

## Chapter 11

# **ULTRA-CLEAN DIESEL FUELS BY DEEP DESULFURIZATION AND DEEP DEAROMATIZATION OF MIDDLE DISTILLATES**

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### **1. INTRODUCTION**

Increasing attention worldwide is being paid to chemistry of diesel fuel processing. This heightened interest is related to both the thermal efficiency and the environmental aspects, which include both the pollutants and greenhouse gas emissions. Clean fuels research including desulfurization and dearomatization has become an important subject of environmental catalysis studies worldwide. The U.S. Clean Air Act Amendments of 1990 and new regulations by the U.S. 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.<sup>1-4</sup> In the mean time, the demand for transportation fuels has been increasing in most countries for the past two decades. According to a recent analysis, diesel fuel demand is expected to increase significantly in the early part of the 21st century and both the U.S. and Europe will be increasingly short of this product.<sup>5</sup> Sulfur content in diesel fuel is an environmental concern because, upon combustion, sulfur is converted to SO<sub>x</sub> during combustion which not only contributes to acid rain, but also poisons the catalytic converter for exhaust emission treatment.

Sulfur content is usually expressed as the weight percent (wt %) of sulfur in the fuel, since there are many different sulfur-containing compounds in petroleum-derived fuels. Dramatic changes occurred in many countries concerning diesel sulfur regulations in the past decade.<sup>6</sup> The maximum sulfur

content of highway diesel fuel in the U.S. was reduced by regulations, from about 0.20-0.50 wt% in late 1980s<sup>7-8</sup>, to 0.05 wt% on October 1, 1993 for all highway (on-road) diesel fuels<sup>3</sup>. The sulfur content of diesel fuel in Western Europe was limited to 0.3 wt% in 1989, to 0.2 wt% in 1994, and further reduced to 0.05 wt% from October 1, 1996. The diesel sulfur content in Japan was reduced by regulation from 0.4 wt% to  $\leq 0.2$  wt% in 1993, and further to  $\leq 0.05$  wt% in 1997. Canadian government regulations required all diesel fuels sold must contain no more than 0.05 wt% sulfur since January 1998.

Tables 1 and 2 show the current US EPA regulations for gasoline<sup>9-11</sup> and diesel fuels<sup>11-13</sup>, including non-road diesel fuels<sup>14</sup>, respectively, along with earlier fuel specification data in the US for comparison<sup>15-17</sup>. Currently the fuel specifications for all highway diesel fuels in the U.S., Japan, and Western Europe limit the sulfur content of the diesel fuels to less than 0.05 wt% or 500 parts per million by weight of sulfur (ppmw). The new government regulations in many countries will further lower the contents of sulfur and aromatics in the year 2004-2007.<sup>12</sup> In January 2001, the U.S. EPA announced new rules that will require a 97% reduction in sulfur content of highway diesel fuel to 15 ppmw from current 500 ppmw, starting from June 2006<sup>18</sup>. New gasoline sulfur regulations will require most refiners to meet a 30 ppmw sulfur average with an 80 ppmw cap for both conventional and reformulated gasoline by January 1, 2006.<sup>9-10</sup>

Table 1. US EPA Tier II Gasoline Sulfur Regulations as of 2002

Category	Year				
	1988 <sup>a</sup>	1995 <sup>b</sup>	2004 <sup>c</sup>	2005 <sup>c</sup>	2006 <sup>c</sup>
Compliance as of year					
Refinery average, ppmw	1000 <sup>a</sup> (maximum)	330 <sup>b</sup> ( $<330$ ppm S and $<29.2\%$ aromatics required for national certification; $< 850$ ppm S and $<41.2\%$ aromatics as national maximum)	--	30	30
Corporate average, ppmw			120	90	--
Per gallon cap, ppmw			300	300	80

Source: (a) SAE, Automotive Gasoline - SAE J312 Oct88, Society of Automotive Engineers, Warrendale, PA, February, 1992; (b) K. Owen, and T. Coley, Automotive Fuels Reference Book, 2<sup>nd</sup> Ed., Society of Automotive Engineers, Warrendale, PA, 1995; (C) US EPA, 2001.

Table 2. US EPA Sulfur Regulations for Diesel and Jet Fuels as of April 2003

Category	Year			
	1989 <sup>a</sup>	1993 <sup>b</sup>	2006 <sup>b</sup>	2010 <sup>b</sup>
Compliance as of year				
Highway diesel, ppmw	5000 <sup>a</sup> (Maximum for No. 1-D & 2-D, with minimum cetane No. of 40)	500 (Current upper limit since 1993)	15 (Regulated in 2001; exclude some small refineries)	15 (Regulated in 2001; apply to all US refineries)
Nonroad diesel, ppmw	20000 <sup>a</sup>	5000 (Current upper limit)	500 (Proposed in 2003 for 2007)	15 (Proposed in 2003 for 2010)
Jet fuel, ppmw	3000	3000	?	?

Source: (a) SAE, Diesel Fuels - SAE J313 Jun89, Society of Automotive Engineers, Warrendale, PA, February, 1992; (b) US EPA, 2003.

More recently, the EPA has announced plan to reduce non-road diesel fuel sulfur from the current average of 3400 ppm to 500 ppm by 2007 and further to 15 ppm by 2010<sup>14</sup>. The U.S. Clean Air Act Amendments of 1990 and related new fuel regulations by the U.S. 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 statistic data.<sup>19-23</sup> 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 [EIA/IEA, 2002]. The total US consumption of petroleum products reached 19.59 MBPD in 2001, about a 39 % increase from 1971 (14.11 MBPD).<sup>19</sup> Of the petroleum products consumed in the US in 2001, 8.59 MBPD was supplied as motor gasoline, 3.82 MBPD as distillate fuels, including 2.56 MBPD as highway diesel fuels and 1.26 MBPD as off-road fuels and industrial fuels, 1.65 MBPD as jet fuel, 0.93 MBPD as residual fuel oil, and 1.13 MBPD as liquefied petroleum gas (LPG), and 3.47 MBPD for other uses in the US.<sup>19</sup>

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 U.S. 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 U.S. known as the 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.<sup>21-23</sup> In the past 2 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 US refineries increased from 12.47 MBPD in 1981 (11.20 MBPD in 1971) to 15.13 MBPD in 2001.<sup>19</sup>

*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 per 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 per day	16.06	16.71	19.59
Total worldwide petroleum consumption, million barrel per day	60.90	66.72	77.12

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.<sup>24</sup> 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 from FCC is used in the diesel pool in the US, which has higher contents of more refractory sulfur compounds (see below). H<sub>2</sub> demand increase is another challenge to the refinery operations. Hydrogen deficits are processing restraints and will impact future hydrotreating capabilities and decisions.<sup>25</sup>

The heightened interests in ultra-clean fuels are also due to the need for using new emission control technologies for IC engines (especially those for diesel fuels), and for using on-board or on-site reforming of hydrocarbon fuels for fuel cells. Our studies on clean fuels have focused on deep desulfurization and dearomatization of diesel and jet fuels as well as gasoline<sup>26-36</sup>. One new application area which presents a great challenge to ultra-deeper desulfurization of liquid hydrocarbon fuels is the hydrocarbon fuel processor for proton-exchange membrane fuel cells, which require essentially zero-sulfur fuels such as gasoline and diesel fuels<sup>26,27,30,37</sup>. The general chemistry of diesel fuels is covered in a recent book<sup>33</sup>. This Chapter is a selective overview on new design approaches and associated catalysis and chemistry as well as processes for deep desulfurization and deep hydrogenation of hydrocarbon fuels, particularly diesel fuels.

## 2. SULFUR COMPOUNDS IN TRANSPORTATION FUELS

There are three major types of transportation fuels: gasoline, diesel and jet fuels that differ in composition and properties. The common types of sulfur compounds in liquid fuels are listed below.

- Gasoline Range: Naphtha, FCC-naphtha (Selective HDS)
  - Mercaptanes RSH; Sulfides R<sub>2</sub>S; Disulfides RSSR
  - Thiophene and its alkylated derivatives
  - Benzothiophene
- Jet Fuel Range: Heavy naphtha, Middle distillate
  - Benzothiophene (BT) and its alkylated derivatives
- Diesel Fuel Range: Middle distillate, Light cycle oil
  - alkylated benzothiophenes
  - Dibenzothiophene (DBT) and its alkylated derivatives
- Boiler Fuels Feeds: Heavy oils and distillation residues
  - ≥3-ring Polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT), phenanthro[4,5-b,c,d]thiophene (PT) and their alkylated derivatives

Table 4. Volume Fraction of U.S. Highway Diesel Pool from Each Feedstock Component

Diesel Blendstock	% of U.S. Highway Diesel Fuel Pool per Blendstock 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	0.3	8.1	41.2	2.3	51.9
Straight Run					
Cracked Stock	-	0.1	0.8	2.2	3.1
Hydrotreated	-	2.1	15.6	1.7	19.4
Cracked Stock					
Coker Gas Oil	-	-	1.0	-	1.0
Hydrotreated	0.1	2.1	3.7	2.3	8.2
Coker Gas Oil					
Hydrocrackate	-	1.3	2.7	-	4.0

Source: EPA, EPA420-R-00-026, 2000.

Table 4 shows the volume fraction of U.S. highway diesel pool, and Table 5 shows the corresponding sulfur levels of U.S. highway diesel blendstocks<sup>12</sup>. Among the diesel blendstocks, the light cycle oil (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 (4-MDBT) and 4,6-dimetyldibenzothiophene (4,6-DMDBT)<sup>12</sup>.

Table 5. Sulfur Levels of U.S. Highway Diesel Blendstocks (CA Excluded)

Diesel Blendstock	Sulfur Content (ppmw) by Boiling Fraction					All Boiling Fractions Combined
	Naphtha	Light Distillate	Heavy Distillate	Light Gas Oil	Gas	
Straight Run	827	1770	2269	4980		2218
Hydrotreated straight Run	362	119	394	548		358
Cracked Stock	-	2219	2892	6347 <sup>c</sup>		5322
Hydrotreated Cracked Stock	18	37	939	1306 <sup>c</sup>		874
Coker Gas Oil	540	1800	3419	-		3419 (?)
Hydrotreated Coker Gas Oil	8	25	310	400		258
Hydrocrackate	-	12	120	-		85

C: Indicating 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 blendstocks by assuming the same relative sulfur levels between boiling fractions. Source: EPA, EPA420-R-00-026, 2000.

There are various 2-ring and 3-ring sulfur compounds in middle distillates from various refinery streams that can be used to make middle distillate fuels—diesel fuels and jet fuels. Kabe and coworkers have analyzed the sulfur compounds in a light gas oil and hydrotreated gas oils using gas-chromatography with atomic emission detector (GC-AED) and GC-mass spectrometer (GC-MS)<sup>38-39</sup>. They identified 42 alkylated benzothiophene compounds and 29 alkylated dibenzothiophene compounds in the oil. Among them the 4,6-DMDBT was found to remain even after deep hydrodesulfurization<sup>38,40</sup>. Ma et al. have analyzed the sulfur compounds in a gas oil and a non-polar fraction of vacuum gas oil<sup>41-43</sup>. They found that the major sulfur compounds are alkyl benzothiophenes in the gas oil, and alkyl thiophenes, alkyl benzothiophenes, alkyl DBT, alkyl BNT and alkyl PT in the vacuum gas oil. The dibenzothiophenes with two alkyl substituents at 4- and 6-positions, respectively, were found to be the most difficult to remove from the oils. Hsu and coworkers have performed mass spectrometric analysis of many diesel fuels and petroleum fractions<sup>44,45</sup>. They have identified not only the major compounds in all classes, but also trace amounts of heteroatom-containing compounds. Trace amounts of nitrogen compounds in diesel fuels include indoles, carbazoles, quinolines, acridines, and phenanthridines. The oxygen compounds include alkylated phenols and dibenzofurans. Formulated diesel fuels also contain trace amounts of additives.

Figure 1 shows the GC-FPD chromatograms of the three transportation fuel samples analyzed in our laboratory.<sup>26,27</sup> For obtaining the results in Figure 1, we have conducted a detailed analysis to identify the type of sulfur compounds and their alkylated isomers in a commercial gasoline sample and a commercial diesel fuel sample, which were purchased in 2001 from a local fuel station in State College, Pennsylvania, and a JP-8 type jet fuel sample from

Wright Laboratory of US Air Force. The identification of different alkylated polycyclic sulfur compounds and their isomers is complicated, since there are few commercially available standards and their mass spectra (e.g., fragmentation patterns) are often similar for most isomers of alkyl thiophenic compounds. In our group, we did the identification of the sulfur components in the gasoline, jet fuel and diesel fuel based on a combination of various techniques, standard sample, HPLC separation<sup>43</sup>, sulfur-selective ligand exchange chromatography<sup>43</sup>, GC-MS<sup>41,43</sup>, retention time comparison with the literature data<sup>46,47</sup>, reactivities of various sulfur compounds in HDS<sup>41,42</sup> and understanding of the elution order of the isomers<sup>48</sup>.

