EVOLUTION OF PROCESS TECHNOLOGY FOR FCC NAPHTHA DESULFURIZATION: 1997 - 2003

AN EXAMPLE OF TECHNICAL PROGRESS INDUCED BY ENVIRONMENTAL REGULATION

Prepared by

MathPro Inc.

P.O. Box 34404
West Bethesda, Maryland 20827-0404
301-951-9006

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1. BACKGROUND

The U.S. EPA has established stringent sulfur control programs for gasoline and diesel fuel. The Tier 2 gasoline sulfur control program begins in 2004 and requires that, by 2006, all U.S. gasoline must have an average sulfur content ≤ 30 ppm.[1] (We call this standard **GSA 30**.) The Ultra-Low-Sulfur Diesel (ULSD) program begins in 2006 and requires that highway diesel fuel must have maximum sulfur content ≤ 15 ppm (**DSC 15**). EPA is likely to initiate a rule-making this year aimed at extending the ULSD program to non-highway diesel fuel (except for railroad and marine diesel), starting in 2008.

Three broad alternatives are available for meeting these sulfur standards:

- *Post-treating*: hydrotreat or otherwise treat part or all of the FCC naphtha[2], and hydrotreat straight run kerosene and distillate, coker distillate, and FCC light cycle oil (LCO).

- *Conventional pre-treating*: hydrotreat FCC feed (to reduce sulfur content, as well as nitrogen and metals content); hydrofinish all or part of the FCC naphtha; and hydrotreat straight run kerosene and distillate, coker distillate, and LCO.

  Under certain conditions, treating the FCC naphtha would be unnecessary because its sulfur content would be sufficiently low without post-treatment.

- *Partial conversion hydrocracking*: partially hydrocrack FCC feed (to reduce sulfur content, as well as nitrogen and metals content, and – importantly – to produce some low sulfur naphtha and distillate), and hydrotreat straight run kerosene and distillate, coker distillate, and LCO.

  With partial conversion hydrotreating, treating the resulting FCC naphtha would not be necessary.

Post-treating FCC naphtha is the *minimum investment, least cost* route for meeting the Tier 2 gasoline sulfur and ULSD standards. Post-treating processes alone are sufficient for meeting these standards, and they entail lower investment and operating costs than the other approaches. Thus far, post-treating has been the approach of choice for most U.S. refineries (with the notable exception of the California refineries, most of which practice pre-treating for reasons unique to California).

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[1] U.S. refineries that (1) meet EPA's definition of "small refinery", (2) can show that timely compliance would induce hardship, or (3) are in the Geographic Preference Area (essentially PADD 4) have additional time to comply with the Tier 2 gasoline sulfur program.

[2] FCC naphtha is the source of 95–97% of the sulfur in gasoline that has not been desulfurized. Hence, controlling the sulfur in FCC naphtha suffices for meeting the GSA 30 standard.

Here, we briefly review the evolution of post-treating technologies for *gasoline* sulfur control since EPA began considering stringent gasoline sulfur control standards (circa 1997). This evolution is perhaps an instructive example of technological progress in the refining industry in response to clean fuels regulations.

2. EVOLUTION OF FCC NAPHTHA DESULFURIZATION TECHNOLOGY: 1997 TO 2003

In 1997, the only commercial technology for controlling the sulfur content of full-range FCC naphtha was what is now called "conventional hydrotreating".[3] A number of technology providers offered conventional hydrotreating processes for full-range FCC naphtha and other naphtha streams. Collectively, these processes had accumulated considerable commercial experience. They were reliable and well-understood, and could accomplish the necessary degree of sulfur control.

Conventional FCC naphtha hydrotreating processes are expensive because they are *non-selective*. In the course of removing sulfur, they also saturate essentially all of the olefins present in FCC naphtha. Olefin saturation leads to high octane loss (> 10 numbers) and high hydrogen consumption, which account for the high cost of conventional hydrotreating. The average cost of achieving the Tier 2 gasoline sulfur standard with conventional hydrotreating was estimated to be in the range of 5¢/gal of complying gasoline (assuming that FCC naphtha constituted 30–40 vol% of the gasoline pool).

At that time, the prevailing view in the refining industry was that, notwithstanding the high cost of conventional hydrotreating, refiners would select it to meet any gasoline sulfur standard that EPA might promulgate, because it was commercially proven technology. In part for this reason the refining industry advocated less stringent sulfur standards than the 30 ppm (avg.) standard that EPA ultimately established in the Tier 2 gasoline sulfur control program.

