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An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel[☆]

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Abstract

This review discusses the problems of sulfur reduction in highway and non-road fuels and presents an overview of new approaches and emerging technologies for ultra-deep desulfurization of refinery streams for ultra-clean (ultra-low-sulfur) gasoline, diesel fuels and jet fuels. The issues of gasoline and diesel deep desulfurization are becoming more serious because the crude oils refined in the US are getting higher in sulfur contents and heavier in density, while the regulated sulfur limits are becoming lower and lower. Current gasoline desulfurization problem is dominated by the issues of sulfur removal from FCC naphtha, which contributes about 35% of gasoline pool but over 90% of sulfur in gasoline. Deep reduction of gasoline sulfur (from 330 to 30 ppm) must be made without decreasing octane number or losing gasoline yield. The problem is complicated by the high olefins contents of FCC naphtha which contributes to octane number enhancement but can be saturated under HDS conditions. Deep reduction of diesel sulfur (from 500 to $<$15 ppm sulfur) is dictated largely by 4,6-dimethyldibenzothiophene, which represents the least reactive sulfur compounds that have substitutions on both 4- and 6-positions. The deep HDS problem of diesel streams is exacerbated by the inhibiting effects of co-existing polyaromatics and nitrogen compounds in the feed as well as H_2S in the product. The approaches to deep desulfurization include catalysts and process developments for hydrodesulfurization (HDS), and adsorbents or reagents and methods for non-HDS-type processing schemes. The needs for dearomatization of diesel and jet fuels are also discussed along with some approaches. Overall, new and more effective approaches and continuing catalysis and processing research are needed for producing affordable ultra-clean (ultra-low-sulfur and low-aromatics) transportation fuels and non-road fuels, because meeting the new government sulfur regulations in 2006–2010 (15 ppm sulfur in highway diesel fuels by 2006 and non-road diesel fuels by 2010; 30 ppm sulfur in gasoline by 2006) is only a milestone. Desulfurization research should also take into consideration of the fuel-cell fuel processing needs, which will have a more stringent requirement on desulfurization (e.g., $<$1 ppm sulfur) than IC engines. The society at large is stepping on the road to zero sulfur fuel, so researchers should begin with the end in mind and try to develop long-term solutions.

Keywords: Desulfurization; Gasoline; Fuels; Diesel fuel; Jet fuel; Catalysis; Adsorption

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1. Introduction

This review discusses fuel specification issues and the problems of sulfur reduction in highway and non-road fuels and presents an overview of new

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Table 1
US EPA Tier II gasoline sulfur regulations as of 2002

Category	Year				
	1988 [7]	1995 [9]	2004 [3]	2005 [3]	2006 [3]
Refinery average (ppmw)	1000 (maximum) [7]	330 (<330 ppm S and <29.2% aromatics required for national certification; <850 ppm S and <41.2% aromatics as national maximum) [9]	–	30	30
Corporate average (ppmw)			120	90	–
Per-gallon cap (ppmw)			300	300	80

approaches to ultra-deep desulfurization of refinery streams for ultra-clean (ultra-low-sulfur) gasoline, diesel fuels and jet fuels.

In the past decade, clean fuels research including desulfurization has become a more important subject of environmental catalysis studies worldwide. Tables 1 and 2 show the current US EPA regulations for gasoline [1–3] and diesel fuels [3–5] including non-road diesel fuels [6], respectively, along with earlier fuel specification data in the US for comparison [7–9]. With the new US EPA Tier II regulations to reduce the gasoline sulfur from current maximum of 350–30 ppm (refinery average, with 80 ppm as per-gallon (1 US gallon = 3.7854 l) cap) by 2006, and to cut the highway diesel fuel sulfur from current 500 ppmw down to 15 ppmw (per-gallon average) by June 2006, refineries are facing major challenges to meet the fuel sulfur specification along with the required reduction of aromatics contents. More recently, EPA has announced plan to reduce non-road diesel fuel sulfur from current average of 3400 ppm down to 500 ppm by 2007 and further to 15 ppm by 2010 [6]. The US Clean Air Act Amendments of 1990 and related new fuel regulations by the US EPA and government regulations in many countries call for the production and use of more environmentally friendly transportation fuels with lower contents of sulfur and aromatics.

Table 3 shows the average properties of crude oils refined in the US during 1981–2001 along with the US and worldwide petroleum consumption during 1981–2001 based on published statistical data [10–14]. The demand for transportation fuels has been increasing in most countries for the past three decades. The total world petroleum consumption increased from 49.42 million barrels per day (MBPD) in 1971 to 77.12 MBPD in 2001, representing a 56% increase [11]. The total US consumption of petroleum products reached 19.59 MBPD in 2001, about 39% increase from 1971 (14.11 MBPD) [10]. Of the petroleum products consumed in US in 2001, 8.59 MBPD was supplied as motor gasoline, 3.82 MBPD as distillate fuels, including 2.56 MBPD as high-way diesel fuels and 1.26 MBPD as off-road fuels and industrial fuels, 1.65 MBPD as jet fuel, 0.93 MBPD as residual

Table 2
US EPA sulfur regulations for diesel and jet fuels as of April 2003

Category	Year			
	1989 [8]	1993 [6]	2006 [6]	2010 [6]
Highway diesel (ppmw)	5000 (maximum for no. 1D and 2D, with minimum cetane no. 40) [8]	500 (current upper limit since 1993)	15 (regulated in 2001; exclude some small refineries)	15 (regulated in 2001; apply to all US refineries)
Non-road diesel (ppmw)	20000 [8]	5000 (current upper limit)	500 (proposed in 2003 for 2007)	15 (proposed in 2003 for 2010)
Jet fuel (ppmw)	3000	3000	3000 maximum?	<3000 maximum?

Table 3
Average properties of crude oils refined in the US during 1981–2001 and US and world petroleum consumption during 1981–2001

Property	Year		
	1981	1991	2001
Total amounts of crude oils refined in US (million barrel/day)	12.47	13.30	15.13
Average sulfur content of crude oils refined in US (wt.% based on sulfur)	0.89	1.13	1.42
API gravity of crude oils refined in US (° API)	33.74	31.64	30.49
Total petroleum products supplied in the US including imported crude and products (million barrel/day)	16.06	16.71	19.59
Total worldwide petroleum consumption (million barrel/day)	60.90	66.72	77.12

fuel oil, and 1.13 MBPD as liquefied petroleum gas (LPG), and 3.47 MBPD for other uses in the US [10].

The problem of deep removal of sulfur has become more serious due to the lower and lower limit of sulfur content in finished gasoline and diesel fuel products by regulatory specifications, and the higher and higher sulfur contents in the crude oils. A survey of the data on crude oil sulfur content and API gravity for the past two decades reveals a trend that US refining crude slates continue towards higher sulfur contents and heavier feeds. The average sulfur contents of all the crude oils refined in the five regions of the US known as five Petroleum Administration for Defense Districts (PADDs) increased from 0.89 wt.% in 1981 to 1.42 wt.% in 2001, while the corresponding API gravity decreased from 33.74° API in 1981 to 30.49° API in 2001 [12–14]. In the past two decades, average sulfur contents in crude oils refined in the US increased by 265 ppm/year and API gravity decreased by 0.16° API/year, while the total crude oil refined in the US refineries increased from 12.47 MBPD in 1981 (11.20 MBPD in 1971) to 15.13 MBPD in 2001 [10].

The crude oils refined in the US tend to have higher sulfur contents than those in the Western Europe. For example, the average crude oil feeds to US refineries in 2000 have 1.35 wt.% sulfur and 31.0° API gravity, whereas European refinery feed by comparison was sweeter at 1 wt.% sulfur and 35° API gravity [15]. The total world consumption of refined petroleum product in 2000 was 76.896 MBPD, in which the consumptions in the US and western Europe were 19.701 and 14.702 MBPD, respectively. The problem for diesel desulfurization is also somewhat more serious in the US because a higher proportion of light cycle oil (LCO) from FCC is used in the diesel pool in the US, which has higher contents of more refractory sulfur compounds (see below). H_2 demand increase is another challenge to the refinery operations. Hydrogen deficits are processing restraints and will impact future hydrotreating capabilities and decisions [16].

2. Reactivity of organic sulfur compounds in hydrodesulfurization (HDS)

Fig. 1 presents a qualitative relationship between the type and size of sulfur molecules in various distillate fuel fractions and their relative reactivities [17]. Various refinery streams are used to produce three major types of transportation fuels, gasoline, jet fuels and diesel fuels that differ in composition and properties. The common types of sulfur compounds in liquid fuels are outlined in Table 4, which corresponds to Fig. 1 for transportation fuels. The reactivity ranking in Fig. 1 is based on well-known experimental observations and a large amount of literature information [18–21]. For the sulfur compounds without a conjugation structure between the lone pairs on S atom and the π-electrons on aromatic ring, including disulfides, sulfides, thiols, and tetrahydrothiophene, HDS occurs directly through hydrogenolysis pathway. These sulfur compounds exhibit higher HDS reactivity than that of thiophene by an order of magnitude [22], because they have higher the electron density on the S atom and weaker C–S bond. The reactivities of the 1- to 3-ring sulfur compounds decrease in the order thiophenes > benzothiophenes > dibenzothiophenes [23–27]. In naphtha, thiophene is so much less reactive than the thiols, sulfides, and disulfides that the latter can be considered to be virtually infinitely reactive in practical high-conversion processes [22,28]. Similarly, in gas oils, the reactivities

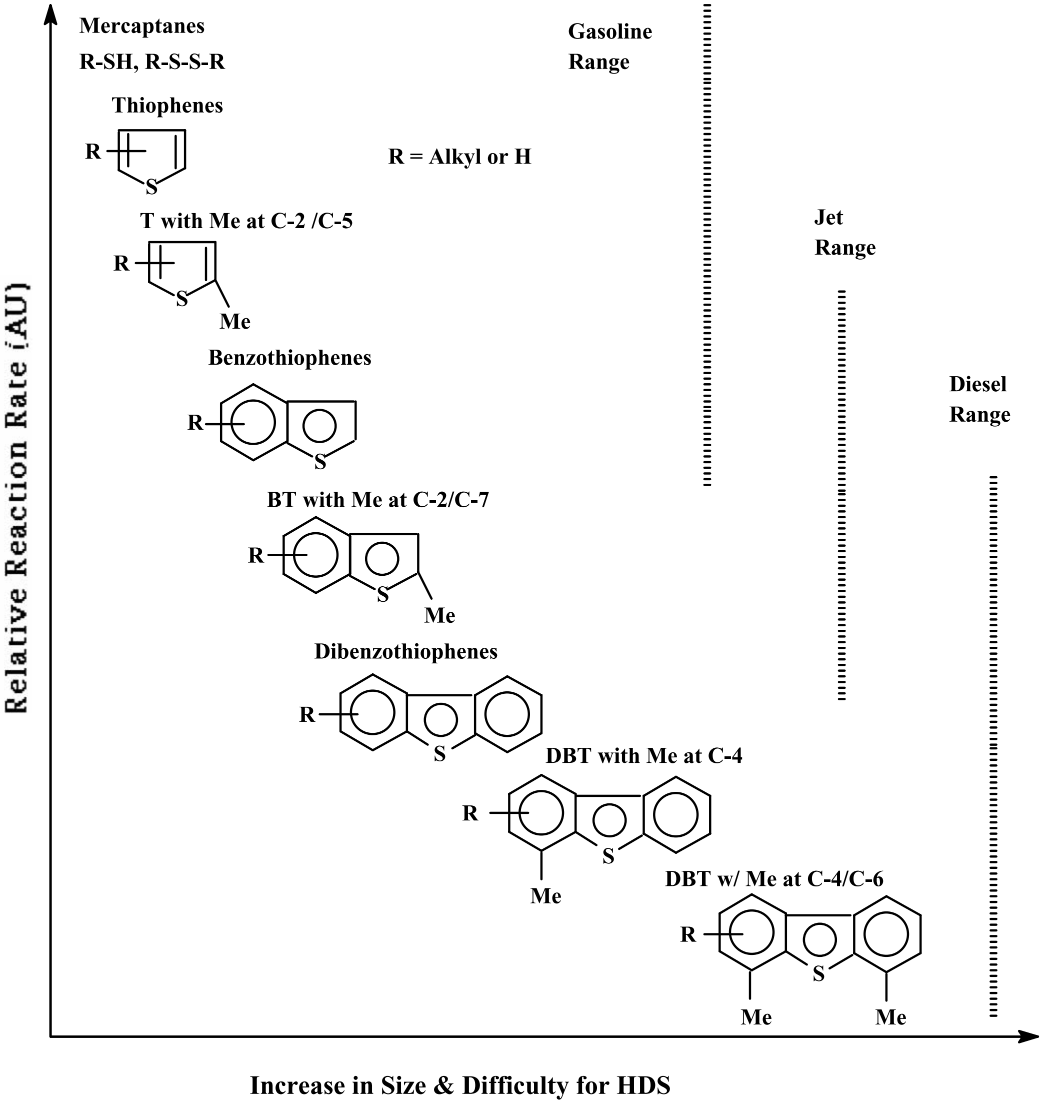


Fig. 1. Reactivity of various organic sulfur compounds in HDS versus their ring sizes and positions of alkyl substitutions on the ring [17].

of (alkyl-substituted) 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are much lower than those of other sulfur-containing compounds [28–31]. Consequently, in deep HDS, the conversion of these key substituted dibenzothiophenes largely determines the required conditions. Gates and Topsoe [28] pointed out in 1997 that 4-methyldibenzothiophene and 4,6-DMDBT are the most appropriate compounds for investigations of candidate catalysts and reaction mechanisms.

Fig. 2 shows the sulfur compounds in the finished products of gasoline, jet fuel, and diesel fuel that are representative of current commercial transportation fuels in the US [32,33]. It can be seen that in each of the fuels, what are left as sulfur compounds in the finished products are those that have lower reactivities among all the sulfur compounds in the corresponding feed shown in Fig. 1, e.g., naphtha range for gasoline, kerosene range for jet fuel, and gas oil range for diesel fuel. Deep desulfurization and ultra-deep desulfuriza-

Table 4
Typical sulfur compounds and corresponding refinery streams for fuels

Sulfur compounds	Refinery streams	Corresponding fuels
Mercaptanes, RSH; sulfides, R_2S; disulfides, RSSR; thiophene (T) and its alkylated derivatives, benzothiophene	SR-naphtha; FCC naphtha; coker naphtha	Gasoline (BP range: 25–225 °C)
Mercaptanes, RSH; benzothiophene (BT), alkylated benzothiophenes	Kerosene; heavy naphtha; middle distillate	Jet fuel (BP range: 130–300 °C)
Alkylated benzothiophenes; dibenzothiophene (DBT); alkylated dibenzothiophenes	Middle distillate; FCC LCO; coker gas oil	Diesel fuel (BP range: 160–380 °C)
Greater than or equal to three-ring polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT), phenanthro[4,5-b,c,d]thiophene (PT) and their alkylated derivatives and naphthothiophenes (NT)	Heavy gas oils; vacuum gas oil; distillation resides	Fuel oils (non-road fuel and heavy oils)

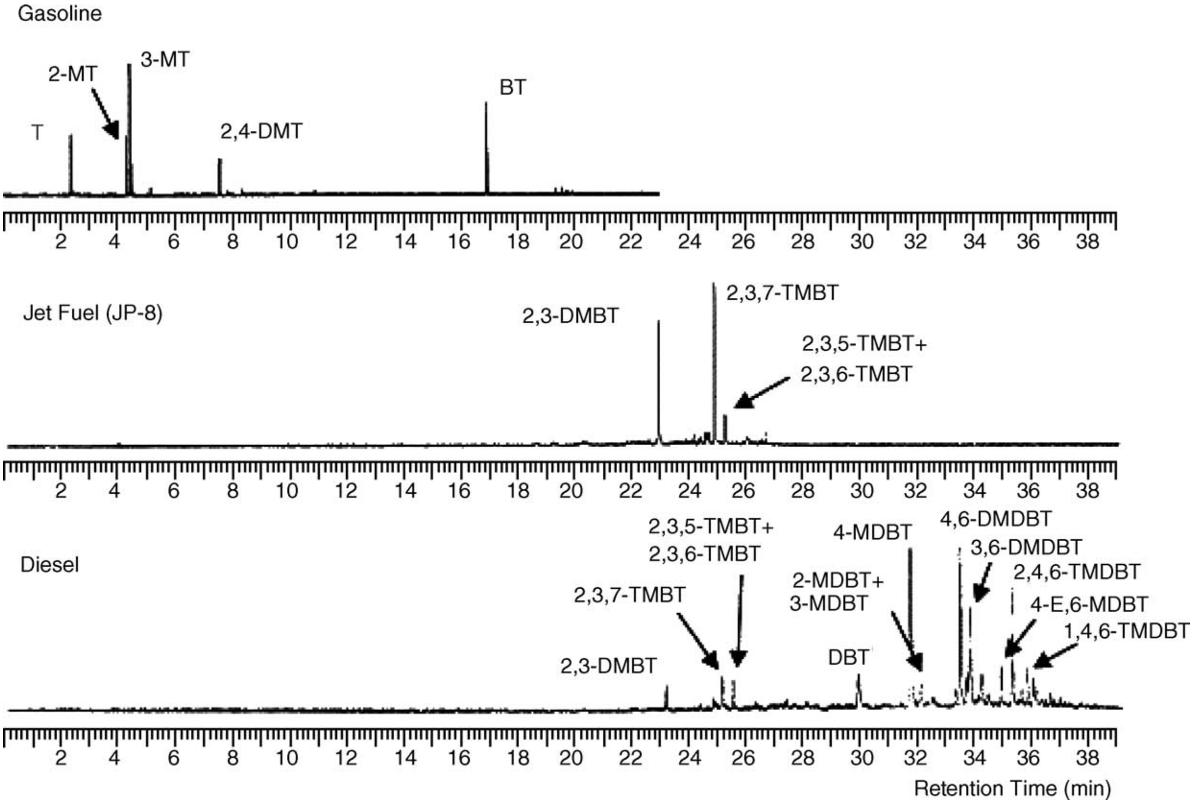


Fig. 2. Sulfur compounds in commercial gasoline, jet fuel and diesel fuel identified by GC-FPD analysis coupled with GC-MS and reaction kinetic analysis [32].

tion refers to processes to remove sulfur (that exists in current gasoline and diesel fuels as shown in Fig. 2) to below 15 ppmw for diesel fuels and to below 30 ppmw for gasoline, respectively.

3. Catalysts for hydrotreating/HDS

3.1. Catalyst formulations

The formulations of modern hydroprocessing catalysts originated from early research in catalytic coal liquefaction and coal liquids upgrading to automotive fuels in the 1920s and the 1930s in Germany which led to catalysts based on molybdenum and tungsten with nickel or cobalt promoters [34–36]. The basic compositions of current hydrotreating catalysts are represented by molybdenum sulfide promoted by cobalt or nickel and supported on porous γ-alumina, Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3, with various modifications by using additives (e.g., boron or phosphorus or silica) or more promoters (e.g., Ni–Co–Mo/Al_2O_3) or improved preparation methods. The activity and selectivity of the hydrotreating catalysts have been improved significantly as a result of continuous research and development in research institutions and catalysts, and petroleum companies worldwide.

An excellent review has been published by Topsoe et al. [37] on chemistry and catalysis by metal sulfides. Design approaches for developing more active catalysts are based on the ideas to tailor the active sites for desired reactions. The exact nature of active sites in Co–Mo or Ni–Mo catalysts is still a subject of debate, but the Co–Mo–S model (or Ni–Mo–S model for Ni–Mo catalysts) is currently the one most widely accepted [37,38]. According to the model, the Co–Mo–S structure or Ni–Mo–S structure is responsible for the catalytic activity of the Co-promoted or Ni-promoted MoS_2 catalyst, although the model does not specify whether the catalytic activity arises from Mo promoted by Co or from cobalt promoted by molybdenum. Density-functional theory (DFT) calculations show that addition of Co–MoS_2 structure lowers the sulfur binding energy at the edges and thereby provides more active sites [39]. Recently, the formation of sulfur vacancy in MoS_2 under H_2 atmosphere has been observed directly for the first time by scanning tunneling microscope (STM) [40]. Comparison of STM images for Mo sulfide-based particles with and without cobalt promoter atoms shows that without cobalt, the MoS_2 particles assume a neat triangular shape. Once cobalt enters the crystals, the particles become truncated hexagons–triangles with clipped-off vertices [41]. These new findings from experimental STM observations are consistent also with the FT-IR studies for NO chemisorption on Co–Mo catalysts. Co–Mo catalysts with more Co sites exposed (Co edge sites) tend to have higher activity for HDS [37], and this trend has been observed also for Co–Mo/MCM-41 and Co–Mo/Al_2O_3 catalysts based on DBT HDS and FT-IR of chemisorbed NO [20].

Among the Co–Mo–S structures for alumina-supported catalysts, the intrinsically more active phase was referred to as type II (Co–Mo–S II), and the less active phase as type I (Co–Mo–S I); type I structure is assumed to be bonded to support through Mo–O–Al linkages and has less stacking, whereas type II structure has higher stacking and few linkages with support [38]. For steric reasons, catalyst–support linkages in Co–Mo–S I probably hinder reactant molecules from approaching the catalytically active sites, and thus Co–Mo–S II is more active than Co–Mo–S I although Mossbauer and EXAFS signals of types I and II structures are the same. Daage and Chianelli [42] reported that the top and bottom layers (rim) of unsupported MoS_2 stacks (slabs) have a much higher activity than the surface of intermediate layers (edge) for hydrogenation of DBT, while the hydrogenolysis of the C–S bond in DBT occurs equally well on all MoS_2 layers. They proposed a rim-edge model, and explained that the flat π-adsorption on MoS_2 surface results in hydrogenation of DBT which can take place on rim sites but this adsorption is more difficult on edge sites, whereas vertical adsorption of sulfur is assumed to be necessary for C–S bond hydrogenolysis which can take place on surface Mo sites of all layers (both rim and edge). The Co–Mo–S model makes no distinction between rim and edge, but Co–Mo–S II would seem to have relatively more rim sites that are not likely to be influenced by steric hindrance of reactant adsorption. Consequently, more Co–Mo–S II structures can lead to more active catalysts for desulfurization of polycyclic sulfur compounds.

