

# **A NOVEL VAPOR-PHASE PROCESS FOR DEEP DESULFURIZATION OF NAPHTHA/DIESEL**

## **FINAL REPORT**

DOE Cooperative Agreement No. DE-FC26-01BC15282

Period of Performance: April 10, 2001 to June 30, 2003

For

U.S. Department of Energy  
National Energy Technology Laboratory  
3610 Collins Ferry Road  
Morgantown, WV 26507

by

B.S. Turk  
R. P. Gupta  
S.K. Gangwal

Research Triangle Institute  
Research Triangle Park, NC 27709

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## ABSTRACT

Tier 2 regulations issued by the U.S. Environmental Protection Agency (EPA) require a substantial reduction in the sulfur content of gasoline. Similar regulations have been enacted for the sulfur level in on-road diesel and recently off-road diesel. The removal of this sulfur with existing and installed technology faces technical and economic challenges. These challenges created the opportunity for new emerging technologies. Research Triangle Institute (RTI) with subcontract support from Kellogg Brown & Root, Inc., (KBR) used this opportunity to develop RTI's transport reactor naphtha desulfurization (TReND) process. Starting with a simple conceptual process design and some laboratory results that showed promise, RTI initiated an accelerated research program for sorbent development, process development, and marketing and commercialization. Sorbent development has resulted in the identification of an active and attrition resistant sorbent that has been prepared in commercial equipment in 100 lb batches. Process development has demonstrated both the sulfur removal performance and regeneration potential of this sorbent. Process development has scaled up testing from small laboratory to pilot plant transport reactor testing. Testing in the transport reactor pilot plant has demonstrated the attrition resistance, selective sulfur removal activity, and regeneration activity of this sorbent material. Marketing and commercialization activities have shown with the existing information that the process has significant capital and operating cost benefits over existing and other emerging technologies. The market assessment and analysis provided valuable feedback about the testing and performance requirements for the technical development program. This market analysis also provided a list of potential candidates for hosting a demonstration unit. Although the narrow window of opportunity generated by the new sulfur regulations and the conservative nature of the refining industry slowed progress of the demonstration unit, negotiations with potential partners are proceeding for commercialization of this process.

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## List of Acronyms and Abbreviations

AI	Attrition Index
°C	Celsius
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COR	Contracting Officer's representative
COS	Carbonyl Sulfide
DI	Davison Index
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
°F	Fahrenheit
FCC	Fluid Catalytic Cracking
GC	Gas Chromatograph
GPA	Geographical Phase-in Area
H <sub>2</sub> S	Hydrogen Sulfide
HDS	Hydrodesulfurization
HPLC	High Pressure Liquid Chromatography
HTHP	High-temperature, High-pressure
IGCC	Integrated Gasification Combined Cycle
KBR	Kellogg Brown & Root, Inc.
kW	kilowatt
LCO	Light Cycle Oil
LOI	Loss on Ignition
MAT	Microactivity Testing
MFC	Mass Flow Controller
N <sub>2</sub>	Nitrogen
NETL	National Engineering Technology Laboratory
O <sub>2</sub>	Oxygen
PONA	Parafins, Olefins, Naphthenes, and Aromatics
ppmv	Parts per Million by Volume
ppmw	Parts per Million by Weight
psig	Pounds per Square Inch Gauge
PTR	Pilot Test Reactor
R&D	Research and Development
RTI	Research Triangle Institute
SCD	Sulfur Chemiluminescence Detection
SCI	Süd Chemie, Inc.
SO <sub>2</sub>	Sulfur Dioxide
SPPCo	Sierra Pacific Power Company
TRTU	Transport Reactor Test Unit
TReND	Transport Reactor Naphtha Desulfurization
XRD	X-ray Diffraction

## Executive Summary

Research Triangle Institute (RTI) with subcontract support from Kellogg Brown & Root, Inc., (KBR) initiated a research program aimed at commercialization of RTI's transport reactor naphtha desulfurization (TReND) process. The U.S. Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) under the Cooperative Program DE-FC26-01BC15282 sponsored this research and development work.

The need for such a technology was based on the predicted impact of the U.S. Environmental Protection Agency's (EPA's) Tier 2 regulations on the sulfur content of gasoline. Analysis of the existing technology indicated that the new sulfur regulations would result in technical challenges to remove the remaining sulfur and economic challenges to minimize the cost impact on the consumer. A similar situation was developing for on-road diesel. However, the compliance date was further in the future.

Based on a simple conceptual process and some promising laboratory results, RTI began a rapid research and development program to commercialize this technology to provide the refining industry with an alternative technology for complying with Tier 2 regulations. Part of this research and development program focused on the technical issues. These included optimizing sorbent composition, sorbent production processes, and process development. Additional work assembled cost information and market analysis. Fitting all these activities into a schedule to meet the commercialization goals required an accelerated research and development program.

Because of this accelerated schedule, a large amount of resources were dedicated to technical issues relating to sorbent and process development. The major accomplishments of this effort were:

- Identified key active components and support materials for desulfurization sorbents
- Designed, constructed, and conducted shakedown of a dedicated testing system
- Developed a bench-scale production method producing active attrition resistant sorbent
- Scaled up the bench-scale production method to produce multiple 100 lb batches with commercial equipment by a catalyst manufacturer
- Conducted process and sorbent optimization testing in bench-scale reactor systems
- Performed pilot plant testing in transport reactor testing system
- Screened sorbent effectiveness for multiple fuels including fluid catalytic cracking (FCC) naphtha, hydrotreated diesel, hydrotreated diesel spiked with light cycle oil (LCO), and Jet-A fuel
- Filed a patent application.

Although the cost analysis for RTI's TReND process showed the process to have a significant cost savings for both capital and operating costs as these estimates were continually revised, market analysis and assessment provided a different point of view about the potential of the TReND process for FCC naphtha desulfurization. This market assessment showed that refiners are extremely conservative investors, particularly in adopting new technology. Refiner's profit margins are relatively low, forcing them to minimize any process investment, particularly capital investment for regulatory compliance, and to maintain productivity and reliability as high as possible. Therefore, refiners typically do not have the risk tolerance necessary for adopting any emerging technology.

Furthermore, the market assessment also indicated that the Tier 2 regulations were a small portion of larger regulatory issues faced by refiners. In response to this larger picture, many refineries were making technology decisions for gasoline in the 2001 and 2002 period. Any emerging technology, which had not developed strong technical and economic incentives and developed a strategy for mitigating technical risks compared to more established technologies during this period, was not a serious contender for the gasoline desulfurization market. After 2002, the number of refineries still actively in the market for desulfurization technology, particularly for an emerging technology, essentially dropped to zero.

The good news was the technology selection for diesel would remain open to late 2003, because the refiners perceived the diesel sulfur problem as more complex and final investment plans needed to take impending regulations for off-road diesel into account. Because of these market factors, in January 2002 a technical redirection was sought, and granted by the DOE, to shift research and development efforts from the desulfurization of FCC naphtha to diesel.

As a result of this technical redirection, efforts were initiated to adapt the sorbent and process technology for desulfurization of diesel. The transport reactor system could be adapted to treat diesel as easily as it could FCC naphtha. Sorbent development had been focused on optimizing removal of refractory cyclic sulfur compounds, in particular thiophenic derivatives. Sorbent testing had also showed that the sorbent was equally effective at removing all thiophenic derivatives. Because the sorbent composition was similar, the same production process could be used to produce active attrition resistant sorbent. Thus, to implement this redirection, the sorbent composition had to be reoptimized for the desulfurization of diesel. This relatively smooth transition from FCC naphtha to diesel demonstrated the versatility of this technology for removing sulfur from various transportation fuels and the unique sulfur removal ability of the RTI's sorbent composition.

The research and development work in this project advanced testing of this technology to pilot plant transport reactor systems with hydrotreated diesel. Because the best available transport reactor system for testing this process was a more generalized single loop testing system at KBR, complete process testing was limited. Although the market analysis did permit the identification of a short list of refiners that might be interested in hosting a demonstration test, the limited test results from the pilot plant transport reactor testing was not sufficient to interest these refiners. This did not stop attempts to find a demonstration partner, but did make locating and negotiating the demonstration testing more difficult. Currently, discussions are underway with a major refinery technology developer to further demonstrate and ultimately commercialize this technology.

# CHAPTER 1

## INTRODUCTION

Research Triangle Institute (RTI) with subcontract support from Kellogg Brown & Root, Inc., (KBR) initiated a research program titled, "A Novel Vapor-Phase Process for Deep Desulfurization of Naphtha" in April 2001. The U.S. Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) under the Cooperative Program DE-FC26-01BC15282 partially sponsored this research and development work.

### 1.1 PROJECT RATIONALE

In March 2000, U.S. Environmental Protection Agency (EPA) issued Tier 2 regulations that require that the sulfur content of gasoline be reduced to a maximum of 30 parts-per-million-by weight (ppmw) of sulfur by the year 2006 (EPA, 2000). It is anticipated that, due to public demand for a cleaner environment, future regulations will have even stricter emission requirements; as a result, fuels containing near zero sulfur levels will be required. Accordingly, these new regulations require sulfur reduction of typically >90% by 2006, and perhaps nearly complete removal thereafter. At the same time, the sulfur content of commercially available crude oils produced in the United States and neighboring countries has been generally increasing. The implication of this increasing sulfur content in crude oil is that compliance with Tier 2 regulations cannot be met by simply switching to low sulfur crudes. With the Tier 2 regulations requiring significantly higher sulfur removal and with the increasing sulfur content of future crudes, marginal improvements in existing desulfurization processes may not be able to produce the amount of gasoline required and achieve regulatory compliance. Therefore, new, cost-effective processes must be developed to minimize the financial impact of these regulations on the American economy and provide the American public with a cleaner environment.

