APPENDIX H

Refining Technology for Low Sulfur Diesel Production

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I. Introduction

Diesel fuel is a middle distillate petroleum product that is generally heavier than jet fuel and lighter than fuel oil. Distillate refers to a range of similar products including kerosene, diesel fuel, No. 2 heating oil and jet fuel. The diesel fuel produced by a refinery is a blend of all the appropriate available refinery streams. The primary refinery components produced for blending diesel are non-hydrotreated straight run diesel, hydrotreated straight run diesel, non-hydrotreated light cat cycle oil (LCCO) from the FCC, hydrotreated LCCO, non-hydrotreated coker diesel, hydrotreated coker diesel, hydrocracker diesel, and gas oil hydrotreater diesel.[1]

The blendstocks used to produce CARB diesel differ from the rest of the nation. As shown in Table 1[2], the results of the 1996 NPRA/API survey of 10 California refineries indicated that CARB diesel fuel is made primarily from hydrotreated and hydrocracked distillates in roughly equal proportions (48 and 47 percent, respectively) with small fractions of hydrotreated cracked stock (2 percent) and hydrotreated coker gas oil (3 percent). Table 2 shows the sulfur content of the different blendstocks used to produce California diesel and Table 3 compares average highway diesel fuel properties by geographic area.

II. Sulfur Compounds in Distillate

Sulfur containing compounds in distillate can be classified according to the ease with which they are desulfurized.[3] Sulfur contained in paraffins or aromatics with a single aromatic ring are relatively easy to desulfurize. The sulfur atom is in a geometric position where it can readily make physical contact with the surface of the catalyst. The more difficult compounds are the aromatics consisting of two aromatic rings, particularly dibenzothiophenes. Dibenzothiophene contains two benzene rings which are connected by a carbon-carbon bond and two carbon-sulfur bonds (both benzene rings are bonded to the same sulfur atom). This compound is essentially flat and the carbon atoms bound to the sulfur atom hinder the approach of the sulfur atom to the catalyst surface. Nevertheless, today's catalysts are very effective in desulfurizing dibenzothiophenes, as long as only hydrogen is attached to the carbon atoms bound directly to the sulfur atom. However, when hydrogen of the aromatic ring is substituted with methyl or ethyl groups, these groups can hinder the approach of the sulfur atom to the catalyst surface when the alkyl groups are next to the sulfur atom. This steric hindrance reduces the effectiveness of the catalytic hydrogenation reaction.

Most straight run distillates (or straight run light gas oil (SRLGO)) contain relatively low levels of these sterically hindered compounds. LCO contains the greatest concentration of sterically hindered compounds, and is generally more difficult to desulfurize than coker distillate which is in turn more difficult to treat than straight run distillate.[4] In addition, cracked stocks, particularly LCO, have a greater tendency to form coke on the catalyst, which deactivates the catalyst and requires its replacement.

Generally, conventional desulfurization is much slower for sterically hindered compounds than it is for those that aren't. Slower reactions mean that either the volume of the reactor must be much larger, or that the rate of reaction must somehow be increased. The latter implies either a more active catalyst, higher temperature, or higher pressure.

III. Hydrodesulfurization

A. Hydrotreating

Catalytic hydrotreating is a hydrogenation process used to remove contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions. Typically hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils. In addition, hydrotreating converts olefins and aromatics to saturated compounds. Hydrotreating for sulfur removal is called hydrodesulfurization.

Liquid distillate from the crude unit is mixed with hydrogen-rich make up gas and recycle gas, heated and pumped to temperatures of 300-380°C and pressures of 500-700 psia, and reacted over a catalyst. Hydrogen reacts with the sulfur and nitrogen compounds in the distillate, forming hydrogen sulfide and ammonia. The resulting vapor is separated from the desulfurized distillate, then the desulfurized distillate is usually mixed with other distillate streams in the refinery to produce diesel fuel and heating oil.

The vapor still contains valuable hydrogen, because the reaction requires the use of a significant amount of excess hydrogen to operate efficiently and practically. However, the vapor also contains a significant amount of hydrogen sulfide and ammonia, which inhibit the desulfurization and denitrogenation reactions and must be removed from the system. Thus, the hydrogen leaving the reactor is usually mixed with fresh hydrogen and recycled to the front of the reactor for reaction with fresh distillate feed. To avoid a build up of hydrogen sulfide and ammonia in the system, the hydrogen sulfide and ammonia are either chemically scrubbed from the hydrogen recycle stream or purged with a portion of the of the recycle stream as a mixture of hydrogen, hydrogen sulfide and ammonia. The latter method of preventing the build up is less efficient since it leads to higher levels of hydrogen sulfide and ammonia in the reactor, but it avoids the cost of building and operating a scrubber.