Table 5 shows typical hydroprocessing conditions used in industry [43]. The choice of commercial hydrotreating catalysts, represented by Co–Mo, Ni–Mo

Table 5
Typical hydroprocessing conditions used in industry [43]

Fuel type and historical conditions	Pressure (MPa)	LHSV (h^{-1})	Temperature (°C)
Recent history			
Naphtha (gasoline)	1.38–3.45	2–8	290–370
Kerosene/gas oil (jet/diesel fuels)	3.45–8.27	2–4	315–400
FCC feed pretreat	5.17–13.80	1.0–3.0	370–425
Current trends			
Naphtha (gasoline)	1.38–5.17	2–6	290–370
Kerosene/gas oil (jet/diesel fuels)	3.45–10.30	0.5–3.0	315–400
FCC feed pretreat	6.90–20.70	0.5–2.0	370–425

and Ni–Co–Mo usually supported on alumina with or without modifiers, depends also on the capability of reactor equipments, operating conditions (pressure, temperature), feedstock type and sulfur contents, and desired level of sulfur reduction. Increasingly more severe conditions and more active catalysts are used today for hydroprocessing. In general, for low-pressure and high-temperature desulfurization of distillate fuels, Co–Mo catalysts may be better than Ni–Mo catalysts. For high-pressure and low-temperature conditions, Ni–Mo catalysts perform better than Co–Mo catalysts. Ni–Mo catalysts generally have higher hydrogenating ability than Co–Mo counterparts, and higher H_2 pressure and lower temperature favor the hydrogenation reactions and thus facilitate HDS by hydrogenation pathway. The trimetallic Ni–Co–Mo catalysts can combine the features of Co–Mo and Ni–Mo, and this new formulation feature is being used in some recent commercial catalysts.

3.2. Global catalyst markets

Table 6 shows the global merchant refinery catalyst market distribution during 1997–2001 with a projection to 2005 [44–47], together with the data for 1992 [46] for comparison. The largest volume gain in refining catalysts was in hydrotreating/HDS catalysts. In fact, HDS catalysts recently overtook FCC as the largest market for refinery catalyst makers. HDS catalysts are playing an increasingly more important role in refineries today for producing clean fuels that meet the regulatory sulfur requirements. A 1999 report puts the 1997 global merchant catalyst market at US$ 7.4 billion, with the following distribution: 28% refinery, 27% chemical, 23% polymerization, and 22% environmental, in which the environmental part excludes the value of the precious metals and substrate used and includes only manufacturing fees [47]. According to a study reported in 2000, the global merchant catalyst

Table 6
Worldwide refinery catalysts markets [44–46]

Category	Year			
	1992 [46]	1997 [44]	2001 [44,45]	2005 [45]
Total catalyst market		US$ 7.40 billion [47]	US$ 10.16 billion	
Total refinery catalyst market	US$ 2.2 billion	US$ 2.07 billion	US$ 2.32 billion	US$ 2.68 billion
By sector in refinery				
Hydrotreating/desulfurization	US$ 265 million (12%)	US$ 723 million (34%)	US$ 789 million (34%)	US$ 965 million (36%)
Catalytic cracking/FCC	US$ 900 million (41%)	US$ 944 million (45%)	US$ 696 million (30%)	US$ 804 million (30%)
Naphtha reforming	US$ 90 million (4%)	US$ 124 million (6%)	US$ 139 million (6%)	US$ 134 million (5%)
Hydrocracking	US$ 200 million (9%)	US$ 155 million (7%)	US$ 116 million (5%)	US$ 134 million (5%)
Others[a]	34%	US$ 125 million (6%)	US$ 580 million (25%)	US$ 643 million (24%)
By region for refinery				
North America (%)			40	38
Western Europe (%)			20	19
Asia/Pacific (%)			19	20
Rest of world (%)[b]			21	23

[a] Include isomerization, alkylation, etherification, polymerization, lubes, sulfur recovery, hydrogen, and purification catalysts.
[b] Includes Eastern Europe, Mid-East, and South America.

market is about US$ 10 billion/year, with the captive market worth an additional US$ 2 billion to US$ 3 billion and total market growth approaching 10% per year [48]. It is clear from these studies that refining catalysts, particularly desulfurization catalysts, represent an important category of growth areas due to the needs for producing cleaner transportation fuels. In addition, some new approaches and new technologies that do not use hydrotreating are also emerging in the past several years [17,21,49].

4. Deep desulfurization of naphtha for ultra-clean gasoline

4.1. Gasoline pool and sources of sulfur

Table 7 shows the typical gasoline pool compositions in the US [50] and in the western Europe [51]. It is well known that naphtha from FCC makes up about 25–40% (average of 36% in the US) of gasoline blend stocks, but accounts for over 90% of the sulfur (up to 90–98%) and essentially all of the olefins in the entire gasoline pool. Therefore, the key to deep desulfurization of gasoline is sulfur removal from FCC naphtha.

It is well known that sulfur removal from FCC naphtha can be achieved by catalytic HDS, but the accompanying decrease of octane number is a significant loss due to the saturation of olefins. Fig. 3 shows the relationship between HDS and octane loss for conventional hydrotreating, in which the plot is made based on data from industrial sources [52]. Because FCC naphtha also has a high content of olefins (e.g., 20%) which have higher octane number, selective sulfur removal without loss of octane number (or without loss of olefins) is desirable. Hydrotreating of FCC naphtha is an attractive process alternative, provided that octane losses are minimized by either minimizing olefin saturation during HDS or restoring the octane number after the HDS.

FCC naphtha can be divided (in a fractionator or splitter) into light cat naphtha (LCN, IBP: 140° F or 60 °C), medium (or intermediate) cat naphtha (MCN or ICN) cut, and heavy cat naphtha (HCN) cuts. Totally debutanized FCC naphtha distills between 80 and 430 °F (27–221 °C) boiling range [53]. A MCN or ICN cut is defined by an initial boiling point that should include thiophene (183 °F, 85 °C) but thiophene begins to distill with C6 hydrocarbons boiling above 140 °F (60 °C) and below 200 °F (93 °C) which makes the better fractionation more important for MCN [53]. The final boiling point of MCN is flexible between 270 and 360 °F (132 and 182 °C) [54].

Sulfur species change from primarily mercaptans in the low boiling IBP: 140 °F (60 °C) LCN to thiophenes and substituted thiophenic sulfur compounds in 140–390 °F (MCN + HCN), and benzothiophenes and substituted benzothiophenes in the 390–430 °F (bottom part of HCN). Above 390 °F (199 °C), total sulfur increases rapidly with boiling point [53]. In general, LCN has most of the olefins and the sulfur in mercaptan form; caustic treatment is used for LCN treatment to remove mercaptans. Thiophene cannot be extracted by caustic treatment and that is why fractionation of FCC naphtha is important. HCN contains much less olefins and most of the thiophenic sulfur, and thus

Table 7
Typical gasoline pool composition in US and western Europe

Gasoline blend stocks	Percentage of gasoline pool volume in US	Percentage of gasoline pool sulfur in US	Percentage of gasoline pool volume in western Europe
FCC naphtha	36	98	27
Naphtha reformate	34	–	40
Alkylate	12	–	9
Light straight-run naphtha	3	1	7.5
Coker naphtha	1	1	∼0
Hydrocracked naphtha	2	–	∼0
Isomerate	5	–	10
Butanes	5	–	5.5
MTBE	2	–	1.0
Total (%)	100	100	100

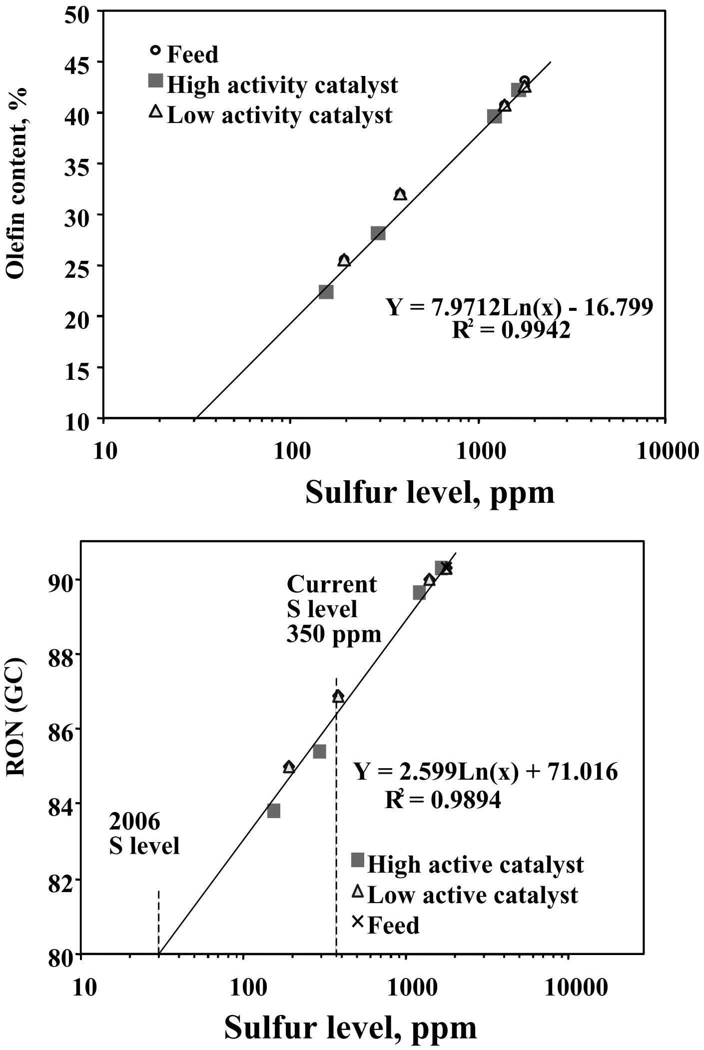


Fig. 3. Relationship between desulfurization and olefin content (top) and octane number of FCC naphtha (plot by Ma et al. based on data from Desai et al. [52]).

can be desulfurized in a hydrotreater. MCN or ICN is the lowest-octane portion of FCC naphtha, and can be desulfurized deeply to produce a blend stock or reformer feedstock [54].

4.2. Approaches to gasoline sulfur removal

Table 8 outlines the catalytic and non-catalytic approaches to gasoline deep desulfurization with general remarks on their features based on published information in the open literature [17,55–57]. Approaches to reducing sulfur content in FCC naphtha include: (1) post-treating product to remove sulfur from FCC naphtha [55,56]; (2) pretreating the FCC feed to remove sulfur [50]; (3) increasing sulfur conversion in situ to hydrogen sulfide during the FCC operation [56]. The principles of these methods are based on one or more of the following processes: catalytic HDS, selective HDS, reactive adsorption using solid sorbent and H_2 at elevated temperature, selective adsorption without using H_2 at ambient temperature, distillation or extraction coupled with HDS, membrane, and

Table 8
Approaches to deep desulfurization of naphtha for cleaner gasoline

Category	Description and representative process	Remarks
(I) Post-FCC sulfur removal	Conventional HDS process without special olefin preservation (many companies)	HDS
	Convert organic sulfur to H_2S by selective HDS while preserving olefins (ExxonMobil's SCANfining; IFP Prime G+)	Selective HDS
	Hydrodesulfurize organic sulfur, saturate olefins but convert paraffins for octane gain (ExxonMobil OCTGain 125; UOP-INTEVEP's ISAL)	HDS plus octane recovery
	Reactive adsorption and capture of sulfur by solid adsorbent at elevated temperatures under low H_2 pressure (Phillips Petroleum S-Zorb Gasoline)	Non-HDS; stoichiometric H_2 consumption
	Sulfur adsorption and capture by solid metal oxide adsorbent at high temperatures (RTI TReND)	Non-HDS; use H_2 atmosphere
	Polar adsorption by using solid adsorbent based on alumina (Black and Veatch Prichard IRVAD)	Polar adsorption
	Selective adsorption for removing sulfur (SARS) as organic compounds by solid adsorbent at ambient temperature without using H_2 (Pennsylvania State University, PSU-SARS)	S adsorption, no H_2; can reach <1 ppm S for fuel cells
	Integrated adsorption and hydrotreating of concentrated sulfur from adsorption (Pennsylvania State University, PSU-SARS-HDSCS)	S adsorption coupled with HDS
	Drop the organic sulfur to heavier fraction by alkylation of thiophenes (BPs OATS process)	Alkylation and boiling point shift
	Remove the organic sulfur by using caustic treatment (Merichem's THIOLEX/REGEN process; Exomer by Merichem and ExxonMobil) or extraction (GTC Technology's GT-DeSulf)	Extraction of sulfur in light fraction of naphtha
	Remove the organic sulfur by using membrane filtration (Grace's S-Brane^{TM} Process)	Membrane separation of light naphtha
(II) Pre-FCC sulfur removal	Deep HDS of feed before catalytic cracking in FCC reactor, which greatly reduces sulfur in FCC naphtha and in LCO (Akzo Nobel, IFP, UOP, etc.)	HDS at higher H_2 pressure
	Physico-chemical treatment such as adsorption or extraction to remove sulfur (concept suggested here as a possible approach based on PSU-SARS)	Adsorption without H_2
(III) In situ FCC sulfur removal	Convert more organic sulfur into H_2S during FCC operation, which can reduce organic sulfur in liquid products (Akzo Nobel's Resolve; Grace Davison's Saturn (GSR-6.1))	Sulfur conversion in FCC
	Capture organic sulfur using metal species to retain sulfur as sulfur oxide, and regenerate it in the regenerator (concept suggested here as a possible approach based on reactive adsorption using sorbent)	Sulfur capture in FCC

biochemical processes. Due to limitation of space and scope, only some of the approaches and processes related to catalysis and adsorption are further elaborated below.

Compared to the diesel sulfur problem, it is not very difficult to remove sulfur from gasoline by HDS. The challenges to the refinery for gasoline deep desulfurization are to meet the new EPA Tier II regulations on sulfur contents (2006–2010) and aromatic contents and still produce high-octane gasoline in a profitable manner. As can be seen from Fig. 3, the increasing extent of sulfur removal by conventional HDS of FCC naphtha also translates into decreasing octane number due to saturation of olefins [52].

4.2.1. Selective HDS of FCC naphtha

Selective HDS could be achieved by designing catalysts that promote thiophene HDS but do not saturate olefins, or by passivating olefin hydrogenation sites on the catalysts. Some reports indicate that there exist different active sites on hydrotreating catalysts (such as sulfided Co–Mo/Al_2O_3) for thiophene desulfurization and for olefin hydrogenation [57–63]. On the other hand, a recent report suggests that selective HDS of FCC naphtha may be due to competitive adsorption of sulfur compounds that inhibit adsorption and saturation of olefins in naphtha [64]. ExxonMobil's SCANfining [65] and IFP's Prime G+ are two representative new processes for gasoline desulfurization based on selective HDS in which organic sulfur is converted to H_2S but olefinic species are largely preserved for preventing octane loss.

Fig. 4 shows the scheme of SCANfining (Selective Cat Naphtha hydrofining), first developed by Exxon (now ExxonMobil). It is a catalytic HDS process that is based on a proprietary catalyst called RT-225 [65,66]. The process flow can be described as follows. The feed is mixed with recycle hydrogen, heated with reactor effluent and passed through the pretreat reactor for diolefin saturation. After further heat exchange with reactor effluent and preheat using a utility, the hydrocarbon/hydrogen mixture enters the HDS reactor containing proprietary RT-225 catalyst. In the reactor, the sulfur is converted to H_2S under conditions which strongly favor HDS while minimizing olefin saturation. The RT-225 catalyst system was jointly developed by ExxonMobil and Akzo Nobel specifically for selective removal of sulfur from FCC naphtha by HDS with minimum hydrogenation of olefins, thus preserving octane. Fig. 5 illustrates the performance of SCANfining catalyst for naphtha HDS and olefin hydrogenation [62]. The SCANfining could be used for wide-cut naphtha and the catalyst causes very little yield loss. Therefore, SCANfining offers the ability to eliminate FCC naphtha product splitting towers and to reduce hydrogen consumption to 30–50% less than in conventional hydrofinishing, resulting in significant investment and operating cost savings. SCANfining can be retrofitted using existing equipment, however, there are multiple configurations that can best adapt

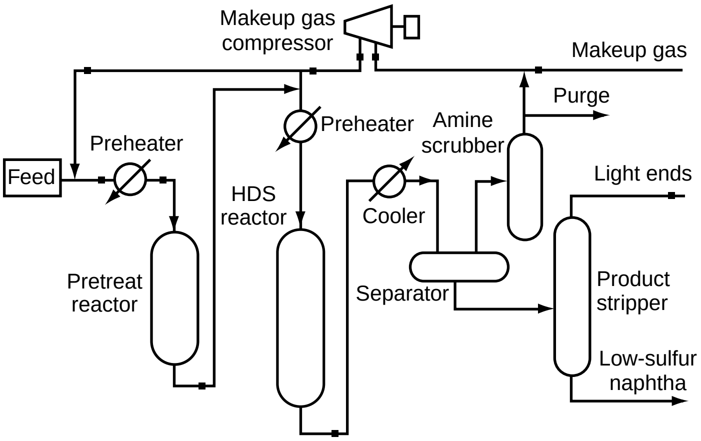


Fig. 4. ExxonMobil's SCANfining process for selective naphtha HDS from Halbert et al. [65]; see also ExxonMobil web site: http://www.prod.exxonmobil.com/refiningtechnologies/ [66].

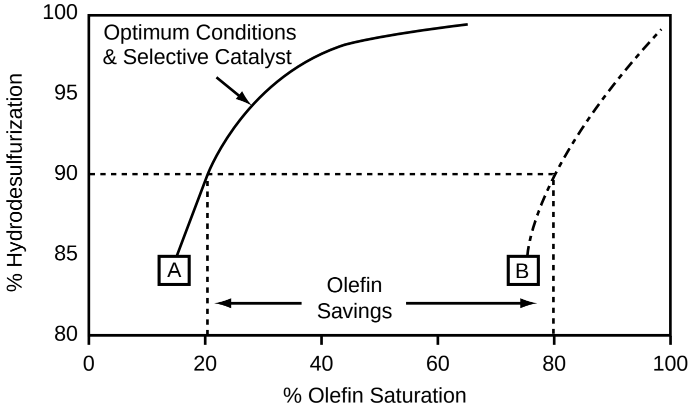


Fig. 5. Relative activities of SCANfining catalyst for selective cat naphtha HDS [62].

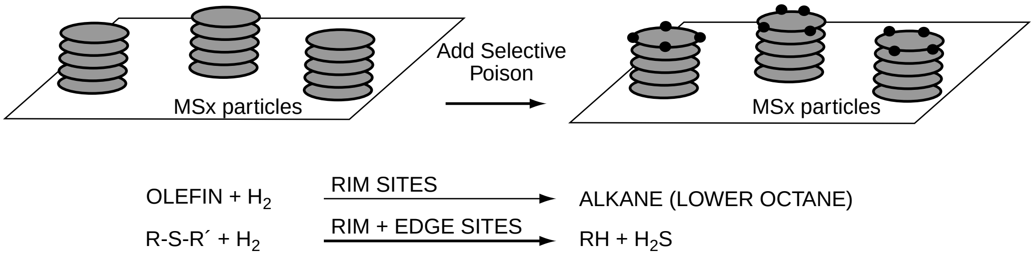


Fig. 6. Catalytic sites on HDS catalysts for naphtha [62].

the process to site-specific conditions. Related to catalyst for SCANfining, Fig. 6 shows a concept to control the catalytically active sites on sulfide catalysts for conversion of sulfur compounds (rim sites and edge sites) and for hydrogenation of olefins (rim sites) [62].

Fig. 7 shows the scheme of Prime G+ desulfurization process, which was developed by IFP (Intitute Francais du Petrole), and largely preserves olefins as its strategy for diminishing octane loss [67–69]. Prime G+ is based on a combination of a selective

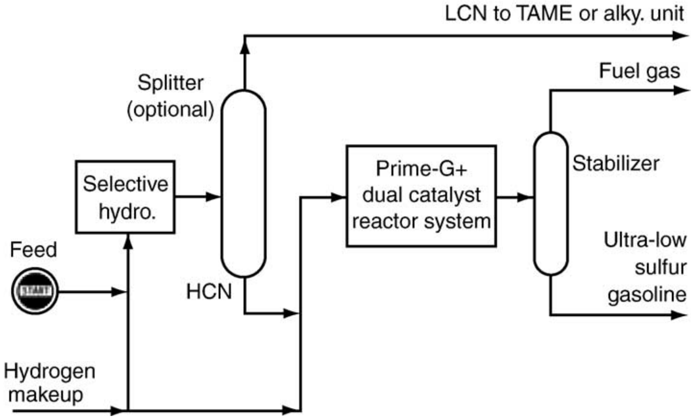


Fig. 7. Prime G+ process developed by IFP [67,68].

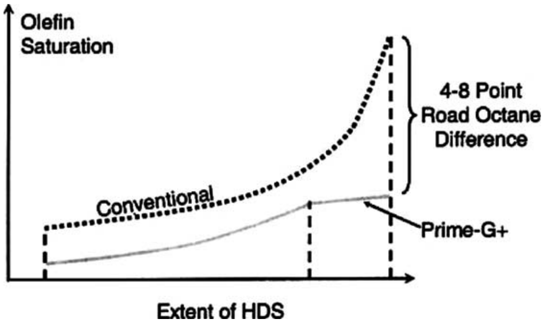


Fig. 8. General performance of Prime G+ process developed by IFP [67,68].

hydrogenation unit which removes diolefins and light mercaptans, a splitter, and a selective HDS of mid- and HCN cut through a dual catalytic system. It is designed for FCC naphtha ultra-deep desulfurization with minimal octane penalty. FCC debutanizer bottoms are fed directly to the first reactor, where under mild conditions diolefins are selectively hydrogenated and mercaptans are converted to heavier sulfur species. The selective hydrogenation reactor effluent is then usually split to produce a LCN and a HCN cut. The LCN stream is mercaptan free with a low-sulfur and diolefin concentration enabling further processing in an etherification or an alkylation unit. The HCN then enters the main Prime G+ section, where it undergoes a deep HDS in a dual catalyst system with very limited olefins saturation and no aromatic losses to produce an ultra-low-sulfur gasoline, as shown in Fig. 8 [67–69]. Catalysts used in this HDS section are a combination of HR-806 and HR-841 catalysts developed by IFP and commercialized by Axens, where HR-806 achieves the bulk of desulfurization, and HR-841 is a polishing catalyst which reduces sulfur and mercaptans with no activity for olefin hydrogenation [70]. Prime G+ is less severe and has been commercially demonstrated for over 7 years in two US refineries, and in an Asian refinery [1]. There are over 10 Prime G+ units, and the economics are estimated to be as follows: capital investment, US$ 600–800/bpsd; combined utilities, US$ 0.32/bbl; H2, US$ 0.28/bbl; catalyst, US$ 0.03/bbl [68].