### 1.2 BACKGROUND

Most of the sulfur found in gasoline comes from the naphtha produced from a fluid catalytic cracking (FCC) unit. FCC naphtha is the primary blending stock of gasoline in conventional petroleum refineries. One recent study (Lamb et al., 2000) of two hypothetical refineries showed that FCC naphtha accounted for 84.5% to 96.5% of the sulfur in each refinery's total gasoline pool, ranging from 81 to 227 ppmw of sulfur. The sulfur content of FCC naphtha typically varies from 150 to 3,000 ppmw depending on the sulfur concentration of the feed and the end point of the gasoline product. By just treating the FCC naphtha, these authors showed that a nominal 30-ppmw-sulfur gasoline could be produced. From this and other references (EPA, 1999), the efforts in this program were focused on the desulfurization of FCC naphtha to reduce the sulfur content of the gasoline pool in order to meet current and future regulations.

In a typical FCC naphtha, sulfur compounds range from  $H_2S$  to the derivatives of dibenzothiophene. Table 1-1 shows the distribution of the various sulfur compounds in a typical FCC naphtha sample with an end point of 430°F. As the end point of naphtha increases, the total sulfur content, the fraction of sulfur present in a carbon ring (like thiophene) and the complexity of the sulfur compounds increase rapidly. Table 1-1 shows that most of the sulfur in FCC naphtha is present as thiophenic derivatives, but the largest and most complex sulfur compound is benzothiophene. For FCC naphtha with an end point >430°F, derivatives of

**Table 1.1. Sulfur Compounds in a Typical FCC Naphtha**

<b>Sulfur Compound</b>	<b>S (ppmw)</b>	<b>Sulfur Compound</b>	<b>S (ppmw)</b>
Hydrogen Sulfide	43	Ethyl Methyl Disulfide	<1
Carbonyl Sulfide	<1	Ethyl Disulfide	<1
Sulfur Dioxide	<1	Thiophene	41
Carbon Disulfide	82	Tetra-Hydro Thiophene	6
Methyl Mercaptan	10	2-Methyl Thiophene	25
Ethyl Mercaptan	4	3-Methyl Thiophene	38
Isopropyl Mercaptan	1	2-Ethyl Thiophene	6
n-Propyl Mercaptan	2	3-Ethyl Thiophene	15
tert-Butyl Mercaptan	<1	2,5-Dimethyl Thiophene	3
sec-Butyl Mercaptan	<1	2,4 & 2,3-Dimethyl Thiophene	11
Isobutyl Mercaptan	<1	3,4-Dimethyl Thiophene	6
n-Butyl Mercaptan	<1	Methyl Ethyl Thiophenes	10
Methyl Sulfide	<1	Trimethyl Thiophenes	8
Ethyl Methyl Sulfide	<1	Benzothiophene	<u>268</u>
Ethyl Sulfide	<1		
Methyl Disulfide	<1	<b>Total</b>	<b>594</b>

dibenzothiophenes are typically found. Thus, any desulfurization process must be capable of removing these high-molecular weight, complex cyclic sulfur compounds from naphtha.

To desulfurize FCC naphtha using a commercially-proven process, a refiner has several options. The traditional route has been to use hydrodesulfurization (HDS), but there are other alternatives as well, as described below and in Table 1-2. In conventional HDS (Rock et al., 1998), the FCC naphtha feedstock is reacted with hydrogen over a catalyst to convert the sulfur into gaseous hydrogen sulfide ( $H_2S$ ). The reaction is typically carried out in a packed-bed or fixed-bed reactor using various well-known catalysts containing sulfided metals on a high-surface-area alumina support. The reactions are exothermic and are conducted at moderate pressure (400-500 psig) with inlet temperature of 550°F to 650°F. The sulfur in the feed is converted to hydrogen sulfide ( $H_2S$ ) and leaves the reactor in the overhead hydrogen stream. A separation step is required for  $H_2S$  removal so that the hydrogen can be recompressed and recycled. Make-up hydrogen is required. The HDS reaction conditions tend to result in some hydrogenation of olefins, which results in loss of octane number rating—as much as a 3 to 8 number loss for full-range (*i.e.*, not prefractionated) naphtha feed.

As refiners and researchers recognize the obvious shortcomings of conventional HDS, several new-generation HDS or HDS-like processes are being developed and commercialized to address the problems of high capital cost associated with large, fixed-bed reactors, and to address the loss in octane number rating.



Table 1-2 summarizes the characteristics of these technologies:

- CD Hydro (CD Tech)
- CD HDS (CD Tech)
- ISAL (UOP)
- Prime G+ (IFP)
- S Zorb (Phillips)
- Scanfining (Exxon)
- Octgain (Mobil)

Of particular interest to this project, as a benchmark, is the S Zorb process (also summarized in Table 1-2) being developed by the Phillips Petroleum Company, now ConocoPhillips. This emerging technology removes sulfur compounds by contacting the vapor-phase naphtha with a solid adsorbent in the presence of hydrogen. The adsorbent is regenerated continuously in a separate regeneration sequence by controlled burning of adsorbed sulfur to sulfur dioxide. The chemical reactions that remove the sulfur from the naphtha are not the same as those occurring in conventional hydrotreating (Greenwood et al., 2000) and only a small amount of hydrogen is consumed, with no olefin saturation. It is claimed that very low levels of sulfur can be attained with high yields. Both the absorber and the regenerator in the S Zorb process are contemplated to be conventional bubbling-bed units. Furthermore, a separate reactor is required upstream of the desulfurizer to reduce the sorbent. No units have been commercialized, although a 6,000 bbl/day demonstration unit was built at Phillips' Borger, TX, refinery and this process was demonstrated in this unit.

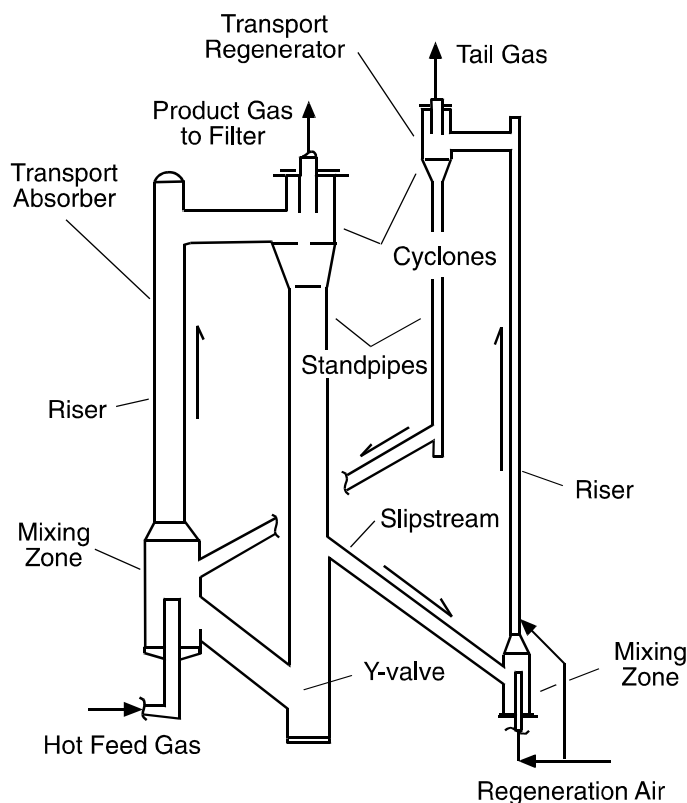
### **1.2.1 The RTI Process**

The RTI process, designated as transport reactor naphtha desulfurization (TReND) process, utilizes an attrition-resistant sorbent in a high-throughput transport reactor system developed by KBR. KBR has successfully used the transport reactor system in the Sierra Pacific Power Company's (SPPCo's) integrated-gasification-combined-cycle (IGCC) system for removal of H<sub>2</sub>S and COS from syngas produced from coal gasification. A schematic of this transport reactor is shown in Figure 1-1. This unit, utilizing KBR's patented transport reactor technology, consists of an absorber (desulfurizer) and a much-smaller diameter regenerator that continuously processes a fraction of the recirculating solid sorbent (arrows show the flow direction).

This transport reactor system provides significant advantages over conventional bubbling bed reactors (used in Phillips' S Zorb process as discussed previously), such as smaller reactor size, higher vapor throughput, and more efficient heat and mass transfer. However, the sorbent must possess extremely high attrition resistance and fast kinetics to be used in a transport reactor. RTI has successfully developed a sorbent that meets these criteria. The unique chemistry (discussed later) combined with high attrition resistance and fast kinetics of the sorbent for a transport reactor form the basis for the TReND process.