EPA promulgated the Tier 2 gasoline sulfur rule in January 2000. In June 2000, the National Petroleum Council issued a report, "*U.S. Petroleum Refining: Assuring the Adequacy and Affordability of Cleaner Fuels*". In connection with that report, the NPC's Technology Task Group surveyed FCC naphtha desulfurization processes on offer by the start of 2000.

Tables 1, 2, and 3 summarize the results of the NPC survey. Table 1 shows the processes that the Task Group identified and the readiness status that the Task Group assigned to each. Tables 2 and 3, respectively, show the commercial readiness categories and the technology categories that the NPC Technology Task Group established for classifying FCC naphtha desulfurization processes.

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[3] For brevity, the discussion does not address caustic treating processes for desulfurizing light FCC naphtha.

Table 1: NPC Assessment of Processes for Full-Range FCC Naphtha Desulfurization (January 2000)

Readiness Classification	Process Licensor	Process[1]	Technology
Proven	Many	Many	Conventional Hydrotreating
Demonstrated	CDTech	CD Hydro	Selective Hydrotreating
	Exxon	SCANfining	Selective Hydrotreating
	IFP	Prime G	Selective Hydrotreating
	Mobil	OCTGAIN 125	Non-selective Hydrotreating + Oct. Rec.[2]
Near-Commercial	CDTech	CD Hydro / CD HDS	Selective Hydrotreating
	Mobil	OCTGAIN 220	Non-selective Hydrotreating + Oct. Rec.
	UOP	ISAL	Non-selective Hydrotreating + Oct. Rec.
Developing	Black & Veatch	IRVAD	Adsorption
	Phillips Petroleum	S Zorb G	Selective Hydrotreating + Sorption

Notes:

1. All process names are trademarked
2. **Oct. Rec.** denotes Octane Recovery, chemical reactions that recover octane lost in non-selective hydrotreating (e.g., isomerization)

Table 2: NPC 2000 Classifications of Commercial Readiness: FCC Naphtha Desulfurization

Proven	In [commercial] use at multiple locations on a variety of feedstocks, at required operating conditions, such that use in another application poses no technology-performance risk.
Demonstrated	In commercial use with demonstrated run lengths [of at least] two years. . . such that scale-up of pilot plant results has been demonstrated. Experience is limited, such that extrapolation of pilot plant or commercial results is required for new operating conditions or feed compositions.
Near-Commercial	In initial phases of commercial demonstration with sufficient pilot plant experience to make scale-up and commercial operating practices the primary technology risk. No commercially demonstrated basis for . . . extrapolation [of pilot plant results] to commercial operation.
Developing	New concept with some limited pilot plant results; significant scale-up and commercial operation issues remain.

Table 3: NPC 2000 Classifications of Technology: FCC Naphtha Desulfurization

Conventional Hydrotreating achieves desulfurization with essentially complete olefins saturation (and hence substantial loss of octane in the treated FCC naphtha (10 octane numbers or more)).

Selective Hydrotreating achieves desulfurization with little olefins saturation (and hence little loss of octane).

Non-selective Hydrotreating + Octane Recovery achieves desulfurization with partial or total olefins saturation (with attendant octane loss), but recovers most of the lost octane by secondary reactions (e.g., isomerization).

Sorption sequesters the sulfur in a solid sorbent medium and achieves desulfurization with little olefins saturation (and hence little loss of octane).

As Table 1 indicates, a number of new processes had reached NPC's Demonstrated or Near-Commercial status by the end of 1999, and several interesting candidates were in the Developing stage. All of these processes promised performance superior to conventional hydrotreating, with respect to octane loss, yield loss, hydrogen consumption, and investment and operating costs.

With regard to costs, analyses by MathPro Inc. in the late '90's indicated that certain of the Demonstrated and Near-Commercial processes offered average costs of achieving the Tier 2 gasoline sulfur standard in the range of 2½¢/gal of complying gasoline – about half that of conventional hydrotreating.

Recognizing the rapid progress in FCC naphtha desulfurization technology, the NPC stated in its June 2000 report that ". . . few refiners are expected to choose [conventional hydrotreating] . . .".

However, the NPC also noted that ". . . conventional hydrotreating is the only process with wide commercial experience currently available."

As the refining industry has geared up for complying with the Tier 2 gasoline sulfur standard, FCC naphtha desulfurization technology has continued to advance. Some processes that were in the Demonstrated and Near-Commercial categories in 2000 have since accumulated considerable commercial experience. Others have been improved significantly. Still others, that were not advanced enough to be considered in the NPC survey, are now commercially available.