4.2.2. Deep HDS combined with octane recovery processing

Another hydrotreating approach is to carry out deep HDS of organic sulfur and saturate olefins, then convert low-octane components such as paraffins to high-octane components for octane gain by isomerization and alkylation. Two representative industrial processes in this category are ExxonMobil's OCTGain and UOP-INTEVEP's ISAL.

The OCTGain process was first developed and initially commercialized in 1991 by Mobil (now ExxonMobil). Fig. 9 shows the scheme of OCTGain process [66,71]. The process, now in its third generation, uses a fixed-bed reactor to desulfurize FCC naphtha while maintaining octane. The process first totally removes sulfur and saturates olefins, and then restores the octane to economically needed levels, thus variation in

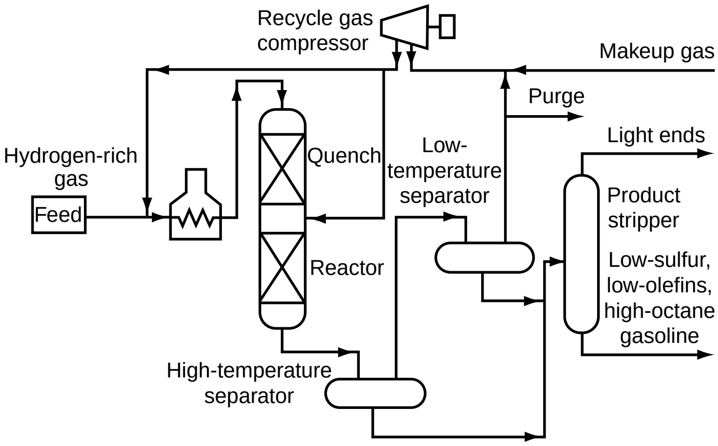


Fig. 9. ExxonMobil's OCTGain process for selective naphtha HDS [66,71].

feed sulfur content does not impact product sulfur and treated products typically contain <5 ppm sulfur and $<1\%$ olefins [72]. The basic flow scheme is similar to that of a conventional naphtha hydrotreater. Feed and recycle hydrogen mix is preheated in feed/effluent exchangers and a fired heater then introduced into a fixed-bed reactor. Over the first catalyst bed, the sulfur in the feed is converted to hydrogen sulfide with near complete olefin saturation. In the second bed, over a different catalyst, octane is recovered by cracking and isomerization reactions. The reactor effluent is cooled and the liquid product separated from the recycle gas using high- and low-temperature separators. The vapor from the separators is combined with makeup gas, compressed and recycled. The liquid from the separators is sent to the product stripper where the light ends are recovered overhead and desulfurized naphtha from the bottoms. The product sulfur level can be as low as 5 ppm. Compared to ExxonMobil's SCANfining, the OCTGain process is run at more severe conditions for it to recover octane, so this process is more appropriate for refiners with higher sulfur levels which requires severe hydrotreating to reach the sulfur target [1]. While octane loss can be eliminated with the proper operating conditions, some yield loss may result [1].

OCTGain has been commercially demonstrated at ExxonMobil's refinery in Joliet, IL [1]. More recently, OCTGain process has been demonstrated for deep desulfurization and octane enhancement of heavy cracked naphtha feeds in its first commercial grassroots application in the Qatar Petroleum OCTGain unit [73]. On the actual refinery feed, an ultra-low-sulfur (<1 ppm), low olefins gasoline is produced, while process flexibility allows the adjustment of octane number between -2 and $+2$ RON of the feed, as refinery economics dictate. Naphtha yield loss and hydrogen consumption were much less than design allowances. The desulfurized gasoline is low in mercaptans and has suitable vapor pressure for direct blending into the refinery's gasoline pool [73].

ISAL process, jointly developed by INTEVEP, SA and UOP, is designed as a low-pressure fixed-bed hydroprocessing technology for desulfurizing gasoline-range feedstocks and selectively reconfigures lower octane components to restore product octane number. Its flow scheme is very similar to that of a conventional hydrotreating process, but a major feature of this process is the catalyst formulation, typically a combination of a HDS catalyst such as Co–Mo–P/Al_2O_3 and octane-enhancing catalyst such as Ga–Cr/H-ZSM-5 catalysts in two beds [49,74]. The naphtha feed is mixed with H_2-rich recycle gas and processed across fixed catalyst beds at moderate temperatures and pressures. Following heat exchange and separation, the reactor effluent is stabilized. The similarity of an ISAL unit to a conventional naphtha hydrotreating unit makes implementation of ISAL simple and straightforward [75]. There are several revamp and several new units based on ISAL process [75].

Researchers from UOP and INTEVEP have discussed the technical aspects of the process and catalyst chemistries leading to these desirable results [76,77]. The ISAL process reduces the naphtha sulfur and nitrogen content, reduces the naphtha olefin content, does not increase the aromatics content, and can maintain or increase the naphtha octane [78]. The ability of the ISAL process to provide both desulfurization and octane flexibility is the result of a development program that was begun by INTEVEP in the early 1990s for possible improvements in fixed-bed isomerization and alkylation technologies. One result of this program was the discovery of a new catalyst system that could increase octane by isomerization of its gasoline-range feedstock [77]. An interesting feature of this system was that an octane boost occurred despite the occurrence of significant olefin saturation [77]. Therefore, INTEVEP and UOP teamed up to develop the ISAL process to enable refiners to hydrotreat highly olefinic feedstocks, such as coker and FCC naphtha, while controlling both the sulfur content and the octane of its product. This flexibility is achieved by the use of a catalyst system that promotes an array of octane-enhancing reactions, including isomerization, conversion, dealkylation, and molecular-weight reduction. The ability of the ISAL process to operate within a wide range of desulfurization and product octane combinations allows the refiner to tailor the unit's operation to the specific processing needs of the refinery. In addition, recent improvements to the ISAL catalyst system and the process configuration allow these tighter gasoline sulfur specifications to be achieved at higher yield and lower capital cost. Its products can meet the most stringent specifications of gasoline sulfur and olefin content. Because the flow scheme and processing conditions of an ISAL unit are similar to a conventional naphtha hydrotreating unit, the process can be implemented as either a new grassroots unit or as a revamp of an existing hydrotreater [77]. The technology is based on typical hydrotreating flow schemes, which imply ease of operation and reliability as a refinery process. The upgraded FCC naphtha from the ISAL process is specifically suited to meet reformulated gasoline specifications in global market [78].

What are the differences between UOP-INTERVEP's ISAL process and ExxonMobil's OCTGain process? The two processes are similar in terms of process design concept and processing schemes, but the catalysts and processing conditions are different. What are the differences between ExxonMobile's SCANfining and OCTGain processes? SCANfining is used for selective HDS (to <30 ppm sulfur) and has a high content of olefins in the product with little reduction in octane number. It was developed by ExxonMobil and Akzo Nobel Catalysts to reduce hydrogen consumption over a low-temperature and a low-pressure fixed-bed reactor. When the new Exomer process (caustic extraction of sulfur) is added to this, the desulfurization capability is extended further to 10 ppm [79]. The Exomer process has been developed by ExxonMobil and Merichem to extract all the mercaptans from the fuel, and provide catalyst stability. The process does not involve the use of a catalytic naphtha splitter, which reduces the capital and operating costs of the motor gasoline desulfurization unit. OCTGain technology is used for deep HDS and the product has little olefins but a high-octane value due to isomerization of paraffins (alkanes) in the process, where the octane gain is at the expense of some yield loss to LPG. The technology can be used to vary product octane on a day-to-day basis, while keeping almost 100% desulfurization.

Isomerization of alkanes in naphtha cuts, as involved in OCTGain and ISAL processes, can be achieved by using catalysts to improve the octane number of gasoline. For example, Jao et al. [80] reported on naphtha isomerization over mordenite-supported Pt catalysts. Their results demonstrated that catalyst performance was determined by Pt dispersion when using pure feed, whereas it was determined by both Pt dispersion and Pt cluster stability for feed containing 500 ppm sulfur. Highest Pt dispersion and, thus, best performance with pure feed was obtained with a catalyst prepared by the ion exchange and pretreated at a low-temperature ramping rate (0.5 °C/min) during calcination and reduction. In addition, this catalyst was pretreated by calcination at 450 °C, followed by reduction at 450 °C. In contrast, the catalyst having the best performance with feed containing 500 ppm sulfur was pretreated by calcination at 450 °C, followed by reduction at 530 °C. The authors suggested that the superior performance may result from a compromise between metal dispersion and metal cluster stability.

As but one example of bimetallic catalysts, Lee and Rhee [81] prepared a series of bifunctional bimetallic M–Pt/H-Beta (M = Cu, Ga, Ni, and Pd) catalysts and examined them for the isomerization of *n*-hexane. The sulfur-containing feed was prepared by addition of thiophene in pure *n*-hexane to have 500 ppmw sulfur. Sulfur in the feed brought about a substantial decrease in the catalyst performance and the sulfur deactivation of bifunctional Pt/H-Beta turned out to be a two-step irreversible process caused by metal poisoning followed by coking. To test their effect on the sulfur tolerance, various second metals (Cu, Ga, Ni, and Pd) were added to monometallic Pt/H-Beta catalysts. Unfortunately, all of these, except for Pd, greatly decreased the sulfur tolerance of the original Pt/H-Beta catalyst. Regardless of the preparation method or the Pd/Pt atomic ratio of the bimetallic Pd–Pt series, all the bimetallic catalysts showed high sulfur tolerance, in comparison to the monometallic Pt/H-Beta and Pd/H-Beta [81]. The metal dispersion and the hydrogenation activity decreased in the Pd–Pt series compared to Pt/H-Beta. However, the amounts of sulfur adsorbed and coke deposited on the sulfur-deactivated Pd–Pt/H-Beta were much lower than those on Pt/H-Beta, Pd/H-Beta, and the other M–Pt/H-Beta catalysts. The authors suggested that the Pd–Pt bimetallic interaction in Pd–Pt/H-Beta increased the amount of electron deficient metal sites, and that Pd–Pt bimetallic interaction inhibits irreversible sulfur adsorption and thereby reduces sulfur-induced coke formation [81]. This is why the Pd–Pt series maintained high activity under sulfur deactivation conditions.

4.2.3. *Catalytic distillation for desulfurization*

The catalytic distillation desulfurization process developed by CDTech is significantly different from conventional hydrotreating [82,83]. The most important portion of the CDTech desulfurization process is a set of two distillation columns loaded with

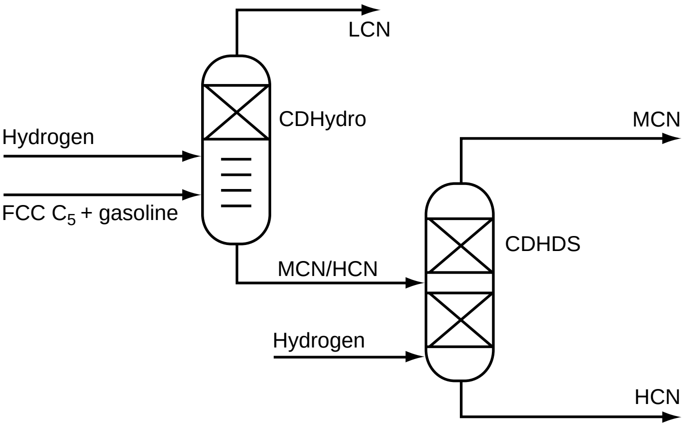


Fig. 10. Flow scheme of CDTech's CDHydro + CDHDS for naphtha desulfurization [82].

desulfurization catalyst in a packed structure. In this process, the LCN, MCN, HCN are treated separately, under optimal conditions for each. The first column, called CDHydro, treats the lighter compounds of FCC gasoline and separates the heavier portion of the FCC gasoline for treatment in the second column. The second column, called CDHDS, removes the sulfur from the heavier compounds of FCC gasoline.

Fig. 10 shows the flow scheme of the process [82,84]. The full-range FCC naphtha is fed to the CDHydro column and the desulfurization begins with fractionation of the light naphtha overhead in CDHydro column. Mercaptan sulfur reacts quantitatively with excess diolefins to product heavier sulfur compounds, and the remaining diolefins are partially saturated to olefins by reaction with hydrogen. Bottoms from the CDHydro column, containing the reacted mercaptans, are fed to the CDHDS column where the MCN and HCN are catalytically desulfurized in two separate zones. HDS conditions are optimized for each fraction to achieve the desired sulfur reduction with minimal olefin saturation. Olefins are concentrated at the top of the column, where conditions are mild, while sulfur is concentrated at the bottom where the conditions result in very high levels of HDS. The temperature and pressure of the CDTech process columns are lower than fixed-bed hydrotreating processes, particularly in the upper section of the distillation column, which is where most of the olefins are located. These operating conditions minimize yield and octane loss.

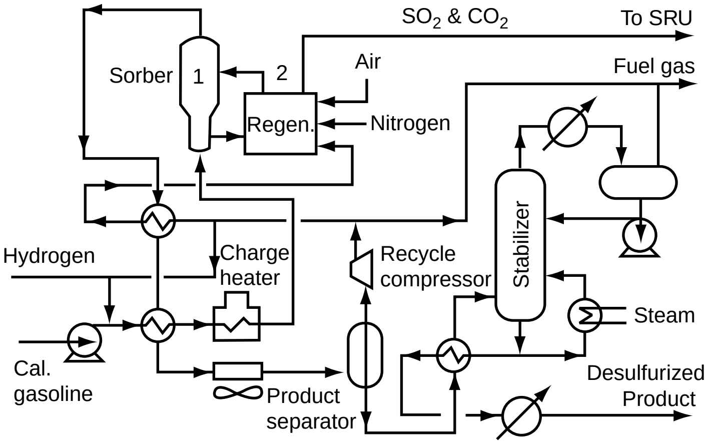
While the CDTech process is very different from conventional hydrotreating, the catalyst used for removing the sulfur compounds is the same [1]. CDHydro combines fractionation and hydrogenation and it is designed to selectively hydrogenate diolefins in the top section of a hydrocarbon distillation column. Conventional hydrotreating requires a distillation column after fixed-bed hydrogenation unit, while CDHydro eliminates the fixed-bed unit by incorporating catalyst in the column. Proprietary devices containing catalysts are installed in the fractionation column's top section, and hydrogen is introduced beneath the catalyst zone. Fractionation carries the light components into the catalyst zone where reaction with H_2 occurs. Fractionation also sends the heavy materials to the bottom. This prevents foulants and heavy catalyst poisons in the feed from contacting the catalyst. In addition, the clean hydrogenated reflux continuously washes the catalyst zone. These factors combine to give a longer catalyst life. In the bottom of catalyst zone, mercaptans react with diolefins to form heavy, thermally stable sulfides. These sulfides have higher boiling points than the C5 fraction and are easily fractionated to the bottom product [83]. This can eliminate a separate mercaptan removal step [82]. There are over 14 commercial CDHydro units in operation for C4, C5, C6 and benzene hydrogenation applications [82].

CDHDS is used in combination with CDHyrdro to selectively desulfurize gasoline with minimum octane loss. Bottoms of CDHydro column, containing the reacted mercaptans, are fed to the CDHDS column where the MCN and HCN are catalytically desulfurized in two separate zones. HDS conditions are optimized for each fraction to achieve the desired sulfur reduction with minimal olefin saturation. Olefins are concentrated at the top of the column, where conditions are mild, while sulfur is concentrated at the bottom, where the conditions results in very high levels of HDS [82].

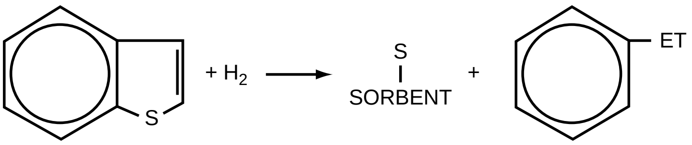
Catalytic distillation essentially eliminates catalyst fouling because the fractionation removes heavy coke precursors from the catalyst zone before coke can form and foul the catalyst bed. The estimated ISBL capital cost for 35,000 bpd CDHydro/CDHDS unit with 92% desulfurization is US$ 25 million, and the direct operating cost including utilities, catalyst, hydrogen, and octane replacement are estimated to be US$ 0.03/gal of full-range FCC naphtha [82]. A recent article discusses the CDHDS technology from CDTech for reliable HDS operation, where the catalyst cycle length for CDTech catalytic distillation technologies can be aligned with the 5-year FCC operating cycles [8].

4.2.4. Reactive adsorption for sulfur capture at elevated temperatures

Reactive adsorption refers to the processes using metal-based sorbent for sulfur capture to form metal sulfide. Phillips Petroleum (now ConocoPhillips) developed a new process called S-Zorb that can be used for making low-sulfur gasoline [85]. Fig. 11 shows the scheme of S-Zorb Gasoline process along with the principle of S-Zorb process [85,86]. The sulfur atom of the sulfur-containing compounds adsorbs onto the sorbent and reacts with the sorbent. Phillips Petroleum uses a proprietary sorbent that attracts sulfur-containing molecules and removes the sulfur atom from the molecule. The sulfur atom is retained on the sorbent while the hydrocarbon portion of the molecule is released back into the process stream. Hydrogen sulfide is not released into the product stream and therefore prevents recombination reactions of hydrogen sulfide and olefins to make mercaptans, which could otherwise increase the effluent sulfur concentration. Based on the principle, it appears that



Flow Scheme of S Zorb Gasoline



Principle of S Zorb process

Fig. 11. ConocoPhillips's S-Zorb sulfur removal process based on solid adsorbent and its continuous regeneration [85,86].

the sorbent is based on reduced metal that reacts with sulfur to become metal sulfide.

The spent sorbent is continuously withdrawn from the reactor and transferred to the regenerator section. In a separate regeneration vessel, the sulfur is burned off of the sorbent and SO_2 is sent to the sulfur plant. The cleansed sorbent is further reduced by hydrogen and the regenerated sorbent is then recycled back to the reactor for removing more sulfur. The rate of sorbent circulation is controlled to help maintain the desired sulfur concentration in the product. Because the sorbent is continuously regenerated, Phillips estimates that the unit will be able to operate 4–5 years between shutdowns [4].

Table 9 shows the performance of S-Zorb process for naphtha under the following general operating conditions: reactor temperature, 650–775 °F (343–413 °C); reactor pressure, 100–300 psig (7–21 atm); space velocity, 4–10 WHSV; H_2 gas purity, >50% [86]. ConocoPhillips's first commercial S-Zorb Gasoline unit began operations successfully in its Borger refinery in Texas, USA, in early 2001, for processing 6000 barrels of gasoline feed per day to produce gasoline with 10 ppmw sulfur [86]. A second S-Zorb Gasoline unit at 25,000 barrels per day is scheduled to be started in late 2003 at the ConocoPhillips refinery in Ferndale, WA [87].

Research Triangle Institute (RTI) is developing another reactive adsorption process called TReND (transport reactor for naphtha desulfurization) which is based on metal oxide sorbent. The feature of TReND process is that supported metal oxide-based regenerable sorbent is used to capture the sulfur in a transport reactor which is similar to FCC reactor [88]. RTI has conducted extensive studies on desulfurization of synthesis gas from coal gasification [89], and recently applied their expertise in H_2S removal using metal oxide to organic sulfur removal from liquid fuels at 800–1000 °F (426–535 °C) with or without the presence of H_2 gas feed in the TReND process [90]. Fig. 12 shows the scheme of the transport reactor for TReND process, and Table 10 shows the results for naphtha desulfurization with RTIs pilot test reactor [91,92]. Mercaptan type sulfur is captured completely without H_2, but thiophenic sulfur capture seems to be

Table 9
Performance of S-Zorb process for FCC naphtha [86]

	Case 1[a]	Case 2[a]
Feed properties		
Unit capacity (bpd)	35000	35000
Sulfur (ppmw)	300	1500
Product properties		
Sulfur (ppmw)	10	10
Volume yield (%)	>99.9	>99.9
RVP change	None	None
(R + M)/2 loss	<0.3	<1.0
Utilities		
Chemical hydrogen consumption (ft^3/bbl)	25	70
Fuel (btu/bbl)	33000	33000
Electricity (kW/bbl)	0.8	1.1
Cooling water (gal/bbl)	115	115
Steam, MP (lb/bbl)	12	12
Nitrogen (ft^3/bbl	4	16
Economics		
Capital cost (ISBL)	US$ 800/bbl	US$ 900/bbl
Operating cost (cent/gal)[b]	0.9	1.2

[a] S-Zorb SRT when processing full-range FCC naphtha (reactor temperature: 650–775 °F (343–413 °C); reactor pressure: 100–300 psig (7–21 atm); space velocity: 4–10 WHSV; H_2 gas purity: >50%).

[b] Includes utilities, 4% per year maintenance and sorbent costs.

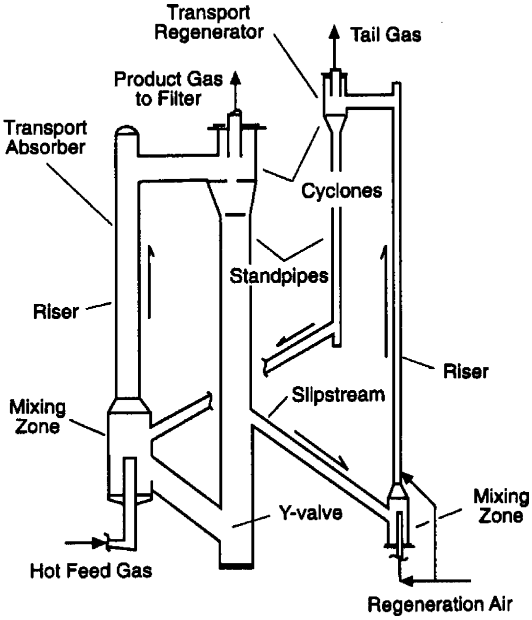


Fig. 12. RTIs transport reactor for naphtha desulfurization (TReND) process [91].