**Table 1-2. Comparison of Proposed TRND Process with Existing and Emerging Naphtha Desulfurization Technologies**

	CD Tech	CD Tech	UOP	IFP	Phillips	Exxon	Mobil
Trade name Suited for boil range	CD Hydro Light naphtha	CD HDS Medium and heavy naphtha	ISAL Medium and heavy naphtha or full range	Prime G+ Any range	S Zorb Any range	Scavfining medium or medium and heavy naphtha	Octgain medium and heavy naphtha
Basic chemistry	Convert mercaptans to heavy boiling sulfides; optional catalyst to convert alpha olefins to beta for octane boost	Selective HDS	Non-selective HDS followed by cracking/isomerization for octane recovery	Mild hydrogenation to convert mercaptans to high boiling sulfides, then selective HDS	Adsorption of sulfur compounds over solid adsorbent	Selective HDS	Non-selective HDS followed by cracking/ isomerization for octane recovery
Process configuration	Catalyst placed on top trays inside LN/MHN naphtha splitter column	Catalyst placed on top and bottom trays inside MN/HN naphtha splitter column	Single reactor with two catalysts, flow scheme like conventional hydrotreater	Full naphtha treated for mercaptan conversion followed by LN splitter, MN+HN then treated over selective HDS catalyst, polishing reactor to further reduce sulfur	Packed bed adsorber vessel with continuous regeneration of catalyst in a separate vessel by controlled oxidation	Conventional HDS scheme	Single reactor with two catalysts, flow scheme like conventional hydrotreater
Reaction conditions	75 psig/ 214°F	250 psig/489°F top 250 psig /623°F bottom	600 psig/NA	235 psig/370°F pre- reaction 320 psig/570°F 1st reaction 270 psig/660°F 2nd reaction	100-300 psig 500-725°F	NA	600 psig 754°F
Strengths	Near complete mercaptan removal, ability to gain octane, avoid Merox, no waste streams	Reasonable octane loss, low hydrogen consumption, high yield	Ability to recover full octane, conventional flow scheme	Low pressure, low capital, low hydrogen rate, high yield, conventional process scheme for the HDS side	Low pressure, low hydrogen rate, in theory simple chemistry and operation	Low pressure, low capital, low hydrogen rate, high yield, conventional process scheme	Ability to recover full octane, conventional flow scheme
Weaknesses	Cost of catalyst, larger column, cannot remove light disulfides	Needs HN to operate column at desired conditions, high catalyst cost	High pressure, high capital; some yield loss esp. at full octane recovery, high H <sub>2</sub> rate, gasoline pool vapor pressure increase	Some octane loss	Technology not adapted commercially	Some octane loss	High pressure, high capital, lower yields, octane loss, high H <sub>2</sub> rate, gasoline pool vapor pressure increase
Commercial unit(s)	Yes	In Design/ Construction	No	Yes	No	Yes	Yes
Reference	Rock et al., 1998	Rock et al., 1998	Martinez et al., 2000	Nocca et al., 2002	Greenwood et al., 2000	Halbert et al., 2000	Halbert et al., 2000



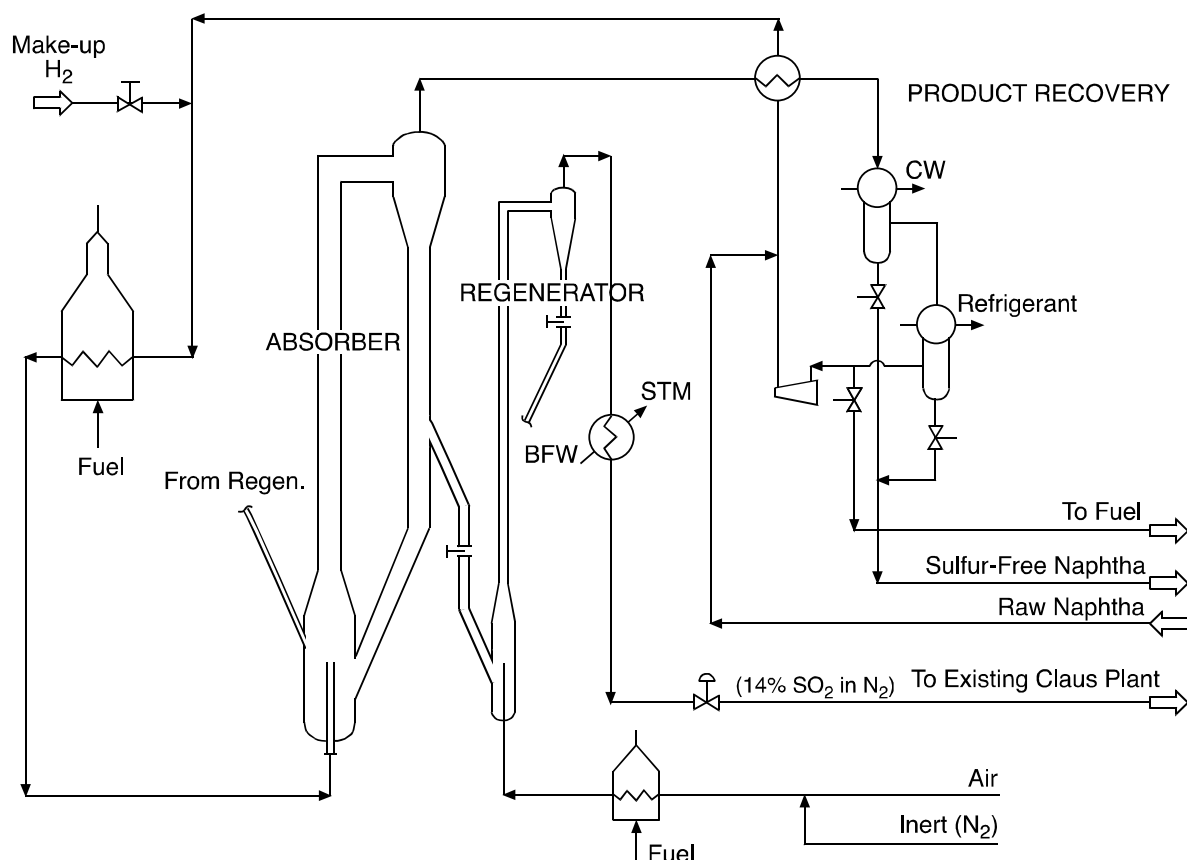
**Figure 1-1. Schematic of the SPPCo hot gas desulfurization system.**

Figure 1-2 shows the process flow diagram of the TReND process in its commercial embodiment. In this process, the liquid naphtha is pumped to pressure, blended with an  $H_2$ -containing stream, and vaporized. A preheater brings the feed to the absorber at a temperature of 600° to 1,000°F. The absorber operates as a transport reactor, where the feed vapor contacts and entrains the sorbent. Contact time is on the order of seconds, sufficient for removal of sulfur compounds in the naphtha. A cyclone separates the sorbent, and sulfur-laden sorbent is returned to the standpipe. The desulfurized naphtha product is then condensed, separated from  $H_2$  and other light ends, and sent to a stabilizer column, if necessary. The light ends are recycled back into the incoming naphtha feed. Some light ends are purged to the fuel system to maintain the desired hydrogen concentration.

A portion of the standpipe sorbent is sent to a regenerator, where the sulfur-laden sorbent is oxidized at a temperature of 800° to 1,000°F, generating  $SO_2$ . Neat air is used as the oxidant without the need for dilution; this is only possible in a transport reactor because high circulation rates help control the temperature rise resulting from the exothermic regeneration reaction. The  $SO_2$  and  $N_2$  mixture is separated from the regenerated sorbent and sent to the refinery sulfur plant, while the regenerated sorbent is returned to the riser of the absorber. The regenerator is also a transport reactor.

The typical transport reactor operating conditions demand a sorbent that has

- high attrition resistance (to withstand 10 to 30 ft/s riser velocity and thermal cycling)
- high reactivity (reaction zone residence time <10 seconds).



**Figure 1-2. Commercial embodiment of the RTI-KBR transport reactor naphtha desulfurization (TReND) process.**

### 1.3 PROJECT OBJECTIVES

The goal of this R&D effort was to develop the TReND process from lab-scale proof-of-concept through pilot-plant testing. To meet this goal, a number of distinct but interrelated research activities were necessary. One of these activities was sorbent development. Sorbent development included identification of suitable active components, development of a production process providing the necessary chemical activity and physical strength, and scale-up of this production process to produce commercially large batches of this sorbent. Another research activity was process development. In this activity, testing was moved from small-scale batch fluidized bed testing to pilot plant transport reactor testing. In addition to assisting sorbent development activities, this testing was to build the basis for technical and economic evaluation of the TReND and design of a demonstration system. The last research activity was market analysis and assessment with the intention of identifying a commercial demonstration partner.

The challenge of meeting the goal for this R&D effort was meeting the time schedule necessary for a larger research effort to make the TReND technology commercially available to comply with the Tier 2 regulations.

## 1.4 CHANGE IN PROJECT DIRECTION

EPA's Tier 2 regulations required refiners to produce 30 ppmw sulfur gasoline by January 2005. There are provisions to allow more time to smaller and financially challenged refiners to extend this deadline, but only a very small number of the refineries fall into this category. To meet this deadline, the refiners are in one of four possible stages of implementing EPA's Tier 2 sulfur regulations for gasoline. These are: (1) evaluating available technologies, (2) developing the engineering design to implement the selected technology, (3) constructing the equipment for installation of the technology, and (4) using of the technology to produce a 30 ppmw gasoline product. Market analysis performed during the development of the TReND process and contacts with potential commercial partners indicated that a majority of the refiners in the United States have already selected the technologies that will enable them to meet EPA's Tier 2 regulations and are actively designing and constructing the equipment necessary for this technology. Some refineries are already producing 30 ppmw gasoline including Chevron at Pascagoula, BP at Texas City, and all California refineries. The small remaining fraction of refiners that have not yet selected a technology will have very little time to test the technology once it is installed and are therefore only interested in commercially mature technologies. Based on this analysis, finding a commercial partner to test the TReND process for FCC naphtha being developed in this project became very challenging. This analysis also demonstrated that the short-term opportunity to enter the gasoline desulfurization market with RTI's TReND process was limited to small refineries, which may have exemption to comply with Tier 2 regulations until 2008 or 2010.

The market analysis and the contacts with potential commercial partners, however, did demonstrate that refiners are more anxious to consider new technologies for diesel desulfurization to meet EPA's sulfur restrictions for on-road diesel. As these regulations are set to take effect during 2006 to 2008, most refiners are still evaluating technologies to meet the regulations. As the operation of a refinery is selected to maximize the profit from a slate of products and not a single product like gasoline or diesel, refiners are also waiting for the regulations for off-road diesel to be announced before choosing a diesel desulfurization technology. Another factor influencing technology decision by refiners for diesel is applying conventional hydrotreating technology for diesel will not be as simple as for naphtha. The lower reactivity of the sulfur species in diesel requires more severe operating pressures and temperatures, and will consume more hydrogen. This will significantly increase the operating and capital expense associated with meeting the sulfur regulations for diesel. According to National Petroleum Council and American Petroleum Institute estimates, the estimated range for the price increase of diesel is between 5.8 to 11.6 cents/gal. With all this uncertainty, refiners are expected to postpone committing to any technology as long as possible. Time constraints, however, will force refiners to begin making their selection in next 1 to 2 years. Table 1-3 summarizes the regulatory schedule and the technical and economic challenges facing production of gasoline and diesel demonstrating the opportunity for rapid commercialization of RTI's TReND process for desulfurization of diesel.