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 ppm or lower. However, a second reactor can be used, particularly to meet lower sulfur levels. Instead of liquid distillate going to the diesel fuel/heating oil pool after the first reactor, it would simply be mixed with fresh hydrogen and sent to the second reactor.

A few refineries also currently hydrotreat their distillate more severely than is typical, but not as severely as hydrocracking. Their intent is to remove the sulfur, nitrogen and metallic contaminants and at the same time saturate most of the aromatics present. This is done primarily in Europe to meet very stringent specifications for both sulfur and aromatics applicable to certain diesel fuels. This severe hydrotreating process is also used in the U.S. to “upgrade” petroleum streams which are too heavy or too low in quality to be blended into the diesel pool. The effect is to crack some of the material to lower molecular weight compounds and saturate some of the aromatics to meet the distillation and cetane requirements. A different catalyst which encourages aromatic saturation is used in lieu of one that simply encourages contaminant removal.

B. Hydrocracking

Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are cracked in the presence of hydrogen to produce more desirable products. The process employs high pressure, high temperature, a catalyst, and hydrogen. Hydrocracking is used for feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstock are characterized usually by a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.

In the process, nearly all of the contaminants are removed and olefins and aromatics are saturated into paraffins and naphthenes. Outside the U.S., this process is commonly used to produce distillate from heavier, less marketable refinery streams.

The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts. When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst. Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.

IV. Catalyst Technology

Because moderate sulfur reduction is often all that is currently required in distillate hydrotreating, catalysts have been developed almost exclusively for contaminant removal. The most commonly used desulfurization catalyst consists of a mixture of cobalt and molybdenum (Co/Mo) which interacts primarily with the sulfur atom and encourage the reaction of sulfur with hydrogen. The CoMo catalyst is very effective in the desulfurizing of distillate, straight run or cracked which contain relatively low levels of the sterically hindered sulfur compounds.

With the 15 ppm sulfur cap there is now a need to desulfurize sterically hindered aromatic sulfur compounds and this has led to greater interest in catalysts that encourage saturation (hydrogenation) of the aromatic rings. This generally improves the quality of the diesel fuel produced from this distillate. These catalysts also indirectly encourage the removal of sulfur from sterically hindered compounds by eliminating one or both of the aromatic rings contained in dibenzothiophene. Without one or both of the rings, the molecule is much more flexible and the sulfur atom can approach the catalyst surface much more easily. Thus, the desulfurization rate of sterically hindered compounds is greatly increased through the hydrogenation route. The most commonly used hydrogenation/desulfurization catalyst consists of a mixture of nickel and molybdenum (Ni/Mo). There is a significant additional cost involved in this method of desulfurization, primarily due to the consumption of additional hydrogen. Consequently, the EPA expects refiners to choose desulfurization processes that minimize the amount of aromatics saturation.

V. Hydrogen Sulfide Scrubbing

During the hydrotreating process, hydrogen reacts with sulfur-containing compounds in the distillate to form hydrogen sulfide (H_2S). The desulfurized distillate is separated from the mixed stream leaving the reactor to yield a gaseous stream containing H_2, some hydrocarbons, and the H_2S by-product. This acid gas stream is sent to an amine absorber unit where the H_2S is removed by the circulating amine stream (MEA, DEA, MDEA). Many refineries have mul;tiple amine absorbers served by a common regeneration unit. The stripped gas or liquid is removed overhead, and the amine is sent to a regenerator where the acidic components are stripped by heat and reboiling action and disposed of, and the amine is recycled.[5]

VI. Sulfur Recovery

The sulfur in the acid gas from the amine regeneration unit is removed first by a Claus sulfur recovery unit that achieves 92 to 96 percent of the overall sulfur recovery and then by a tailgas cleanup unit that can increase overall sulfur recovery to 99.9 percent.