As a group, the FCC naphtha desulfurization processes now on offer have technical capabilities far superior to those available in 1997 and even in 2000:

- Minimal octane loss (≈1 number)
- Little or no volume loss
- Low hydrogen consumption (< 100 SCF/B)
- Low capital investment and operating expenses
- Flexibility for co-processing other sulfur-bearing streams

- Capability to economically produce ultra-low-sulfur FCC naphtha ($\leq$ 10 ppm)

The last item, production of ultra-low-sulfur FCC naphtha, requires reliable techniques for avoiding production of recombinant mercaptans, which can occur in hydrotreating processes at reactor exit temperatures and relatively high concentrations of H_2S.

With regard to costs, recent data obtained by MathPro Inc. suggests that processes now on offer have average costs of achieving the Tier 2 gasoline sulfur standard in the range of 2¢/gal of complying gasoline.

Table 4, based on publicly available information in March 2003, shows processes that the refining industry has selected to date for complying with the Tier 2 gasoline sulfur standard and the indicated number of installations for each. Note that the indicated number of refineries includes both U.S. and foreign refineries.

Table 4: Refiners' Choices of Processes for Full-Range FCC Naphtha Desulfurization, as of March 2003

Jan. 2000 NPC Classification	Process Licensor	Process	Technology	Number of Refineries
Demonstrated	Exxon Mobil	SCANfining	Selective HDS	26
Near-Commercial	CD TECH	CD Hydro / CD HDS	Selective HDS	≈ 30
	UOP	ISAL	HDS + Oct. Recovery	≈ 5
Developing	Phillips	S Zorb G	Sorption	≈ 10
Not Considered	IFP	Prime G+	Selective HDS	> 60
By NPC in 2000	Grace Davison	SuRCA	Sulf. Reduc. FCC Cat.	≈ 10
	Grace Davison	S-Brane	Membrane Separation	--

Notes:

1. All process names are trademarked
2. HDS denotes Hydrodesulfurization
3. SuRCA™ is a sulfur-reducing FCC catalyst

Table 4 contains some striking information. First, processes that the NPC considered Demonstrated in 2000 account for only about 20% of the refining industry's reported selections. Second, processes that were not sufficiently advanced to be candidates for consideration in 2000 account for about 50% of the refining industry's reported selections. Third, the indicated processes come from six different technology providers. In addition, though not shown in Table 4, several other processes are available for licensing from other technology providers.

3. TECHNOLOGICAL PROGRESS INDUCED BY CLEAN FUELS REGULATIONS

We have identified a number of factors that account for the advance in FCC naphtha desulfurization technology triggered first by the prospect and then by the establishment of Tier 2 gasoline sulfur control.

- The Tier 2 gasoline sulfur control established a strong economic driving force for technological progress in FCC naphtha desulfurization. As noted above, conventional hydrotreating is expensive. From the standpoint of the refining industry, improved technology that reduces capital expenditures and operating costs offers large economic benefits. Across the entire U.S. gasoline pool, every 1¢/gal reduction in the average cost of gasoline production amounts to about $1¼ billion per year. From the standpoint of the technology providers, the Tier 2 gasoline sulfur program opened up a large new market; virtually every U.S. refinery (other than the California refineries) became a potential licensor of an FCC naphtha desulfurization process. This new market was augmented by new gasoline sulfur control programs adopted in Canada and the European Union.

- The refining sector has a competitive market for new technology in general and for FCC naphtha desulfurization technology in particular. Many established and capable technology providers are vying for a share of the latter market, as Tables 1and 4 indicate.

- The regulatory process that led to the Tier 2 gasoline sulfur program provided adequate lead time for technology providers to develop improved technology and for the refining industry to evaluate and compare the new processes and then to install the necessary process units. EPA began considering gasoline sulfur control in 1997, and it was clear then that EPA would ultimately promulgate a gasoline sulfur control program. EPA promulgated the Tier 2 gasoline sulfur rule in January 2000, with the program to start in January 2004. Many U.S. refiners were able to defer making commitments on gasoline sulfur control until early 2002.

- The chemistry of naphtha hydro-desulfurization is well-established and relatively well-understood. Except for S Zorb G™ and S-Brane™, the processes listed in Tables 1 and 4 embody refinements and enhancements to established technology.

We draw several conclusions from this example of technological progress induced by environmental regulation.

First, when technological progress is rapid and a competitive market for new technology exists, being an “early adopter” may not be advantageous. The longer one waits before committing to a particular process, the greater the chances of (1) having more options and (2) realizing technical and economic benefits from improving technology.

Second, developing objective estimates of the refining costs of a prospective clean fuels regulation requires consideration of the technological progress the regulation is likely to induce. In particular, such estimates should reflect the projected economics of identifiable new technologies and processes likely to be ready for commercial use when the new regulation takes effect.