Based on the foregoing discussion, the selection for a diesel desulfurization technology would be driven primarily by operating and capital cost advantages. A request was made to DOE/NETL in January 2002 for technical redirection to focus the efforts on adapting the TReND process for desulfurization of diesel. This request was granted by DOE and hence a majority of work reported in this report deals with desulfurization of diesel.

**Table 1-3. Summary of Regulatory Requirements and Technology Challenges Facing Gasoline and Diesel Production**

	<b>Gasoline</b>	<b>Diesel</b>
EPA sulfur limits	30 ppmw	15 ppmw
Compliance date	Jan 1, 2005	June 1, 2006
Sulfur in untreated products	500 ppm with benzothiophene being most complex	30,000 ppm with very complex sulfur compounds <sup>+</sup>
Available desulfurization technology	Hydrotreating	Hydrotreating
Operating conditions	Moderate	Severe
Cost of new technology ¢/gal of gasoline/diesel product	5-8	6-12

<sup>+</sup>Based on using FCC light cycle oil as a feed. Refineries that have installed hydrotreating capacity can produce a diesel with 500 ppmw sulfur.

## **1.5 REPORT ORGANIZATION**

The strong motivation to move the TReND process technology to commercialization in time for complying with the Tier 2 regulations required simultaneous activity in many different parallel, but interrelated research areas. Because of this research approach, effectively describing this R&D effort was challenging. Thus, this report has been organized around sorbent development, testing, and market analysis and technical assessment activities. The testing activities have been further broken down to describe RTI's testing systems, results for bench-scale testing, and pilot plant transport reactor testing.

## **CHAPTER 2**

### **EXPERIMENTAL AND ANALYTICAL SYSTEMS**

In this research project, a number of reactor systems available at RTI were used to conduct the R&D work. The unique process requirements and necessity of a dedicated research reactor system prompted the design and construction of the RTI's Pilot Test Reactor (PTR) system. Descriptions of RTI's reactor systems, supporting analytical systems, and characterization techniques used in this development program are provided in the following sections. Further commercialization efforts required testing in transport reactor systems at KBR. Documentation of testing in these pilot plant transport reactor systems is provided in Section 4.

#### **2.1 RTI'S MICROREACTOR SYSTEM**

The primary use of RTI's microreactor system was as a screening tool for active sulfur materials, support materials, sorbent formulations, and desulfurization testing conditions. Although the system was ideally suited for gas phase testing, the system could be used to vaporize and test liquid hydrocarbons. This system required only 50 g of test material and could tolerate a higher portion of fines than other reactor systems. Disadvantages of this system were only very small amounts of liquid hydrocarbon could be processed in a given period, limited and fractional collection of liquid product, and minimal instrumentation for monitoring regeneration. A simplified schematic diagram of this system is provided in Figure 2-1.

The heart of the microreactor system consisted of a 1-in diameter quartz reactor. The total length of the quartz reactor was 48 in. A coarse quartz frit was fixed in roughly the middle of the reactor during reactor production. The two ends of this quartz reactor were flanged. This allowed a set of metal flanges to attach and seal inlet and outlet process piping. A majority of the reactor was surrounded by a 3-ft clamshell furnace with a single zone furnace. The reactor was aligned to place the center of the sorbent or catalyst bed supported on the coarse quartz frit at roughly the middle of the furnace's single heating zone. The heating control system used the temperature from a thermocouple inserted through the upper flange into the center of the sorbent bed.

The feed system for this reactor system began with a pair of mass flow controllers (MFCs) for metering in known quantities of gas. The gas from this pair of MFCs flowed into the lower inlet of the liquid vaporization system shown in Figure 2-1. This liquid vaporization system was heated externally with heat tapes and internally with a small heating rod. Any liquid to be vaporized was fed into the preheater at the top. Either a syringe pump or HPLC pump controlled the liquid flow into the preheater. This liquid flowed down the internal heating rod due to gravity. As the liquid vaporized, the vapor was swept up and out of the preheater with the gas flow. The preheated feed gas/vapor mixture was fed into the heated zone of the reactor below the coarse quartz frit through the bottom flange in a 1/4-in stainless steel tube.

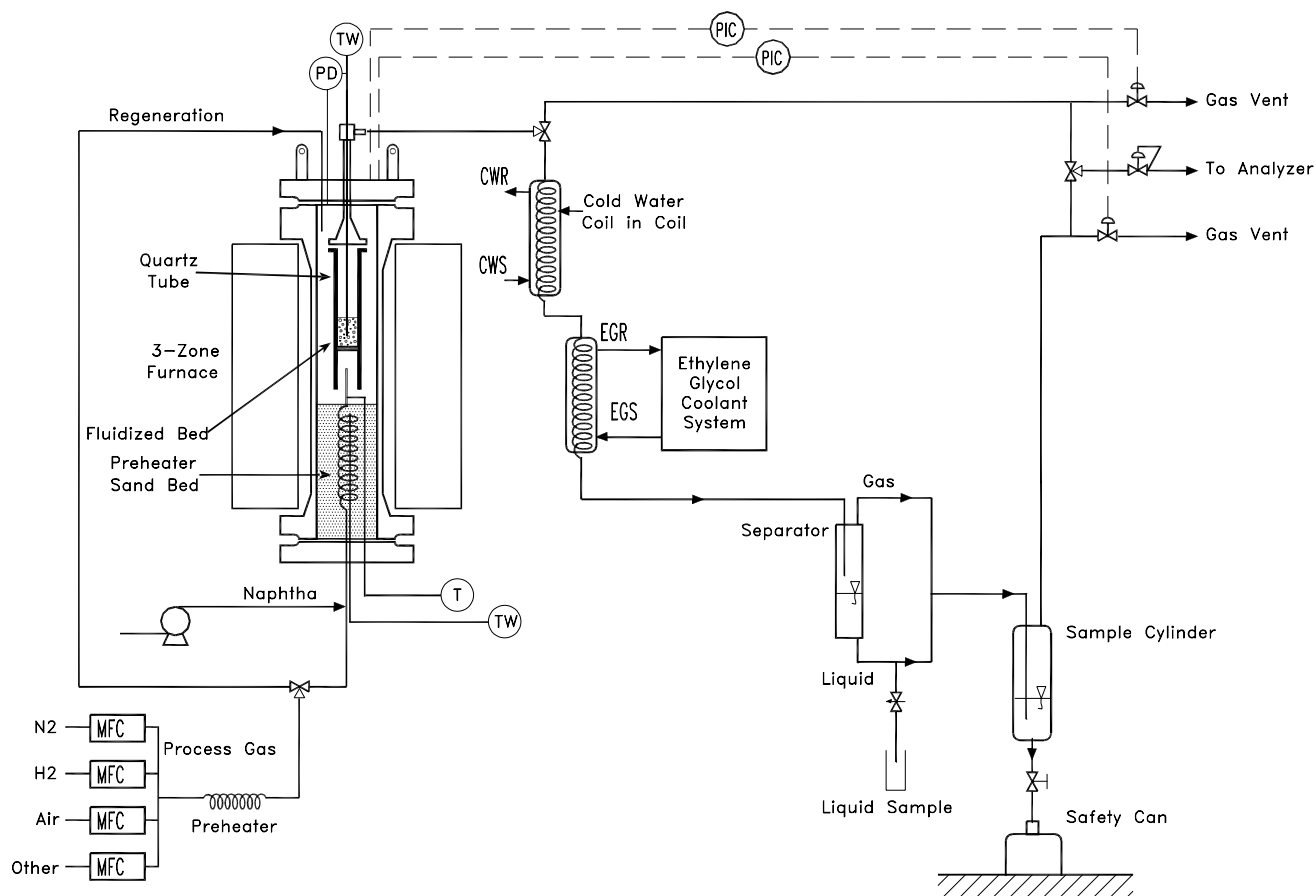




naphtha product. This fact seriously complicated the measurement of sulfur concentrations for individual species. The next approach involved trapping the naphtha smoke in a sparger filled with ceramic packing and maintained at  $\leq 5^{\circ}\text{C}$  with an ice bath, dry ice or ethyl glycol system. Although this system did manage to trap the naphtha smoke, it had a tendency to freeze any water or heavier hydrocarbons in the fine pores of the sparger stopping effluent flow. The latest approach involved narrowing the bore of the tube from  $\frac{1}{4}$  in to  $\frac{1}{16}$  in and spraying the effluent from the  $\frac{1}{16}$  in tube onto the cooled walls of a stainless steel collection vessel. The vessel was cooled to  $5^{\circ}\text{C}$  in a glycol cooled water bath. This approach was compact and relatively effective for condensation of naphtha, diesel, and jet fuels.

## 2.2 RTI'S PILOT TEST REACTOR SYSTEM (PTR)

Although RTI's microreactor system was extremely well suited for screening tests, this system was not appropriate for rigorous process development and preparation for transport reactor testing. To fulfill these needs, a larger, dedicated, and specialized reactor system was built. This system was designed to provide the potential for high liquid feed rates, better feed vaporization, and analytical analysis of the product. A simplified schematic of the process can be seen in Figure 2-2. The PTR system was designed with a maximum operating pressure of 150 psig and maximum reactor temperature of  $1400^{\circ}\text{F}$ .