Table 10
PONA and octane analysis for FCC naphtha testing in RTIs PTR [91]

	Feed	Product
PONA analysis (%)		
Paraffins	41.45	40.9
Olefins	19.7	22.1
Monocycloparaffins	12.84	11.1
Dicycloparaffins	0.85	0.3
Alkylbenzenes	22.38	19.6
Indanes/tetralins	2.28	2.4
Naphthalenes	0.5	0.5
Octane number		
Research	91.0	90.8
Motor	80.8	81.5

better in the presence of H_2 [90]. The octane number is preserved in general in naphtha desulfurization. RTI has also conducted pilot plant test with an engineering company.

Tawara et al. [93–95] reported their study on using Ni/ZnO catalyst as sorbent for adsorptive HDS of kerosene for fuel-cell applications, where Ni reacts with sulfur under H_2 to form NiS which then pass the sulfur to ZnO to form ZnS and regenerate Ni. The more recent paper describes Ni/ZnO as an autoregenerative nickel catalyst for adsorptive HDS [95]. Based on the work of Tawara et al., Babich and Moulijn [49] discussed the mechanism of reactive adsorption using Ni/ZnO shown in Fig. 13. This may provide some fundamental understanding regarding what may happen under reactive adsorption using metal or metal oxide under H_2 atmosphere, such as the S-Zorb and TReND process.

4.2.5. *Polar adsorption using alumina-based adsorbents*

The IRVAD process by Black and Veatch Pritchard and Alcoa Industrial Chemicals is claimed to be a low-cost process for making low-sulfur gasoline [96–98]. The process uses an alumina-based adsorbent to counter-currently contact liquid hydrocarbon in a multistage adsorber. The adsorbent is regenerated in a continuous cross-flow reactivator using heated reactivation gas. The process operates at lower pressure, does not consume hydrogen or saturate olefins. The adsorption mechanism is based on the polarity of sulfur, and nitrogen compounds in gasoline range. The adsorbent is fluidized and continuously removed and regenerated, using hydrogen, in a second column. The regenerated adsorbent is then recycled back into the reactor vessel at the rate which it is being removed. In the regeneration column, the adsorbed heteroatom containing petroleum compounds, which is about 4% of the refinery stream being treated, are removed from the adsorbent [1]. However, since it is based on polarity, it is not expected to be very selective towards sulfur compounds in liquid fuels such as gasoline, diesel fuels and jet fuels. Work on the IRVAD process is currently discontinued [49].

4.2.6. *Selective adsorption for removing sulfur*

Pennsylvania State University is exploring a new desulfurization process by selective adsorption for

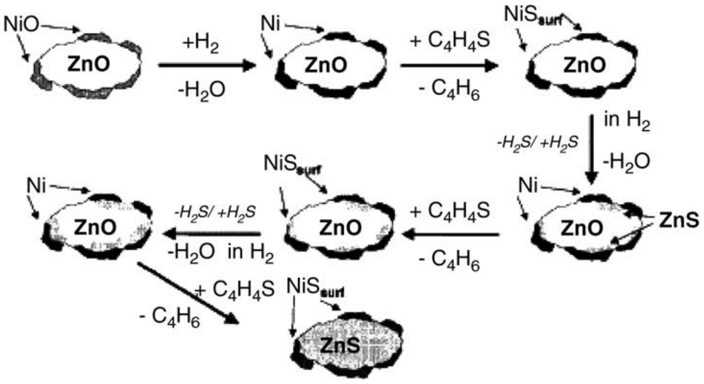


Fig. 13. Mechanism of reactive adsorption desulfurization [49].

removing sulfur (PSU-SARS) at ambient temperature without using hydrogen or any other reactive gas [21]. In general, adsorption of sulfur compounds has been studied and reported in both open literature and patent literature for many years, but not successfully developed for liquid fuels because there are major problems with selectivity towards sulfur compounds in the presence of many other compounds such as aromatics and polar species in refinery streams. In developing the PSU-SARS concept, the key consideration is to design the adsorbent materials to selectively interact with sulfur in the presence of large excess of aromatic compounds, which exist in concentrations of >20% in comparison with less than 1 wt.% sulfur compounds [32,33,99].

The scientific basis behind the experimental approach for PSU-SARS is that there exists site-specific interactions between sulfur and metal species that are known to be possible with some organometallic complexes [32,33]. Penn State is preparing and examining various new adsorbent materials for selective adsorption desulfurization process concept based on sulfur-selective adsorption of liquid hydrocarbon fuels (gasoline, diesel fuel and jet fuel) for producing ultra-clean transportation fuels and for fuel-cell applications. There are several recent reports on PSU-SARS for deep desulfurization of distillate fuels (diesel, gasoline and jet fuels) based on selective adsorption for removal of sulfur compounds at ambient conditions without using H_2 [21,32,33,99–102]. Ambient temperatures for various application environments range from room temperature to about 250 °C.

Fig. 14 illustrates the known coordination geometries of thiophene in organometallic complexes, which indicate likely adsorption configurations of thiophenic compounds on the surface of adsorbents [32]. Both thiophenic compounds and non-sulfur aromatic compounds can interact with metal species by π-electrons. However, in Fig. 14 only two types of interaction of thiophene with metal involve sulfur atom in thiophene, the η^1-S bonding interaction between the sulfur atom and one metal atom, and the S-μ_3 bonding interaction between the sulfur atom and two metal atoms. Several adsorbents based on transition metal complexes supported on porous materials, zeolites, supported transition metals, mixed metal oxides, activated carbon, etc. have been developed and used for selective adsorption desulfurization of diesel fuel, gasoline and jet fuel at ambient temperatures. The results from testing various liquid fuels show that selective adsorption of sulfur compounds can be achieved using PSU-SARS process in laboratory scale [17,21,32,33,99–102].

Fig. 15 shows the breakthrough curves for the adsorptive desulfurization of commercial real gasoline containing about 210 ppmw of sulfur over Ni-based supported adsorbents, PSU A-2 at room temperature (30 °C) and PSU A-5 at different temperatures [101]. Fig. 16 shows the sulfur-selective GC-pulsed flame

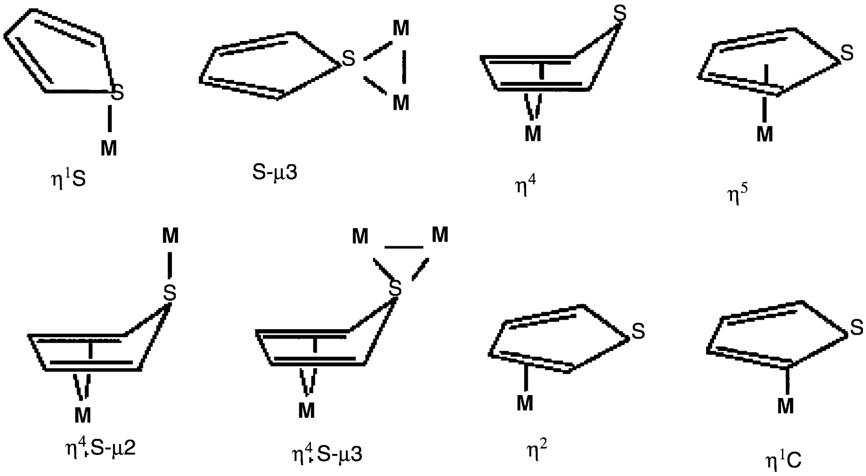


Fig. 14. Known coordination geometries of thiophene in organometallic complexes, indicating likely adsorption configurations of thiophenic compounds on the surface of adsorbents [32].

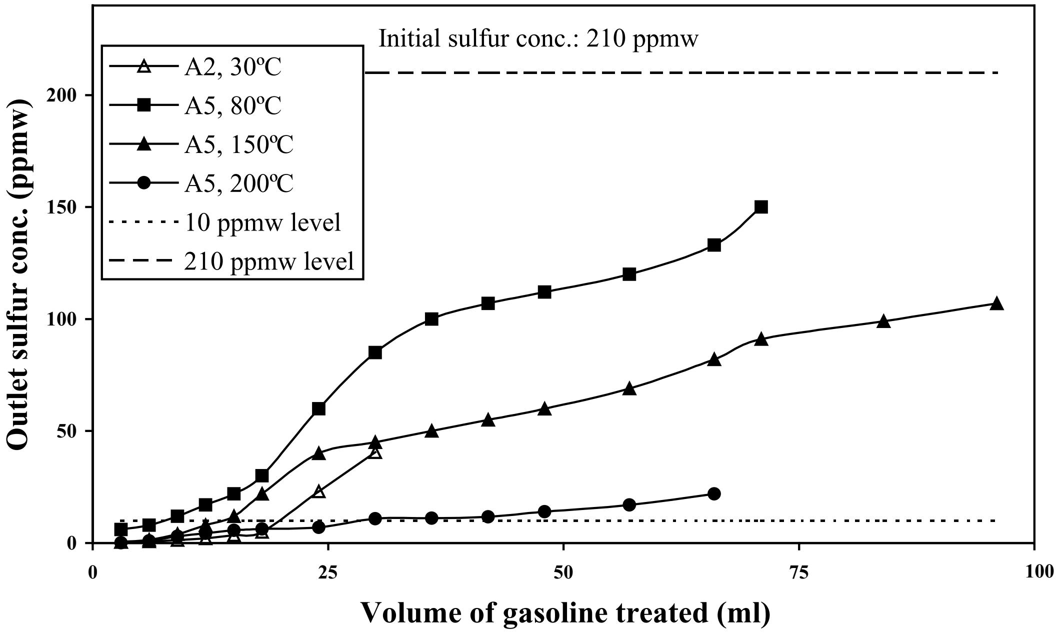


Fig. 15. Breakthrough curves for the adsorptive desulfurization of real gasoline over PSU A-5 adsorbent at different temperatures. The breakthrough curve of PSU A-2 adsorbent at 30 °C also is included for comparison [101].

photometric detector chromatogram of real gasoline used in this study and the gasoline samples collected after the adsorption treatment. The results indicate that the A-2 adsorbent removes sulfur compounds from gasoline to below 1 ppmw even at room temperature. The A-5 adsorbent also is capable of desulfurizing real gasoline to below 1 ppmw, but relatively more effective at elevated temperatures, above 150 °C. The outlet sulfur content remains below 20 ppmw even after 60 ml of gasoline treatment at 200 °C. The adsorbent continuously removes sulfur compounds without reaching the saturation value even after 100 ml treatment in the temperature range studied.

The PSU-SARS can be applied for on-site or on-board organic sulfur removal for producing ultra-low-sulfur liquid fuels before the reformer for either high-temperature or low-temperature fuel cells, which require sulfur contents to be <1 ppmw [103]. The on-site or on-board removal of sulfur from liquid fuels for fuel-cell applications represents another major challenge for fuel desulfurization at places where neither high-pressure reactor nor high-pressure H_2 is available, yet near-zero sulfur fuel (<1 ppm) must be made available either on-site or on-board [103]. The PSU-SARS process uses neither H_2 gas nor high temperatures (>300 °C) and is therefore different from the well-known ConocoPhillips S-Zorb process that uses low-pressure H_2 at elevated temperatures [86] and different from the RTI TReND desulfurization process that uses solid adsorbent at high temperatures under H_2 atmosphere [90,91].

Separation of sulfur from hydrocarbons has been reported and discussed in several publications [104–107]. Naphtha desulfurization by adsorption has been studied using activated carbon and zeolite 13X [105,106]. Zeolite 13X showed some capacity for sulfur at low concentration ranges. At higher ranges the capacity of activated carbon was three times greater than that of 13X zeolite at 20 °C. Zeolite 5A was unfavorable for sulfur sorption from naphtha. The activated carbon and zeolite 13X were compared for naphtha desulfurization at 80 °C [106]. The activated carbon was found to be superior to zeolite 13X at such high temperatures. A new formula based on the Langmuir model has been found to fit the experimental data satisfactorily. Comparison of the findings of the high-temperature (80 °C) adsorption study [106] with those of a previous one conducted at ambient

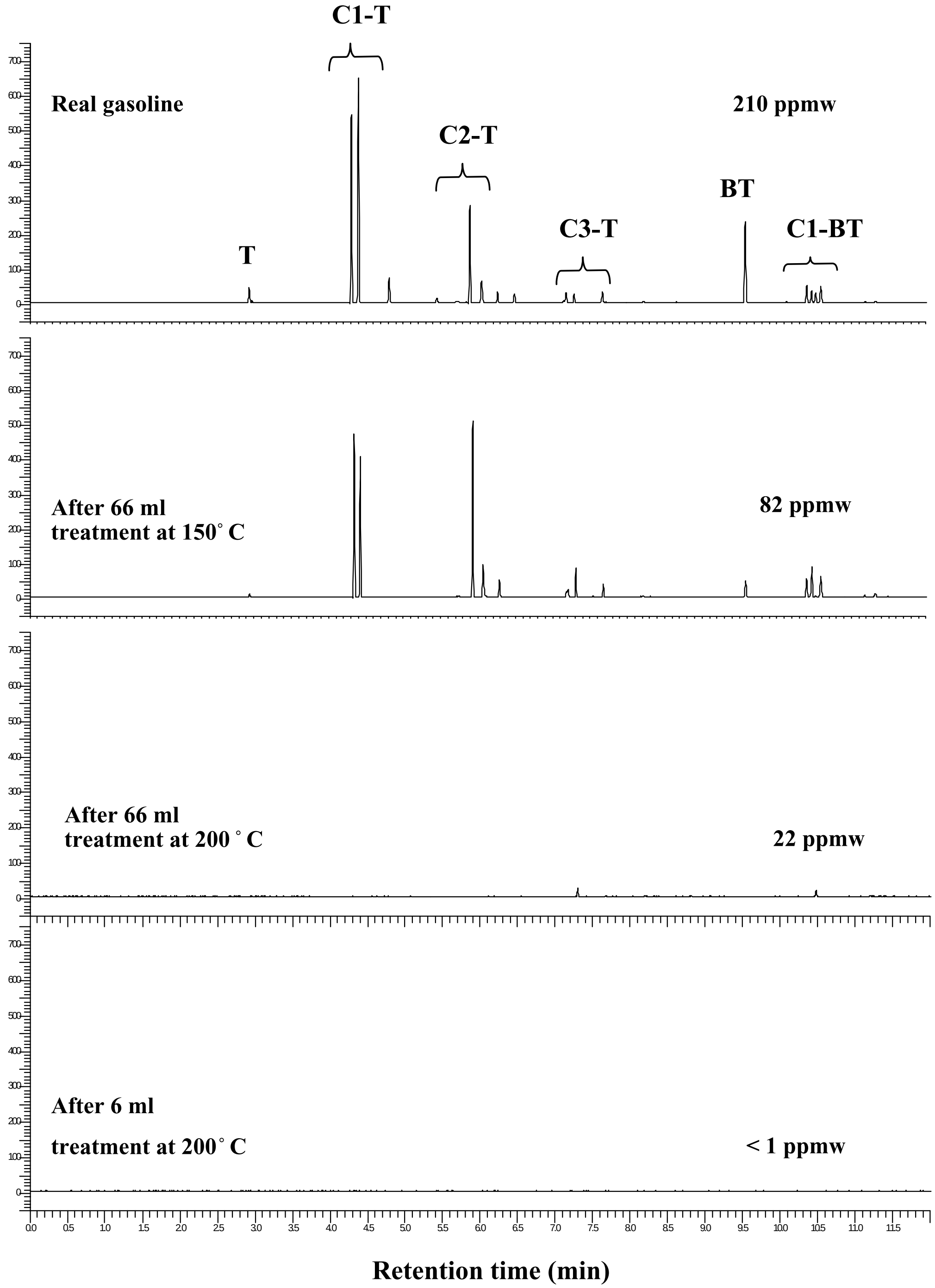


Fig. 16. Sulfur-selective GC-pulsed flame photometric detector chromatograms of real gasoline and treated gasoline over PSU A-5 adsorbent [101].

temperatures [105] indicates that such treatment generally gives better results at low temperature where almost complete recovery of the sulfur compounds can be performed by using zeolite 13X.

More recently, Yang et al. [108–111] have reported on adsorption separation of thiophenic sulfur compounds from aromatic compounds based on π-complexation using Cu- and Ag-exchanged Y zeolites. The Cu(I)-Y zeolite was prepared by reducing the Cu(II)-Y zeolite at 450 °C in He atmosphere. Better adsorption performance was noticed over Cu(I)-Y zeolites. However, it is not clear how the π-complexation can differentiate between sulfur-containing aromatic compounds and non-sulfur-containing aromatic compounds in real liquid fuels although they have shown by theoretical calculations that the π-complexation strength is higher for thiophene compared to benzene [109]. The authors have noted that the adsorption performance of the Cu(I)-Y zeolite is decreased when aromatics are present in the fuel [110,111] probably due to the competitive adsorption of sulfur compounds and aromatics by π-complexation.

4.2.7. Selective extraction of sulfur for subsequent HDS

GTC is developing a GT-Desulf process for desulfurizing the FCC stream with no octane loss and decreased hydrogen consumption by using a proprietary extractive distillation system, and the process also recovers aromatic compounds [112]. FCC naphtha with end point of 210 °C is fed to the GT-Desulf unit, which extracts sulfur and aromatics from the hydrocarbon stream. The sulfur and aromatic components are processed in a conventional hydrotreater to convert the sulfur to H_2S. Because the portion of gasoline being hydrotreated is reduced in volume and free of olefins, hydrogen consumption and operating costs are reduced. The unique part of the extractive distillation unit is that it segregates the sulfur and aromatic components prior to the hydrotreater [113]. Conventional HDS schemes process the majority of the gasoline through hydrotreating and caustic washing units to eliminate sulfur, which results in olefin saturation, octane downgrade and yield loss [112]. The production cost is estimated to be US$ 0.50/bbl of feed for desulfurization and dearomatization [112]. UOP is developing a process for FCC naphtha (MCN or heart-cut) desulfurization by solvent extraction [113], in addition to the well-known extractive Merox for removing mercaptan sulfur from LCN. The extracted thiophene sulfur from MCN is sent to ISAL process unit for HDS and octane control. It appears that the solvents used for BTX extraction are actually more effective for removing thiophenic sulfur compounds and the preferred solvent would be sulfolane [114].

4.2.8. Other approaches to gasoline sulfur reduction

There are several other emerging processes for post-FCC desulfurization, such as BPs OATS (olefin alkylation of thiophenic sulfur) process which shifts boiling points of sulfur compounds [115], Grace's S-Brane^{TM} Process for separation of sulfur compounds using a polymer membrane [116–118], and Exomer process jointly developed by Merichem and ExxonMobil for caustic extraction of sulfur compounds using fiber film [119], and exploratory studies for extraction of sulfur compounds using ionic liquid such as 1-butyl-3-methylimidazolium hexafluorophosphate [120,121], as also outlined in Table 7.

4.3. Pretreat the FCC feed to remove sulfur before FCC

Hydrotreating (process that consumes <300 scf H_2/bbl) can effectively remove sulfur, nitrogen and metals in heavy feeds without excessive hydrogenation of aromatic ring structures. Removing these contaminants can also preserve the activity of FCC catalysts and, thus lengthen their service. Therefore, there are advantages for doing deep HDS of FCC feed before catalytic cracking in FCC reactor, which can also reduce sulfur in FCC naphtha and in LCO. Upgrading pretreatment and/or deeper hydrotreatment for desulfurization of FCC feed are optional sulfur reduction solutions [16]. Results from UOP have shown that deep HDS of FCC feed (89.1 wt.% straight-run VGO containing 2.5 wt.% sulfur + 10.9 wt.% delayed coker CGO containing 3.4 wt.% sulfur) has very positive impacts on reduction of sulfur in FCC naphtha and in LCO oil [50].

According to Akzo Nobel, if a FCC feed pretreater exists in a refinery, by far the least expensive way to reduce gasoline sulfur is to increase the HDS level in the FCC feed hydrotreater [54]. The recent catalysts recommended by Akzo Nobel for FCC feed hydrotreating include Ni–Co–Mo trimetallic (KF 901 and KF 902) systems that maintain the HDN and aromatics saturation activity of a conventional Ni–Mo catalyst while providing the HDS activity of Co–Mo catalysts. Therefore, a change from a conventional Ni–Mo to KF 902 Ni–Co–Mo can result in a significantly lower sulfur at essentially the same operating conditions and cycle life [54]. Ni–Co–Mo catalysts typically cost more than Ni–Mo catalysts because cobalt is more expensive than nickel [54].

On the other hand, not all refineries have the capability to carry out FCC feed deep hydrotreating. As shown in Table 5, FCC feed hydrotreating requires more severe conditions and thus the reactor needs to operate at higher temperature and higher pressure [43]. In the US, 47 refineries (with 150,000+ bpd processing capacity) operate an FCC unit; only 15 refineries actually hydrotreat the FCC feed [16]. At least a part of the reason is that hydrotreating gas oil must be severe enough to get the sulfur that is embedded in the hetero-polycyclic hydrocarbon rings.

4.4. In situ desulfurization during FCC

As a way to enhance organic sulfur conversion, research and developments are in progress for promoting in situ desulfurization during FCC operation by adding catalyst additives. Cracking and hydrogen transfer are two important elementary reaction steps for thiophene and alkyl-thiophene species desulfurization via cracking. Higher temperature favors the former, while lower does the latter. The contradiction leads to about 400 °C to be the optimal temperature for thiophene and alkyl-thiophene species to desulfurize via cracking [122]. Thiophene can crack over acidic USY zeolite, which is used as FCC catalyst, to propylene, butane, butene and H_2S. Cracking desulfurization is the dominant reaction although 2-methyl thiophene, 3-methyl thiophene, dimethyl thiophene, trimethyl thiophene and benzothiophene are also formed. Compared to thiophene, alkyl-thiophene species in gasoline are easier to desulfurize via cracking over the specially prepared sulfur removal catalyst with the USY zeolite as the cracking component, and the conversion increases with the alkyl carbon number of alkyl-thiophene [122].

