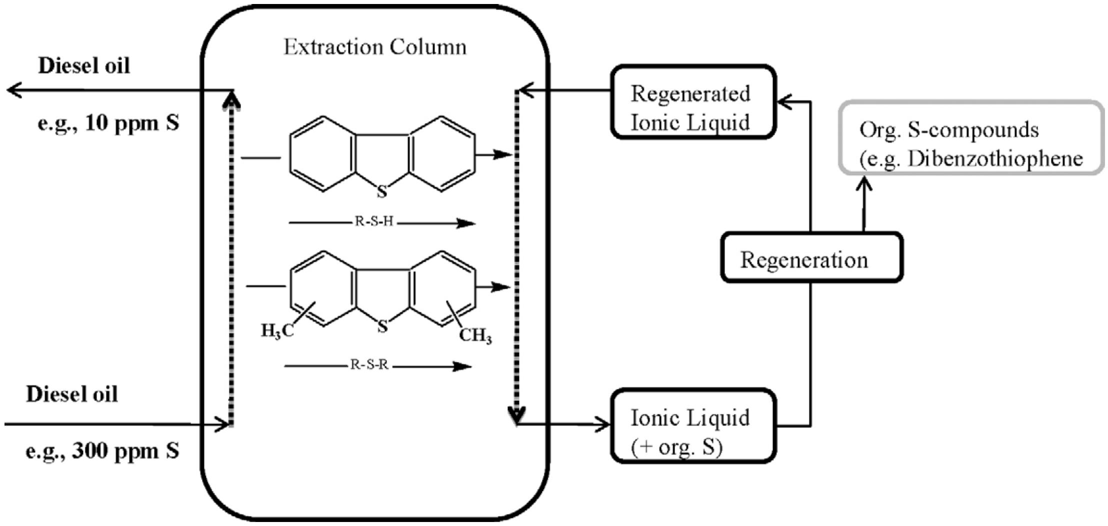


Fig. 83. Concept of deep desulfurization of refinery streams by extraction with ionic liquids (ILs) [537].

also tested by a model cracking gasoline. During the course of these experiments the "cross-solubility" of hydrocarbons, and, vice versa, the absolute unwanted "contamination" of the desulfurized oil with IL were also investigated. Extraction experiments were then also done with selected organic N-compounds. In addition to the fundamental experiments with model oils, the desulfurization of real FCC gasoline and diesel oil was also investigated with selected ILs. With a view to develop a continuous extraction process, the regeneration of S-loaded ILs was studied. The continuous operation of the extraction was tested in a two-step mixer-settler miniplant. Based on the screening tests alkyl imidazolium type ILs such as ILs are 1-n-butyl-3-methylimidazolium octylsulfate ([BMIM][$OcSO_4$]), l-ethyl-3-methyl-imidazolium ethylsulfate [EMIM][$EtSO_4$] and 1,3-dimethylimidazolium dimethylphosphate ([MMIM][Me_2PO_4]) were found to be very promising for the extraction of DBT and alkyl DBTs.

The formation of liquid-clathrates and π–π interaction is between aromatic structures of the DBTs and the imidazolium ring system was assumed to be the main driving force for extraction. The sulfur content of a model oil that contained 500 ppm sulfur as DBT in n-dodecane was reduced to less than 10 ppm by a five-stage extraction using the ionic liquid [BMIM][$OcSO_4$] at room temperature (Fig. 82). The ionic liquids used in their study also showed amazingly high partition co-efficient for nitrogen compounds. The process concept illustrated in Fig. 83 is still in the laboratory experimentation stage. Several issues, such as regeneration of sulfur-loaded ionic liquids, minimization of cross solubility of valuable hydrocarbon liquids in the ionic liquids, reducing the number of stages for efficient separation, cost-effectiveness of the process, etc. have to be resolved before any attempt to commercialize the process is made.

Recently an integrated approach has been reported [677b] by using oxidative desulfurization and ionic liquids. By this approach they succeeded sulfur removal from the DBT model molecule to 96.1%, which was obviously superior to mere solvent extraction with [BMIM]BF4 (28.5%) or catalytic oxidation without [BMIM]BF4 (7.3%). It was also found that in a combination of extraction and oxidation, the sulfur content decreased from 500 ppm to 5 ppm when H_2O_2 was added into the desulfurization system.