As shown in Figure 1, the major sulfur compounds existing in the commercial gasoline are thiophene, 2-methylthiophene, 3-methylthiophene, 2,4-dimethylthiophene and benzothiophenes, indicating that most sulfur compounds with higher HDS reactivity, including thiols (mercaptanes), disulfides and sulfides, have been removed in current processes for making the commercial gasoline. The major sulfur compounds in the commercial and military jet fuel JP-8 are dimethylthiophenes and trimethylthiophenes with two methyl groups at the 2- and 3-positions, respectively, implying that these alkyl benzothiophenes are more difficult to be removed than their isomers. No alkyldibenzothiophenes were detected in the JP-8. The sulfur compounds in the commercial diesel fuel include alkyl benzothiophenes and alkyl dibenzothiophenes, but the major sulfur compounds are the alkyl dibenzothiophenes with alkyl groups at the 4- or/and 6-positions, indicating that the major sulfur compounds remaining in the commercial diesel fuel are the refractory sulfur compounds, which are difficult to be removed by the conventional HDS process.

Figure 1 also clearly demonstrates that sulfur compounds tend to become larger in ring size and higher in number of substitutes as the fuel becomes higher in boiling point ranges from gasoline to jet fuels to diesel fuels. The current sulfur contents in highway (on-road automotive) diesel fuel and gasoline are limited to 500 ppm and 350 ppmw, respectively, by regulations in the U.S. The jet fuel sulfur is limited to 3000 ppmw. The sulfur content of off-road diesel fuels is limited to 2000 to 3000 ppmw. The real sulfur contents in commercially available gasoline and diesel fuel samples are typically lower than the regulatory upper limits. This statement applies to commercial and military jet fuels as well. The average content of sulfur in typical jet fuels was reported to be 490 ppmw.<sup>49</sup>

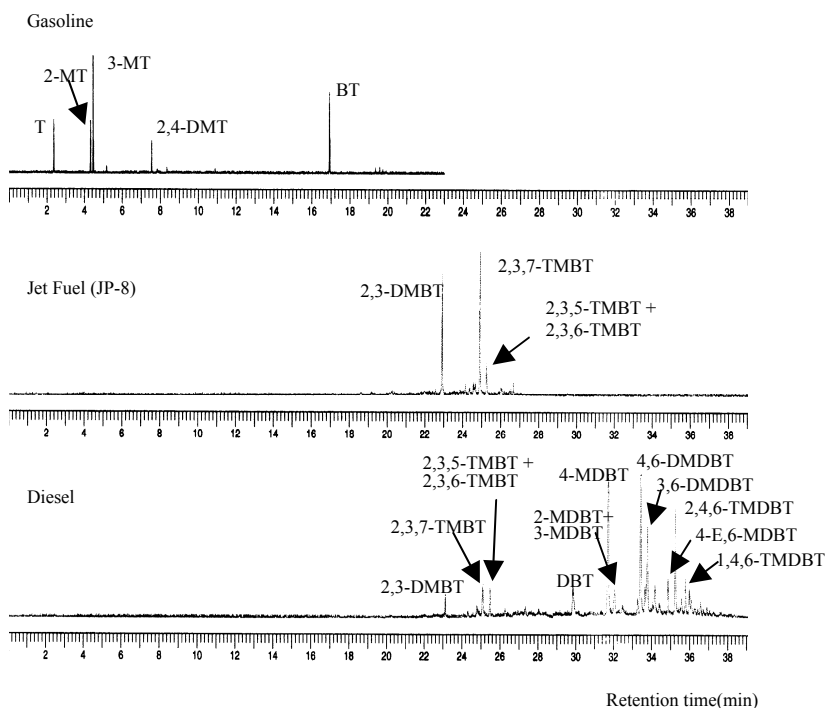


Figure 1. GC-FPD Chromatograms of Commercial Gasoline, Jet Fuel and Diesel

### 3. CHALLENGES OF ULTRA DEEP DESULFURIZATION OF DIESEL FUELS

#### 3.1 Reactivities of Sulfur Compounds in HDS

Figure 2 shows the qualitative relationship between reactivities of sulfur compounds and their ring size and substitution patterns. It covers the gasoline, jet fuel and diesel fuel ranges. Figure 2 illustrates that there are major differences in reactivity of sulfur compounds depending on both their ring size and substitution pattern. In particular, differences in the position of alkyl groups on benzothiophene and on dibenzothiophene can have major impacts on their reactivity due to steric hindrance. The organic sulfur compounds present in petroleum vary widely in their reactivities in catalytic hydrodesulfurization. Deeper hydrodesulfurization (HDS) is not a simple increase in conversion of total sulfur compounds by a pseudo first order. There are many different sulfur compounds in diesel fuels. Earlier research has shown that certain sulfur compounds are easier to convert. The reactivities



of the 1- to 3-ring sulfur compounds decrease in the order of thiophenes > benzothiophenes > dibenzothiophenes<sup>50-54</sup>. 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<sup>55,56</sup>.

Figure 3 shows the GC-FPD chromatograms that illustrate reactivities of various sulfur compounds in gas oil HDS for diesel fuel production. In deep HDS, the conversion of these key substituted dibenzothiophenes largely determines the required conditions. In gas oils, the reactivities of (alkyl-substituted) 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are much lower than those of other sulfur-containing compounds<sup>38,41,56,57</sup>. Gates and Topsoe<sup>56</sup> pointed out in 1997 that 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are the most appropriate compounds for investigations of candidate catalysts and reaction mechanisms.

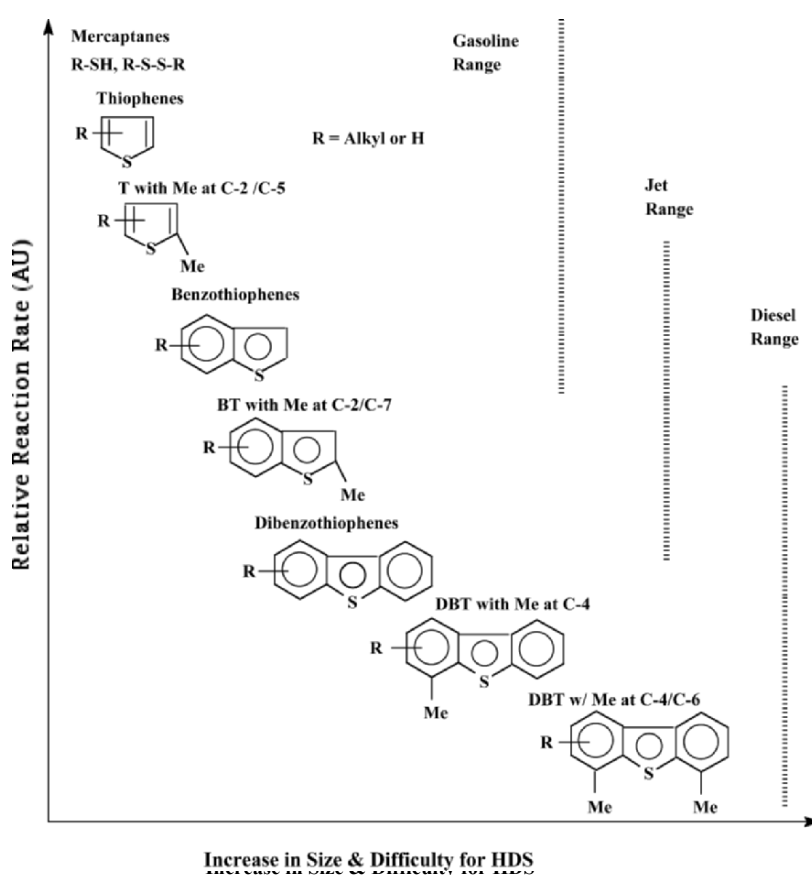


Figure 2. Dependence of reactivity of sulfur compounds vs their ring size and substitution patterns (for sulfur compounds in gasoline, jet fuel and diesel fuel feedstock)<sup>37</sup>.

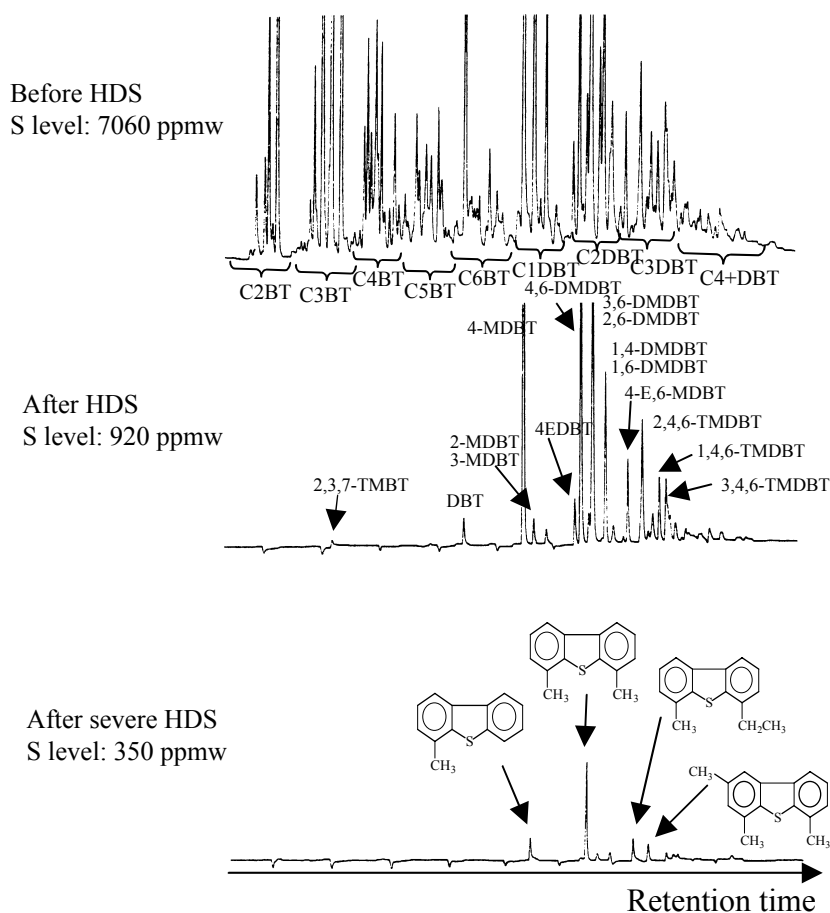


Figure 3. GC-FPD Chromatograms showing Reactivities of Various Sulfur Compounds in Gas Oil in HDS<sup>181</sup>

While the new regulation will further reduce the environmental impact of diesel emissions, it creates a major technical challenge for fuel processing<sup>58,59</sup>. It is the most refractory sulfur species that remains in the diesel fuel after the sulfur reduction to 500 ppmw level by conventional hydrodesulfurization<sup>38,41,42,56,57,60,61</sup>. For desulfurization of sulfur species in it gasoline, is not difficult to remove the sulfur compounds in the naphtha range by current catalytic HDS processes. For the U.S. refineries, most sulfur in the gasoline pool is found in FCC naphtha. The challenge in deep desulfurization of FCC naphtha is selective conversion of sulfur compounds without saturation of olefinic compounds, which contribute to octane number enhancement. For straight run kerosene that is used for making jet fuels, the sulfur removal by HDS is

more difficult than that from naphtha, but less difficult compared to that from gas oil.

Recently, investigations have demonstrated that sulfur compounds remaining in diesel fuels at sulfur levels lower than 500 ppm are the dibenzothiophenes (DBTs) with alkyl substituents at the 4- and/or 6-position, and are lower in HDS reactivity<sup>38,41,42,56,62</sup>. These species are termed refractory sulfur compounds. Both steric hindrance and electronic factors are responsible for the observed low reactivity of 4- and 6-substituted DBTs<sup>63,64</sup>.

Based on recent studies on gas oil HDS<sup>41,57</sup>, the sulfur compounds can be classified into four groups according to their HDS reactivities that were described by the pseudo-first-order rate constants. The first group is dominantly alkyl BTs; the second, DBT and alkyl DBTs without alkyl substituents at the 4- and 6-positions; the third, alkyl DBTs with only one alkyl substituent at either the 4- or 6-position; the fourth, alkyl substituents at the 4- and 6- positions (as shown in Scheme 1). The sulfur distribution of the four groups in the gas oil is 39, 20, 26 and 15 wt %, respectively, and the relative rate constant of HDS for each of the four groups is 36, 8, 3, and 1, respectively<sup>41,57</sup>.

Figure 4 shows the relative reactor volume requirements for various degrees of sulfur removal by conventional single-stage HDS of diesel fuels. The estimation of volume requirements is based on the results from HDS kinetics studies using a commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst 41, assuming 1.0 wt% S in feed. When the total sulfur content is reduced to 500 ppmw, the sulfur compounds remaining in the hydrotreated oil are the third and fourth group sulfur compounds. When the total sulfur content is reduced to 30 ppmw, the sulfur compounds remaining in the hydrotreated oil are only the fourth group sulfur compounds, indicating that the less the sulfur content is the lower the HDS reactivity, which has been discussed by Whitehurst et al. in their review<sup>60</sup>. More recent studies using various straight-run gas oils from different crude oils confirmed the differences in reactivity between different sulfur compounds<sup>65,66</sup>.