Akzo Nobel's Resolve and Grace Davison's Saturn (GSR 6.1) are representative FCC catalyst additives that have been commercialized recently to convert more organic sulfur into H_2S during FCC operation, which can reduce organic sulfur in liquid products including naphtha and LCO. The FCC catalyst additive "Resolve" developed by Akzo Nobel is the "no capital" alternative for lowering gasoline sulfur. Since the molecules of mid- and heavy-range sulfur compounds are too large to enter the zeolite cage, the potential of FCC catalysts to reduce gasoline sulfur has become clear only recently with the development of Akzo Nobel's unique active selective matrix technology [123]. The new FCC catalyst additives developed at Akzo Nobel Catalysts (Resolve 700, 750, 800, 850) and their effects on gasoline sulfur reduction have been discussed in a recent article [124].

Grace Davison has developed a series of FCC catalysts and additives, as summarized in some recent publications [125–127]. In one case, the use of Saturn (GSR 6.1) additive can result in 32% sulfur reduction gasoline [125]. A more recent article discussed the state-of-the-art of technologies developed at Grace Davison in FCC catalyst technologies for clean fuels including new FCC catalyst additives (SuRCA^{TM}, SATURN^{TM}, D-PriSM^{TM} and RFG^{TM}) for desulfurization during FCC along with the S-Brane^{TM} membrane process for removal of sulfur-containing molecules from gasoline [127].

5. Deep desulfurization for highway and non-road diesel fuels

5.1. Sulfur issues of highway and non-road diesel fuels

Table 11 shows the distribution of distillate fuels consumed in the US including highway diesel fuels and non-road fuels such as locomotive fuels and marine diesel fuels [128]. The data in Table 11 represents the estimated US consumptions of distillate fuels and diesel fuels in non-road applications including farms, construction machines, industrial, commercial, military, electric utilities, railroad (locomotive), vessel bunkering (marine), and residential uses, together with on-highway diesel fuels consumed in the US in calendar year 2000. In 2000, of the 39,248 million gal (1 barrel = 42 US gal) supplied as highway diesel fuel, 33,130 million gal were actually consumed on-highway, with the rest as spillover for other applications such as locomotive and marine diesel fuels. Both highway diesel and non-road

Table 11
US consumption of non-road distillate fuels and highway diesel fuels in 2000 (million US gallons; 1 barrel = 42 US gal) [128]

End use	Fuel grade	Distillate (Mgal)	Diesel (%)	Diesel (Mgal)	Non-road (%)	Non-road (Mgal)
Farm	Diesel	3080	100	3080	100	3080
	Distillate	89	0	0	0	0
Construction	Distillate	1900	95	1805	100	1805
Other/(logging)	Distillate	431	95	409	100	409
Industrial	No. 2 fuel oil	357	0	0	0	0
	No. 4 distillate	39	0	0	0	0
	No. 1 distillate	54	40	22	100	22
	No. 2 low-S (<500 ppm) diesel	810	100	810	100	810
	No. 2 high-S (>500 ppm) diesel	889	100	889	100	889
Commercial	No. 2 fuel oil	1576	0	0	0	0
	No. 4 distillate	198	0	0	0	0
	No. 1 distillate	64	40	25	50	13
	No. 2 low-S (<500 ppm) diesel	1061	100	1061	0	0
	No. 2 high-S (>500 ppm) diesel	475	100	475	100	475
Oil company	Distillate	685	50	342	100	342
Military	Diesel	180	100	180	85	153
	Distillate	54	0	0	0	0
Electric utility	Distillate	793	100	793	0	0
Railroad (locomotive)	Distillate	3071	95	2917	1.0	29
Vessel bunkering (marine)	Distillate	2081	90	1873	0	0
On-highway (road diesel)	Diesel (<500 ppm)	33130	100	33130	0.7	229
Residential	No. 2 fuel oil	6086	0	0	0	0
	No. 1 distillate	118	0	0	0	0
Total		57217		47800		8254

distillate fuels are important, accounting for 58 and 42% of distillate fuels, respectively.

Table 12 shows the amounts and types of diesel fuels consumed in the whole US and in California State in 2000 in million gallons [128]. Although CA has essentially eliminated high-sulfur diesel fuels for all non-road applications in addition to highway diesel fuels, US as a whole still consumes a significant amount of high-sulfur diesel fuels in non-road applications, as can be seen from Table 12. Non-road diesel fuel currently has high sulfur levels of about 3400 parts per million (ppm) on average [6]. According to the new EPA proposal, fuel sulfur levels in non-road diesel fuel would be limited to a maximum of 500 ppm starting in 2007, the same as for current highway diesel fuel, and further reduced to 15 ppm limit in 2010 [6].

Table 13 shows the volume fraction of US highway diesel pool, and Table 14 shows the corresponding sulfur levels of US highway diesel blend stocks [4]. Among the diesel blend stocks, the LCO from fluid catalytic cracking (FCC) contains highest amount of sulfur and aromatics, and the LCO also tends to have the highest contents of refractory sulfur compounds, especially 4-methyldibenzothiophene and dibenzothiophene [4].

The key to ultra-deep desulfurization is the removal of refractory sulfur compounds, particularly 4,6-DMDBT, from diesel fuels. In addition to straight-run gas oil, the LCO from FCC of heavy oils is a major blend stock for diesel fuels in the US. LCO has higher sulfur contents, in which the content of 4,6-DMDBT is higher than other middle distillates in diesel pool. LCO also has higher aro-

Table 12
Summary of types of diesel fuels consumed in US in 2000 (million gallons) [128]

Category	Fuel type	US National and California State		
		CA	US	US–CA
Revised highway	Total	2614	32902	30288
	High S	n/a	n/a	n/a
Land-based non-road	Total	539	8255	7716
	Low S	539	2871	2332
	High S	0	5384	5384
Locomotive	Total	178	2889	2711
	Low S	178	1011	833
	High S	0	1878	1878
Marine	Total	91	1872	1781
	Low S	91	520	429
	High S	0	1352	1352
Subtotal (NR, LOC, marine)	Total	808	13016	12208
	Low S	808	4402	3594
	High S	0	8614	8614
Other non-highway	Total	131	11065	10934
	Low S	131	1868	1737
	High S	0	9197	9197
Total	Total	3553	56983	53430
	Low S	3553	39171	35618
	High S	0	17812	17812

Table 13
Volume fraction of US highway diesel pool from each feedstock component [4]

Diesel blend stock	Percentage of US highway diesel fuel pool per blend stock boiling fraction				
	Naphtha	Light distillate	Heavy distillate	Light gas oil	All boiling fractions combined
Straight run	0.1	6.4	4.9	1.0	12.4
Hydrotreated straight run	0.3	8.1	41.2	2.3	51.9
Cracked stock	–	0.1	0.8	2.2	3.1
Hydrotreated cracked stock	–	2.1	15.6	1.7	19.4
Coker gas oil	–	–	1.0	–	1.0
Hydrotreated coker gas oil	0.1	2.1	3.7	2.3	8.2
Hydrocrackate	–	1.3	2.7	–	4.0

Table 14
Sulfur levels of US highway diesel blend stocks (CA excluded) [4]

Diesel blend stock	Sulfur content (ppm) by boiling fraction				
	Naphtha	Light distillate	Heavy distillate	Light gas oil	All boiling fractions combined
Straight run	827	1770	2269	4980	2218
Hydrotreated straight run	362	119	394	548	358
Cracked stock	–	2219	2892	6347[a]	5322
Hydrotreated cracked stock	18	37	939	1306[a]	874
Coker gas oil	540	1800	3419	–	3419 (?)
Hydrotreated coker gas oil	8	25	310	400	258
Hydrocrackate	–	1.3	2.7	–	4.0
	–	12	120	–	85

[a] Indicate properties that were not reported in the refiner survey. These values were calculated by EPA using the reported sulfur contents of like boiling fractions in other diesel blend stocks by assuming the same relative sulfur levels between boiling fractions.

matics contents, which makes the dearomatization necessary for producing low-aromatic diesel fuel. The general chemistry of diesel fuel processing and HDS have been discussed in several recent reviews and books [18–21,28,37]. Described below are some of the processing approaches for ultra-deep desulfurization to produce ultra-low-sulfur (ultra-clean) diesel fuels.

5.2. Design approaches to deep desulfurization of diesel

Approaches to ultra-deep desulfurization include: (1) improving catalytic activity by new catalyst formulation for HDS of 4,6-DMDBT; (2) tailoring reaction and process conditions; (3) designing new reactor configurations; and (4) developing new processes. Design approaches for ultra-deep HDS focus on how to remove 4,6-DMDBT more effectively. One or more approaches may be employed by a refinery to meet the challenges of producing ultra-clean fuels at affordable cost.

Fig. 17 shows the relative volume of catalyst bed required for achieving various levels of diesel sulfur using conventional HDS of gas oil over a commercial hydrotreating catalyst [21]. The modeling is based on HDS using a commercial catalyst reported in 1994 [30,129,130], so it is not a state-of-the-art catalyst. However, it clearly illustrates the key issue. The problem of deep HDS of diesel fuel is caused by the lower reactivity of 4,6-disubstituted dibenzothiophene, as represented by 4,6-DMDBT which has much lower reactivity than any other sulfur compounds [30,129,130] in diesel blend stocks. The methyl groups at 4- and 6-positions create steric hindrance for the interaction between sulfur and active sites on the catalysts. The problem is exacerbated by the inhibiting effects of polyaromatics and nitrogen compounds in some diesel blend stocks for diesel as well as H_2S that exist in reaction system on deep HDS. Based on experimental results, polyaromatics compete with sulfur compounds on the surface of hydrotreating catalyst, perhaps more for the flat chemisorption thereby influencing the hydrogenation and subsequent HDS,

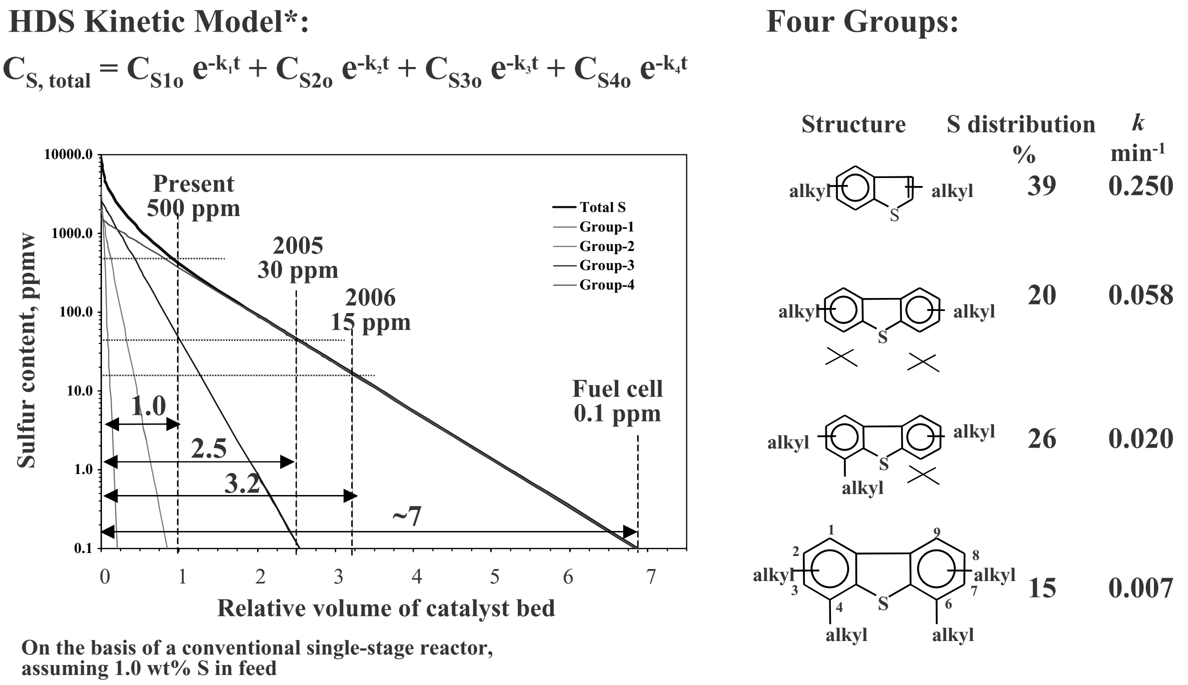


Fig. 17. Relative volume of catalyst bed required for achieving various levels of diesel sulfur using conventional HDS of gas oil over a commercial hydrotreating catalyst [21].

whereas H_2S compete with sulfur compounds, affecting more of the direct C–S hydrogenolysis route.

Table 15 outlines processing approaches for ultra-deep desulfurization to produce ultra-low-sulfur diesel [17,21], where the processes for reducing sulfur content in diesel feedstock can be grouped according to the treatment around FCC, including: (1) post-treating product to remove sulfur from FCC LCO as well as other gas oil streams; (2) pretreating the FCC feed to remove sulfur; (3) increasing sulfur conversion in situ to hydrogen sulfide during the FCC operation, as in the case of naphtha desulfurization. The general approach #2 for pretreating before FCC and #3 for in situ desulfurization during FCC would be the same as that discussed above for naphtha. General processing methods and developers are listed below for desulfurization of gas oil streams (including LCO from FCC, CGO from delayed coker, and straight-run gas oil, etc.), and most of them have been discussed elsewhere [21,49]. Only some selected approaches based on catalysis or adsorption are further elaborated below.

5.2.1. Improving catalytic activity by new catalyst formulation

Design approaches for improving catalytic activity for ultra-deep HDS focus on how to remove 4,6-DMDBT more effectively, by modifying catalyst formulations to: (1) enhance hydrogenation of aromatic ring in 4,6-DMDBT by increasing hydrogenating ability of the catalyst; (2) incorporate acidic feature in catalyst to induce isomerization of methyl groups away from the 4- and 6-positions; and (3) remove inhibiting substances (such as nitrogen species in the feed, H_2S in gas) and tailoring the reaction conditions for specific catalytic functions. The catalytic materials formulations may be improved for better activity and/or selectivity by using different supports (MCM-41, carbon, HY, TiO_2, TiO_2–Al_2O_3, etc.) for preparing supported CoMo, NiMo and NiW catalysts; by increasing loading level of active metal (Mo, W, etc.); by modifying preparation procedure (using different precursor, using additives, or different steps or sequence of metal loading); by using additives or additional promoters (P, B, F, etc.); by adding one more base metal (e.g., Ni–CoMo or Co–NiMo, Nb, etc.); and by incorporating a noble metal (Pt, Pd, Ru, etc.).

New and improved catalysts and different processing schemes are among the subjects of active research on deep HDS [18–20,131]. For example, some recent studies examined carbon-supported CoMo catalysts for deep HDS [132–135]. Binary oxide supports such as TiO_2–Al_2O_3 have been examined for making improved HDS catalysts [136–138].

In 1992, novel mesoporous molecular sieve MCM-41 was invented by Mobil researchers [139,140]. The novel mesoporous molecular sieve of MCM-41 type has also been examined as support for Co–Mo/MCM-41 catalyst for HDS. Al-MCM-41 has been synthesized with improved aluminum incorporation into framework [141–144] and applied to prepare Co–Mo/MCM-41 for deep HDS of diesel fuels [20,145–147] and for HDS of petroleum resid [148].

The design approach makes use of high surface area of MCM-41 for higher activity per unit weight, uniform mesopore to facilitate diffusion of polycyclic sulfur compounds, and mild acidity of Al-containing MCM-41 to facilitate metal dispersion and possible isomerization [145]. Reddy and Song synthesized MCM-41 type aluminosilicate molecular sieves using different Al sources, and established a proper procedure for making acidic MCM-41 [141–144]. Several recent studies have explored the design of new catalysts for HDS of refractory DBT-type sulfur compounds, based on synthesis and application of mesoporous aluminosilicate molecular sieves of MCM-41 type [146,149–151]. Compared to Co–Mo/Al_2O_3, higher activity for HDS has been observed for Co–Mo/MCM-41 with a higher metal loading. When MCM-41 with proper SiO_2/Al_2O_3 ratio was used to prepare Co–Mo/MCM-41 at suitable metal loading, the catalyst is much more active for HDS of dibenzothiopene, 4-methyl- and 4,6-dimethyl dibenzothiopene than a commercial Co–Mo/Al_2O_3 catalyst [146,149–152].

Fig. 18 shows the FT-IR spectra of chemisorbed NO on sulfided Co–Mo/MCM-41 and in comparison the sulfided Co–Mo/Al_2O_3 catalyst [20,153]. Examination of IR profiles in Fig. 18 revealed that there is a higher degree of Co edge site exposure on sulfided Co–Mo/MCM-41 as compared to that on sulfided Co–Mo/Al_2O_3 catalyst [20], since Co site has a distinct NO chemisorption peak [153]. The reason for higher degree of Co site exposure in Co–Mo on MCM-41 relative to Co–Mo on Al_2O_3 (based on

Table 15
Approaches to deep desulfurization for cleaner diesel fuels

Category	Description and representative process	Remarks
(I) Post-FCC and non-FCC distillate S removal	Apply conventional HDS of middle distillates with higher process severity (many companies can apply hydrotreating with longer residence time or at higher temperature)	HDS at higher severity
	Ultra-deep HDS of middle distillate (MAKFining premium distillates technology (PDT) by Akzo Noble, ExxonMobil, and Kellog Brown)	HDS with more active catalysts
	Ultra-deep HDS (SynHDS) and hydrodearomatization (SynSat) and cetane improvement by ring-opening (SynShift) of middle distillate (SynTechnology including new reactor design by SynAlliance including ABB Lummus, Criterion Catalyst, and Shell Global)	HDS with new reactor design and better catalysts
	Two-stage hydrotreating for ultra-low-sulfur diesel fuel using industrially proven high-activity TK catalysts (Haldor-Topsoe)	HDS in staged operation
	Ultra-deep HDS, hydrodenitrogenation and hydrogenation of distillate fuels (Unionfining by UOP; Prime-D by IFP)	HDS, HDN and HDAr
	Hydrodearomatization (HDAr) of middle distillate in the second stage (MAKFining Premium Distillates Technology (PDT) by Akzo Noble, ExxonMobil, and Kellog Brown)	HDAr after HDS
	Sulfur adsorption and capture by solid metal-based adsorbent at elevated temperatures under low H_2 pressure (Phillips Petroleum S-Zorb Diesel)	Non-HDS, stoichiometric H_2 consumption
	Sulfur adsorption and capture by solid metal oxide sorbent at high temperatures (RTI TReND)	Non-HDS, with H_2 atmosphere
	Selective adsorption for removing sulfur (SARS) as organic compounds by solid adsorbent at ambient temperature without using H_2 (Pennsylvania State University, PSU-SARS)	Adsorption, no H_2; can reach <1 ppm S for fuel cells
	Integrated adsorption and hydrotreating of concentrated sulfur from adsorption (Pennsylvania State University, PSU-SARS-HDSCS)	Adsorption plus HDS
	Oxidative desulfurization (SulphCo DeS; Unipure ASR-2; PetroStar DeS)	Use peroxide as oxidant
	Biochemical desulfurization (Energy BioSystems DeS)	Use bacteria for sulfur oxidation
(II) Pre-FCC sulfur removal	Deep HDS of feed before catalytic cracking in FCC reactor, which greatly reduces sulfur in FCC naphtha and in LCO (Akzo Nobel, IFP, UOP, etc.)	HDS at higher H_2 pressure and longer residence time
	Physico-chemical treatment such as adsorption or extraction to remove sulfur (concept suggested here as a possible approach based on PSU-SARS)	Adsorption without H_2
(III) In situ FCC sulfur removal	Convert more organic sulfur into H_2S during FCC operation, which can reduce organic sulfur in liquid products (Akzo Nobel's Resolve; Grace Davison's Saturn (GSR-6.1))	Sulfur conversion to H_2S in FCC
	Capture organic sulfur using metal species to retain sulfur as sulfur oxide, and regenerate it in the regenerator (concept suggested here as a possible approach based on reactive adsorption using sorbent)	Sulfur capture in FCC

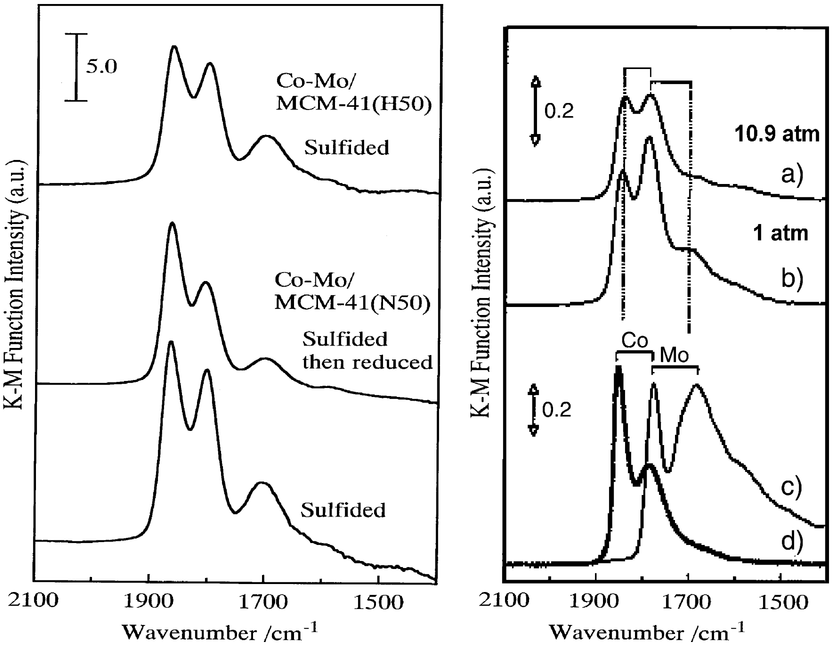


Fig. 18. FT-IR spectra of chemisorbed NO on in situ sulfided Co–Mo/MCM-41 (left, top: sulfided (H50), bottom: sulfided (N50), middle: sulfided and then reduced (N50)) in comparison with the Co–Mo/Al_2O_3 catalyst sulfided at low (a) and high pressure (b) and specific Mo species (c) and Co species (d) [20,153].