9.4. Biodesulfurization

In the biodesulfurization (BDS) process, the sulfur present in the organosulfur compounds is removed by bacteria without degrading the carbon skeleton. The process operates in the presence of water and oxygen under mild operating conitions (i.e. at room temperature and pressure) and requires no hydrogen. Both these features can lead to substantial energy savings. As a result, the BDS process

Table 22
Desulfurization of crude oil fractions by some bacterial strains.

Bacterium	Crude oil fraction + and its sulfur content	Total sulfur reduction (%)	Ref.
Gordona sp. CYKS1 (resting cells)	MDUF (1500 ppm)	70	[690]
	Light gas oil (3000 ppm)	50	
Gordoniasp. SYKS1 (resting cells)	HDS-untreated light gas oil (3000 ppm)	35	[691]
	HDS-untreated middle distillate unit feed Diluted with hexadecane (1500 ppm)	60	
Gordonia sp. SYKS1 (resting cells)	Diesel oil (250 ppm)	76	[692]
Rhodococcus erythropolis XP	HDS-treated diesel oil (259 ppm)	94.5	[525]
Rhodococcus sp. ECRD-1 (growing cells)	Middle-distillate (diesel range) fraction of Oregon Basin crude oil (20,000 ppm)	8.1	[693]
Rhodococcus sp. ECRD-1 (growing cells)	Catalytic cracker middle-distillate light cycle oil Light gas oil (669 ppm)	92	[694]
Rhodococcus sp. P32C1 (resting cells)	HDS-treated light diesel oil (303 ppm)	48.5	[695]
Rhodococcus erythropolis I-19 (resting cells)	HDS-treated-middle distillate (1850 ppm)	67	[696]
Sphingomonas subarctica T7b (growing cells)	HDS-treated light gas oil (280 ppm)	59	[697]
Mycobacterium phlei WU-0103 (growing cells)	12-fold-diluted straight-run light gas oil (1000 ppm)	52	[698]
Mycobacterium sp. X7B (resting cells)	HDS-treated diesel oil (535 ppm)	86	[682]
Pseudomonas delafieldii R-8 (resting cells)	HDS-treated diesel oil (591 ppm)	90.5	[699]
Pseudomonas delafieldii R-8 (growing cells)	HDS treated diesel oil (591 ppm)	47	[700]

has attracted attention as a complementary and promising alternative to the conventional HDS process used in petroleum refineries.

Numerous studies have been made to develop biocatalysts (micro-organism) that are active in the desulfurization of organosulfur compounds present in petroleum fractions. In 1990, Kilbane and Bielaga [678] reported the isolation of a Rhodococcus rhoochrous strain, designated IGTS8, which possessed a stable sulfur specific oxidative desulfurization pathway. Subsequently, many other strains such as, Gordona sp. CYKD1 [679], Peanibacillus sp. A11–2 [680], and Rodococcus sp. Strain P 32C1 [681], Mycobacterium sp. [682] and Pseudomonas sp. [683], which can desulfurize DBT and alkyl DBTs have been isolated. The desulfurization activity of these naturally occurring bacterial cultures are relatively low and genetic manipulation has been used to improve their HDS activity [523,684,685]. Several studies have revealed that BDS process can specifically remove sulfur from the sterically hindered alkyl DBTs that are least reactive in the conventional catalytic HDS process [522,524]. A sulfur specific desulfurization pathway, named as 4S route has been proposed for the biodesulfurization of DBT and alkyl DBT molecules by microorganisms such as rhodococcus, bacillus, corynebacterium and anthrobacter. This reaction scheme [522,523,686–689] shown in Fig. 84 involves four consecutive reaction steps: (i) DBT is oxidized to DBTO (DBT sulfoxide), (ii) DBTO is transformed to DBT sulfone ($DBTO_2$) and (iii) to sulfinate (HPBS), (iv) hydrolytic cleavage to 2-hydroxylbiphenyl (2-HBP) and subsequent release of sulfite or sulphate. In this pathway the sulfur of DBT is selectively removed without destroying the hydrocarbon skeleton so that the thermal value of the fuel is not destroyed.

Significant research has also been made during the last 10 years in the application of the BDS process for desulfurization of diesel [522–525,686,687,689]. A summary of the biocatalysts tested is given in Table 22. It is evident from the results reported in Table 22 [522,690–700] that the BDS process is not very effective for ultra deep desulfurization of diesel to ultra low sulfur levels (15 ppm or less) as required by new diesel fuel specifications. Some companies such as Energy Bio-systems Company (EBC) and Diversa which were actively involved in the development of commercial BDS process for desulfurization of diesel have stopped further work [523]. The biodesulfurization rates are still relatively low compared with the requirements of an industrial hydrotreating process for ULSD production. The currently available biocatalysts require an activity increase in desulfurization rate of about 500-fold [523]. Improved thermal stability of the desulfurization enzymes is also needed. Another limiting factor in the BDS process is the transport rate of the sulfur compounds from the oil phase to the bacterial cell membrane. Efficient separation of desulfurized oil fraction, recovery of the biocatalyst and its return to the bioreactor are also important issues which need attention. It has been suggested [522,523] that more work is needed in the above areas to make a BDS process competitive with catalytic deep HDS processes currently used in the refineries.