To put these problems into perspective based on conventional approaches for HDS of diesel fuels, for reducing the sulfur level from current 500 ppmw to 15 ppmw (the regulation in 2006) by conventional HDS processing, the volume of catalyst bed will need to be increased by 3.2 times as that of the current HDS catalyst bed. This is consistent in general with the analysis on a typical Co-Mo catalyst by Haldor Topsøe regarding the required increase in catalyst activity and bed temperature for further reduction of sulfur from 500 to 50 ppmw<sup>61,67</sup>. Furthermore, as shown in Figure 3, for reducing the sulfur level to 0.1 ppmw by conventional HDS process for fuel cell applications, the volume of catalyst bed will need to be increased by about 7 times. Increasing the volume of the high-temperature and high-pressure reactor is very expensive. In another scenario, with current commercial HDS processes

without changing the reactor volume the catalyst activity will have to be increased by a factor of 3.2 and 7 to meet the new regulation and fuel cell applications, respectively. It is difficult to meet such a demand by making small incremental improvements in the existing hydrotreating catalysts that have been developed during the last 50 years.

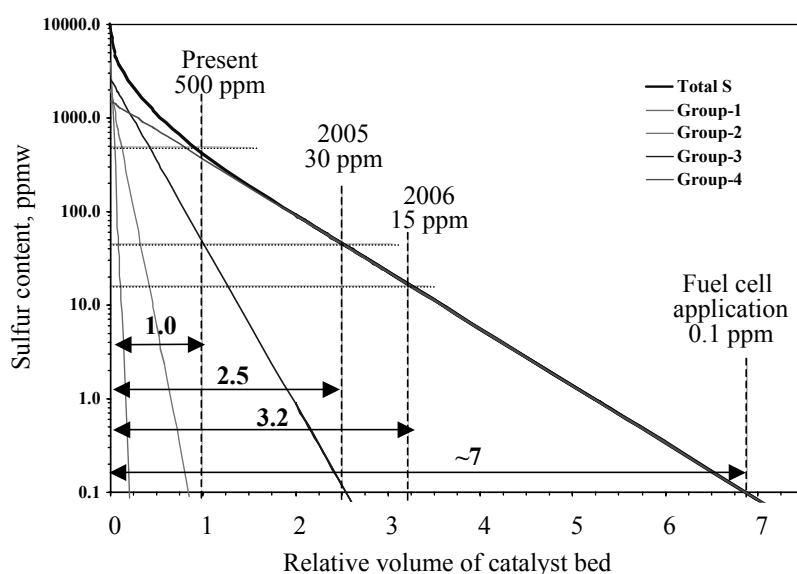


Figure 4. Simulated HDS of diesel to meet 15 and 0.1 ppm level on the basis of a conventional single-stage reactor, assuming 1.0 wt% S in feed; HDS kinetic model:  $C_{S, total} = C_{S10} e^{-k1t} + C_{S20} e^{-k2t} + C_{S30} e^{-k3t} + C_{S40} e^{-k4t}$

The NPRA (National Petroleum Refiners Association) estimates that imposing a 15-ppmw sulfur maximum on diesel could result in a 10% to 20% shortfall in supply<sup>68</sup>. The above trends and discussion indicate that the petroleum refining industry is facing a major challenge to meet the new stricter sulfur specifications for producing ultra clean transportation fuels in the early 21<sup>st</sup> century<sup>69</sup> when the quality of the crude oils continue to decline in terms of increased sulfur content and decreased API gravity.

### 3.2 Mechanistic Pathways of HDS

Substantial progress has been made in fundamental understanding and practical applications of hydrotreating catalysis and metal sulfide-based catalysts for HDS, as discussed in several excellent reviews<sup>40,60,61,64,67,70,71</sup>. The following discussion focuses on deep desulfurization of polycyclic sulfur compounds as shown in Scheme 1.

HDS of thiophenic compounds proceeds through two pathways: hydrogenation pathway (hydrogenation followed by hydrogenolysis) and the

direct hydrogenolysis pathway (direct elimination of S atom via C-S bond cleavage)<sup>31,32,62,72-77</sup>. A third pathway is isomerization of alkyl groups on the rings which affect the HDS conversion and selectivity<sup>31</sup>. Hydrogenation and hydrogenolysis may occur at different active sites. Polyaromatic compounds have been found to be the main inhibitors towards the hydrogenation pathway<sup>78-81</sup>. Girgis and Gates published an excellent review on reactivities of various compounds and their reaction networks as well as kinetics of high-pressure catalytic hydroprocessing<sup>53</sup>. Kabe et al.<sup>82</sup> compared the reactivities of DBT, 4-MDBT and 4,6-DMDBT under deep hydrodesulfurization conditions (sulfur concentration < 0.05 wt.%) using Co-Mo/Al<sub>2</sub>O<sub>3</sub>. The conversion of DBTs into cyclohexylbenzenes (CHBs) was nearly the same while that of DBTs into biphenyls (BPs) decreased in order DBT > 4-MDBT > 4,6-DMDBT. Data for DBTs could be arranged by the Langmuir-Hinshelwood rate equation. Activation energies of DBT, 4-MDBT and 4,6-DMDBT were 24, 31 and 40 kcal/mol, respectively<sup>82</sup>. Heats of adsorption for DBT, 4-MDBT and 4,6-DMDBT were 12, 20 and 21 kcal/mol, respectively<sup>82</sup>. Kabe et al. proposed that 4-MDBT or 4,6-DMDBT can be adsorbed on the catalyst through a pi-electron in the aromatic rings more strongly than that of DBT, and that the C-S bond cleavage of adsorbed DBTs is disturbed by steric hindrance of the methyl group<sup>82</sup>. Previous studies by Mochida and coworkers<sup>62,83-85</sup> have demonstrated that over the industrial HDS catalysts, the refractory sulfur compounds, particularly 4,6-DMDBT, are desulfurized dominantly by the hydrogenation pathway as the alkyl groups at the 4 and/or 6-position of DBT strongly blocks the hydrogenolysis pathway. The rate constant of DBT and 4,6-DMDBT for hydrogenation pathway is similar, being 0.015 and 0.010 min<sup>-1</sup> over a commercial Co-Mo catalyst, while the rate constant of 4,6-DMDBT for hydrogenolysis pathway is 0.004 min<sup>-1</sup>, less than that of DBT (0.048) by 12 times. Quantum chemical calculation on the conformation and electronic property of the various sulfur compounds and their HDS intermediates by Ma et al. shows that the hydrogenation pathway favors desulfurization of the refractory sulfur compounds by both decreasing the steric hindrance of the methyl groups and increasing the electron density on the sulfur atom in the sulfur compounds<sup>63</sup>. As desulfurization of the refractory sulfur compounds occurs dominantly through the hydrogenation pathway, the inhibition of the coexistent aromatics towards HDS of the refractory sulfur compounds by competitive adsorption on the hydrogenation active sites becomes stronger in deep HDS<sup>80,81</sup>. H<sub>2</sub>S produced from reactive sulfur compounds in the early stage of the reaction is one of the main inhibitors for HDS of the unreactive species.<sup>41,86</sup>

Computer modeling and simulation in the active sites on the catalyst surface and their interaction with sulfur compounds have also been applied in our laboratory to understand the reaction pathways and mechanism<sup>87-90</sup>. Figure 5 shows 2 types of chemisorption patterns of 4,6-DMDBT on MoS<sub>2</sub>, the flat adsorption and S-μ<sub>3</sub> type adsorption. Semi-empirical calculations have

been carried out to illustrate the difference in chemisorption patterns between DBT and 4,6-DMDBT. Both DBT and 4,6-DMDBT can interact well with 3030 edge of MoS<sub>2</sub> catalyst by flat chemisorption. The chemisorption of 4,6-dialkyldibenzothiophenes, different from that of the DBTs without any alkyl group at both 4- and 6-positions, is difficult by the S- $\mu_3$  type coordination due to the steric hindrance of the alkyl groups. This steric hindrance is expected to increase with increasing size of the alkyl groups (from methyl to ethyl to propyl). Milenkovic et al.<sup>91</sup> synthesized various alkyldibenzothiophenes bearing bulky groups in positions 4 and 6 and compared their sensitivity to HDS over a NiMo/Al<sub>2</sub>O<sub>3</sub> industrial catalyst in a batch reactor at 573 K and under 5 MPa H<sub>2</sub> pressure. It was further demonstrated that their reactivity is correlated to the steric hindrance near the sulfur atom. Some recent studies were directed at understanding the surface reaction pathways for deep HDS of alkyldibenzothiophenes<sup>92</sup>.

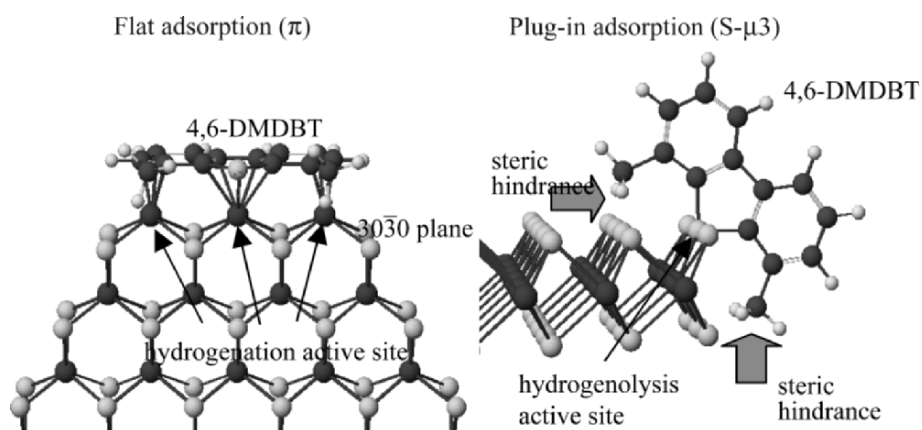


Figure 5. Adsorption conformations of 4,6-DMDBT at the hydrogenation active site and the hydrogenolysis active site. There is a strong steric hindrance in the plug-in adsorption<sup>181</sup>.

#### 4. DESIGN APPROACHES TO ULTRA DEEP DESULFURIZATION

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. One or more approaches may be employed by a refinery to meet the challenges of producing ultra-clean fuels at affordable cost.

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<sup>70,71</sup>. 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<sub>2</sub> 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 to MoS<sub>2</sub> structure lowers the sulfur binding energy at the edges and thereby provides more active sites<sup>93</sup>. Recently, the formation of sulfur vacancy in MoS<sub>2</sub> under H<sub>2</sub> atmosphere has been observed directly for the first time by scanning tunneling electron microscope (STM)<sup>94</sup>. Comparison of STM images for Mo sulfide based particles with and without cobalt promoter atoms shows that without cobalt, the MoS<sub>2</sub> particles assume a neat triangular shape. Once cobalt enters the crystals, the particles become truncated hexagons--triangles with clipped-off vertices.<sup>94</sup> 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<sup>70</sup>, and this trend has been observed also for Co-Mo/MCM-41 and Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts based on DBT HDS and FT-IR of chemisorbed NO<sup>33</sup>.

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); the type I structure is assumed to be bonded to support through Mo-O-Al linkages and has less stacking, whereas the type II structure has higher stacking and few linkages with support<sup>71</sup>. 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 type I and type II structures are the same. Daage and Chianelli reported that the top and bottom layers (rim) of unsupported MoS<sub>2</sub> 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<sub>2</sub> layers<sup>64</sup>. They proposed a rim-edge model, and explained that the flat pi-adsorption on MoS<sub>2</sub> 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.

## 4.1 Improving Catalytic Activity by New Catalyst Formulation

Design approaches for improving catalytic activity for ultra deep hydrodesulfurization 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<sub>2</sub>S 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<sub>2</sub>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 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 to CoMo or Co to 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<sup>33,60,61,67</sup>. For example, some recent studies examined carbon-supported CoMo catalysts for deep HDS<sup>81,95,96</sup>. Binary oxide supports such as TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> have been examined for making improved HDS catalysts<sup>97-99</sup>.

In 1992, novel mesoporous molecular sieve MCM-41 was invented by Mobil researchers<sup>100,101</sup>. 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<sup>102-104</sup> and applied to prepare Co-Mo/MCM-41 for deep HDS of diesel fuels<sup>31,32,105,106</sup> and for HDS of petroleum resid<sup>104</sup>.