**Figure 2-2. Simplified schematic of RTI's pilot test reactor (PTR) system.**

For safety considerations, the system was broken into two parts. A majority of the process equipment necessary to operate the PTR was conveniently mounted on a 6-ft by 4-ft skid. The reactor furnace; gas feed mixing and control systems; product condensation, collection, and separation for analysis; as well as pressure control systems were mounted on this skid. The liquid processing and liquid feed pumping system were located in a walk-in fume hood. With this arrangement, the liquid hydrocarbon could be effectively isolated and maintained in a small well-ventilated space, reducing the potential for generating explosive mixtures of hydrocarbon vapors and air.

The equipment on the skid primarily consisted of a controlling scheme for mixing and metering of feed gases; the high pressure, high temperature preheating and reactor system; and product cooling, separation, and analytical processing system.

### **2.2.1 Hydrocarbon Feed System**

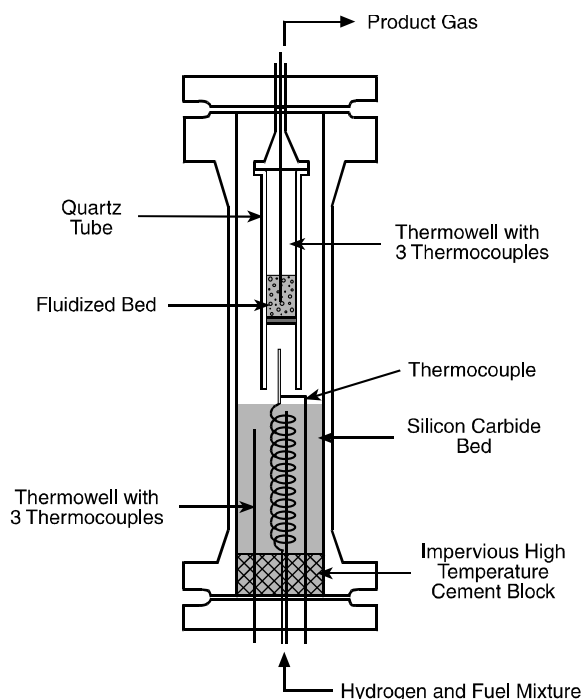
The liquid hydrocarbon was stored in a feed tank in a walk-in hood to ensure that any fugitive hydrocarbon vapors generated were not allowed to collect and concentrate, but were dissipated and vented. This feed tank was maintained under a nitrogen blanket by means of a small nitrogen purge at roughly atmospheric pressure. The liquid hydrocarbon was transported from the feed tank to the preheater by means of a high pressure metering pump located near the feed tank in the fume hood. Initially, a Milton Roy Model MD1-M30-P025 metering pump was used. However, at the lower pumping rates  $\leq 25$  ml/min, this pump was not capable of providing continuous flow. For these lower flow rates, a high pressure Thermo Separations Products P-100 pump was used. The high pressure liquid hydrocarbon from the pump was pumped from the fume hood to the liquid/gas mixing zone downstream of the preheater/vaporization system.

### **2.2.2 Gas Feed System**

The permanent gases were supplied to the system from gas cylinders through the gas supply system. This gas supply system consisted of four MFCs and a switching panel. For sulfidation, the MFCs were used to meter the appropriate amount of a hydrogen and argon mixture and nitrogen if necessary to the mixing zone. In this mixing zone, the hydrogen mixture and liquid hydrocarbon feed were combined and fed into the preheater coil. For regeneration, the MFCs were used to generate mixtures of air and nitrogen with the correct amount of oxygen for regeneration. The mixture was fed into the annulus between the quartz reactor and the pressure vessel bypassing the heating coil. The MFC and switching arrangement also allowed both house and tank nitrogen to be fed into either feed point in the reactor instead of the reactive feed gas.

### **2.2.3 Preheater and Reactor System**

The preheater and reactor were enclosed in a single pressure vessel that was externally heated by a three-zone electric furnace with individual temperature control in each zone. The schematic arrangement of the preheater and reactor in this stainless steel pressure shell can be seen in Figure 2-3. Pressure drop across the reactor was measured with a Foxboro electronic pressure transducer.



**Figure 2-3. Schematic of contents of pressure shell for PTR system.**

The liquid hydrocarbon and gas mixture were fed into the preheating zone at the bottom of the reactor. The preheating zone consisted of 3/8-in inner diameter stainless steel tube coil that was roughly 3 in in diameter and 12 in tall. The lower portion of the coil was embedded in a thermal concrete block to prevent accumulation of a pool of hydrocarbon liquid in the cooler portion of the pressure vessel. In the heated zone above the concrete block, the coil was immersed in a bed of granular silicon carbide. Because silicon carbide has a high thermal conductivity, heat entering through the wall of the pressure vessel from the furnace was rapidly transferred to heating the coils and heating and vaporizing the liquid/gas feed mixture. A total of three thermocouples were mounted at different lengths along the axis of the preheater to monitor temperature during preheating. A final thermocouple was mounted in the process gas outlet of the heating coil to monitor the temperature of the feed mixture to the reactor.

The sorbent was supported on a coarse quartz frit fused into the walls of a 2-in inner diameter quartz reactor. This quartz reactor was mounted to a Hastelloy flange attached to the top flange of the pressure vessel. The vaporized feed mixture was forced to flow through the quartz reactor fluidizing the sorbent bed supported on the frit. The reactor effluent flowed out of the top of the reactor through the pressure vessel flange and on to the condensers. Three thermocouples were mounted in a thermal well inserted into the sorbent bed through the top flange on the pressure vessel. These thermocouples were positioned to provide temperature measurements at 1 in, 3 in, and 5 in above the frit supporting the fluidized sorbent bed. These thermal couples are referred to as B1, B3, and B5, respectively.

During regeneration, the mixture of oxygen and nitrogen was introduced in the annulus between the quartz reactor and the stainless steel pressure shell. The gas flowed through this annulus and was heated to the same temperature as the sorbent bed. After the regeneration gas had flowed through the annular zone, the gas then flowed through and fluidized the sorbent bed. The regeneration effluent flowed out of the reactor through the process tubing in the top flange.

## **2.2.4 Liquid Product Condensation**

The effluent hydrocarbon vapor from the reactor was cooled in three sequential tube-in-tube heat exchangers. A small compact water-cooled heat exchanger was used initially to drop the temperature of the reactor effluent to below 200°F. The reduction of temperature was used to protect gas routing valves used for sending the hydrocarbon vapor mixture to the condensation and collection system or directly routing the regeneration tailgas to the backpressure regulator and analytical system. After this first heat exchanger, the hydrocarbon vapor was forced through a second water-cooled coiled heat exchanger designed to cool the hydrocarbon vapor mixture to roughly 70°F. Finally, the hydrocarbon product mixture was forced through a third coiled heat exchanger designed to drop the temperature of the mixture to 40°F. In this heat exchanger an ethylene glycol/water mixture was chilled to 40°F with a Lauda WK-2200 refrigerated circulator. Temperature of the product mixture was monitored at the outlet of each of the heat exchangers by means of a thermocouple mounted in the process tubing.

## **2.2.5 Liquid Product Sampling**

Liquid product samples were only collected during the desulfurization of the liquid hydrocarbon feed. The liquid samples collected included time dependent samples of roughly 10 ml collected at approximately 10-minute intervals and a larger cumulative samples collected over the desulfurization and subsequent purge periods.

After the effluent mixture had been cooled to approximately 40°F, the mixture was forced through a series of parallel process tubing. One of these sections of tubing had a needle valve, whereas the other had a special sampling valve. By closing the needle valve, more of the product mixture was forced to flow in process tubing with the sampling valve. Using this sampling valve, small time-dependent liquid samples of roughly 10 ml could be collected at 10-minute intervals.

After the time-dependent sampling section, the product mixture was fed into a large collection vessel by means of a dip tube designed to separate the liquid phase hydrocarbon product from the gas phase product. These large cumulative sample vessels could be removed from the system for conveniently weighing and processing of the collected liquid sample. Processing, performed in the fume hood station, involved collecting at least two representative samples of 40 ml each and disposing of any excess liquid product.

## **2.2.6 Gas Sampling**

After separation of the liquid and gas phase product mixture from the desulfurization process, a backpressure control valve was used to drop the operating pressure to roughly 20 psig. Using a small MFC, a slipstream of the gas phase effluent was collected in a 1-liter gas canister for analysis. The remainder of the gas phase effluent was vented. The gas phase sample trapped in the gas canister was analyzed for hydrogen, helium, argon, hydrocarbon distribution, and total sulfur with the aid of three distinct GC systems. The GC systems are described in Sections 2.3 and 2.4.

During regeneration, the reactor effluent was routed to bypass the condensation system and feed directly to a backpressure control valve. Using a line regulator, the regeneration effluent gas was maintained at 20 psig. A slipstream of this effluent was routed to a series of continuous analyzers for CO, CO<sub>2</sub>, SO<sub>2</sub>, and O<sub>2</sub>.

### **2.2.7 Data Logging**

A LabView program was used to monitor and record the process information being obtained from the PTR. The information collected by this data acquisition system included the MFC output; thermocouples in the preheater, reactor, and condensation systems; pressure transducers, differential pressure transducer for the reactor; and the continuous analyzers for CO and CO<sub>2</sub>, SO<sub>2</sub>, and O<sub>2</sub>. This information was systematically recorded at 30-second intervals.

### **2.2.8 Additional Safety Activities**

Based on the process objectives to vaporize and react naphtha and diesel at rates as high as 1 gallon per hour and temperatures between 800°F and 1000°F, a detailed hazard review of the PTR system was conducted prior to construction. Facility and personnel training recommendations from the hazard safety review that were implemented included the installation of two fire extinguishers near the unit, refresher training for all personnel involved with the unit on fire extinguisher operation, and installation of explosive limit detectors on the unit that were tied into a central building alarm system. Special safety features built into the operating unit included a explosive limit detector for determining safe operating conditions to switch from absorption to regeneration, storage and liquid processing in a dedicated fume hood, and installation of an overhead winch system to help install and remove the reactor system.