FT-IR spectra for NO on Co–Mo/MCM-41 in Fig. 16) remains to be clarified. It is possible that relatively more hydrophobic support could lead to higher layer of stacking and more Co site on the edge when compared to a more hydrophilic surface such as Al_2O_3, but it is difficult to quantify such an effect due to support surface hydrophobicity. In this context, the surface hydrophobicity consideration may partially rationalize why carbon-supported MoS_2 catalyst can be more active than alumina-supported MoS_2 catalyst for desulfurization of dibenzothiophene-type sulfur compounds. Recently, the use of silicalite MCM-41 without aluminum has also been reported for DBT HDS [154].

5.2.2. New commercial HDS catalysts developed for ultra-low-sulfur diesel

For practical applications, Ni–Mo catalysts generally have higher hydrogenation ability for saturating aromatic ring that is connected to thiophenic sulfur, while Co–Mo catalysts generally have higher selectivity towards C–S bond cleavage without hydrogenation of neighboring aromatic rings. For HDS under higher H_2 pressure, Ni–Mo catalysts tend to be more active than Co–Mo catalysts, and this advantage becomes more apparent with ultra-deep desulfurization of diesel fuels. A combination of Ni and Co together with Mo (such as Ni–Co–Mo) is also a practical way to take advantage of both Ni–Mo and Co–Mo catalysts. The catalyst development has been one of the focuses of industrial research and development for deep HDS [155]. For example, new and improved catalysts have been developed and marketed by Akzo Nobel, Criterion, Haldor-Topsoe, IFP, United Catalyst/Sud-Chemie, Advanced Refining, ExxonMobil, Nippon Ketjen in Japan, and RIPP in China.

Akzo Nobel has developed and commercialized various catalysts that can be used for HDS of diesel feed: KF 752, KF 756 and KF 757, and KF 848 [156]. KF 752 can be considered to be typical of an Akzo Nobel catalyst of the 1992–1993 timeframe. KF 756 is a Co–Mo catalyst with high HDS activity; it was jointly developed by Akzo Nobel and Exxon Research and Engineering by applying a new alumina-based carrier technology and a special promoter impregnation technique to allow high and uniform dispersion of metals such as Co and Mo on support with moderate density [62]. KF 757 is Akzo Nobel's latest Co–Mo with higher HDS activity and optimized pore structure; it was announced in 1998 [156]. Akzo Nobel estimates that under typical conditions (e.g., 500 ppmw sulfur), KF 756 is 25% more active than KF 752, while KF 757 is 50% more active than KF 752 and 30% more active than KF 756 [157]. KF 756 is widely used in Europe (20% of all distillate hydrotreaters operating on 1 January 1998), while KF 757 has been used in at least three hydrotreaters commercially [4]. Under more severe conditions (e.g., <50 ppmw sulfur), KF 757 is 35–75% more active than KF 756.

KF 757 (Co–Mo) and KF 848 (Ni–Mo) were developed by using what Akzo Nobel calls STARS (super type II active reaction sites) technology. Type II refers to a specific kind of catalyst site for hydrogenation, which is more effective for removing sulfur from sterically hindered compounds. KF 848 was announced in 2000 [157]. KF 848 Ni–Mo STARS is 15–50% more active than KF 757 Co–Mo STARS under medium to high pressure. Commercial experience exists for both advanced catalysts at BP refineries. In terms of sulfur removal, Akzo Nobel projects that a desulfurization unit which produces 500 ppmw sulfur with KF 752, would produce 405, 270 and 160 ppm sulfur with KF 756, KF 757, and KF 858, respectively [4].

As evidenced by the STARS technology, the advances in basic understanding of fundamental reaction pathways of HDS reactions over transition metal sulfides has also resulted in major advances in commercial catalyst developments. Akzo Nobel recently reported on their commercial experience of their STARS catalyst for diesel fuel feedstock HDS at two BP refineries (Grangemouth and Coryton) in UK. The original unit at Grangemouth refinery was designed to produce 35,000 barrels per day of diesel fuel at 500 ppmw treating mostly straight run material, but some LCO was treated as well. Akzo Nobel's newest and best catalyst (KF 757 at that time) was dense-loaded into the reactor to produce 45,000 barrels per day diesel fuel at 10–20 ppmw (to meet the 50 ppmw cap standard). As the space velocity changed, the sulfur level changed inversely proportional to the change in space velocity. Usually when the space velocity decreased to below 1.0, the sulfur level dropped below 10 ppmw. At that refinery, however, it was not necessary to maintain the sulfur level below 10 ppmw [4].

More recently, NEBULA catalyst has been developed jointly by ExxonMobil, Akzo Nobel, and Nippon Ketjen and commercialized in 2001 [158]. NEBULA stands for New Bulk Activity and is bulk base metal catalyst without using a porous support. Figs. 18–20 show the recent results published by Akzo Nobel on relative activity of the new NEBULA and STARS catalysts compared to conventional $CoMo/Al_2O_3$ developed over the last 50 years [159]. The NEBULA-1 catalyst is even more active than KF 848 STARS catalyst with respect to HDS and HDN and diesel hydrotreating; it has been successfully applied in several diesel hydrotreaters for months as of early 2002 [158]. Hydrocracking pretreatment was the first application where very high activity was found for NEBULA-1. As shown in Fig. 19, the improvement in the HDN performance over NEBULA-1 compared to KF 848 is indeed very significant. Moreover, KF 848 was already an enormous improvement over the previous generation, KF 846. The advantage in activity is 18 °C (32 °F) compared to KF 848 and about 25 °C (45 °F) compared to KF 846 [159]. The performance data shown in Fig. 19 are for feeds boiling in the LCO boiling range, for typical VGO applications the activity advantage is less great [159]. For good hydrocracking pretreatment one traditionally needs the best possible HDN catalyst and since HDN usually correlates with good hydrogenation the typical hydrocracking pretreat catalysts have excellent HDN and HDA combined. HDS activity used to be of secondary importance for hydrocracking pretreatment but with the new low-sulfur specifications it can also limit the performance of the pretreater [159]. A similar improvement in activity is found for HDS and hydrogenation over NEBULA, this will lead to highly improved product qualities like lower sulfur, higher cetane, lower density, etc. Fig. 21 compares NEBULA-1 and KF 848 catalysts at equal product sulfur level corresponding to different weighted-average bed temperatures (WABT), for which long-term tests were run using an SR gas oil with 1.2 wt.% sulfur and a density of 0.86 g/ml. Test conditions are: $P = 56$ bar, LHSV $= 2.5$ and hydrogen to oil $= 208$ NL/l [159].

Researchers at Haldor-Topsoe and their collaborators in academic institutions have contributed significantly to both the advances in research on fundamental aspects of catalytically active sites of transition metal sulfides [37,131] and the development of new and

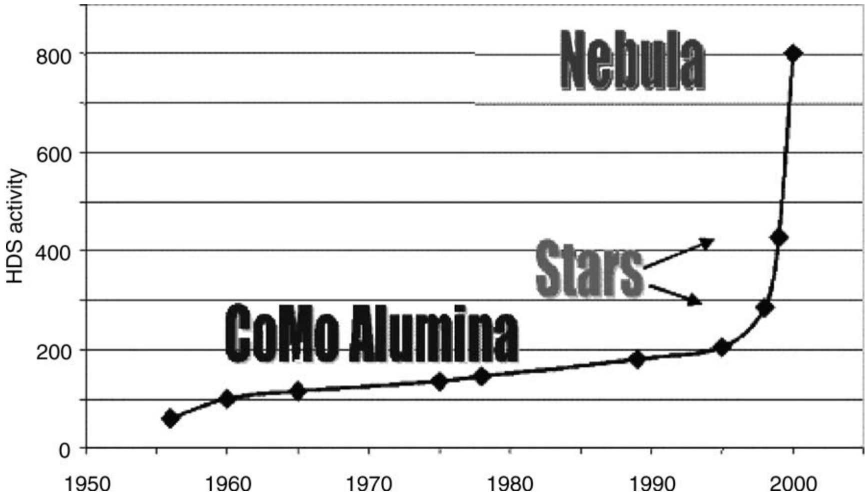


Fig. 19. Relative activity of the new NEBULA and STARS catalysts compared to conventional CoMo/Al_2O_3 developed over the last 50 years [159].

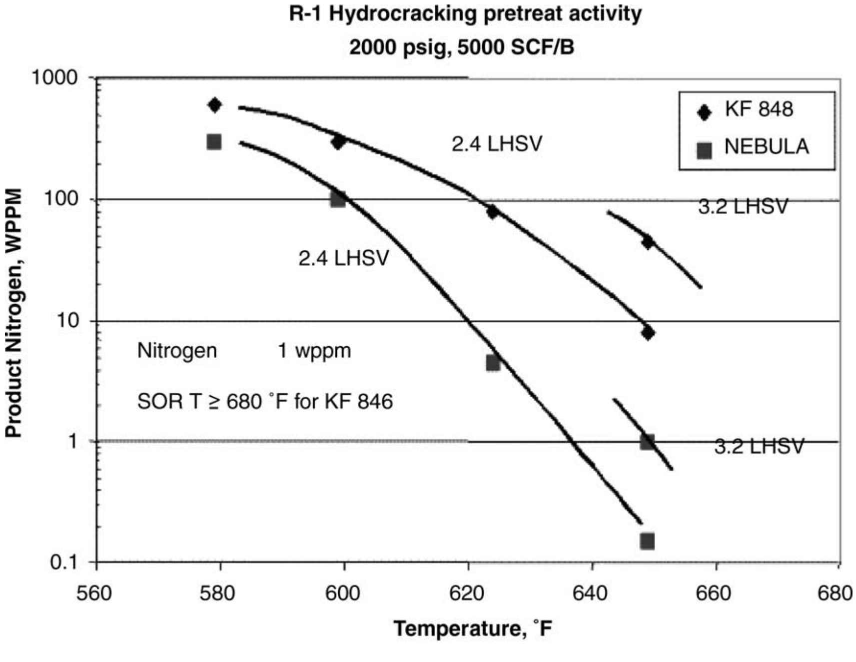


Fig. 20. Hydrodenitrogenation (HDN) activity of NEBULA-1 compared with KF 848 NiMo STARS catalysts [159].

more active commercial hydrotreating catalysts and processes [18]. Haldor-Topsoe has commercialized more active catalysts for HDS. Its TK-554 catalyst is analogous to Akzo Nobel's KF 756 catalyst, while its newer, more active catalyst is termed TK-574. For example, in pilot plant studies, under conditions where TK-554 produces 400 ppmw sulfur in SRGO, TK-574 will produce 280 ppmw. Under more severe conditions, TK-554 will produce 60 ppmw, while TK-574 will produce 30 ppmw, and similar benefits are found

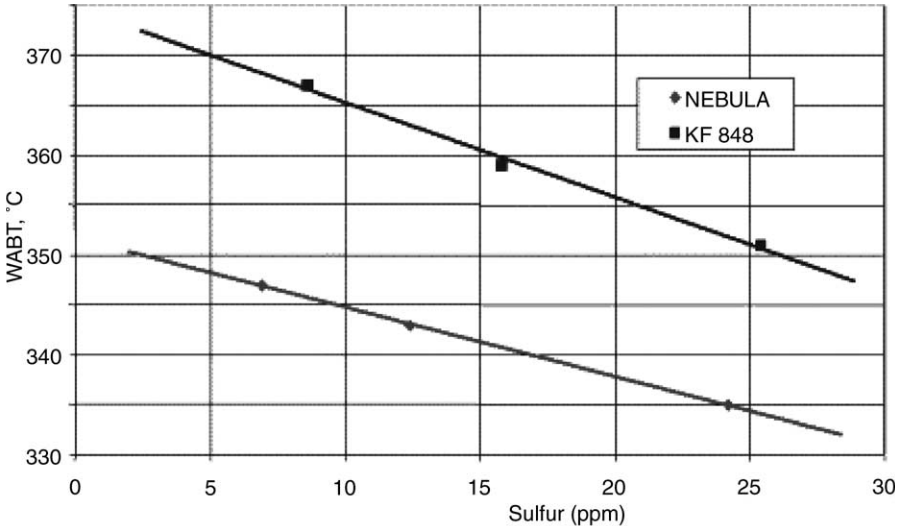


Fig. 21. HDS activity of NEBULA-1 compared with KF 848 NiMo STARS catalysts [159]. The feed used in this test was an SR gas oil with 1.2 wt.% sulfur and a density of 0.86 g/ml. Test conditions are: $P = 56$ bar, LHSV = 2.5 and hydrogen to oil = 208 NL/l.

with a mixture of straight run and cracked stocks [4]. In addition to catalyst development, Haldor-Topsoe has also developed new processes for HDS.

Criterion Catalyst announced two new lines of catalysts. One is called Century, and the other is called Centinel. These two lines of catalysts are reported to be 45–70 and 80% more active, respectively, at desulfurizing petroleum fuel than conventional catalysts used in the mid-1990s [4]. These improvements have come about through better dispersion of the active metal on the catalyst substrate. The advanced refining technologies (ART) LP, a joint venture between Chevron and Grace Davison, has developed SMART (*S*ulfur *M*inimization by *ART*) catalyst system for diesel deep HDS [160]. The SMART catalyst takes advantages of different reaction pathways of deep HDS for DBT and 4,6-DMDBT type sulfur compounds and is made using a combination of a high-activity Co–Mo catalyst (for C–S bond direct hydrogenolysis of unhindered sulfur such as DBT) and a specialized Ni–Mo catalyst (for aromatic ring hydrogenation followed by C–S bond hydrogenolysis for sterically hindered sulfur such as 4,6-DMDBT). In addition to improving HDS activity over conventional catalysts, the SMART system can be tailored to optimize hydrogen consumption, especially when hydrogen availability is limited [160].

5.2.3. *Tailoring reaction and processing conditions*

Tailoring process conditions aims at achieving deeper HDS with a given catalyst in an existing reactor without changing the processing scheme, with no or minimum capital investment. The parameters include those that can be tuned without any new capital investment (space velocity, temperature, pressure), and those that may involve some relatively minor change in processing scheme or some capital investment (expansion in catalyst volume or density, H_2S scrubber from recycle gas, improved vapor–liquid distributor) [161,162]. First, space velocity can be decreased through increasing the catalyst bed volume or reducing the flow rate of liquid feedstock to increase the reactant–catalyst contact time. More refractory sulfur compounds would require lower space velocity for achieving deeper HDS. Second, temperature can be increased, which increases the rate of HDS. Higher temperature facilitate more of the high activation-energy reactions. Third, H_2 pressure can be increased. Fourth, improvements can be made in vapor–liquid contact to achieve uniform reactant distribution, which effectively increases the use of surface area of the catalyst. Finally, the concentration of hydrogen sulfide in the recycle stream can be removed by amine scrubbing. Since H_2S is an inhibitor to HDS, its build-up in high-pressure reactions through continuous recycling can become significant.

Some of these factors are elaborated further below. It should be noted that conventional approaches for fuel desulfurization in response to the 1993 diesel fuel sulfur regulation (500 ppmw sulfur) in the US were to increase process severity of HDS, increase catalysts to fuel ratio, increase residence time, and enhance hydrogenation, or to use additional low-sulfur blending stocks either from separate process streams or purchased. It is becoming more difficult to meet the ultra-low-sulfur fuel specifications by fuel HDS using the conventional approaches.

Liquid-hourly space velocity (LHSV) and catalytic bed volume are inter-related parameters that control both the level of sulfur reduction and the process throughput. Increase in catalyst bed volume can enhance desulfurization. UOP projects that doubling reactor volume would reduce sulfur from 120 to 30 ppmw [4]. Haldor-Topsoe reports that doubling the catalyst volume results in a 20 °C decrease in average temperature if all other operating conditions are unchanged, and there is a double effect of the increased catalyst volume [18]. The deactivation rate decreases because the start-of-run temperature decreases, and the lower LHSV by itself reduces deactivation rate even at the same temperature.

Increasing the temperature of reaction can enhance the desulfurization of more refractory sulfur compounds. Haldor-Topsoe has shown that an increase of 14 °C while processing a mix of SRLGO and LCO with its advanced TK-574 Co–Mo catalyst will reduce sulfur from 120 to 40 ppmw [4]. UOP projects that a 20 °F increase in reactor temperature would decrease sulfur from 140 to 120 ppmw [4]. The downside of increased temperature is the reduction of catalyst life (i.e., the need to change catalyst more frequently) [161]. This increases the cost of catalyst, as well as affects highway diesel fuel production while the unit is down for the catalyst change. Still, current catalyst life ranges from 6 to 60 months, so some refiners could increase temperature and still remain well within the range of current industry performance. The relationship between temperature and life of a catalyst is a primary criterion affecting its marketability; thus, catalyst suppliers generally do not publish these figures [4].

Role of H_2S in deep HDS of gas oils has been discussed in detail by Sie [163]. The decrease in the concentration of hydrogen sulfide in gas phase could reduce the inhibition of the desulfurization [30,129,164,165] and hydrogenation reactions. H_2S can be removed by chemical scrubbing. Haldor-Topsoe indicates that decreasing the concentration of H_2S at the inlet to a co-current reactor by 3–6 vol.% can decrease the average temperature needed to achieve a specific sulfur reduction by 15–20 °C, or reduce final sulfur levels by more than two-thirds [4]. UOP projects that scrubbing H_2S from recycle hydrogen can reduce sulfur levels from roughly 285 to 180 ppmw in an existing hydrotreater [4].

The increase in H_2 partial pressure and/or purity can improve HDS and hydrogenation. Haldor-Topsoe indicates that increasing hydrogen purity is preferable to a simple increase in the pressure of the hydrogen feed gas, since the latter will also increase the partial pressure of hydrogen sulfide later in the process, which inhibits both beneficial reactions [4]. Haldor-Topsoe projects that an increase in hydrogen purity of 30% would lower the temperature needed to achieve the same sulfur removal rate by 8–9 °C. Or temperature could be maintained while increasing the amount of sulfur removed by roughly 40%. Hydrogen purity can be increased through the use of a membrane separation system or a PSA unit. UOP project that purifying hydrogen can reduce distillate sulfur from 180 to 140 ppmw from an existing hydrotreater [4].

Increasing the recycle gas/oil ratio (increase in the amount of recycle gas sent to the inlet of the reactor) could increase the degree of desulfurization, but the effect is relatively small so a relatively large increase is needed to achieve the same effect as scribing recycle gas [8]. Haldor-Topsoe indicates that a 50% increase in the ratio of total gas/liquid ratio only decreases the necessary reactor temperature by 6–8 °C; or the temperature can be maintained and the final sulfur level reduced by 35–45% [4].

The improvement in vapor–liquid contact can enhance the performance of distillate hydrotreaters. As an example, in testing of an improved vapor–liquid distributor in commercial use, Haldor-Topsoe and Phillips Petroleum found that the new Topsoe Dense Pattern Flexible Distribution Tray (installed in 1996 to replace a chimney type distributor installed in 1995 in a refinery) allowed a 30% higher sulfur feed to be processed at 25 °C lower temperatures, while reducing the sulfur content of the product from 500 to 350 ppmw [18]. Akzo Nobel estimates that an improved vapor–liquid distributor can reduce the temperature necessary to meet a 50 ppmw sulfur level by 10 °C, which in turn would increase catalyst life and allow an increase in cycle length from 10 to 18 months [4]. Based on the above data from Haldor-Topsoe, if temperatures were maintained, the final sulfur level could be reduced by 50% [4]. Maintaining temperature should have allowed an additional reduction in sulfur of more than two-thirds. Thus, ensuring adequate vapor–liquid contact can have a major impact on final sulfur levels.

The above-mentioned individual improvements described cannot be simply combined, either additively or multiplicatively. As mentioned earlier, each existing distillate hydrotreater is unique in its combination of design, catalyst, feedstock, and operating conditions. While the improvements described above are probably indicative of improvements which can be made in many cases, it is not likely that all of the improvements mentioned are applicable to any one unit; the degree of improvement at one refinery could either be greater than, or less than the benefits that are indicated for another refinery.

5.2.4. Designing new reactor configurations

Industrial reactor configuration for deep HDS of gas oils in terms of reaction order and effect of H_2S has been discussed by Sie [163]. The reactor design and configuration involve one-stage and two-stage desulfurization. Desulfurization processes in use today in the US generally use only one reactor, due to the need to only desulfurize diesel fuel to 500 ppmw or lower. Hydrogen sulfide strongly suppresses the activity of the catalyst for converting the refractory sulfur compounds which should occur in the major downstream part of a co-current trickle-bed reactor during deep desulfurization. The normally applied co-current trickle-bed single reactor is therefore not the optimal technology for deep desulfurization [163]. However, a second reactor can be used, particularly to meet lower sulfur levels. Adding a second reactor to increase the degree of desulfurization is an option, and both desulfurization and hydrogenation in the second reactor can be improved by removing H_2S and NH_3 from the exit gas of first reactor before entering the second reactor. This last technical change is to install a complete second stage to the existing, one-stage hydrotreater. This second stage would consist of a second reactor, and a high pressure, hydrogen sulfide scrubber between the first and second reactor. The compressor would also be upgraded to allow a higher pressure to be used in the new second reactor. Assuming use of the most active catalysts available in both reactors, UOP projects that converting from a one-stage to a two-stage hydrotreater could produce 5 ppm sulfur relative to a current level of 500 ppm today [4].

A new way of reactor design is to have two or three catalyst beds, that are normally placed in separate reactors, within a single reactor shell and have both co-current and counter-current flows [163]. This new design was developed by ABB Lummus and Criterion, as represented by their SynSat process [166,167]. The SynAlliance (consisting of ABB Lummus, Criterion Catalyst, and Shell Oil) has patented a counter-current reactor design called SynTechnology. With this technology, in a single reactor design, the initial portion of the reactor will follow a co-current design, while the last portion of the reactor will be counter-current [4]. Traditional reactors are co-current in nature. The hydrogen is mixed together with the distillate at the entrance to the reactor and flow through the reactor together. Because the reaction is exothermic, heat must be removed periodically. This is sometimes done through the introduction of fresh hydrogen and distillate at one or two points further down the reactor. The advantage of co-current design is practical, it eases the control of gas–liquid mixing and contact with the catalyst. The disadvantage is that the concentration of H_2 is the highest at the front of the reactor and lowest at the outlet. The opposite is true for the concentration of H_2S. This increases the difficulty of achieving extremely low-sulfur levels due to the low H_2 concentration and high H_2S concentration at the end of the reactor. A new solution to this problem is to design a counter-current reactor, where the fresh H_2 is introduced at one end of the reactor and the liquid distillate at the other end. Here, the hydrogen concentration is highest (and the hydrogen sulfide concentration is lowest) where the reactor is trying to desulfurize the most difficult (sterically hindered) compounds. The difficulty of counter-current designs in the case of distillate hydrotreating is vapor–liquid contact and the prevention of hot spots within the reactor.