The design approach makes use of high surface area of MCM-41 for higher activity per unit weight, uniform meso pore to facilitate diffusion of polycyclic sulfur compounds, and mild acidity of Al-containing MCM-41 to facilitate metal dispersion and possible isomerization<sup>31</sup>. We synthesized MCM-41 type aluminosilicate molecular sieves using different Al sources, and established a proper procedure for making acidic MCM-41<sup>31,103</sup>. 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<sup>32,34,35</sup>. Compared to Co-Mo/Al<sub>2</sub>O<sub>3</sub>, higher activity for HDS has been observed for Co-Mo/MCM-41 with a higher metal loading. When MCM-41 with proper SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was used to prepare Co-Mo/MCM-41 at suitable metal loading, the catalyst is much more active for HDS of dibenzothiophene, 4-



methyl- and 4,6-dimethyl dibenzothiophene than a commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>32,34,35</sup>

Figure 6 shows the results for HDS of various polycyclic sulfur compounds in a light cycle oil (LCO) over Co-Mo/MCM-41 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 50) and Co-Mo/Al<sub>2</sub>O<sub>3</sub> (C-344)<sup>107</sup>. The conversions of refractory sulfur compounds in LCO such as 4-MDBT and 4,6-DMDBT are much higher with the Co-Mo/MCM-41 catalyst than with the Co-Mo/Al<sub>2</sub>O<sub>3</sub>. FT-IR spectra of chemisorbed NO on sulfided Co-Mo/MCM-41 and in comparison the sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>108,109</sup> 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<sub>2</sub>O<sub>3</sub> catalyst,<sup>108</sup> since Co site has a distinct NO chemisorption peak<sup>109</sup>. The reason for the higher degree of Co site exposure in Co-Mo on MCM-41 relative to Co-Mo on Al<sub>2</sub>O<sub>3</sub> (based on FT-IR spectra for NO on Co-Mo/MCM-41) remains to be clarified. It is possible that relatively more hydrophobic support could lead to a higher layer of stacking and more Co site on the edge when compared to a more hydrophilic surface such as Al<sub>2</sub>O<sub>3</sub>, 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<sub>2</sub> catalyst can be more active than alumina-supported MoS<sub>2</sub> catalyst for desulfurization of dibenzothiophene-type sulfur compounds. Recently, the use of silicalite MCM-41 without aluminum has also been reported for DBT HDS.<sup>110</sup>

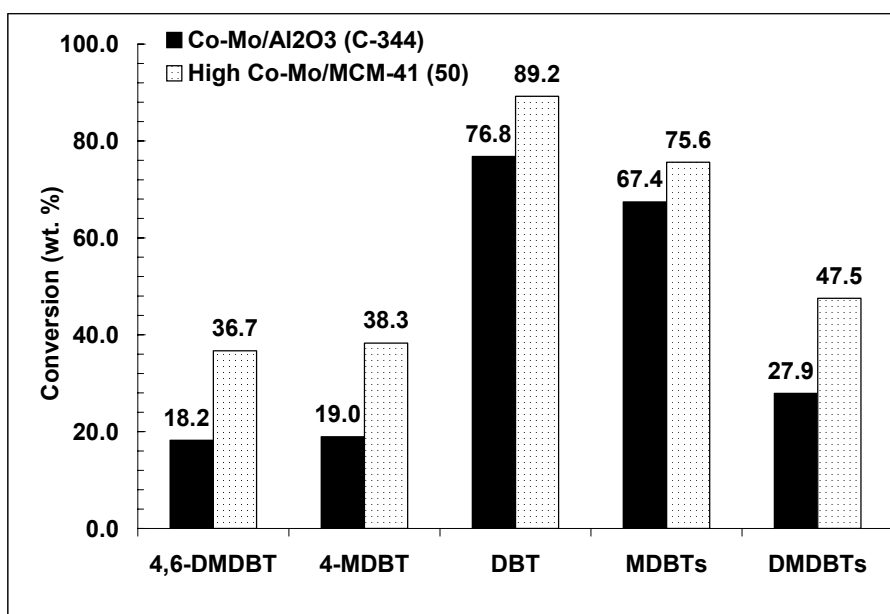


Figure 6. HDS of various PASCs in LCO over Co-Mo/MCM-41 (50) and Co-Mo/Al<sub>2</sub>O<sub>3</sub> (C-344) (Temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h<sup>-1</sup>; hydrogen/hydrocarbon, 300 ml/ml; conversion data obtained after 4 h of time on stream)<sup>107</sup>.

The catalyst development has been one of the focuses of industrial research and development for deep hydrodesulfurization.<sup>69</sup> For example, new and improved catalysts have been developed and marketed by Albemarle, Haldor Topsøe, Criterion, IFP, United Catalyst/Sud-Chemie, Advanced Refining, and ExxonMobil.

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<sup>111</sup>. KF 752 can be considered to be typical of an Akzo Nobel catalyst of the 1992-93 timeframe. KF 756 is a Co-Mo catalyst with high HDS activity; it was jointly developed by Albemarle and Exxon Mobil 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<sup>112</sup>. KF 757 is Albemarle's latest Co-Mo with higher HDS activity and optimized pore structure; it was announced in 1998<sup>111</sup>. Albemarle 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<sup>113</sup>. KF 756 is widely used in Europe (20 % of all distillate hydrotreaters operating on January 1, 1998), while KF 757 has been used in a large number of hydrotreaters commercially<sup>12</sup>. Under more severe conditions (e.g., <50 ppmw sulfur), KF 757 is 35-75 % more active than KF 756.

KF 757 and KF 848 were developed by using what Albemarle calls STARS (Super Type II Active Reaction Sites) technology. Type II refers to a specific kind of catalyst site, which is more effective for removing sulfur from sterically hindered compounds. KF 848 was announced in 2000<sup>113</sup>. KF 848 is 15-50% more active than KF757 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, KF757, and KF 842, respectively<sup>12</sup>. As evidenced by the STARS technology, the advances in basic understanding of fundamental pathways of HDS reactions over transition metal sulfides has also resulted in major advances in commercial catalyst developments.

Researchers at Haldor Topsøe 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<sup>61,70</sup> and the development of new and more active commercial hydrotreating catalysts and processes<sup>67</sup>. Haldor Topsøe 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 with a mixture of straight run and

cracked stocks<sup>12</sup>. In addition to catalyst development, Haldor Topsøe has also developed new processes for HDS.

Criterion Catalyst Company 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-90s<sup>12</sup>. These improvements have come about through better dispersion of the active metal on the catalyst substrate.

Albemarle 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. Albemarle'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<sup>12</sup>.

More recently, NEBULA catalyst has been developed jointly by Exxon Mobil, Albemarle, and Nippon Ketjen and announced in 2001<sup>114</sup>. The NEBULA catalyst is even more active than KF 848 STARS catalyst with respect to HDN and diesel hydrotreating; it has been successfully applied in several diesel hydrotreaters for months as of early 2002<sup>114</sup>. Hydrocracking pretreatment was the first application where very high activity was found for NEBULA-1. 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<sup>115</sup>. 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.

The choice of commercial hydrotreating catalysts, represented by alumina-supported Co-Mo, Ni-Mo and Ni-Co-Mo, depends on the capability of reactor equipments, operating conditions (pressure, temperature), feedstock type and sulfur contents, and desired levels of sulfur reduction. 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<sub>2</sub> 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.

## 4.2 Tailoring Reaction and Processing Conditions

Tailoring process conditions aims at achieving deeper hydrodesulfurization 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 the processing scheme or some capital investment (expansion in catalyst volume or density, H<sub>2</sub>S scrubber from recycle gas, improved vapor-liquid distributor)<sup>116,117</sup>. First, space velocity can be decreased to increase the reactant-catalyst contact time. More refractory sulfur compounds would require lower space velocity for achieving deeper HDS. Second, temperatures can be increased, which increases the rate of HDS. Higher temperatures facilitate more of the high activation-energy reactions. Third, H<sub>2</sub> pressure can be increased. Fourth, improvements can be made in vapor-liquid contact to achieve uniform reactant distribution, which effectively increases the use of the surface area of the catalyst. Fifth, the concentration of hydrogen sulfide in the recycle stream can be removed by scrubbing. Since H<sub>2</sub>S is an inhibitor to HDS, its build-up in high-pressure reactions through continuous recycling can become significant. Finally, more volume of catalyst can be used, either through catalyst bed volume expansion or more dense packing.

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 U.S. 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 hydrodesulfurization 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<sup>12</sup>. Haldor-Topsøe 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<sup>67</sup>. The deactivation rate decreases because the

start-of-run temperature decreases, and the lower LHSV by itself reduces the deactivation rate even at the same temperature.

Increasing the temperature of reaction can enhance the desulfurization of more refractory sulfur compounds. Haldor Topsøe 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 ppmw to 40 ppmw<sup>12</sup>. UOP projects that a 20 °F increase in reactor temperature would decrease sulfur from 140 to 120 ppmw<sup>12</sup>. The downside of increased temperature is reduced catalyst life (i.e., the need to change catalyst more frequently). 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<sup>12</sup>.

The decrease in the concentration of hydrogen sulfide in the gas phase could reduce the inhibition of the desulfurization<sup>41,85,86,118</sup> and hydrogenation reactions. The role of H<sub>2</sub>S in deep HDS of gas oils has been discussed in detail by Sie<sup>119</sup>. H<sub>2</sub>S can be removed by chemical scrubbing. Haldor-Topsøe indicates that decreasing the concentration of hydrogen sulfide at the inlet to a co-current reactor by three to six volume% 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<sup>12</sup>. UOP projects that scrubbing hydrogen sulfide from recycled hydrogen can reduce sulfur levels from roughly 285 to 180 ppmw in an existing hydrotreater<sup>12</sup>.

The increase in hydrogen partial pressure and/or purity can improve hydrodesulfurization and hydrogenation. Haldor-Topsøe 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<sup>12</sup>. Haldor-Topsøe projects that an increase in hydrogen purity of 30% would lower the temperature needed to achieve the same sulfur removal rate by eight to nine °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<sup>12</sup>.

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 scrubbing the recycle gas<sup>67</sup>. Haldor-Topsøe indicates that a 50% increase in the ratio of total gas/liquid ratio only decreases the necessary reactor temperature by 6 to 8°C; or the temperature can be maintained and the final sulfur level reduced by 35-45%<sup>12</sup>.

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 Topsøe 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<sup>67</sup>. Albemarle 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<sup>12</sup>. Based on the above data from Haldor-Topsoe, if temperature were maintained, the final sulfur level could be reduced by 50%<sup>12</sup>. 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.

### 4.3 Designing New Reactor Configurations

Industrial reactor configuration for deep hydrodesulfurization of gas oils in terms of reaction order and effect of H<sub>2</sub>S has been discussed by Sie<sup>119</sup>. The reactor design and configuration involve 1-stage and 2-stage desulfurization. Desulfurization processes in use today in the U.S. 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 cocurrent trickle-bed reactor during deep desulfurization. The normally applied cocurrent trickle-bed single reactor is therefore not the optimal technology for deep desulfurization<sup>119</sup>. 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<sub>2</sub>S and NH<sub>3</sub> 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<sup>12</sup>.

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<sup>119</sup>. This new design was developed by ABB Lummus and Criterion, as represented by their SynSat process<sup>120,121</sup>. The SynAlliance (consisting of ABB Lummus, Criterion Catalyst Corp., and Shell Oil Co.) 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<sup>12</sup>. Traditional reactors are cocurrent in nature. The hydrogen is mixed together with the distillate at the entrance to the reactor and the mixture flows through the reactor. 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 cocurrent design is practical; it eases the control of gas-liquid mixing and contact with the catalyst. The disadvantage is that the concentration of H<sub>2</sub> is the highest at the front of the reactor and lowest at the outlet. The opposite is true for the concentration of H<sub>2</sub>S. This increases the difficulty of achieving extremely low sulfur levels due to the low H<sub>2</sub> concentration and high H<sub>2</sub>S concentration at the end of the reactor. A new solution to this problem is to design a counter-current reactor, where the fresh H<sub>2</sub> 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<sup>12</sup>. 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 countercurrent 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. Some novel reactor concepts based on special structured packings or monoliths that allow such countercurrent operation have been presented<sup>119</sup>.

## 4.4 Developing New Processes

Among the new process concepts, design approaches for ultra deep desulfurization focus on (1) 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.

### 4.4.1 S Zorb Process for Sulfur Absorption and Capture.

Phillips Petroleum (now Conoco Phillips) conducted an internal study of its refineries and concluded that the use of hydrotreating technologies to reach ultra-low sulfur levels in gasoline to be a cost-prohibitive option<sup>122</sup>. A new diesel desulfurization process called S Zorb Diesel, was recently announced by Phillips Petroleum. This is an extension of their S Zorb Gasoline process for gasoline (at 377-502°C, 7.0-21.1 kg/cm<sup>2</sup>)<sup>122</sup>. S-Zorb for diesel contacts highway diesel fuel (typically with about 350 ppm sulfur) 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. 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 would otherwise increase the effluent sulfur concentration.

Scheme 2 illustrates the principle of S Zorb process<sup>122</sup>. Based on the principle, it appears that 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<sup>12</sup>.

Phillips Petroleum'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<sup>123</sup>. The S Zorb diesel desulfurization process has been demonstrated in the laboratory using two different diesel feedstocks, which has shown that diesel feeds containing 17-20% hydrotreated LCO can be desulfurized down below 10 ppmw sulfur<sup>123</sup>.

Table 6 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<sub>2</sub> gas purity, > 50%<sup>123</sup>. The S Zorb diesel desulfurization process has been demonstrated in the laboratory using two different diesel feedstocks (Table 6), which has shown that diesel feeds containing 17-20% hydrotreated LCO can be desulfurized down below 10ppmw sulfur<sup>123</sup>. Conoco Phillips 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<sup>124</sup>. A recent article from Conoco Phillips presents a summary of S-Zorb process performance, historical development and future perspective of S-Zorb for gasoline and diesel desulfurization<sup>125</sup>. RTI group also tested their TreND process, initially developed for gasoline, for diesel desulfurization<sup>126</sup>.

Table 6. Impact of Hydrodesulfurization on FCC Feed Properties

	Raw Feed		HDS	
	Untreated	90% HDS	98% HDS	99% HDS
Operating pressure, psig	—	900	1,000	1,000
Feed properties				
Gravity, °API	20.5	23.5	24.8	26.0
Sulfur, wt%	2.6	0.25	0.06	0.02
Nitrogen, wppm	880	500	450	400
Carbon residue, wt%	0.4	0.25	0.1	0.1
Metals (Ni + V), wppm	1	<1	<1	<1
Hydrogen addition to feed, wt%	0	0.51	0.74	0.94

Source:<sup>160</sup>.