## **2.3 SULFUR ANALYSIS**

Sulfur was analyzed by a number of different techniques. The sample type, form of sulfur, and the type of sulfur information desired dictated the appropriate sulfur analysis technique. For analysis of process gas streams with sulfur compounds, excluding SO<sub>2</sub> above 100 ppmv, gas chromatography with sulfur chemiluminescence detection (SCD) was employed. Gas chromatography with SCD was also used to quantify the amount of each sulfur species present in liquid samples. For total sulfur analysis of either liquid or solid samples, an Antek total sulfur analyzer was used. For analysis of gas samples with SO<sub>2</sub> particularly in concentrations exceeding 500 ppmv, a Bovar ultraviolet photometric analyzer was used.

### **2.3.1 Gas Phase Sulfur Species Analysis**

For the analysis of sulfur species in gas phase samples, the samples were injected into a Hewlett-Packard Model 5890 gas chromatograph GC with a capillary column and a Sievers Model 355 SCD. Specifications for this chromatographic analysis are provided in Table 2-1.

The Sievers SCD provided high sensitivity and selectivity for detection of sulfur containing compounds. Selectivity of sulfur to carbon response on the SCD was 10<sup>6</sup> or better. The sulfur in a compound eluting from the capillary column is oxidized to sulfur dioxide and then reduced to hydrogen sulfide in the flameless burner. The hydrogen sulfide is reacted with ozone in the reaction chamber to produce an activated form of sulfur dioxide, which emits light. A photomultiplier tube detects the light and the resulting signal is amplified to produce an analog voltage output.

The Sievers SCD was calibrated periodically with hydrogen sulfide in nitrogen at concentrations from 250 ppbv to 100 ppmv. The calculated response factors were also used for carbonyl sulfide and sulfur dioxide. Standards containing carbonyl sulfide in nitrogen and sulfur dioxide

**Table 2-1. Hewlett-Packard GC with SCD – Specifications for Gases**

Gas chromatograph	Hewlett-Packard Model 5890
SCD	Sievers Model 355
Sample injection technique	6-port gas sampling valve
Sample loop volume	250 $\mu$ L
Capillary column	J&W, 30 meter long, 0.32 mm ID, with GS-GasPro stationary phase
Column head pressure with helium carrier gas (column oven at 50°C)	18 psig
Column temperature program	50°C for 2 min., 30°C/min. to 140°C, hold for 1.5 min.
Carbonyl sulfide retention time	2.07 min.
Hydrogen sulfide retention time	2.48 min
Sulfur dioxide retention time	4.51 min.
Air flow to SCD burner	40 sccm
Hydrogen flow to SCD burner	100 sccm
SCD burner temperature	800°C
SCD burner pressure	238 mm Hg
SCD reaction chamber pressure	6 mm Hg

in nitrogen were analyzed periodically to establish retention times and equivalence of response to hydrogen sulfide. A daily calibration check was performed with a hydrogen sulfide in nitrogen standard at a nominal concentration of 4.8 ppmv.

### 2.3.2 Liquid Sulfur Species Analysis

For liquid samples and particularly with samples for which the objective was to determine the quantitative amounts of each sulfur species within the naphtha and diesel range, a second chromatographic technique was used. These liquid samples were loaded in a suitable sample vial for a Hewlett-Packard Model 6890 autosampler and spiked with a known amount of an internal standard solution containing 3,6-dithiaoctane. These samples were loaded into the sample carousel. Approximately 1  $\mu$ L was removed from each sample and injected into a Hewlett-Packard GC Model 6890 GC equipped with a capillary column and Antek Model 7090 SCD. The specifics of this chromatographic setup are provided in Table 2-2.

**Table 2-2. Hewlett-Packard GC with SCD – Specifications for Liquids**

Gas chromatograph	Hewlett-Packard Model 6890
SCD	Antek Model 7090
Sample injection technique	10 $\mu$ L syringe
Sample volume	1 $\mu$ L
Capillary column	Hewlett-Packard, 30 meter long, 0.32 mm ID, with Hewlett-Packard-1 stationary phase
Column head pressure with helium carrier gas (column oven at 70°C)	6.47 psig
Column temperature program	40°C for 3 min., 10°C/min. to 250°C, hold for 36 min.
Oxygen flow to SCD burner	10 sccm
Hydrogen flow to SCD burner	150 sccm
SCD burner temperature	950°C
SCD burner pressure	156 mm Hg
SCD reaction chamber pressure	13 mm Hg

The theoretical operation of the Antek SCD is exactly the same as the Sievers SCD. The primary difference between the two detectors is the burner configuration. The burner configuration on the Antek SCD was found to be less sensitive to coke formation from repeated exposure to samples with large hydrocarbon content, i.e., liquid hydrocarbons. The Sievers SCD would lose sensitivity as coke was formed in the burner. When sensitivity degraded beyond the acceptable limit, a coke burn-off and reconditioning sequence was necessary. As limited exposure to gas phase carbon compounds, particularly CO and CO<sub>2</sub>, did not affect the stability or sensitivity of the response for the Sievers SCD, the Sievers SCD was dedicated to gas phase sulfur analysis and the Antek SCD was used exclusively for analysis of sulfur species in liquid hydrocarbon samples.

The Antek SCD was calibrated with standards prepared by diluting weighed quantities of sulfur compounds in isooctane. An internal standard compound (3,6-dithiaoctane) was included in each calibration standard to enable the quantitation of sulfur compounds based on their relative response to the internal standard.

The analog signal from both the Sievers and Antek detectors was converted to a digital signal by an analog to digital converter that was interfaced with a Hewlett-Packard ChemStation data acquisition/data processing system. This system provided for raw data file storage and the production of external standard report (Sievers SCD) and internal standard report (Antek SCD) for the samples that were analyzed.

### **2.3.3 Total Sulfur Analysis**

For liquid and solid samples, the total sulfur content was measured by an Antek Model 9000HS Total Sulfur Analyzer. In this apparatus, either liquid or solid samples are loaded into a quartz boat that is pushed into a combustion chamber with high partial pressures of O<sub>2</sub> in excess of 1000°C. The solid or liquid samples are combusted with the sulfur compounds being converted to SO<sub>2</sub>. Ultraviolet light is used to excite the SO<sub>2</sub>, which subsequently fluoresces, and the light emission is detected by a photomultiplier.

The response of the Total Sulfur Analyzer was calibrated with gravimetrically made samples of dibenzothiophene in C<sub>15</sub>H<sub>32</sub>. Samples generated for this application were essentially identical to diesel samples and were only slightly affected by extended storage time and/or volatility of the hydrocarbon solvent. This technique was used to set up multiple ranges from roughly 5 to 2000 ppmw sulfur.

### **2.3.4 Sulfur Dioxide (SO<sub>2</sub>) Analysis**

Concentrations of SO<sub>2</sub> in excess of 500 ppmv were continuously measured with a Bovar Model 921 photometric detector. The Bovar 921 uses the absorption of a particular wavelength of light through an optical cell purged continuously with sample gas compared with the absorption in an identical optical cell filled with inert gas. The response from the Bovar 921 was calibrated with a calibrated SO<sub>2</sub> standard with 9776 ppmv and a pure nitrogen purge.

## 2.4 HYDROGEN ANALYSIS

Specifications for the Hewlett-Packard GC with TCD are given in Table 2-3.

**Table 2-3. Hewlett-Packard GC with TCD – Specifications**

Gas chromatograph	Hewlett-Packard Model 5890 Series II
Sample injection technique	6-port gas sampling valve
Sample loop volume	500 $\mu$ L
Packed column	Carboxen 1000, 15 ft. x 1/8 in. OD stainless steel
Nitrogen carrier gas flow rate	30 sccm
Column head pressure (column oven at 35°C)	16 psig
Column temperature	40°C isothermal for 2.5 min.
TCD reference gas flowrate	75 sccm
TCD sensitivity	Low
Detector temperature	250°C

The TCD is a non-selective detector that responds to a given compound based on its thermal conductivity being different from nitrogen (the reference gas). The TCD response was calibrated with standard containing argon and hydrogen. Initially the concentration of the mixture was 1 vol% argon and 10 vol% hydrogen in nitrogen.

The TCD signal was acquired over a Hewlett-Packard interface bus (HPIB) and stored and processed with a Hewlett-Packard GC ChemStation.

## 2.5 CARBON DIOXIDE ANALYSIS

Carbon dioxide concentration in the reactor effluent during regeneration was continuously measured with a Hartmann & Braun Optima Activa infrared detector. The response from this analyzer was also calibrated with a certified CO<sub>2</sub> standard containing 10 vol% CO<sub>2</sub> and a pure nitrogen sample.

## 2.6 OXYGEN ANALYSIS

The oxygen content of the reactor effluent during regeneration was continuously monitored with a Teledyne Instant Trace Model 3001 oxygen sensor. This sensor uses the oxygen content of the sample gas to operate a fuel cell. The electrochemical response of the fuel cell is proportional to the oxygen concentration of the sample gas. The response of this detector was also calibrated with a certified oxygen standard and pure nitrogen sample.

## 2.7 CATALYST CHARACTERIZATION

During the development of a commercially viable production process for sorbent material for desulfurization of naphtha and diesel, a number of characterization techniques were used to help guide and assess the performance of this development process. These techniques included BET surface area measurement, mercury porosimetry, and ASTM D5757 attrition measurements. In addition to these tests, the sorbent material was tested in the microreactor system and possibly in the Pilot Test Reactor, if performance warranted.



Other specialized test programs involve temperature program reduction studies and acidity. Although the standard ASTM D 4824 test was used to measure the acidity of the sorbent, the catalytic activity and/or activated state of the sorbent might influence the results from this test. These issues were addressed by testing the sorbent after an appropriate activation process with ASTM method D 4824 and additional acidity test using n-butylamine as the base adsorbent instead of ammonia. More detailed description of the testing procedures with n-butylamine are provided in Section 4.4 and Appendix A.