In a two-reactor design, the first reactor will be co-current, while the second reactor will be counter-current. ABB Lummus estimates that the counter-current design can reduce the catalyst volume needed to achieve 97% desulfurization by 16% relative to a co-current design [4]. The impact of the counter-current design is even more significant when aromatics control (or cetane improvement) is desired in addition to sulfur control. However, operation of counter-current flow reactor might not be possible in packed beds of the usual catalyst particles because of the occurrence of flooding at industrially relevant fluid velocities. Criterion offers the catalysts for the SynSat and SynShift processes. SynShift involves deep heteroatom removal, ring-opening, and aromatic saturation thus decreasing (shifting) boiling range. Some novel reactor concepts based on special structured packings or monoliths that allow such counter-current operation have been presented [163].

5.2.5. Developing new processes

Among the new process concepts, design approaches for ultra-deep desulfurization focus on: (1) reactive adsorption and sulfur atom extraction—remove sulfur by using reduced metals or metal oxides to react with sulfur to form metal sulfides at elevated temperatures under H_2 atmosphere without hydrogenation of aromatics; (2) selective adsorption for removing sulfur compounds (SARS)—remove sulfur by selective interaction with sulfur compounds in the presence of aromatic hydrocarbons under ambient or mild conditions without using hydrogen; (3) oxidation and extraction—oxidize sulfur compounds by liquid-phase oxidation reactions with or without ultrasonic radiation, followed by separation of the oxidized sulfur compounds and (4) biodesulfurization-attack sulfur atoms by using bacteria via microbial desulfurization.

5.2.5.1. Reactive adsorption for sulfur capture from diesel streams. A new diesel desulfurization process called S-Zorb Diesel, was recently announced by Phillips Petroleum (now ConocoPhillips), which is an extension of their S-Zorb Gasoline process for naphtha (at 377–502 °C, 7.0–21.1 kg/cm^2) [85]. S-Zorb for diesel contacts diesel fuel streams with a solid sorbent in a fluid bed reactor at relatively low pressures and temperature in the presence of hydrogen. The sulfur atom of the sulfur-containing compounds adsorbs onto the sorbent and reacts with the sorbent. It should be mentioned that Phillips Petroleum conducted an internal study of its refineries and concluded the use of hydrotreating technologies to reach ultra-low-sulfur levels in gasoline to be a cost-prohibitive option [85]. As in the case of S-Zorb Gasoline, hydrogen sulfide is not released into the diesel product, which makes the products separation/handling easier.

Table 16
Performance of S-Zorb process for diesel stream [86][a]

	Diesel A	Diesel B	LCO
Feed properties			
Sulfur (ppmw)	523	460	2400
Nitrogen (ppmw)	124	67	755
API gravity (°)	33.20	36.05	20.38
Hydrogen (wt.%)	12.72	13.13	10.47
ASTM color	0.5	0.5	1.5
Cetane index	44.4	46.4	29.7
Product properties			
Sulfur (ppmw)	6	<1	10
Nitrogen (ppmw)	80	30	445
Basic nitrogen	n/a	n/a	n/a
API gravity (°)	33.22	36.23	21.99
Hydrogen (wt.%)	12.72	13.11	10.74
ASTM color	0.5	0.5	1.5
Cetane index	44.4	46.4	31.3
Utilities and economics			
Unit capacity (bpd)	36000	36000	36000
H_2 consumption (ft^3/bbl)	−5	−15	186
Capital cost (ISBL)	US$ 1000–1200/bbl		
Operating cost	US$ 5–10 million less than a hydrotreater		

[a] S-Zorb SRT when treating diesel streams (reactor temperature: 650–775 °F (343–413 °C); reactor pressure: 100–300 psig (7–21 atm); space velocity: 4–10 WHSV; H_2 gas purity: >50%).

Table 16 shows the performance of S-Zorb process for diesel streams under the following general operating conditions: reactor temperature, 650–775 °F (343–413 °C); reactor pressure, 100–300 psig (7–21 atm); space velocity, 4–10 WHSV; H_2 gas purity, >50% [86]. The S-Zorb Diesel desulfurization process has been demonstrated in the laboratory using two different diesel feedstocks (Table 16), which has shown that diesel feeds containing 17–20% hydrotreated LCO can be desulfurized down below 10 ppmw sulfur [86]. ConocoPhillips is currently operating a S-Zorb Diesel pilot plant unit where they are processing feeds with a wide range of sulfur content. Plans are underway for a commercial S-Zorb Diesel unit [87]. A recent article from ConocoPhillips presents a summary of S-Zorb process performance, historical development and future perspective of S-Zorb for gasoline and diesel desulfurization [168]. RTI group is also testing their TReND process, initially developed for gasoline, for diesel desulfurization [91].

5.2.5.2. Selective adsorption for deep desulfurization at ambient temperature. An alternate process is being explored in our laboratory for deep desulfurization of distillate fuels (diesel, gasoline and jet fuels) based on selective adsorption for removal of sulfur (PSU-SARS) compounds at ambient conditions without using H_2 [32,33,99,100]. The possible coordination geometries of thiophene in organometallic complexes (Fig. 14) suggest likely adsorption configurations of thiophenic compounds on the surface of transition metal-based adsorbents. Both thiophenic compounds and non-sulfur aromatic compounds can interact with metal by π-electrons. However, in Fig. 14 only two types of interactions of thiophene with metal involve sulfur atom in thiophene, the η^1-S bonding interaction between the sulfur atom and one metal atom, and the S-μ_3 bonding interaction between the sulfur atom and two metal atoms.

A wide variety of adsorbents based on transition metal complex supported on porous materials, zeolites, supported transition metals, mixed metal oxides, activated carbon, etc. tested in the adsorptive desulfurization of gasoline have also been tested in the desulfurization of diesel and jet fuel (JP-8) fuels [17,21,32,33,99–102]. Our group is also exploring methods for the regeneration of spent adsorbent for the subsequent use. Methods such as solvent washing, oxidative regeneration and reductive regeneration are being investigated.

Fig. 22 shows breakthrough curves for the adsorptive desulfurization of a model diesel fuel containing 220 ppmw of 4,6-DMDBT in a mixture of *n*-decane and hexadecane at 60 °C over transition metal oxides supported on MCM-41 and activated carbon [169]. The results show that over both adsorbents, the 4,6-DMDBT has been completely removed. The MCM-41-based adsorbent exhibits a breakthrough capacity of 3.5 mg sulfur/g of adsorbent while the transition metal supported on activated carbon shows very high breakthrough capacity of 12.6 mg/g of adsorbent.

Attempt has been made to regenerate these adsorbents by flushing with a 1:1 mixture of methanol and toluene at 70 °C. In order to estimate the amount of solvent required to completely recover the 4,6-DMDBT and to regenerate the adsorbent for subsequent use, the fractions of the solvent have been collected and analyzed using the total sulfur analyzer. The profile for recovering the 4,6-DMDBT by solvent washing from the spent activated carbon-based adsorbent is shown in Fig. 23 [169]. The sulfur content in the initial few fractions exceeded 1000 ppmw and then decreases exponentially. The results indicate that most of the sulfur compounds could be recovered using 20 cm^3 of the solvent per gram of adsorbent. However, about 50–80 cm^3 of the solvent is required under the present experimental condition for the complete removal of all the sulfur compounds adsorbed on this particular adsorbent. After the solvent washing, the regenerated adsorbent has been flushed with N_2 gas (40 ml/min) for about 1 h at 300 °C in order to remove any adsorbed solvent molecules. Desulfurization of model diesel fuel over regenerated adsorbent has been performed under the same experimental condition as that of fresh sample and the sulfur breakthrough curve obtained on the regenerated sample is shown in Fig. 22 itself along with that of fresh samples. The breakthrough curves of fresh and regenerated samples are close to coincidence and this indicates that solvent washing can regenerate the adsorbent almost completely.

Fig. 24 shows the GC-PFPD chromatograms of a commercial JP-8 jet fuel provided by the US Air Force Research Laboratory and that of processed fuel obtained by a fractionation to cut-off about 30 wt.% of the heavy fraction [170]. The sulfur concentration in the commercial JP-8 was about 800 ppmw while that in the processed fuel was about 400 ppmw. The major sulfur compounds in the JP-8 are the alkyl benzothiophenes with two or three carbon atoms in the alkyl group(s). The distillation removes most of the sterically hindered C3-BT and 2,3,7-TMBT. These two fuels were desulfurized over PSU A-2 and A-5 adsorbents and the results are presented in Fig. 25 [170]. It is clear that at 27 °C the sulfur concentration in the processed JP-8 after treatment is below 1 ppmw before the effluent amount increases to 8 g/g, indicating that almost all sulfur in the JP-8 has been removed by the selective adsorption. After 8 g/g of effluent amount, the sulfur concentration increases sharply with increasing effluent amount. At 200 °C, the breakthrough curve is similar to that at 27 °C before 8 g/g of effluent amount, but after this point, the sulfur concentration increases slowly with increasing effluent amount, being only

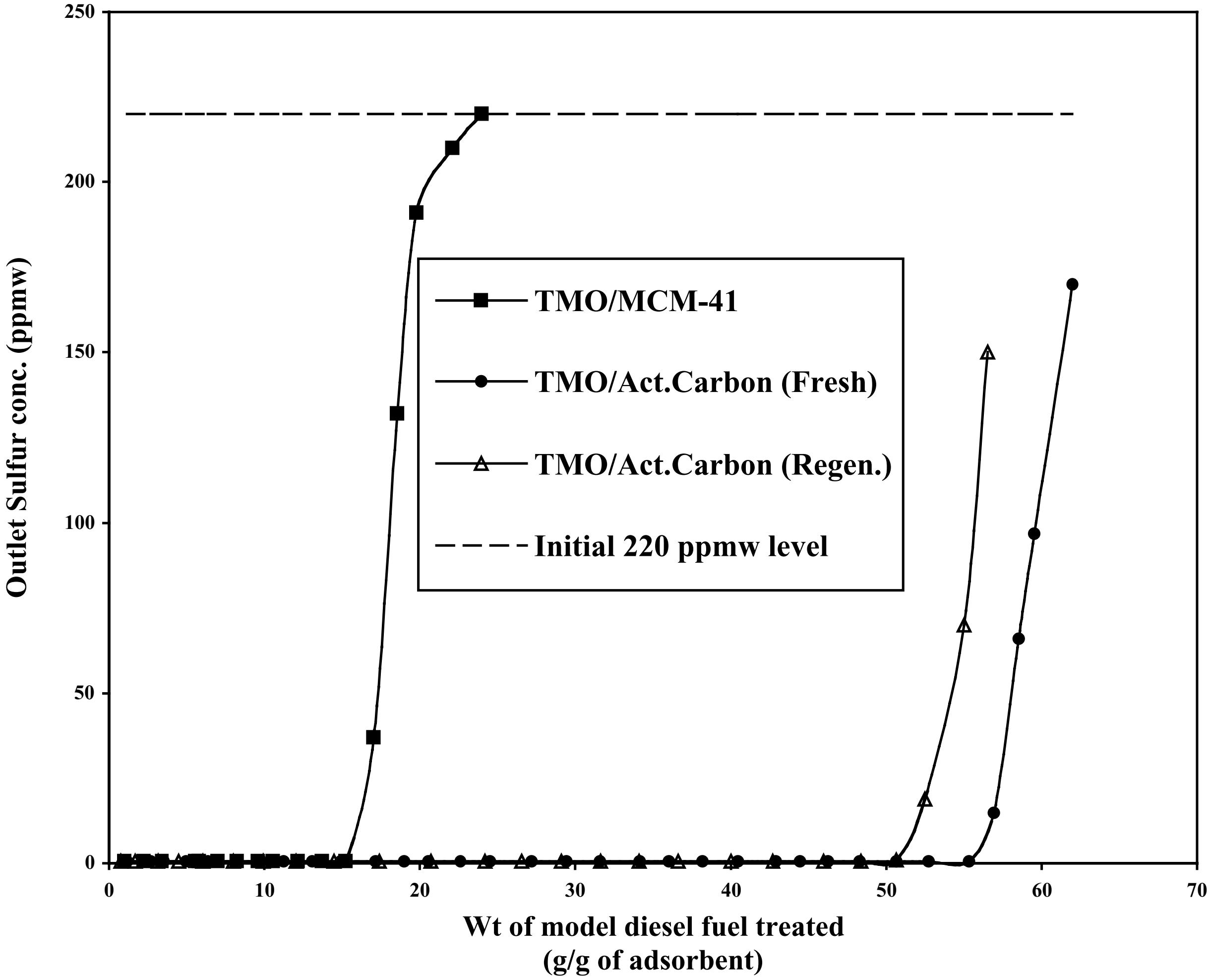


Fig. 22. Breakthrough curves for the adsorptive desulfurization of a model diesel fuel containing 4,6-DMDBT at 60 °C over transition metal oxides supported on MCM-41 and activated carbon [169].

60 ppmw at 56 g/g of effluent amount. Under similar experimental conditions, the only about 2 g/g of the commercial JP-8 could be treated with an outlet sulfur concentration of below 1 ppmw. Thus, fractionation of JP-8 improves the adsorption performance at least by four times because of the removal of sterically hindered C3-BT and 2,3,7-TMBT. Thus, a breakthrough capacity between 4 and 16 mg/g of adsorbent could be obtained over A-2 adsorbent depending upon the nature of sulfur compounds in the fuel and the adsorption temperature. The PSU A-5 adsorbent exhibits better performance at 200 °C compared to PSU A-2.

Current maximum sulfur contents in jet fuels is 3000 ppm. There is not yet a more strict sulfur regulation on jet fuels, but it is expected that further reduction in jet fuel sulfur content may be regulated in the future. Although the maximum allowed sulfur can be up to 3000 ppm, most commercial and military jet fuels in the US have sulfur contents below 1500 ppm, because of the modern refining processes used. We have analyzed various commercial and military jet fuel sam-

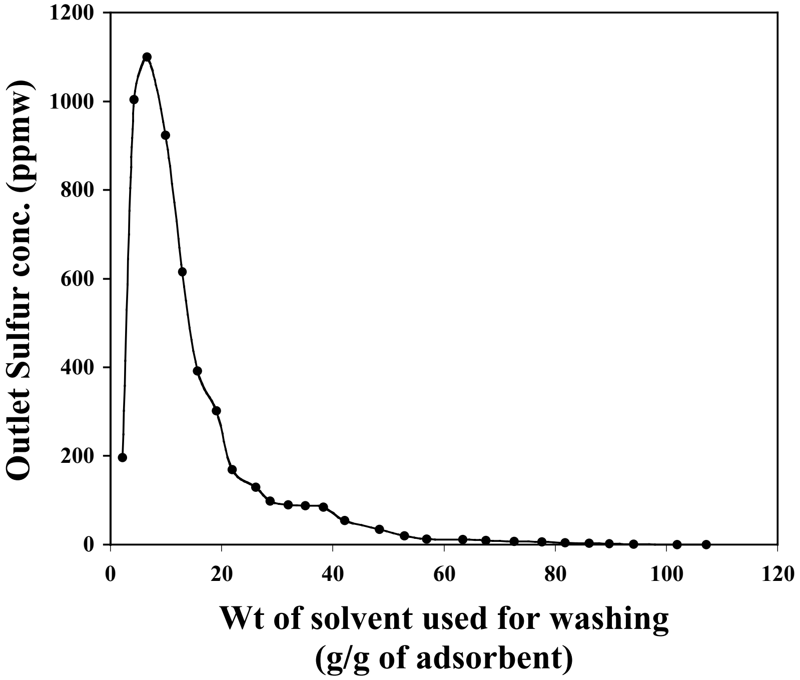


Fig. 23. Profile for recovering the adsorbed 4,6-DMDBT by solvent washing from the spent activated carbon-based adsorbent at 70 °C [169].

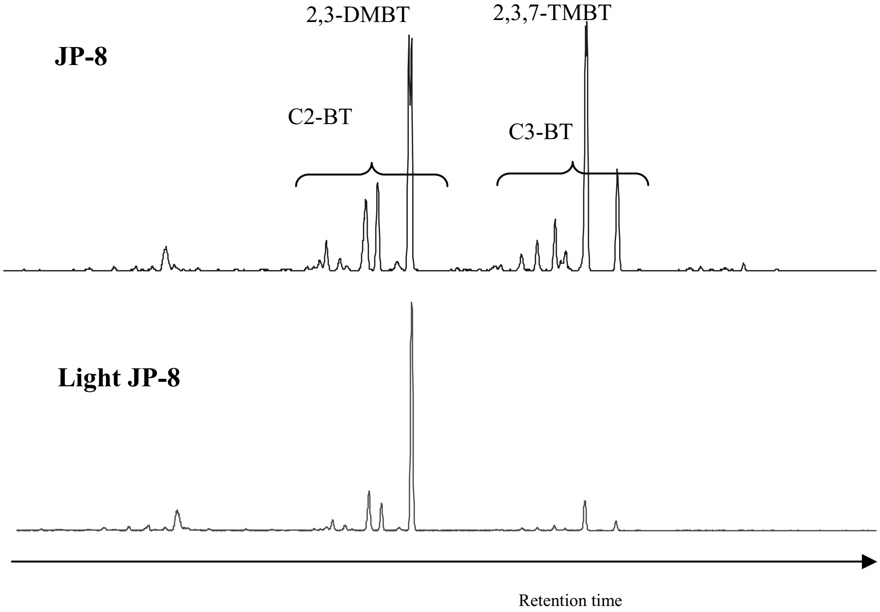


Fig. 24. Sulfur-selective GC-PFPD chromatogram of commercial JP-8 and processed JP-8 [170].

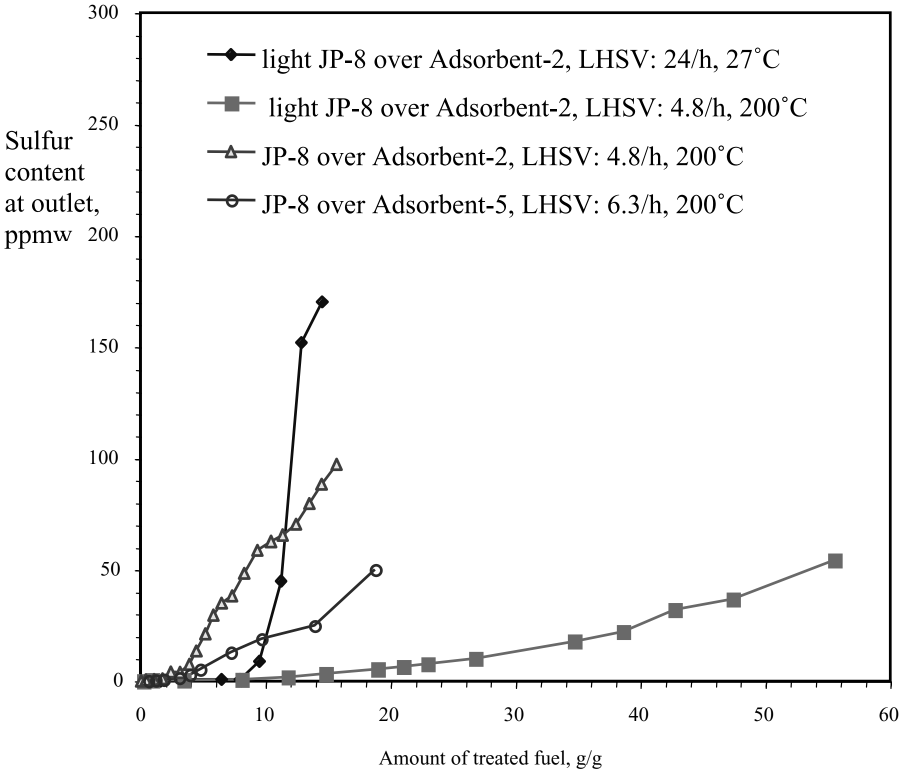


Fig. 25. Breakthrough curves for the adsorptive desulfurization of real jet fuel (JP-8) over PSU A-2 and A-5 adsorbents [170].

ples from US sources in our laboratory, and the sulfur contents were generally between 400 and 800 ppm.

There is an ongoing research at the Pennsylvania State University for developing advanced thermally stable jet fuels [171–174] that have higher thermal stability and lower sulfur contents and can withstand much higher temperatures up to 482 °C (900 °F). LCO from FCC and refined chemical oil from coal tar could be feedstock for producing advanced thermally stable jet fuels [175–177]. However, severe HDS and also denitrogenation will be required [151] in order to produce advanced jet fuels that have superior properties. For use of regular jet fuel in stationary and mobile fuel-cell applications, the PSU-SARS approach appears to be a promising method for on-board and on-site jet fuel desulfurization.

The results in Figs. 15, 16 and 22–25 show that selective adsorption of sulfur compounds from gasoline and diesel fuels as well as jet fuels can be achieved by using PSU-SARS process in laboratory scale [17,21,32,33,99–102,169,170]. Selective separation of sulfur compounds has also been conducted in analytical characterization using ligand-exchange chromatography. For example, Pyell et al. [178] has examined 2-amino-1-cyclopentene-1-dithiocarboxylic acid silica gel (ACDA-SG) loaded with Ag(I) or Pd(II) ions for the group fractionation of polycyclic aromatic sulfur heterocycles (PASH) from polycyclic aromatic hydrocarbons (PAH) via ligand-exchange chromatography in the normal phase mode. It is shown that metal loading has a great impact on the selectivity of ACDA-SG for PASH and PAH. Pd(II) loaded ACDA-SG proved to be suitable for the group isolation of PASH from the aromatic fractions of petroleum mixtures (number of condensed rings less than or equal to 3) [178]. Rudzinski et al. [179] analyzed the Maya crude oil by the saturates-aromatics-resins-asphaltenes (SARA) method. They separated sulfur-containing compounds in the saturate and aromatic fractions using a ligand-exchange chromatography method based on organosulfur affinity for Cu^{2+} and Pd^{2+}, respectively.