#### 4.4.2 Selective Adsorption for Deep Desulfurization at Ambient Temperature

An alternate process is being explored at Pennsylvania State University for deep desulfurization of distillate fuels (diesel, gasoline and jet fuels) based on selective adsorption for removal of sulfur compounds (PSU-SARS) at ambient conditions without using H<sub>2</sub><sup>26,36,127</sup>. Figure 7 illustrates the known coordination geometries of thiophene in organometallic complexes, which indicate likely adsorption configurations of thiophenic compounds on the surface of adsorbents. Both thiophenic compounds and non-sulfur aromatic

compounds can interact with metal by pi-electrons. However, in Figure 5 only two types of interaction of thiophene with metal involve the sulfur atom in thiophene, the  $\eta^1\text{S}$  bonding interaction between the sulfur atom and one metal atom, and the S- $\mu$ 3 bonding interaction between the sulfur atom and two metal atoms.

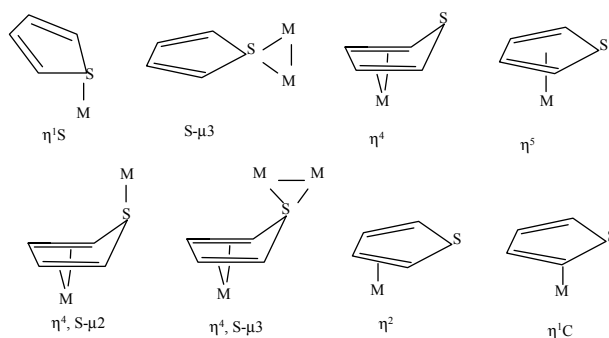


Figure 7. Known coordination geometries of thiophene in organometallic complexes, indicating likely adsorption configurations of thiophenic compounds on the surface of adsorbents<sup>127</sup>

Figure 8 shows the preliminary results from our laboratory for selective adsorption of sulfur compounds from a commercial diesel fuel using a transition metal complex based adsorbent A-1<sup>127</sup>. Figure 9 shows the corresponding results for a model diesel fuel that contains naphthalene, 2-methylnaphthalene, DBT and 4,6-DMDBT<sup>127</sup>. Based on the computational and experimental results, it is theoretically possible and experimentally doable to distinguish between sulfur compounds and aromatic compounds in diesel fuels using a solid adsorbent.

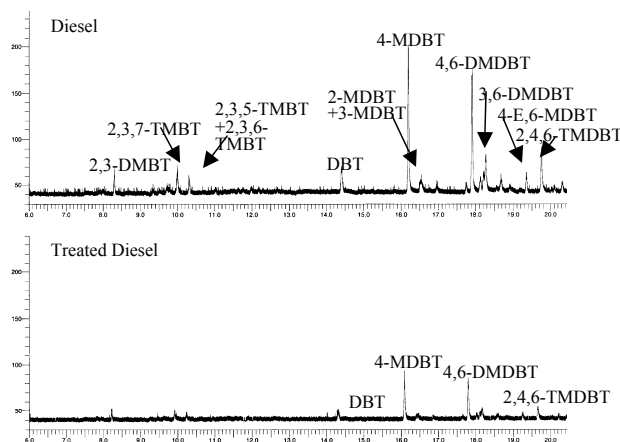


Figure 8. GC-FPD chromatogram of diesel and treated diesel. Adsorbent: A-1, Feed: a commercial diesel

Selective separation of sulfur compounds has also been conducted in analytical characterization using ligand-exchange chromatography. For example, Pyell et al.<sup>128</sup> 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)<sup>128</sup>. Rudzinski et al.<sup>129</sup> 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  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$ , respectively.

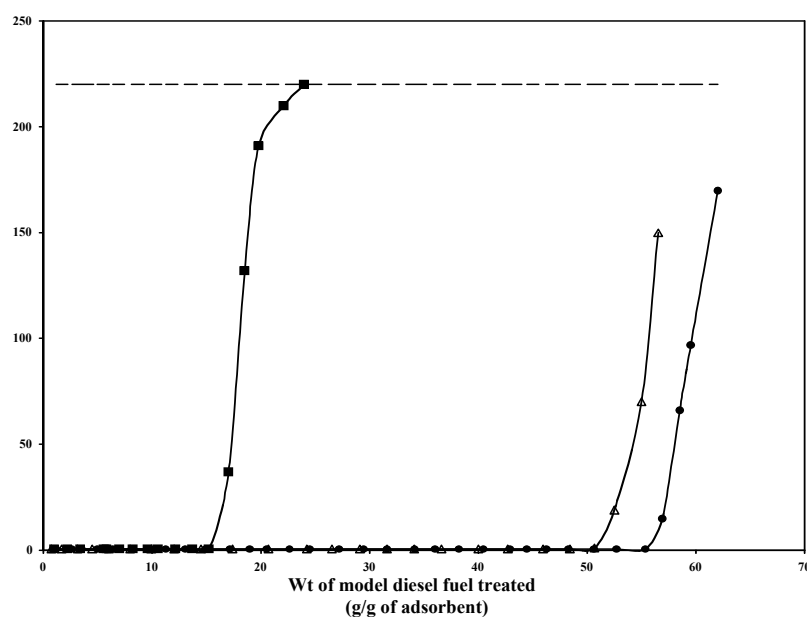


Figure 9. Breakthrough curves for the adsorptive desulfurization of a model diesel fuel containing 4,6-DMDBT at 60°C over Transition metal oxides supported on MCM-41 and activated carbon

More recently, Yang and coworkers<sup>130-134</sup> have reported on adsorption separation of thiophenic sulfur compounds from aromatic compounds based on  $\pi$ -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  $\pi$ -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  $\pi$ -complexation strength is higher for thiophene compared to benzene<sup>131</sup>. The authors have noted that the adsorption performance of the Cu(I)-Y zeolite is decreased when aromatics are present in the fuel<sup>132-134</sup> probably due to the competitive adsorption of sulfur compounds and aromatics by  $\pi$ -complexation.

#### 4.4.3 New Integrated Process Concept Based on Selective Adsorption

By using existing HDS processes, we will need to process 100% of the fuel to deal with sulfur compounds that account for less than 0.3 wt% of the feed with 500 ppmw sulfur level. We are proposing a new approach for an integrated process. Figure 10 shows the flow diagram of the proposed concept of the new integrated desulfurization process, which consists of selective adsorption for removal of sulfur compounds (PSU-SARS)<sup>26,36,127</sup> followed by HDS of concentrated sulfur compounds (HDSCS) using high-activity catalysts such as Co-Mo/MCM-41<sup>34,35</sup>. The subsequent hydrodesulfurization 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.

The PSU-SARS-HDSCS concept 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 for 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  $Nm^3/m^3$  feed (110-120 SCFB) of  $H_2$  consumption; each 1000 ppm nitrogen removal results in about 5.9-6.1  $Nm^3/m^3$  (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 volume %); each one unit increase in  $^\circ API$  gravity requires about 17  $Nm^3/m^3$  feed (100 SCFB) of  $H_2$  consumption, as does each one unit increase in cetane number for diesel stocks<sup>69</sup>.

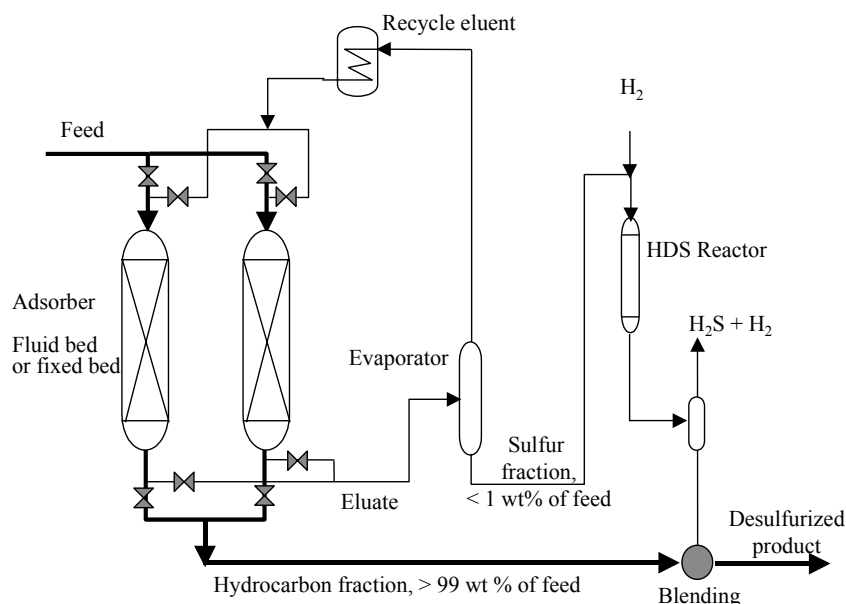


Figure 10. The proposed integrated PSU-SARS-HDSCS process based on adsorption for deep desulfurization<sup>127</sup>

#### 4.4.4 Adsorption Desulfurization Using Alumina Based Adsorbents

The IRVAD process by Black & Veatch Pritchard Inc. and Alcoa Industrial Chemicals is claimed to be a low-cost process for low-sulfur gasoline<sup>135,136</sup>. The process uses an alumina-based selective 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, and does not consume hydrogen or saturate olefins. The adsorption mechanism is based on the polarity of sulfur compounds. It is not very selective for gasoline sulfur, and no information is available on diesel sulfur.

#### 4.4.5 Charge Complex Formation

It is well established that among all sulfur-containing compounds present in gas oil, alkyldibenzothiophenes are the most refractory to the achievement of deep classical hydrodesulfurization. Focusing on these refractory sulfur compounds in gas oil, Milenkovic et al.<sup>91,137</sup> explored an approach to selective elimination of alkyldibenzothiophenes from gas oil by formation of insoluble charge-transfer complexes. They have noted the electron-rich structure of alkyl DBTs and studied their ability to form charge-transfer complexes (CTC) with pi-acceptors in order to develop a new highly

selective method for their specific removal from gas oil. A new method based on the selective formation of insoluble charge transfer complexes for removing the refractory compounds is described. They reported the selective formation of insoluble CTC between dibenzothiophene derivatives and tetranitrofluorenone in synthetic solutions, which model the gas oil matrix. By the same procedure the global sulfur level was lowered in gas oils. Furthermore, they have shown that the charge transfer complexation method is specific for dibenzothiophenes with regard to benzothiophenes. The complexation activity and selectivity have been correlated to the frontier molecular orbital energies and their shapes<sup>137</sup>.

#### 4.4.6 Oxidative Desulfurization

Oxidation of sulfur atoms in liquid phase into corresponding sulfones, with or without radiation by ultrasound or UV light, followed by extraction of oxidized species can lead to desulfurization of diesel fuels. As the regulations for sulfur in fuels become more and more stringent, it becomes increasingly more difficult for existing hydrodesulfurization processes to achieve affordable “ultra-deep desulfurization” to produce ultra-low-sulfur diesel fuels. Oxidative desulfurization is an alternative process, which may have niche applications<sup>138</sup>. Otsuki et al.<sup>139</sup> studied the oxidation of dibenzothiophene (DBT) using t-butyl hypochlorite (t-BuOCl) in the presence of several catalysts. In a flow reactor under ambient pressure at 30-70 °C, more than 90% of DBT could be oxidized in the decahydronaphthalene (decalin) solution. The catalyst was necessary to oxidize dibenzothiophene with t-BuOCl, and gamma-Al<sub>2</sub>O<sub>3</sub> supported catalysts have relatively high activities. At the same time, the activities of the metal-loaded Al<sub>2</sub>O<sub>3</sub> catalysts showed the same activities as those of the Al<sub>2</sub>O<sub>3</sub> support, indicating that the Al<sub>2</sub>O<sub>3</sub> support itself possessed such activity<sup>139</sup>. Aida et al.<sup>140</sup> discussed the oxidation processes for reducing the sulfur content in diesel fuel. The oxidation method has capabilities, not only to decrease the sulfur content in light oil below 0.1 ppm, but also to recover the sulfur component as an organic sulfur compound such as sulfone or dibenzothiophene derivatives that has a potential industrial use<sup>140</sup>. Hangun et al.<sup>141</sup> studied oxidative desulfurization using a series of iron (III) complexes (tetra amido macrocyclic ligand) as activators that enhance the oxidizing ability of hydrogen peroxide for dibenzothiophene derivatives at low catalyst concentrations and mild conditions such as 40 °C. Otsuki et al.<sup>139</sup> also examined the effect of a variety of model compounds found in light gas oil (LGO) such as n-pentadecane, 2,4,4-trimethylpentene, xylene, and indole on the oxidation of DBTs.