The increasingly stringent environmental regulation regarding the sulfur content of diesel, and other transportation fuels, requires that the final desulfurization step be capable of reliably achieving ultra low sulfur levels. The most attractive option at present for industrial application of the BDS process in deep desulfurization of diesel is to integrate it with existing HDS units in the refineries. Biodesulfurization process could complement the hydrotreating process, as sterically hindered alkyl DBTs are least reactive in hydrodesulfurization, but are the preferred substrates for biodesulfurization. The appropriate placement and integration of the biodesulfurization process with the existing diesel hydrotreating unit in a refinery should be carefully planned to achieve the ultra low sulfur target cost-effectively (Fig. 85). Some researchers have proposed that hydrodesulfurization should occur first, and then the final removal of the remaining organosulfur compounds that are resistant to hydrotreating should be accomplished by biodesulfurization [686]. Another alternative is to employ biodesulfurization before hydrotreating. In this way a significant portion of organosulfur compounds that are resistant to hydrotreating can be removed, allowing the hydrotreating process to function more efficiently and consume less hydrogen. At the same time, improved hydrodesulfurization catalysts can be used to reliably achieve environmentally mandated levels of sulfur in the final product. The operations costs will be reduced and the process economics will be improved when BDS and catalytic HDS are integrated.

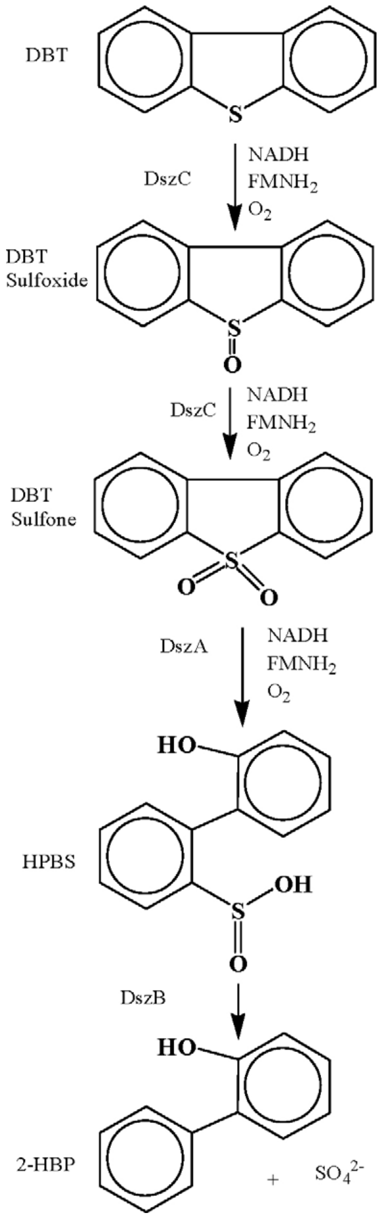


Fig. 84. The 4S pathway for the biocatalytic desulfurization of DBT and its derivatives. DBT, dibenzothiophene; HPBS, hydroxyphenyl-benzene sulfonate; 2-HBP, 2-hydroxybiphenyl; DszA, DBT sulfone monooxygenase; DszB, HPBS desulfinase; DszC, DBT mono-oxygenase [522].

10. Current ULSD challenges

The reduction of sulfur content of diesel fuel to ultra low levels (<15 ppm) reliably and cost-effectively by catalytic hydrotreating process was initially considered as a tough technological challenge for the petroleum refining industry because of the low reactivity of