5.2.5.3. Selective adsorption of organic sulfur coupled with HDS. Our group is proposing a new integrated process concept (SARS-HDSCS) that combines selective adsorption for removing sulfur (PSU-SARS), recovery of concentrated sulfur compounds, and HDS of concentrated sulfur (HDSCS) fraction [32]. This represents an attempt to make deep desulfurization in a future refinery fundamentally more efficient and consumes less hydrogen which is a significant cost factor for both capital investment (H_2S scrubber from recycle H_2 gas, compressor) and process operation (consumption of H_2).

It is known that for current commercial hydrotreater operations, each 1 wt.% sulfur removal results in about 18–20 N m^3/m^3 feed (110–120 SCFB) of H_2 consumption; each 1000 ppm nitrogen removal results in about 5.9–6.1 N m^3/m^3 (35–36 SCFB) of H_2 consumption; each 1 wt.% aromatics removal yields about 5.0–8.4 (use half of these numbers if aromatics are reported as vol.%); each one unit increase in ° API gravity requires about 17 N m^3/m^3 feed (100 SCFB) of H_2 consumption, as does each one unit increase in cetane number for diesel stocks [43].

By using conventional HDS processes, the refiners need to process 100% of the fuel for dealing with sulfur compounds that account for less than 0.3 wt.% of the feed with 500 ppmw sulfur level. This results in larger amount of fuel processed and a larger amount of H_2 required and also larger equipments for recycle H_2 gas scrubbing (to remove H_2S) and H_2 compressor.

Fig. 26 shows the flow diagram of the proposed concept of the new integrated desulfurization process, which consists of SARS compounds [32,33,99,100] followed by HDSCS compounds using high-activity catalysts such as Co–Mo/MCM-41 [146,149–151]. The subsequent HDS of sulfur compounds removed by selective adsorption is expected to be much easier than conventional HDS of diesel streams for two reasons. First, it is more concentrated and thus reactor utilization is more efficient. Second, the rate of HDS reaction is faster because of the removal of aromatics which inhibit the HDS by competitive adsorption on the hydrogenation sites. Third, and most importantly for practical application, the required reactor volume can be substantially smaller because the amount of fuel to be processed is smaller by 95% or more.

5.2.5.4. Adsorption of polar nitrogen compounds before diesel HDS. Adsorption of polar substances can

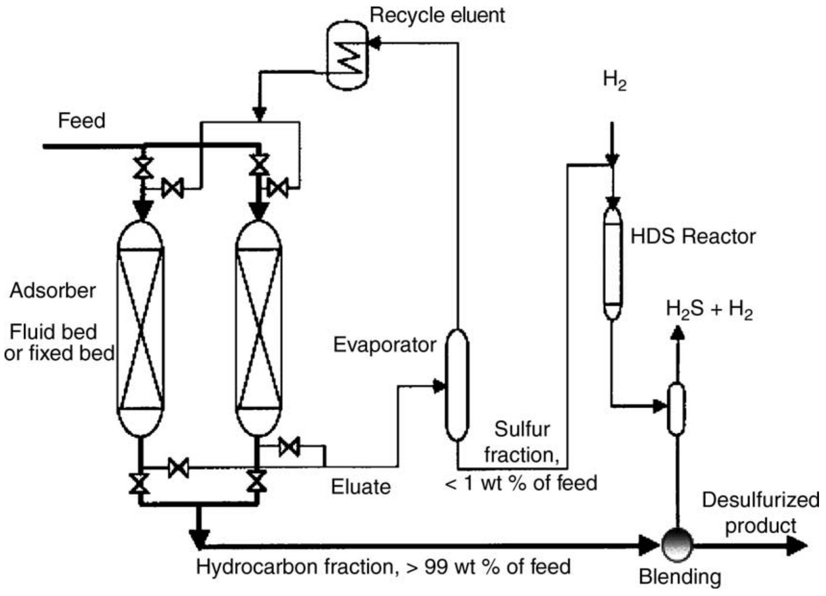


Fig. 26. The proposed adsorption process integrated with HDS in a refinery (SARS-HDSCS) for deep desulfurization [32].

be used as a pretreatment to remove nitrogen before HDS of fuels. Feedstocks for diesel fuel, such as atmospheric gas oil and LCO from FCC, contain some nitrogen compounds [180]. Recently, SK in Korea has developed a new process, SK HDS pretreatment process that enables the refiners to produce economically ultra-low-sulfur-diesel of below 10 ppm [181]. It is known that nitrogen compounds can inhibit HDS on catalyst surface due to competitive adsorption. Adsorption removal of nitrogen compounds is used as a pretreatment before conventional HDS processing. Using a solid adsorbent, this process is based on the adsorptive removal of nitrogen containing compounds (NCCs) from the feedstock prior to conventional HDS units. As is well known, NCC inhibits the activity of HDS catalysts. In the SK HDS pretreatment process, the feedstock to the HDS unit is pretreated, and 90% or more of NCC in the feedstock is removed, resulting in higher desulfurization in a conventional HDS unit. It was found that the degree of improvement in HDS is proportional to the degree of NCC removal. SK HDS pretreatment process is claimed to be a cost-effective method for refineries to choose for 10 ppm ULSD production.

5.2.5.5. Other emerging processes for diesel desulfurization. There are other emerging processes and concepts outlined in Table 15 that are not covered in this article due to the limitation of space and scope of the journal. Some specific information and references on these approaches are given below. More information on diesel desulfurization approaches are available in two recent reviews [21,49]:

- Oxidative desulfurization by chemical oxidation in liquid phase [182–185], such as oxidative desulfurization process ASR-2 by Unipure [186–188]; oxidative desulfurization process by SulphCo using H_2O_2 under ultrasound radiation [189–192]; chemical oxidation by Petrostar using peroxyacetic acid [193,194].
- Biodesulfurization of distillate fuels [195,196] such as microbial desulfurization process by Energy BioSystems [197].
- Precipitation of polycyclic sulfur compounds by charge transfer complex formation [198].
- Temporary solution: Undercutting of sulfur-rich narrow fraction of LCO from FCC to remove a narrow BP range that is rich in refractory sulfur compounds (such as 4,6-DMDBT), and use it for off-road distillate fuels [56].

6. Deep hydrogenation of diesel fuels

6.1. Need for aromatic saturation

High aromatic content in distillate fuels lowers the fuel quality and contributes significantly to the formation of environmentally harmful emissions [199,200]. Reducing aromatic content along with sulfur content is generally desirable with respect to diesel fuel quality, as aromatic reductions increase cetane levels and generally improve combustion characteristics. Furthermore, aromatic saturation followed by ring-opening can significantly increase the cetane number of diesel fuels. California Air Resources Board (CARB) passed legislative measures to limit the sulfur and aromatic contents of diesel fuel to 0.05 wt.% and 10 vol.%, respectively, effective since October 1993. More recently, Texas state government also announced plan to reduce diesel aromatics from 35% down to 10 vol.%. Previously hydrogenating aromatics was viewed as an expensive and unnecessary reaction as it consumes hydrogen and increases the cost of desulfurization relative to a case where only sulfur was being removed. However, with the potential new regulation on aromatics reduction and with the benefit of aromatic saturation followed by selective ring-opening, hydrogenation of aromatics has become more important for diesel fuels.

Currently, conventional hydrotreating technology is adapted for aromatics saturation [199]. Typical conventional catalysts for fuel hydroprocessing are sulfided Co–Mo and Ni–Mo supported on alumina. Some studies have shown that complete hydrogenation of aromatics is not possible owing to equilibrium limitations under typical hydrotreating conditions. Conventional middle distillate hydrotreaters designed to reduce sulfur and nitrogen levels would lower the diesel aromatics only marginally [199,200]. For example, Ali and Siddiqui [201] compared three types of hydrotreating catalysts, $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and NiW/Al_2O_3, for dearomatization of LCO. They observed that the type of catalyst has a critical influence on the composition and properties of the product.

Their data show that it was not possible to obtain a diesel product that meets stringent specifications using one type of catalyst in a single-stage reactor even under severe operating conditions [201].

While noble metals are active for hydrogenation at low temperatures, their use is limited because of their sensitivity to sulfur poison. In current processing schemes involving noble metal catalysts, two or more stages with multiple catalyst beds are used to achieve deep desulfurization and deep hydrogenation. HDS occurs in the first stage over a Ni–Mo or Co–Mo catalyst, followed by intermediate by-product gas removal. Finally, hydrogenation over the noble metal catalyst operates in the last stage or bottom bed where the concentrations of catalyst poisons (organosulfur and H_2S) are extremely low [166,202].

6.2. Saturation of aromatics in commercial process

Commercial examples of two-stage or multi-stage hydroprocessing technology include the Shell middle distillate hydrogenation process by Shell [202,203], the dual-stage process by Haldor-Topsoe [204], and hydrotreating process by IFP [205], and the SynSat process developed by Criterion/Lummus [166,206]. There are no reports of noble metal catalysts that can operate without such intermediate H_2S removal [202].

Haldor-Topsoe has developed a two-stage HDS/HDA process for deep hydrogenation of aromatics in distillate fuels, in which the first stage uses their base metal catalyst such as TK-573 for HDS, while the second stage uses their noble metal catalysts, either TK-907/TK-908 or TK-915 which is a newly developed high-activity dearomatization catalyst [207]. United Catalysts and Sud-Chemie AG have published data on the performance of their ASAT catalyst, which uses platinum and palladium [4]. The focus of their study was to reduce aromatics to less than 10 vol.% starting with a feed distillate containing up to 500 ppmw sulfur and at least 100 ppmw nitrogen. Starting with a feed distillate containing 400 ppmw sulfur and 127 ppmw nitrogen and 42.5 vol.% aromatics, the ASAT catalyst was able to reduce sulfur to 8–9 ppmw, essentially eliminate nitrogen and reduce aromatics to 2–5 vol.%. Hydrogen consumption was 800–971 standard cubic feet per barrel (SCFB) [4].

IFP, in conjunction with various catalyst manufacturers, offers its Prime D technology for deep desulfurization, aromatics saturation and cetane improvement. Using a NiMo catalyst, IFPs Prime D process can produce distillate sulfur levels of 10 ppmw from SRLGO and of less than 20 ppmw from distillate containing 20–100% cracked material using a single-stage reactor. With a two-stage process, less than one ppmw sulfur can be achieved [4].

Fig. 27 illustrates the SynSat/SynShift process using Criterion/Lummus catalytic hydrotreating reactor technology, with intermediate by-product gas removal and counter-current gas-flow [166,206]. The SynTechnology includes SynHDS for ultra-deep

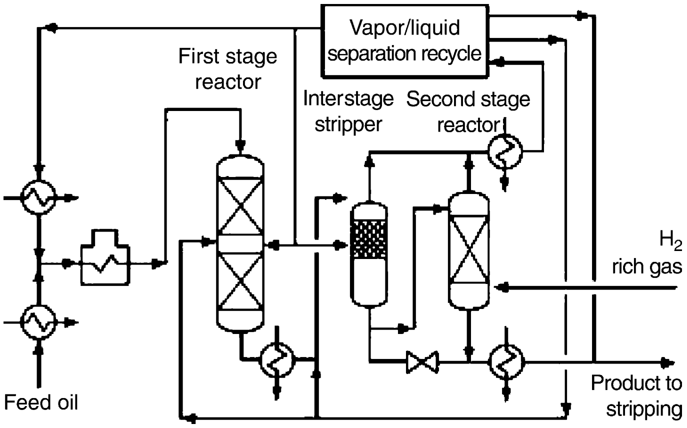


Fig. 27. SynSat/SynShift process with Criterion/Lummus catalytic hydrotreating reactor technology, with intermediate by-product gas removal and counter-current gas-flow [206].

desulfurization and SynSat/SynShift for cetane improvement, aromatics saturation and density/T95 reduction. A single-stage or integrated two-stage reactor system provides various process configuration options and revamp opportunities. In a two-stage reactor system, the feed, makeup and recycle gas are heated and fed to a first-stage co-current reactor. Effluent from the first stage is stripped to remove impurities and light ends before being sent to the second-stage counter-current reactor. When a counter-current reactor is used, fresh makeup hydrogen can be introduced at the bottom of the catalyst bed to achieve optimum reaction conditions [206]. Criterion and ABB Lummus have been licensing their SynTechnology, and there are more than 24 units either in operation or in the process of being constructed. Their purposes range from desulfurization to desulfurization plus dearomatization to mild hydrocracking [4]. ABB Lummus and Criterion indicate that their catalyst technology is sufficiently flexible to focus on the deep desulfurization with or without the significant aromatics reduction seen [4]. Of particular interest here is a revamp of an existing two reactor distillate hydrotreater at the Lyondell/Citgo refinery in Texas. The revamped unit was designed to process a low-cost feed very heavily weighted towards cracked material (65–70% LCO and LCGO) [4]. One existing reactor was converted to SynSat Technology, while the other was used simply as a flash drum. A new first-stage reactor was added. Both reactors were designed to operate in a co-current fashion. Pilot plant studies predicted average sulfur and aromatics levels of 7 ppmw and 31 vol.%, respectively, based on feed sulfur and aromatics levels of 11,900 ppmw and 53 vol.%, respectively. The unit exceeded expectations in the case of sulfur, producing an average sulfur level of less than five ppmw from a feed sulfur level of 13,800 ppmw. The actual aromatic level achieved was above the target by 4 vol.%, but the feed aromatic level was 5 vol.% higher than expected. Thus, the net reduction in aromatic content in terms of vol.% was still higher than found in the pilot plant.

6.3. *A new approach for design of sulfur-tolerant LT-HDA catalyst*

Because of its importance, sulfur resistance of noble metal catalysts has been the subject of a number of studies [200,208–212]. More recently, a new approach has been proposed for the design of sulfur-resistant noble metal catalysts for low-temperature hydrotreating of sulfur-containing distillates to produce clean distillate fuels [211,213] such as diesel fuels and jet fuels. The proposed design concept [211] invokes some unique zeolites as supports for noble metals and utilizes: (1) bimodal molecular sieving zeolite support that have desired pore structures, (2) shape-selective exclusion, (3) hydrogen spillover, and (4) two types of sulfur resistance. Unique zeolite supports can be used to prepare bimodal distributions of noble metal particles. Some metals are located in small pores (Sm: pore opening less than about 5 Å); whereas, others will be contained in large pores (La: pore opening larger than 6 Å). Preferably, the two pore systems inter-connect, or are at least uniformly distributed so that they are in close proximity. Diffusion of organosulfur compounds such as thiophenic molecules into the small pores would be inhibited by size (shape-selective exclusion). The large pores (large micropore or mesopore range) would preferably allow fast diffusion and reaction of bulky polycyclic aromatic and sulfur compounds. The thiophenic molecules could enter the large pores, but not the small pores. However, H_2 molecules can readily enter both types of pores, dissociatively adsorb on metal contained within, and be transported between pore systems by spillover. When the metal in the large pores becomes inactivated by adsorbed sulfur, spillover hydrogen could recover the poisoned metal sites by elimination of R–S–R and R–S–H. It is also of interest to classify sulfur resistance as either type I, resistance to organic sulfur compounds, or type II, resistance to inorganic H_2S [211]. The metal species, particularly those in small pores, should have higher type II sulfur resistance.

Fig. 28 shows a simplified representation of the proposed new concept [211,212]. In our laboratory, we are exploring new catalysts and further developing our proposed LT-HDA concept for design of sulfur-resistant noble metal catalyst for low-temperature hydrotreating and dearomatization [211–216]. It appears that several companies in petroleum refining and catalyst industry are exploiting this LT-HDA catalyst design concept [217–219], and a paper studying this design concept was published by an industrial researcher in Japan [217] based on initial publications [211–213].

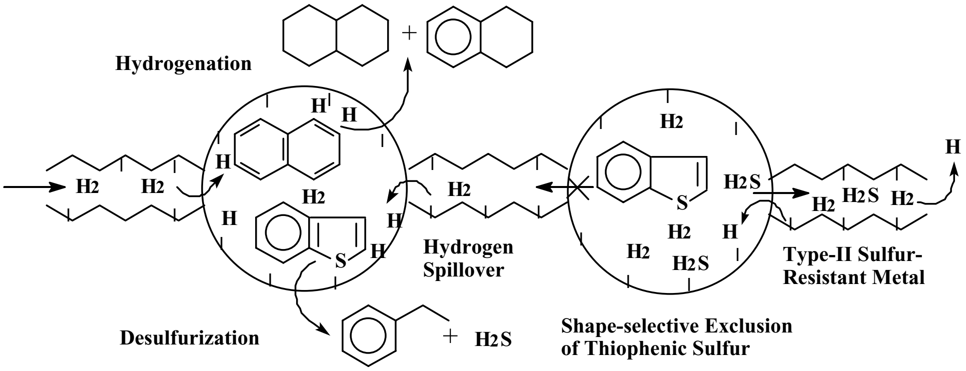


Fig. 28. The proposed new concept for catalyst design based on shape-selective exclusion, hydrogen spillover, and two types of sulfur resistance. The black dots indicate metal particles on internal surface [211].

7. Conclusions

Heightened concerns for cleaner air and increasingly more stringent regulations on sulfur contents in transportation fuels and non-road fuels will make desulfurization more and more important. The sulfur problem is becoming more serious in general, because the regulated sulfur contents are getting an order of magnitude lower, while the sulfur contents of crude oils refined in the US are becoming higher.

The challenge for gasoline deep desulfurization is the selective HDS of thiophenic compounds in FCC naphtha without a significant loss in octane number and in yield of naphtha. Octane loss can be avoided by preserving olefinic components in FCC naphtha, or by isomerizing paraffinic components of naphtha after deep HDS. More selective catalysts for naphtha desulfurization without hydrogenating olefins can further improve the desulfurization efficiency to meet EPA 2006 regulations (<30 ppm sulfur in gasoline). New approaches, such as reactive adsorption for sulfur capture at high temperatures, may become necessary with further deeper desulfurization for next higher level of sulfur reduction (<10 ppm sulfur). Selective adsorption at ambient temperatures without using H_2 may be promising for reaching near-zero sulfur (<1 ppm) for fuel-cell applications.

The challenge for deep desulfurization of diesel fuels is the difficulty of removing refractory sulfur compounds, particularly 4,6-DMDBT, with conventional HDS processes. The problem is exacerbated by the inhibiting effects of polyaromatics and nitrogen compounds as well as H_2S on deep HDS. New catalysts that have been developed in the recent past focus on higher activity for hydrogenation to enhance 4,6-DMDBT conversion and higher activity for HDN (for removal of nitrogen compounds at low concentrations). New and improved catalysts with higher hydrogenation activity coupled with improved reactor operation under more severe conditions can improve deep HDS for meeting EPA 2006 regulations (15 ppm sulfur in highway diesel by 2006 and in non-road diesel by 2010). Some new processing approaches show advantages with further deeper desulfurization (<5 ppm sulfur). For both jet fuel and diesel fuels, selective adsorption at ambient temperatures without using H_2 may be promising for reaching near-zero sulfur (<1 ppm) for fuel-cell applications.

New design approaches are necessary for more efficient production of near-zero sulfur (<1 ppm) ultra-clean fuels. The chemistries of gasoline and diesel fuel processing have evolved significantly around the central issue of how to produce cleaner fuels in a more efficient, environmentally friendly and affordable fashion.

The global society is stepping on the road to zero sulfur fuel, with only differences in starting point of sulfur level and rate of sulfur reduction between different countries. Therefore, researchers should begin with the end in mind and try to develop long-term solutions.

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Glossary

CDHDS: Catalytic distillation for desulfurization, developed by CDTech.
CDHydro: Catalytic distillation for hydrogenation, developed by CDTech.
EPA: Environmental protection agency.
FCC: Fluid catalytic cracking.
FPD: Flame photometric detector, for sulfur-specific analysis.
HCN: Heavy cat naphtha cut from FCC.
HDN: Hydrodenitrogenation.
HDS: Hydrodesulfurization.
IBP: Initial boiling point.
ICE: Internal combustion engines.
ICN: Intermediate cat naphtha cut from FCC.
IRVAD: A process for adsorption desulfurization announced by Black Veatch and Pritchard Corp.
ISAL: Desulfurization process for gasoline, developed by INTEVEP and UOP.
LCN: Light cat naphtha cut from FCC.
LCO: Light cycle oil from fluid catalytic cracking.
LPG: Liquefied petroleum gas.
LT-HDA: Low-temperature hydrotreating and dearomatization.
MBPD: Million barrels per day.
MCN: Medium cat naphtha cut from FCC.
NEBULA: New bulk activity catalyst developed jointly by Akzo Nobel, Nippon Ketjen and ExxonMobil.

OCTGain: Desulfurization process for gasoline, developed and initially commercialized in 1991 by Mobil (now ExxonMobil).

PADD: Petroleum Administration for Defense Districts.

ppmw: Parts per million by weight.

Prime G+: Desulfurization process for gasoline, developed by IFP (Intitute Francais du Petrole).

PSU-SARS: Selective adsorption for removing sulfur, being developed at the Pennsylvania State University.

S-Zorb: A process for reactive adsorption desulfurization developed by Phillips Petroleum (now ConocoPhillips Petroleum).

SARS-HDSCS: Integrated process consisting of selective adsorption for removing sulfur and HDS of concentrated sulfur fraction recovered by desorption being developed at the Pennsylvania State University.

SCANfining: Selective cat naphtha hydrofining process developed by Exxon (now ExxonMobil).

SCFB: Standard cubic feet per barrel of liquid feed.

SRGO: Straight (distillation) run gas oil.

SynSat: Distillate fuel hydrotreating and saturation process developed jointly by ABB Lummus and Criterion.

SynShift: Distillate fuel hydrotreating and saturation coupled with selective ring opening, process developed jointly by ABB Lummus and Criterion.

TReND: Transport reactor for naphtha desulfurization, developed by Research Triangle Institute.