Shiraishi et al.<sup>142</sup> explored a new two-stage oxidative desulfurization process of light oil, effected by a combination of photochemical reaction and organic two-phase liquid-liquid extraction. The first consists of the transfer of the sulfur-containing compounds from the light oil to an aqueous-soluble

polar solvent. This is then followed by the photooxidation and photodecomposition of the sulfur-containing compounds in the solvent by UV irradiation, using a high-pressure mercury lamp. The operations are carried out under conditions of room temperature and atmospheric pressure. Acetonitrile was found to be the most suitable polar solvent for the process. The same group<sup>143</sup> reported photochemical desulfurization using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) aqueous solution extraction system for high-sulfur-content straight-run light gas oil and aromatic-rich light cycle oil. Photochemical desulfurization of light oils of different sulfur contents and aromatic components, such as straight-run light gas oil (LGO) and light cycle oil (LCO), in an oil/hydrogen peroxide aqueous solution two-phase liquid-liquid extraction system was investigated<sup>143</sup>. The entire wavelength region of light from a high-pressure mercury lamp was utilized to realize the direct excitation of sulfur-containing compounds. In the case of LGO of high sulfur content, 77% of the sulfur is removed by 36 h of photo-irradiation, and the quantity of sulfur removed from LGO is six-fold greater than in the case of commercial light oil. Although the desulfurization of LCO is suppressed by the presence of a large quantity of 2-ring aromatics, the sulfur content is reduced to less than 0.05 wt% to meet with regulations in Japan<sup>143</sup>. GC-AED analysis shows that benzothiophenes in all the feedstocks are more easily desulfurized than dibenzothiophenes. Highly substituted dibenzothiophenes in LCO, especially those having substituted carbon number of 4-6, are hardly desulfurized by the proposed method<sup>143</sup>.

With respect to commercial oxidation process development, Petro Star Inc. recently announced a desulfurization technology which removes sulfur from diesel fuels using chemical oxidation<sup>144,145</sup>. Desulfurization of diesel fuel is accomplished by first forming a water emulsion with the diesel fuel. In the emulsion, the sulfur atom is oxidized to a sulfone using peroxyacetic acid<sup>138,145</sup>. This is followed by liquid/liquid extraction to remove the oxidized sulfur compounds using a solvent such as DMSO<sup>145</sup>. With oxygen atoms attached to the sulfur atom, the sulfur-containing molecules (sulfones) becomes polar and hydrophilic and then move into the aqueous phase. The overall oxidative desulfurization process may include liquid-phase oxidation, solvent extraction, solvent recovery, raffinate polishing by adsorption onto silica or alumina, and extract treatment such as chemical reaction or biochemical digestion<sup>138,145</sup>. Like biodesulfurization, some of the sulfones could be converted to a surfactant which could be sold to the soap industry at an economically desirable price; the earnings made from the sales of the surfactant could offset some of the cost of oxidative desulfurization<sup>144</sup>. Oxidative desulfurization has also been studied by other companies such as Unipure and Texaco<sup>146</sup>.

#### 4.4.7 Biodesulfurization

Biodesulfurization is a process that removes sulfur from fossil fuels using a series of enzyme-catalyzed reactions.<sup>147</sup> Biodesulfurization is another alternative processing method that has some similarity to the above-mentioned oxidative desulfurization, in that both methods oxidize sulfur atoms in the sulfur-containing compounds. Certain microbial biocatalysts have been identified that can biotransform sulfur compounds found in fuels, including ones that selectively remove sulfur from dibenzothiophene-type heterocyclic compounds.<sup>147</sup> Biocatalytic sulfur removal from fuels may have applicability for producing low sulfur gasoline and diesel fuels.

Figure 11 shows the general steps in the biodesulfurization system based on studies of various bacterial species.<sup>148</sup> Attention has been given to the microbial chemical pathway which can remove sulfur from substituted dibenzothiophenes with alkyl groups that hinder chemical catalysis and that resist removal by hydrodesulfurization. Monticello recently outlined sulfur-specific C<sub>x</sub>-DBT metabolism via the hydrocarbon-conserving (4S) pathway first proposed by Campbell and Kee Rhee<sup>148</sup>. The activity has been observed in many species of bacteria since the first confirmed isolation by Kilbane in 1988<sup>148</sup>. In most cases, the bacteria have been closely related and catalyze the same reaction.

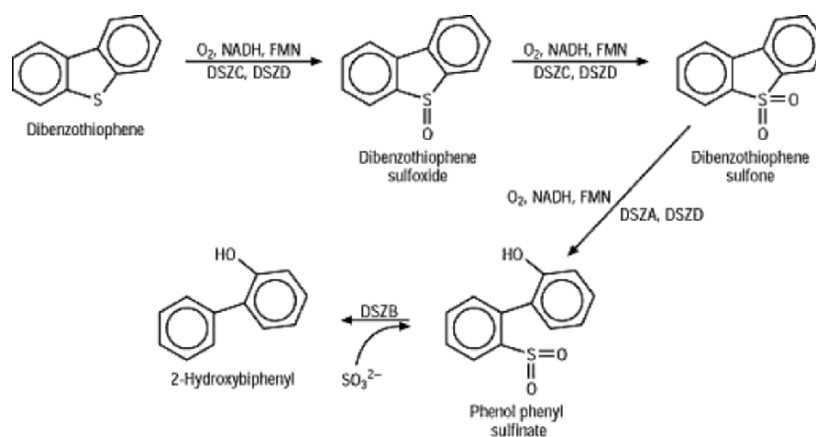


Figure 11. The pathway of biological desulfurization of model compound dibenzothiophene relies on biocatalysts for specificity. NADH is reduced nicotinamide adenosine dinucleotide; FMN is flavin mononucleotide; DSZA, DSZB, DSZC, and DSZD are the catalytic gene products of *dszA*, *dszB*, *dszC*, and *dszD*, respectively<sup>148</sup>.

A biodesulfurization process has been reported by Energy Biosystems<sup>148</sup>. It involves the removal of sulfur-containing hydrocarbon compounds from distillate (diesel) fuel or naphtha (gasoline) streams using bacteria. The distillate stream is first mixed with an aqueous media containing the bacteria,



caustic soda and nutrients for the bacteria. Enzymes in the bacteria first oxidize the sulfur atoms and then cleaves some of the sulfur-carbon bonds. Designs based on pilot plant studies combine biodesulfurization with conventional hydrotreating to produce diesel fuel containing 50 ppmw sulfur<sup>12</sup>. The sulfur leaves the process in the form of hydroxyphenyl benzene sulfonate, which can be used commercially as a feedstock to produce surfactants. Recently, utilization of by-products from biodesulfurization has also been reported and the process system is being explored<sup>149</sup>.

Better understanding of the mechanism of biodesulfurization, as shown in Figure 8, may be gained from some recent studies<sup>150-153</sup>. Gallagher et al.<sup>150</sup> reported a sulfur-specific pathway in microbial desulfurization of DBT. *Rhodococcus rhodochrous* strain IGTS8 metabolizes DBT in a sulfur-specific manner. Two routes of desulfurization have been identified. Under growth conditions, the intermediates are dibenzothiophene sulfoxide, dibenzothiophene sulfone, 2'-hydroxybiphenyl-2-sulfonate, and 2,2'-dihydroxybiphenyl<sup>150</sup>. Stationary phase cells produce 2-hydroxybiphenyl as the desulfurized product and use the 2'-hydroxybiphenyl-2-sulfinate, rather than the sulfonate, as the key intermediate<sup>150</sup>.

Piddington et al.<sup>152</sup> studied the sequence and molecular characterization of a DNA region encoding the DBT desulfurization operon of *Rhodococcus* sp. strain IGTS8. DBT can be desulfurized to 2-hydroxybiphenyl (2-HBP) by *Rhodococcus* sp. strain IGTS8<sup>152</sup>. Izumi et al.<sup>154</sup> isolated a DBT-degrading bacterium, *Rhodococcus erythropolis* D-1, which utilized DBT as a sole source of sulfur from soil. DBT was metabolized to 2-hydroxybiphenyl (2-HBP) by the strain, and 2-HBP was almost stoichiometrically accumulated as the dead-end metabolite of DBT degradation. DBT degradation by this strain was shown to proceed as DBT --> DBT sulfone --> 2-HBP. DBT at an initial concentration of 0.125 mM was completely degraded within 2 days of cultivation. DBT at up to 2.2 mM was rapidly degraded by resting cells within only 150 min. It was thought this strain had a higher DBT-desulfurizing ability than other microorganisms reported previously<sup>154</sup>.

Gray et al.<sup>153</sup> reported on the molecular mechanisms of biocatalytic desulfurization of DBT. *Rhodococcus* sp. strain IGTS8 has the ability to convert DBT to 2-hydroxybiphenyl (HBP) with the release of inorganic sulfur. The conversion of DBT to HBP is catalyzed by a multienzyme pathway consisting of two monooxygenases and a desulfinate. The final reaction catalyzed by the desulfinate appears to be the rate limiting step in the pathway<sup>153</sup>. Each of the enzymes has been purified to homogeneity and their kinetic and physical properties studied. Neither monooxygenase has a tightly bound cofactor and each requires an NADH-FMN oxidoreductase for activity (NADH is reduced nicotinamide adenosine dinucleotide; FMN is flavin mononucleotide). An NADH-FMN oxidoreductase has been purified from *Rhodococcus* and is a protein of approximately 25,000 molecular weight with no apparent sequence homology to any other protein in the databases. Gray et

al.<sup>153</sup> described a unique sulfur acquisition system that *Rhodococcus* uses to obtain sulfur from very stable heterocyclic molecules. According to Denome et al.<sup>151</sup>, *Rhodococcus* sp. strain IGTS8 possesses an enzymatic pathway that can remove covalently-bound sulfur from DBT without breaking carbon-carbon bonds. The DNA sequence of a 4.0-kb BstBI-BsiWI fragment that carries the genes for this pathway was determined. Frameshift and deletion mutations established that three open reading frames were required for DBT desulfurization, and the genes were designated soxABC (for sulfur oxidation). Each sox gene was subcloned independently and expressed in *Escherichia coli* MZ1 under control of the inducible lambda p(L) promoter with a lambda cII ribosomal binding site. SoxC is similar to the 45-kDa protein that oxidizes DBT to DBT-5,5'-dioxide. SoxA is similar to the 50-kDa protein responsible for metabolizing DBT-5,5'-dioxide to an unidentified intermediate. SoxB is similar to the 40-kDa protein that, together with the SoxA protein, completes the desulfurization of DBT-5,5'-dioxide to 2-hydroxybiphenyl. Protein sequence comparisons revealed that the predicted SoxC protein is similar to members of the acyl coenzyme A dehydrogenase family but that the SoxA and SoxB proteins have no significant identities to other known proteins. The sox genes are plasmidborne and appear to be expressed as an operon in *Rhodococcus* sp. strain IGTS8 and in *E. coli*<sup>151</sup>.

Kobayashi et al.<sup>155</sup> studied the reaction mechanism of biodesulfurization using whole cells of *Rhodococcus erythropolis* KA2-5-1, which have the ability to convert DBT into 2-hydroxybiphenyl. The desulfurization patterns of alkyl DBTs were represented by the Michaelis-Menten equation. The values of rate constants, the limiting maximal velocity (V-max) and Michaelis constant (K-m), for desulfurization of alkyl DBTs were calculated. The relative desulfurization activities of various alkyl DBTs were reduced in proportion to the total carbon numbers of alkyl substituent groups. Alkyl DBTs that had a total of six carbons of alkyl substituent groups were not desulfurized. The type or position of alkyl substituent groups had little effect on desulfurization activity<sup>155</sup>. The desulfurization activity of each alkyl DBT, when mixed together, was reduced. This phenomenon was caused by apparent competitive inhibition of substrates. Using the apparent competitive inhibition model, the desulfurization pattern of a multiple components system containing alkyl DBTs was elucidated. This model was also applicable for biodesulfurization of light gas oil<sup>155</sup>.

Lee et al.<sup>156</sup> studied microbial desulfurization of DBTs bearing alkyl substitutions adjacent to the sulfur atom, such as 4,6-diethyldibenzothiophene (4,6-DEDBT), which are referred to as sterically hindered with regard to access to the sulfur moiety. By using enrichment cultures with 4,6-DEDBT as the sole sulfur source, bacterial isolates which selectively remove sulfur from sterically hindered DBTs were obtained. The isolates were tentatively identified as *Arthrobacter* species, 1,6-DEDBT sulfone was shown to be an

intermediate in the 4,6-DEDBT desulfurization pathway, and 2-hydroxy-3,3'-diethylbiphenyl (HDEBP) was identified as the sulfur-free end product<sup>156</sup>.

Omori et al.<sup>157</sup> isolated Strain SY1, identified as a *Corynebacterium* sp., on the basis of the ability to utilize DBT as a sole source of sulfur. Strain SY1 could utilize a wide range of organic and inorganic sulfur compounds, such as DBT sulfone, dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, CS<sub>2</sub>, FeS<sub>2</sub>, and even elemental sulfur. Strain SY1 metabolized DBT to dibenzothiophene-5-oxide, DBT sulfone, and 2-hydroxybiphenyl, which was subsequently nitrated to produce at least two different hydroxynitrobiphenyls during cultivation<sup>157</sup>. These metabolites were separated by silica gel column chromatography and identified by nuclear magnetic resonance, UV, and mass spectral techniques. Resting cells of SY1 desulfurized toluenesulfonic acid and released sulfite anion. On the basis of these results, a new DBT degradation pathway is proposed.<sup>157</sup>

Several recent reviews outline the progress in the studies of the microbial desulfurization from the basic and practical point of view<sup>117,148,158</sup>. Biocatalytic sulfur removal from fuels has potential applicability for producing low sulfur gasoline and diesel. Microbial biocatalysts (microorganisms) have been identified that can biotransform sulfur compounds found in fuels, including ones that selectively remove sulfur from dibenzothiophene heterocyclic compounds to form 2-hydroxyl biphenyl and similar compounds. They are promising as biocatalysts in the microbial desulfurization of petroleum because, without assimilation of the carbon content, they remove only sulfur from the heterocyclic compounds, which are refractory to conventional chemical desulfurization<sup>158</sup>. Various bioreactor and bioprocess designs are being tested for use with biocatalysts, including recombinant biocatalysts, for use in removing sulfur from fuels and feedstocks within the petroleum refinery stream<sup>147</sup>. Both enzymological and molecular genetic studies are now in progress for the purpose of obtaining improved desulfurization activity of organisms. The genes involved in the sulfur-specific DBT desulfurization were identified and the corresponding enzymes have been investigated. Most attention is given to the 4S pathway of *Rhodococcus*, which can remove sulfur from substituted and unsubstituted dibenzothiophenes, including sulfur compounds that hinder chemical catalysis and that resist removal by mild hydrotreatment<sup>147</sup>. From the practical point of view, it has been proved that the microbial desulfurization proceeds in the presence of high concentrations of hydrocarbons, and more complicated DBT analogs are also desulfurized by the microorganisms<sup>148</sup>.