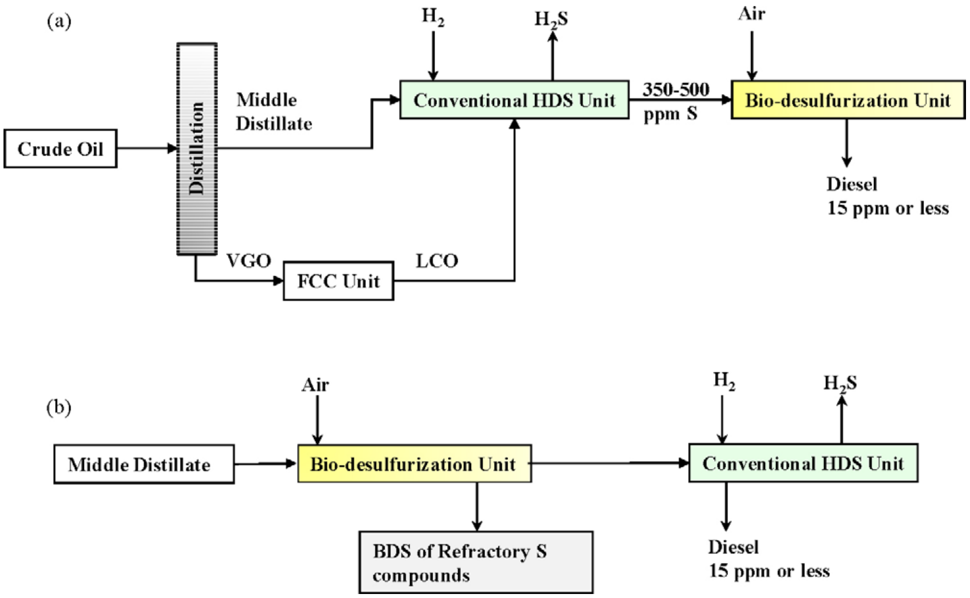


Fig. 85. Options of biodesulfurization in the upgrading of petroleum middle distillates (diesel) to ultra low sulfur levels (a) BDS unit after conventional HDS unit, (b) BDS unit before conventional HDS unit.

some alkyl DBTs and the complex chemistry involved in the desulfurization of such low reactive sulfur species. However, through coordinated efforts of scientists, catalyst manufactures, and process licensers this challenge has been met. Significant improvements in HDS catalysts and reactor design have been made and optimum operating strategies have been developed to enhance the removal of the last traces of refractory sulfur compounds, and the refiners are currently able to produce ULSD by revamping existing hydrotreaters or by installing new grassroots units. However, several issues such as changes in the properties of the diesel fuel, contamination during transportation and delivery of ULSD to customers, engine problems and higher prices remain as causes for concern.

10.1. *ULSD property issues*

The changes in diesel properties as a consequence of ultra deep desulfurization by the hydrotreating process include the following:

i. Lubricity reduction because of the removal of naturally occurring lubricity compounds in diesel fuel.
ii. Reduced density resulting in a slight reduction in energy content (approximately 1%).
iii. Decrease of the fuel's electrical conductivity which increases the risk of static electricity accumulation.
iv. Reduction of anti-oxidants that help in preventing the formation of gums and sledges.
v. Degradation of anti-corrosive property, and
vi. Modification of cold flow property.

Suitable additives have to be added to the ULSD to improve the lubricity, anti-oxidant, anti-corrosion, electrical conductivity and cold-flow properties in accordance with the ASTM standards. This will add to the cost of producing ULSD.

10.2. *ULSD cost issue*

ULSD fuel costs more to produce and distribute than the conventional low sulfur diesel (LSD). The refiners have to make additional capital investment in revamping existing hydrotreating plants to take sulfur down to ultra low levels below 15 ppm. The operating cost will also be more in ULSD units compared to that of conventional low sulfur diesel (500 ppm sulfur) producing units. Investments will also have to be made for reliable transport of ULSD throughout the supply and distribution chain. All these will contribute to the increased cost of producing and delivering ULSD. USEPA estimated that ULSD will cost 5–6 cents more per gallon to refine. The retail price increase at the pump will be, however, much higher depending on many factors such as the cost of crude oil to refineries, diesel fuel demand and supply, refining costs and profits, cost of additives, distribution and marketing costs and taxes. The retail price could be different in different countries, and would vary over time.

Significant reduction in the production cost of ULSD can be achieved if the conventional hydrotreating units that were designed to produced 500 wppm sulfur-containing LSD are combined with non-hydrogenation process such as ODS instead of costly revamping which as mentioned earlier typically require addition of significant catalyst volume (i.e. additional reactor), higher hydrogen consumption, higher operating severity, equipment modifications to increase the hydrogen purity and circulation rate, and installation of improved reactor internals. The HDS/ODS combination will be more cost-effective than the HDS revamp alternatives available to refiners. According to a recent estimate [701] the ODS/HDS cost ratios fall in the range 0.3–0.6 for capital cost and 0.7–0.9 for operating cost. The ODS technology offers a non-hydrogen consuming low-cost alternative to deep HDS technology and it is well suited for reducing the sulfur content of low sulfur diesel from 500 ppm to less than 10 ppm in combination with the existing hydrotreaters. However, the process is still in the developmental stage, and a number of issues still remain to be resolved before industrial scale-up and commercialization.