Sulfur recovery converts hydrogen sulfide in sour gases and hydrocarbon streams to elemental sulfur. The most widely used recovery system is the Claus process, which uses both thermal and catalytic-conversion reactions. A typical process produces elemental sulfur by burning hydrogen sulfide under controlled conditions. Knockout pots are used to remove water and hydrocarbons from feed gas streams. The gases are then exposed to a catalyst to recover additional sulfur. Sulfur vapor from burning and conversion is condensed and recovered. The tail gas from the Claus unit contains H_2S, SO_2, CS_2, S vapor and entrained S liquid. Most tail gas cleanup processes hydrogenate/hydrolyze the sulfur compounds to H2S, and then either recover or convert the H2S. The H2S recovery is usually by a selective amine while the H2S conversion may use a liquid redox or catalytic process.[5]

Table 1[a]

Volume Fraction of CARB Diesel From Each Blendstock Component

Diesel Blendstock	Percent of CARB Diesel Fuel Per Blendstock Type				
	Naphtha	Light Distillate	Heavy Distillate	Light Gas Oil	All Boiling Fractions Combined
Straight Run	-	-	-	-	0.0
Cracked, Unhydrotreated	-	-	-	-	0.0
Non-Cracked, Hydrotreated	-	-	48.0	-	48.0
Cracked and Hydrotreated	-	-	1.6	-	1.6
Hydrocracked	-	1.9	45.4	-	47.3
Coker Streams, Unhydrotreated	-	-	-	-	0.0
Coker Streams, Hydrotreated	-	-	3.1	-	3.1
Total					100.0

Table 2[b]

Sulfur Content (ppm) by Boiling Fractions of Blendstocks

Diesel Blendstock	Sulfur Content (ppm)			
	Naphtha	Light Distillate	Heavy Distillate	Light Gas Oil
Straight Run	—	1,034	6,360	—
Cracked, Unhydrotreated	—	—	—	—
Non-Cracked, Hydrotreated	—	255	162	375
Cracked and Hydrotreated		97	80	—
Hydrocracked	—	7	10	—
Coker Streams, Unhydrotreated	—	—	—	—
Coker Streams, Hydrotreated	—	70	151	—

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[a] Data from Table 4B (pages 1 and 2) of 1997 API/NPRA report on survey of refining operations and product quality.

[b] Data from Table 4B (pages 3 and 4) of 1997 API/NPRA report on survey of refining operations and product quality

Table 3[a]
Average Highway Diesel Fuel Parameter Levels by Geographic Area

Fuel Parameter		PADD 1	PADD 2	PADD 3	PADD 4	PADD 5 (OC)*	California		U.S. (OC)*
							CARB	EPA	
API Gravity		34.6	34.2	34.3	36.2	33.8	36.5	33.6	34.4
Sulfur, ppmw		340	350	360	330	280	140	200	340
Cetane Number Unadditized		-	42.9	43.8	-	46.5	50.1	42.6	44.1
Cetane Additive (ppmv)		0	83	2	12	0	274	183	27
Cetane Number [additized]		-	-	-	-	-	53.8	-	-
Pour Point (F) [additized]		[10]	[10]	[2]	0	[2]	8	6	[5]
Pour Point Depressant Additive (ppmw)		7	47	7	11	0	0	0	19
Distillation (°F)	T10	426	427	436	405	432	440	447	431
	T30	458	470	478	435	472		-	471
	T50	497	505	514	495	521	531	525	510
	T70	549	549	557	519	554		-	551
	T90	609	600	610	598	611	623	612	606
Aromatics (Vol %)		28.9	25.8	37.0	27.1	-	18.2	28.8	32.3
Polynuclear Aromatics (Vol %)							2.8		

* Outside of California

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[1] Moncrieff, T. Ian, Montgomery, W. David, Ross, Martin T., Charles River Associates Inc., Ory, Raymond E., Carney, Jack T., Baker and O'Brien Inc., An Assessment of the Potential Impacts of Proposed Environmental Regulations on U.S. Refinery Supply of Diesel Fuel, A study prepared by Charles River and Associates Inc. and Baker and O'Brien Inc. for the American Petroleum Association, August 2000.

[2] Final Report, 1996 American Petroleum Institute/National Petroleum Refiners Association, Survey of Refining Operations and Product Quality, July 1997.

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[a] Final Report, 1996 American Petroleum Institute / National Petroleum Refiners Association, Survey of Refining Operations and Product Quality, July 1997.

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[3] United States Environmental Protection Agency, Assessment and Standards Division, Office of Transportation and Air Quality. *Regulatory Impact Analysis: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements*. EPA420-R-00-026, Chapter IV. December 2000, Chapter IV.

[4] Mayo, S.W., "Mid-Distillate Hydrotreating: The Perils and Pitfalls of Processing LCO," Akzo Nobel Catalysts.

[5] Robert A. Meyers, Handbook of Petroleum Processes. 2d ed., McGraw Hill, 1996, Chapter 11.