As summarized by McFarland et al.<sup>147</sup>, microbial sulfur-specific transformations have been identified that selectively desulfurize organic sulfur compounds in fossil fuels. Recent discoveries related to biodesulfurization mechanisms may lead to commercial applications of biodesulfurization through engineering recombinant strains for over-expression of biodesulfurization genes, removal of end product repression,

and/or by combining relevant industrial and environmental traits with improvements in bioprocess design<sup>147,159</sup>. With bioprocess improvements that enhance biocatalyst stability, achieve faster kinetics, improve mass transfer limitations, temperature and solvent tolerance, as well as broaden substrate specificity to attack a greater range of heterocyclic compounds, biocatalysis may be a cost-effective approach to achieve the production of low sulfur gasoline<sup>147</sup>. The challenge will be to accomplish these improvements by the time the regulations for ultra low sulfur gasoline and other vehicle fuels go into effect in order to be competitive with emerging non-biological desulfurization technologies<sup>147</sup>.

## **5. FCC FEED HYDROTREATING AND LCO UNDERCUTTING**

### **5.1 FCC Feed Hydrotreating for Sulfur Reduction in LCO**

Tables 6 and 7 show the properties of raw FCC feed and hydrotreated FCC feedstock<sup>160</sup>. The diesel fuel is produced from several blending stocks, of which light cycle oil (LCO) from FCC is a major blending stock that contributes to the sulfur in diesel pool. The FCC unit primarily produces gasoline, but it also produces a significant quantity of LCO. LCO is high in aromatics and sulfur and contains a relatively high fraction of the sterically hindered DBT-type compounds such as 4-MDBT and 4,6-DMDBT<sup>35,107</sup>. In general, sulfur could be removed before, after, or during FCC. Early in the processing train prior to the FCC unit, the most practical place to remove sulfur is feed hydrotreater. Many refineries already have an FCC feed hydrotreating unit; the LCO from these refineries should contain a much lower concentration of sterically hindered DBT compounds than refineries without hydrotreating their FCC feed<sup>12</sup>. However, adding an FCC feed hydrotreating unit is much more costly than distillate hydrotreating. Just on the basis of sulfur removal, FCC feed hydrotreating is more costly than distillate hydrotreating, even considering the need to reduce gasoline sulfur concentrations<sup>111</sup>. On the other hand, FCC feed hydrotreating provides environmental and economic benefits.

In conjunction with Tables 5 and 6, the data in Table 7 shows the impact of feed hydrotreating on FCC product yield and quality<sup>160</sup>. FCC feed hydrotreating decreases the sulfur contents of gasoline and diesel fuel significantly. It also increases the yield of relatively high value gasoline and LPG from the FCC unit and reduces the formation of coke on the FCC catalyst. For individual refiners, these additional benefits may offset the cost of FCC feed hydrotreating to make it more economical than post-FCC distillate hydrotreating. There are newly developed catalysts that have

optimized activity and pore structure for FCC feed hydrotreating, such as Akzo Nobel's KF 841 (NiMo) and KF 902 (NiCoMo).<sup>111</sup>

Table 7. Impact of Feed Hydrotreating on FCC Unit Performance

	Raw Feed		HDS	
	Untreated	90% HDS	98% HDS	99% HDS
<b>Yields, wt%</b>				
H <sub>2</sub> S	1.1	0.1	0.0	0.0
C <sub>2</sub> -	3.3	3.5	3.2	2.8
C <sub>3</sub> +C <sub>4</sub>	16.3	17.6	18.7	19.9
Full-range naphtha	48.3	51.5	52.5	53.6
LCO	16.7	15.7	15.0	14.0
CSO	9.0	6.6	5.9	5.2
Coke	5.4	5.0	4.7	4.4
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>
<b>Conversion, vol%</b>	74.3	77.7	79.1	80.8
<b>Key product properties</b>				
Naphtha RON	93.2	93.0	92.9	92.7
Naphtha MON	80.5	80.8	81.1	81.0
LCO cetane index	25.7	25.7	26.4	26.5
<b>Product sulfur, wppm</b>				
H <sub>2</sub> S	10,066	753	188	94
Naphtha	3,600	225	55	18
LCO	29,700	3,400	900	300
CSO	57,800	11,000	3,000	1,100
Coke	30,300	5,700	1,554	516
SOx, vppm	2,030	410	120	42

Source:<sup>160</sup>

## 5.2 Undercutting LCO

It is conceivable that the sulfur-rich fractions, if they have a narrow boiling range, could be separated out (undercut) by a distillation operation. Undercutting has been considered for both gasoline feed<sup>162</sup>, which may require better naphtha fractionation<sup>163</sup>, and for diesel feeds, in which sulfur compounds and nitrogen compounds tend to concentrate more in high boiling point range of 300-400 °C<sup>164</sup>. A major stumbling block to ultra deep hydrodesulfurization to sulfur levels meeting the 15 ppm cap is the presence of sterically hindered DBT-type compounds, particularly those with two methyl or ethyl groups at 4- and 6-positions blocking the sulfur atom. These compounds are found in greatest concentration in LCO, which itself is highly aromatic. These compounds can be desulfurized readily if saturated. However, due to the much higher hydrogen cost of doing so, it is better economically if this can be avoided. One option is to drop the sulfur-rich fraction out of diesel feed. Because these compounds are inherently large in molecular weight due to their chemical structure, they distill near the high end of the diesel range of distillation temperatures. This makes it possible to segregate these compounds from the rest of the cracked stocks via distillation

and avoid the need to desulfurize them. Once separated, this LCO material could be mixed into the refinery streams currently being used to produce off-highway diesel fuel (maximum sulfur: 2000 ppmw to 3000 ppmw) and heating oil (maximum sulfur: 2000 ppmw to 5000 ppmw depending on the state). These fuels would still have to meet applicable quality specifications, such as cetane, density, sulfur and distillation. For example, the industry specification for non-road diesel fuel is a minimum of 40 cetane number, and a maximum sulfur concentration of 5,000 ppm. An analysis of off-highway diesel fuel shows that off-highway diesel fuel averages 44.4 cetane number, 3,300 ppm sulfur, 34.5 API gravity, T10 of 438 °F, T50 of 517 °F, and T90 of 600 °F<sup>165</sup>. Refiners may need to use cetane additives to compensate for the addition of LCO to maintain off-highway fuel cetane levels similar to those of current in-use fuels. Additional cold-flow additives<sup>166</sup> might also be necessary for off-highway diesel fuel in the winter to maintain cold-flow performance at current levels. Refiners would allow other off-highway and heating oil properties to change as a result of the addition of LCO, while continuing to ensure that all specifications on these fuels are met<sup>12</sup>.

Since LCO contains more refractory sulfur compounds, shifting LCO to off-highway diesel fuel and heating oil could prevent the need to desulfurize a sizeable fraction of the sterically hindered DBT compounds currently present in highway diesel fuel. For example, Albemarle studies indicate that a drop of 10 °C in the T95 (temperature for 95 % distillation) of diesel fuel decreases sulfur from 50 - 60 ppmw<sup>12,167</sup>. Of course, such a shift to non-highway diesel fuel markets would decrease the amount of highway diesel fuel produced, about 3 % for the typical refinery, if more easy-to-hydrotreat material was not switched from non-highway diesel fuels to the highway diesel fuel pool. A decrease of T95 of this magnitude effected by undercutting only LCO would decrease sulfur even more because the sulfur levels in the heaviest portions of LCO are much greater than those in SRLGO and are the most difficult to be desulfurized. Shifting only heavy LCO would increase the sulfur reduction per volume of highway diesel fuel lost, but would still result in a net loss of highway diesel fuel production if no other feedstocks replaced it.

While this heavy LCO material could be shifted to other markets, this does not necessarily have to be the case. Under certain conditions, this material can be recycled to the FCC unit<sup>168</sup>. For this to be feasible, the refiner must hydrotreat the FCC feed at a pressure sufficient to desulfurize the sterically hindered sulfur containing compounds and the feed hydrotreater must have sufficient excess capacity to handle the additional material. This material could also be sent to an existing hydrocracker, if sufficient capacity existed, and converted into gasoline blendstock. Alternatively, it could be hydrotreated separately under more severe conditions to remove the sulfur, such as with SynAlliance's SynShift process<sup>169</sup>. This would entail higher hydrogen consumption per barrel of treated material because of some aromatic saturation. However, the amount of material being processed would

be small, so overall hydrogen consumption would still be low. There are various projections on the distillate hydrodesulfurization technology needed to meet a range of highway diesel fuel sulfur levels<sup>12</sup>. These projections were developed to support refining cost studies conducted by the Engine Manufacturers Association and the American Petroleum Institute, and the National Petroleum Council<sup>12</sup>. These projections addressed compliance with three different average sulfur levels: 10, 30 and 100 ppmw. Generally, these projections indicate that it will be possible for refiners to meet the 10 ppmw average sulfur level without resorting to catalysts and operating conditions which reduce aromatic levels dramatically.

## 6. DEEP HYDROGENATION OF DIESEL FUELS

### 6.1 Benefits of Aromatics Reduction

High aromatic content in distillate fuels lowers the fuel quality and contributes significantly to the formation of environmentally harmful emissions<sup>170,171</sup>. 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. 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 October 1993<sup>1,3</sup>. More recently, the Texas Natural Resources Conservation Commission<sup>172</sup> has announced new Low Emission Diesel Fuel Program. This program, which begins April 1, 2005, limits all diesel fuel sold or supplied for use in on-road vehicles and in nonroad equipment in the affected 110 county region in Texas, to a maximum sulfur content of 500 ppmw, a maximum aromatic hydrocarbons content of 10%, and a minimum cetane number of 48. Beginning June 1, 2006, the maximum sulfur content of LED (low emission diesel) used in both on-road vehicles and non-road equipment in the affected 110 county regions in Texas will be reduced to 15 ppm<sup>172</sup>.

Aromatics saturation by catalytic hydrotreating can increase cetane number significantly<sup>1</sup>. One of the significant findings by the US Auto/Oil Air Quality Improvement Research Program (which involved Ford, General Motors, Chrysler, and the 14 largest US petroleum companies) is that lowering aromatic content lowers toxic emissions<sup>2,173</sup>. The significant findings of the European Program on Emissions, Fuels, and Engine Technologies (EPEFE) also include the following related to aromatics: 1) decreasing aromatics reduces catalytic converter light-off time, improves the converter efficiency and decreases exhaust hydrocarbons; and 2) decreasing fuel polyaromatics reduces light-duty diesel exhaust nitrogen oxides, particulate material and

heavy-duty exhaust hydrocarbons, nitrogen oxides, and particulate material<sup>173</sup>.

## 6.2 Challenges of Deep Dearomatization

Currently, conventional hydrotreating technology is adapted for dearomatization by aromatics saturation<sup>170</sup>. 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.<sup>170,174</sup> For example, Ali and Siddiqui<sup>175</sup> compared 3 types of hydrotreating catalysts, CoMo/Al<sub>2</sub>O<sub>3</sub>, NiMo/Al<sub>2</sub>O<sub>3</sub> and NiW/Al<sub>2</sub>O<sub>3</sub>, for dearomatization of light cycle oil. They observed that the type of catalyst has a critical influence on the composition and properties of the product<sup>175</sup>. Divergent effects of aromatics content and molecular weight on the cetane index by these catalysts occurred. 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<sup>175</sup>.

Deep hydrogenation may become necessary in the near future for reducing aromatic contents of distillate fuels to meet increasingly stringent regulations. As hydrogenation is exothermic, deep hydrogenation is favored at a lower temperature. However, conventional hydrotreating catalysts are active only at relatively high temperatures (e.g., >300°C). It is therefore natural to consider deep hydrogenation at low temperatures (e.g., <300°C). The potential candidate catalysts for low-temperature hydrotreating include noble metals. Since it is known that noble metal catalysts are easily deactivated by sulfur compounds, a two-stage processing strategy is being adopted. The first stage involves deep desulfurization of the fuels using metal sulfide catalysts, and the second stage deals with hydrogenation over a noble metal catalysts. Such a two-stage processing scheme is being practiced by the industry in both the U.S. and Europe, as discussed below. Aromatic structures in diesel fuels are shown in Scheme 3.