## 2.8 SPECIALIZED LIQUID PRODUCT ANALYSIS

A number of other product specifications for both the naphtha and diesel were required to evaluate adequately the desulfurization performance on the hydrocarbon product. These evaluations included research and motor octane, boiling point distribution, cetane number, cetane index, density, cold flow plugging point, pour point, and color. These tests, which were outside RTI's capability, were conducted by Core Laboratories, Inc. A comprehensive list of these test are provided in Table 2-4.

**Table 2-4. List of Tests Services Supplied by CORE Laboratories**

Test Description	Naphtha	Hydrotreated Diesel
Cetane Index (ASTM D 975)		Yes
Cetane Number (ASTM D 613)		Yes
Cloud Point (ASTM D 2500)		Yes
Cold Filter Plugging Point		Yes
Color (ASTM D 1500)		Yes
Nitrogen (ASTM D 4629, 5762))	Yes	
Sulfur (ASTM D 5453)	Yes	
Motor Octane (ASTM D 2700)	Yes	
Research Octane (ASTM D 2699)	Yes	
Paraffins, Olefins, Naphthalenes and Aromatics		
Density (ASTM D 4052)	Yes	Yes
Atmospheric Distillation (ASTM D 86)	Yes	Yes
Pour Point (ASTM D 97)		Yes
Vapor Pressure Reid (ASTM D 323)	Yes	

## **CHAPTER 3**

### **SORBENT DEVELOPMENT**

The objective of this sorbent development effort was to develop a sorbent for the RTI TReND process. This objective was broken down into the following activities:

- Preparation and screening of materials and mixtures for activity for removal of thiophenic sulfur, potential support materials, and as promoters
- Development of a sorbent production method for preparing a sorbent with the necessary chemical and physical properties for use in a transport reactor system
- Scale up sorbent production to prepare large batches of the sorbent.

To complete these activities, RTI drew upon expertise acquired from sorbent development programs for high temperature desulfurization of syngas produced from carbonaceous fuels (such as coal, coke, biomass, etc.) in other DOE sponsored projects. Some of this expertise relates to valuable knowledge about high temperature chemistry of metal oxides and sulfur, particularly hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbonyl sulfide ( $\text{COS}$ ) (Woods et al., 1989; Gupta and Gangwal, 1992; Gupta et al., 2001).

Other expertise includes development of sorbents with suitable chemical and physical properties for transport reactors. Part of this experience comes from the development and commercialization of EX-S03, a zinc titanate based sorbent, for the KBR transport syngas desulfurization system at the 100 MWe Sierra-Pacific integrated gasification combined cycle power plant (Gupta et al., 1998). Additional experience with developing active attrition resistant materials comes from RTI's development of a patented iron-based Fischer Tropsch catalyst (Gangwal and Jothimurugensan, 1999). Both of these development programs led to successful processes for preparing material that was eventually scaled up to larger batches.

Therefore, RTI had both the technical expertise and equipment to successfully complete a sorbent development program for the RTI TReND process. The specific activities and accomplishments of this program are described in this chapter. In order to protect the proprietary nature of the sorbent, some of the information on sorbent compositions and preparation methods is not disclosed in this report.

#### **3.1 SORBENT COMPOSITION**

The first critical component for this sorbent was identification of a material that actively removed thiophenic derivatives. A logical starting point for this material was the various active components used in syngas desulfurization sorbents. Thermodynamic analysis showed that the equilibrium concentration at 450°C for thiophene and  $\text{ZnO}$ , one of the most widely used commercial materials for  $\text{H}_2\text{S}$  removal, was less than 1 ppmv. This provided a number of different ready-made materials for initial screening.

A literature survey repeatedly showed that  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  had catalytic activity for removing and polymerizing sulfur on the surface of these materials (Balko et al., 2000; Andersson et al., 1999; Cheng et al., 1997). In the presence of a hydrogen environment, this catalytic activity could result in the formation of  $\text{H}_2\text{S}$  that could readily be removed by any of the active components for syngas desulfurization.

Initial screening activities investigated these possibilities with a thermogravimetric analyzer and RTI's microreactor system. The results were very encouraging, particularly with EX-S03 doped with iron oxide. The results of this initial screening test were described in the technical proposal for this project. However, at the start of this project, a more elaborate and intensive screening program was initiated. In addition to actively attempting to identify materials that would remove thiophenic derivatives, screening activities also investigated oxygen regeneration activity, sulfur removal activity after regeneration, effects of pretreatment, and conversion and selectivity between different sulfur species. Screening activities also investigated other potential sorbent components including support material and promoters. As support materials are rarely completely inert, screening was used to identify support materials that could provide physical strength for attrition resistance, thermal stability against degradation of chemical and physical properties at high temperatures and enhanced chemical activity for sulfur removal. More details about the results of this sorbent screening program are provided in Section 4.1.

During these screening tests, the focus was primarily on the chemical behavior of the sorbent. Because of this focus, simple mixing and impregnation were more than adequate for preparing the sorbent materials for these screening tests. A generic preparation recipe for these sorbent materials is provided in Table 3-1.

**Table 3-1. Generic Preparation Method for Sorbent Screening Tests**

1. Mix support precursor A and support precursor B. Facilitate intimate mixing by stirring the dry powder in water.
2. Dry the resulting cake overnight at 120°C.
3. Calcine the cake at 800°C for 6 hours.
4. Impregnate active component on the cake and calcine at 280°C to achieve desired concentration. Repeating the impregnation and intermediate drying/calcinations steps could be required to load sufficient active component and/or promoters.

As this screening effort progressed, the key materials to be incorporated into the sorbent for the RTI TReND process elements were identified. Multiple large batches of optimal blend of key components, labeled NWA, were prepared for testing. Testing of NWA in RTI's PTR for FCC naphtha desulfurization is described in Section 4.1. This material was also tested for potential use as a desulfurization additive for FCC catalyst with microreactivity testing (MAT) that is described in Section 5.1. Table 3-2 provides the physical properties of the NWA sorbent that served as a basis for subsequent development of the sorbent preparation method discussed in the next section.

**Table 3-2. Physical Properties of NWA Sorbent**

Physical Properties	Value
BET surface area	61.2 m <sup>2</sup> /g
Pore volume	0.25 cm <sup>3</sup> /g
Bulk density	1.35 g/cm <sup>3</sup>
Average particle size	~500 µm
Attrition resistance	Unacceptable

### 3.2 DEVELOPMENT OF SORBENT PRODUCTION METHOD

Although the composition of the NWA sorbent showed promising chemical performance as a regenerable sorbent for removing thiophenic derivatives, the physical properties, particularly the particle size and attrition, were not suitable for transport reactor applications. Furthermore, the mixing and impregnation technique used to prepare the NWA sorbent was adequate for preparing small batches, but completely inadequate for production of large commercial batches. Therefore, development of a sorbent production method that would produce sorbent with the following attributes was initiated:

- Readily fluidizable with an average particle size of 60 to 80  $\mu\text{m}$
- Attrition index (AI) or Davison index (DI) similar to that of a commercial FCC catalyst
- Highly active for both removal of thiophenic sulfur and oxygen regeneration.

Desirable features for this production method included:

- Minimal number of processing steps
- Scalable for production of large batches
- Suitable for production in standard commercial catalyst preparation equipment
- High yields of sorbent with appropriate specifications.

The preferred industrial means of preparing microspheroidal (typically 40 to 150  $\mu\text{m}$  with 80  $\mu\text{m}$  average) particles suitable for fluidized-bed and/or transport reactors is spray drying. For spray drying, a slurry containing the desired components or precursors of the desired components is prepared. The slurry is then pumped into a drying chamber, fed with hot air, through an atomizer or nozzle to produce a spray containing small droplets of water and solid. As the droplet dries, the particle is formed and is collected at the bottom of the chamber, or depending on its size, in the down stream cyclone.

Spray drying provides a convenient method for producing particles with the appropriate size and shape for transport reactor applications, but the important chemical and physical properties are determined by slurry preparation. Perhaps the simplest means of producing a slurry is to disperse the commercially available precursors in water. Although this is extremely simple, it offers only limited ability to control both the physical and chemical properties of the sorbent. Coprecipitation, on the other hand, offers much more flexibility with regards to the nature of the precursors, level of mixing of the precursors, and many other properties. RTI has also used this technique to successfully prepare active attrition resistant catalysts for Fischer-Tropsch reaction (Zhao et. al, 2001).

Using coprecipitation and spray drying as key elements for sorbent preparation, development of a sorbent production method was initiated. Because the objective of this effort was to produce a sorbent with specific chemical and physical properties and a preparation method for this sorbent (attributes for both are listed above), parametric sorbent preparation varied materials, compositions, and processing steps and conditions. Materials produced during this method development effort were characterized for physical properties and tested for chemical performance in RTI's microreactor and PTR as warranted. By eliminating samples that did not meet the limits for either the physical or chemical specifications, this sorbent development effort was able to rapidly focus on the most promising production method. At this stage, more

parametric testing refined and optimized this production method. A list of the various variables tested during different parametric tests is provided in Table 3-3.

**Table 3-3. List of Parametric Variables Tested**

- 
- Method of incorporation active component – impregnation vs. coprecipitation
  - Coprecipitation processing – single vs. multiple
  - Calcination temperature
  - Binder
  - Relative concentration of active component, support, and promoters
  - pH of slurry prior to spray drying
  - Starting material – solid nitrate vs. commercial nitrate solution
  - Washing and filtration
  - Coprecipitation base.
- 

The ultimate result of the method development work was a sorbent production method with promising characteristics for scale-up that produced a sorbent material with suitable activity and attrition resistance. This sorbent was designated RTI-4 and was extensively tested with hydrotreated diesel. While the focus of the project was still FCC naphtha desulfurization, another sorbent, called RTI-2, exhibited promising results. These two sorbents share the same production method, but have slightly different compositions. A summary of the properties for these two sorbents is provided in Table 3-4.