10.3. *ULSD contamination and transportation problems*

The likelihood of contamination in the transportation and distribution ULSD is one of the major concerns of ULSD markets and pipeline operators, particularly during the period of transition to ULSD. Both ULSD and LSD will co exist side by side, during the transition period until June 1, 2010. Other distillates fuels with widely varying sulfur content such as jet fuel, heating oil, locomotive and marine diesel also will be shipped along with ULSD. As a result, ULSD can be easily contaminated from the leftover higher sulfur fuels in the pipeline, and in bulk storage tanks so that it no longer meets the required 15 ppm maximum sulfur specification. The contaminated ULSD may be downgraded to 500 ppm low sulfur diesel (LSD) or to non-sealable transmix that must be reprocessed prior to distribution. These are expensive options.

Moreover, the liability for off-specification fuel could be another major challenge for petroleum marketers. In USA, the federal fine for dispensing ULSD fuel that does not meet the spec is $32,500 per day per incident [702]. Under the ULSD regulations, all parties along the distribution are presumed liable for on-road diesel fuel that exceeds EPA sulfur limits of 15 ppm. Consequently, each party must prove they did not cause the violation. This is achieved by producing compliant product transfer documents and demonstrating the existence of a comprehensive quality assurance program. Thus, product contamination, downgrading, segregating, tracking multiple products in a single tank and the regulatory reporting, present increasing complications to those handling and distributing ULSD to customers. This is, however, only a temporary problem and will disappear once complete switch over to ULSD occurs for all types of diesel engines.

11. Concluding remarks

Research on the deep desulfurization of diesel fuel to ultra low sulfur levels has gained considerable importance in recent years, and a growing number of articles have been published in the scientific literature concerning various aspects of ULSD production by academic research institutions and industrial research laboratories during the past 7 years. The renewed interest in ULSD research is driven by the need to have a thorough understanding of the various factors influencing deep desulfurization of diesel to ultra low levels as well as to find cost-effective ways to produce ULSD which is expected to quickly dominate the distillates fuels market worldwide. ULSD fuel will enable the use of advanced emission control devices in diesel engines for lowering harmful exhaust emissions. Remarkable progress has been made in recent years in our understanding of the key factors such as catalytic sites, inhibitory effects, feed quality, hydrogen partial pressure and other process variables, kinetic and thermodynamic effects, etc. influencing the desulfurization of the least reactive sterically hindered alkyl DBTs (e.g. 4,6-DMDBT). Significant improvements in HDS catalysts and reactor design have been made, and optimum operating strategies have been developed to minimize the inhibition effects of H_2S and N-compounds and to enhance the removal of the last traces of refractory sulfur compounds. Revamping of the conventional diesel hydrotreating units for ULSD production have been achieved based on the results of these research and developments. In addition, new hydrotreating process concepts and technologies, and alternative non-hydrogenation routes have been developed for ULSD production.

The refiners are currently able to produce ULSD by revamping existing hydrotreaters that were designed in the 1990s to produce low sulfur diesel with 500 ppm sulfur. In the future, the global demand for ULSD will increase remarkably, and the refiners will be required to upgrade poor quality feedstocks such as LCO, heavy gas oils, etc. to produce the additional volume of ULSD. Furthermore, future ULSD specifications may require improvements in other diesel properties such as higher cetane number, lower aromatics content, density reduction, etc. Production of such high quality ULSD from low quality feeds is a tough challenge, but the economic incentive is high.

High hydrogen consumption is a serious problem affecting the process economics in ULSD production. Some recently developed hydrotreating technologies such as Isotherming and POLF which use less hydrogen may receive increased attention for ULSD production in the future. The use of non-hydrogenation processes such as ODS will also gain increasing importance for ULSD production in the future. The refractory sulfur species (e.g. 4,6-DMDBT) are preferentially attacked and desulfurized in the ODS process. Because of the mild process conditions with no hydrogen requirement, the capital and operating costs of the ODS process will be substantially low, and it could be used in combination with existing conventional hydrotreaters for desulfurizing moderately hydrotreated low sulfur diesel having sulfur content around 500 ppm to ULSD (<10 ppm sulfur).

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