## 6.3 Application of Noble Metal Catalysts

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. Hydrodesulfurization occurs in the first stage over a Ni-Mo or Co-Mo catalyst, followed by intermediate byproduct 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  $\text{H}_2\text{S}$ ) are extremely low<sup>120,176</sup>. Commercial examples of two-stage or multi-stage hydroprocessing technology include the Shell Middle Distillate Hydrogenation process by Shell<sup>176,177</sup>, the Dual-Stage Process by Haldor-Topsøe<sup>171</sup>, and hydrotreating process by IFP<sup>178</sup>, and the SynSat process developed by Criterion/Lummus<sup>120,179</sup>. There are no reports of noble metal catalysts that can operate without such intermediate  $\text{H}_2\text{S}$  removal<sup>176</sup>.

Figure 12 shows the SynSat process based on published information.<sup>120,179,180</sup> The SynSat process is considered to be an innovation across the boundary between catalysis and reactor engineering<sup>120</sup>. SynSat employs several different catalyst beds within a single reactor shell with intermediate by-product gas ( $\text{H}_2\text{S}$  etc.) removal, and optional counter-current gas-flow. Catalysts **A** and **B** in Figure 9 are metal sulfide catalysts such as sulfided Ni-Mo. Catalyst **C** is a noble metal loaded on an acidic support such as zeolite. There is an intermediate gas removal between the beds of Catalysts **B** and **C**. Nearly all the sulfur compounds must be converted and removed as  $\text{H}_2\text{S}$  on beds **A** and **B** before the fuel feed reaches the noble metal catalyst bed **C**.

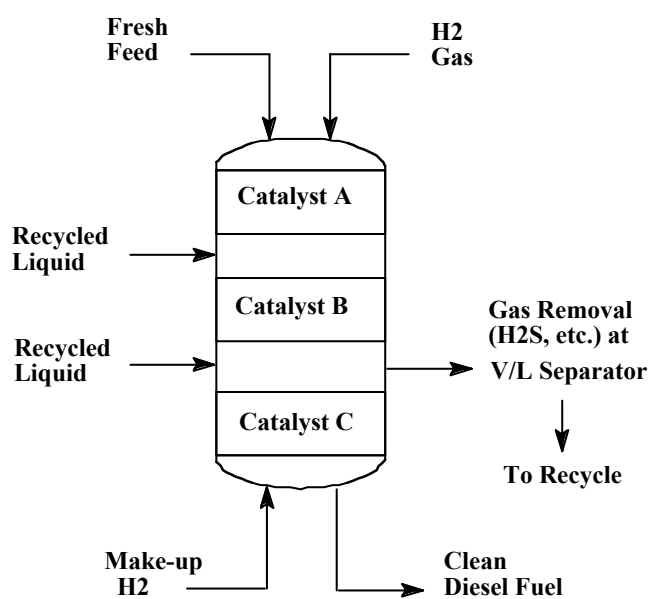


Figure 12. SynSat/SynShift process with Criterion/Lummus catalytic hydrotreating reactor technology, with intermediate by-product gas removal and counter-current gas-flow<sup>181</sup>.

In addition to the SynSat process, which was developed to provide an economic solution to aromatic reduction of diesel fuels, the SynShift process was recently developed for making high-quality diesel fuels with higher cetane number<sup>169,179</sup>. SynShift is a selective ring-opening process; it aims at not only heteroatom removal, but also ring-opening, thus shifting the product

boiling range for the production of lighter diesel fuel with higher quality. The typical reactor pressures and temperatures in SynSat and SynShift process range from 30 to 61 atm (450-900 psig) and from 315 to 400 °C (600 to 750 °F), depending on the feedstocks and required product properties<sup>180</sup>. SynShift upgrading of a feed that was made of 28% SRGO, 33% LCO, and 39% LCGO gave the following improvements<sup>180</sup>:

Property	Feed	Product
Gravity, °API	25.0	33.1
Sulfur, ppmw	15,150	2
Nitrogen, ppmw	631	<1
Aromatics, wt%	64.7	34.3
Cetane Index, D-976	34.2	43.7
Liquid Yield on feed, vol%	103.5	

A recent report by Shell Research and Technology Center<sup>176</sup> showed that commercial noble metal-based catalysts for deep hydrogenation of fuels operate in a regime where the large majority of the metal sites are poisoned by sulfur, even when sulfur tolerance has been improved by choosing modern support functions and metals. Thus, these catalysts are currently used only after a deep desulfurization over Ni-Mo catalysts and subsequent removal of H<sub>2</sub>S, as is also the case in the Shell Middle Distillate Hydrogenation process and the Lummus/Criterion SynSat process<sup>120,176</sup>. Noble metal catalysts that can operate in a stacked-bed reactor with a Ni-Mo catalyst without intermediate H<sub>2</sub>S removal have not been reported<sup>176</sup>.

## 7. DESIGN APPROACHES TO DEEP HYDROGENATION

### 7.1 Deep Hydrogenation at Low Temperatures

We have been exploring sulfur-resistant noble metal catalysts for more efficient hydrotreating of sulfur-containing distillates at low temperatures to produce cleaner transportation fuels. More recently, a new approach has been proposed for the design of sulfur-resistant noble metal catalysts for low-temperature hydrotreating and dearomatization (LTHDA) of sulfur-containing distillates to produce clean distillate fuels<sup>28,29</sup> such as diesel fuels and jet fuels. The proposed concept invokes the use of acidic zeolite support, shape-selective exclusion, differentiation of sulfur resistance, and hydrogen spillover for the design of highly sulfur-tolerant noble-metal catalysts<sup>29</sup>. Because of its importance, sulfur resistance of noble metal catalysts has been the subject of a number of studies<sup>32,106,174,182-185</sup>.

Figure 13 shows a simplified representation of the LTHDA catalyst design concept recently proposed<sup>28</sup>. It invokes some unique acidic zeolites with bimodal pore structure as supports for noble metals and utilizes (1) shape-selective exclusion, (2) hydrogen spillover, and (3) 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<sub>2</sub> 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<sub>2</sub>S. The metal species, particularly those in small pores, should have higher type II sulfur resistance.

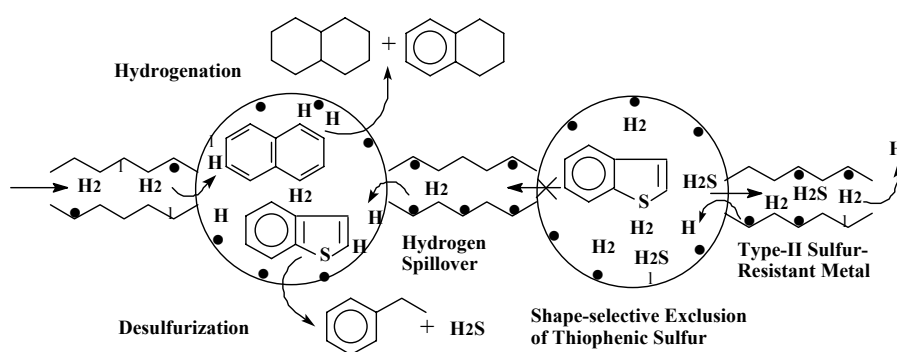


Figure 13. The proposed new concept for LTHDA catalyst design based on shape-selective exclusion, hydrogen spillover, and two types of sulfur resistance. The black dots indicate metal particles on internal surface<sup>28</sup>.

Mesoporous molecular sieve MCM-41 has been used as support for new hydrogenation catalysts<sup>186-188</sup>. In the study by Corma et al., the hydrogenation activity of Pt supported on two mesoporous MCM-41 samples differing in their chemical composition has been examined by following the kinetics of the hydrogenation of naphthalene at 225-275 °C and 5.0 MPa total pressure and by comparing the kinetic parameters obtained with Pt supported

on a mesoporous amorphous silica-alumina (MSA) and other conventional supports, such as commercial amorphous silica-alumina (ASA), zeolite USY, gamma-alumina, and silica. The two mesoporous MCM-41 and MSA materials having very high surface areas allowed for a better dispersion of the Pt particles, and they showed a superior overall hydrogenation activity as compared to the other supports. However; Pt/USY displayed the highest turnover (activity per exposed surface Pt), owing to the interaction of small Pt aggregates in the supercage of the zeolite with the strong Bronsted acid sites associated to framework aluminum forming electron-deficient Pt species of known enhanced activity<sup>188</sup>. Moreover, both the Al-MCM-41 and USY-based catalysts presented the highest sulfur tolerance during the hydrogenation of a naphthalene feed containing 200 ppmw sulfur added as DBT<sup>188</sup>. The high metal dispersion and the interaction of the small Pt clusters with the mildly acidic sites present in Al-MCM-41 may account for its high sulfur tolerance. The superior hydrogenation activity and sulfur tolerance of Pt-MCM-41 catalyst observed in the naphthalene experiments were further confirmed during the hydrogenation of a hydrotreated LCO feed containing about 70 wt% aromatics and 400 ppmw sulfur<sup>188</sup>.

Fujikawa et al.<sup>189</sup> examined the potential of B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-supported bimetallic Pt-Pd catalysts for aromatic hydrogenation of middle distillate fuels. The activity measurements were carried out with hydrotreated LCO/straight-run light gas oil (SRLGO) feed containing 33 vol% aromatics and 320 ppm sulfur under practical conditions. They observed that Pt-Pd/B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts have much higher activity for aromatic hydrogenation as compared to Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts

## 7.2 Saturation of Aromatics in Commercial Process

Haldor Topsøe 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 hydrodesulfurization, while the second stage uses their noble metal catalysts, either TK-907/TK908 or TK-915, which is a newly developed high-activity dearomatization catalyst<sup>190</sup>. United Catalysts and Sud-Chemie AG have published data on the performance of their ASAT catalyst, which uses platinum and palladium<sup>12</sup>. The focus of their study was to reduce aromatics to less than 10 volume % 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 volume % aromatics, the ASAT catalyst was able to reduce sulfur to eight to nine ppmw, essentially eliminate nitrogen and reduce aromatics to two to five vol%. Hydrogen consumption was 800-971 standard cubic feet per barrel (SCFB).<sup>12</sup>

IFP, in conjunction with various catalyst manufacturers, offers its Prime D technology for deep desulfurization, aromatics saturation and cetane

improvement. Using a NiMo catalyst, IFP's 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.<sup>12</sup>

Criterion and ABB Lummus have been licensing their SynTechnology, and as of August 2, 1999, there were 24 units either in operation or in the process of being constructed. Their purposes range from desulfurization to desulfurization plus dearomatization to mild hydrocracking. 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).<sup>12</sup> 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 seven ppmw and 31 volume %, respectively, based on feed sulfur and aromatics levels of 11,900 ppmw and 53 volume %, 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 four volume %, but the feed aromatic level was five volume % higher than expected. Thus, the net reduction in aromatic content in terms of volume % was still higher than found in the pilot plant. 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.<sup>12</sup>

## 8. SUMMARY AND CONCLUSIONS

There exist various sulfur compounds in transportation fuels that differ in ring size, substitution pattern, and reactivities. Heightened concerns for cleaner air and increasingly more stringent regulations on sulfur contents in transportation fuels will make desulfurization more and more important. The sulfur problem is becoming more serious in general, particularly for diesel fuels, as the regulated sulfur content is getting an order of magnitude lower, while the sulfur contents of crude oils refined in the U.S. are becoming higher and higher.

The chemistry of diesel fuel processing has evolved significantly around the central issue of how to produce ultra-low sulfur diesel fuels and low-aromatic diesel fuels in a more efficient and environmentally friendly fashion. New design approaches are necessary for making affordable ultra-clean diesel and gasoline.

Design approaches include (1) shift in thinking paradigms; (2) new catalyst design concepts; (3) new processing schemes; (4) novel integrated and compact sulfur removal systems. It has become more and more difficult for making ultra-low-sulfur fuels by using conventional processes, and new approaches are needed to remove sulfur more effectively and to even far below sulfur levels required by US EPA Tier II regulations in 2006.

Catalysis, adsorption, material formulation, reactor configuration, processing and engineering studies all have important roles to play for developing affordable ultra-clean fuels.

We need to begin with end in mind: road to zero-sulfur. One case which presents a great challenge to ultra-deeper desulfurization of liquid hydrocarbon fuels is the fuel processor for proton-exchange membrane fuel cells and also solid oxide fuel cells, which require essentially near zero-sulfur fuels.

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## 10. GLOSSARY OF TERMS

DBT: dibenzothiophene  
4,6-DMDBT: 4,6-dimethyldibenzothiophene  
4,6-DEDBT: 4,6-diethyldibenzothiophene  
EIA: Energy Information Administration  
EPA: Environmental Protection Agency  
FCC: Fluid catalytic cracking  
GO: gas oil, a middle distillate fraction from  
HBP: hydroxybiphenyl  
HDS: hydrodesulfurization  
HDSCS: HDS of concentrated sulfur fraction  
LCO: light cycle oil, derived from FCC

LED: low emission diesel  
LGO: light gas oil  
LHSV: liquid hourly space velocity  
LTHDA: low-temperature hydrotreating and dearomatization  
MBPD: million barrels per day  
4,6-MDBT: 4-methyldibenzothiophene  
ppm: parts per million  
ppmw: parts per million by weight  
RIA: regulatory impact analysis  
PASH: polycyclic aromatic sulfur heterocycles  
SARS: selective adsorption for removing sulfur  
SRGO: straight-run gas oil  
ULSD: ultra low sulfur diesel fuel

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