**Table 3-4. Comparison of RTI-2 and RTI-4**

	<b>RTI-2</b>	<b>RTI-4</b>
Intended Fuel	FCC Naphtha	Hydrotreated Diesel
Bulk Density (g/cm <sup>3</sup> )	1.20	1.28
Surface Area (m <sup>2</sup> /g)	53.7	57
Pore Volume (cc/g)	0.24	0.163
Davison Index *	13.4	5.5

\* Values determined using Sud Chemie's Davison index procedure

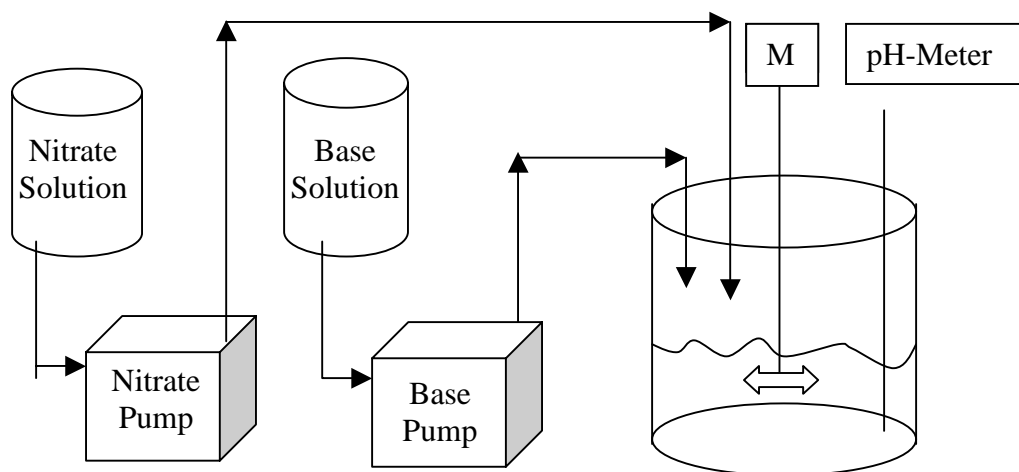
A summary of the production method, consisting primarily of the coprecipitation and spray drying processes, is provided in the following sections.

### **3.2.1 Coprecipitation**

The coprecipitation process begins by preparing solutions with the appropriate concentrations of key elements. For a majority of the samples prepared during this development work, the solutions were prepared from solid chemical nitrates obtained from major chemical suppliers, like Aldrich or Alfa Aesar. However, commercial catalyst manufacturers prefer to use commercially available solutions for coprecipitation processes, if possible. Commercial solutions of the key elements in this sorbent material were available and were used for several preparations. The resulting sorbents from these preparations showed no difference from sorbents prepared from solid starting chemicals using similar preparation steps.

Once the appropriate nitrate solutions were prepared, the precursor materials were coprecipitated with the aid of a coprecipitating base. The coprecipitation apparatus used is shown in Figure 3-1. The nitrate solution and base solution are individually pumped using two peristaltic pumps into a 8.0 liter precipitation vessel provided with a stirrer and pH meter. The

rate of pumping of the two solutions is adjusted to achieve the desired pH or range of pH over which the precipitation occurred.



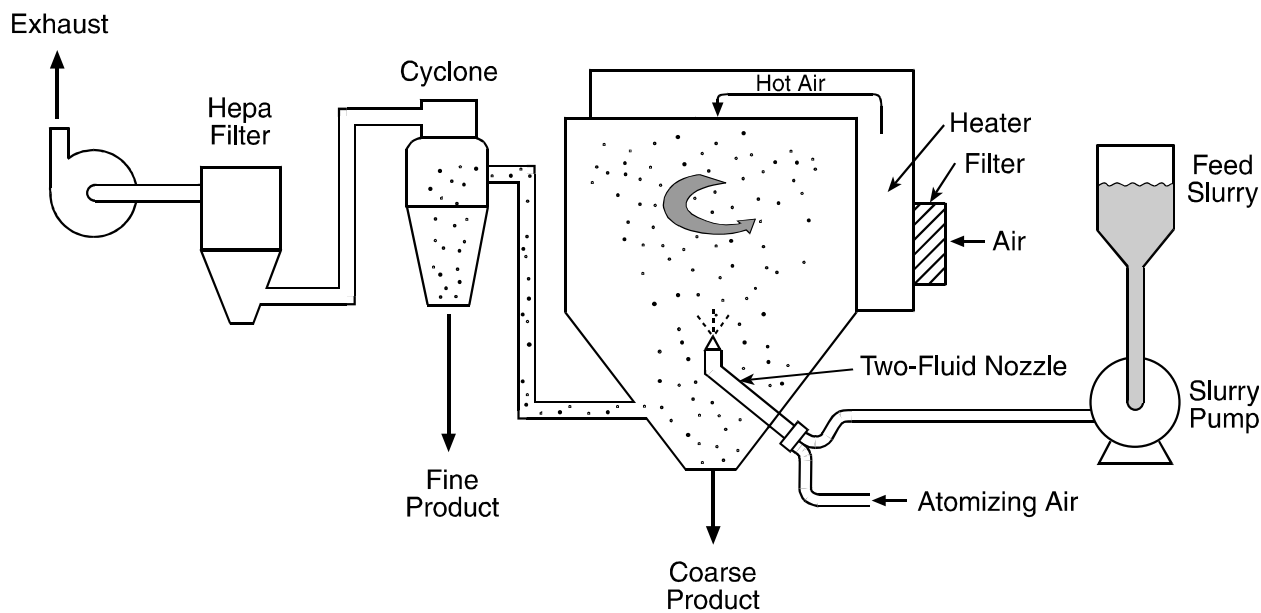
**Figure 3-1. Coprecipitation apparatus.**

### **3.2.2 Spray Drying**

Following completion of the coprecipitation process, the precipitate was washed and filtered to produce a cake. This cake was then rehomogenized with enough water to produce a slurry with a loss on ignition (LOI) between 85% and 90%. The pH of the slurry was adjusted as necessary prior to spray drying.

This slurry was spray dried in a NIRO Mobile Minor 2000 Model H spray dryer. A schematic of RTI's spray drying system is shown in Figure 3-2. The drying chamber on the Mobile Minor is 0.8 m in diameter, 1.5 m high with a 60° cone base and has a 316 stainless steel surface. An accessory that increases the total height of the drying chamber to 1.7 m was also used during all sorbent development for this project. The slurry was fed to the spray dryer by means of a Model 7553-80 Cole Parmer peristaltic pump with Masterflex speed control through a fountain two-fluid nozzle. The outlet air temperature was maintained at about 130°C by adjusting the inlet air temperature. Coarse particle collection occurred at the base of the cone section of the drying chamber. Finer particles were collected in a secondary 6-in diameter cyclone. Any additional dust in the effluent gas was trapped in a HEPA filter prior to venting.

The material collected from the spray dryer was calcined in a muffle furnace at temperatures between 400 and 800°C. Following calcinations, the samples were sized as necessary for subsequent physical characterization or reactor testing. Typical batches of sorbent prepared by this method produced between 100 to 500 g of final calcined material.



**Figure 3-2. NIRO spray dryer system at RTI.**

### 3.3 SORBENT PRODUCTION

One of the primary reasons the sorbent production method was assumed to be scalable was early interaction with Sud-Chemie, Inc. (SCI) in Louisville, KY. This early interaction provided positive feedback from SCI that the sorbent production method RTI was developing could be produced commercially. Some of the parametric testing incorporated in the development of the sorbent production method was based on suggestions from SCI.

However, the real test for the production method came when SCI began preparation of a small batch of RTI-4 in anticipation of producing an even larger batch for bench-scale and transport reactor testing. SCI prepared a trial batch (PP-6649) of RTI-4 and sent it to RTI for evaluation. Comparison of the physical properties of RTI-4 produced by RTI and SCI are provided in Table 3-5. Testing of these materials in RTI's microreactor system showed similar sulfur removal and regeneration performance.

**Table 3-5. Comparison of RTI-4 with SCI Trial Batch (PP-6649)**

	<b>RTI-4 (041102-4)</b>	<b>PP-6649</b>
Bulk Density (g/cm <sup>3</sup> )	1.28	1.44
Surface Area (m <sup>2</sup> /g)	57	70
Pore Volume (cc/g)	0.163	0.148
Davison Attrition Index (DI)*	34.0	21.9

\*Typical for FCC catalyst is 24.0

With the success of this trial batch, SCI made preparations to produce a 100 lb batch of RTI-4. Because SCI's large scale spray drying facilities use atomizer wheels rather than spray nozzles, an atomizer wheel was used for preparation of the large 100 lb batch. A 24 ft diameter spray dryer was used to spray dry this large batch. A number of disappointing features were observed during this spray-drying test. These included a lower than anticipated yield in desired size range and a smaller mean particle size. In smaller spray drying equipment, atomizers are notorious for producing both a lower mean particle size and lower yield in the typical range of interest for

fluidization. Consequently, RTI had to abandon sorbent production using a spray dryer with an atomizer early in the development of the sorbent production method.

Because the spray dryer did have the option for either a rotary atomizer or spray nozzles, a second large batch of RTI-4 was spray dried with spray nozzles instead of the rotary atomizer. Both the yield and mean particle size were larger with the spray nozzle. A comparison of the yields for the rotary atomizer and spray nozzles is shown in Table 3-6.

**Table 3-6. Comparison of Scaled-up RTI-4 Using Nozzle or Atomizer**

	RTI-4 atomizer	RTI-4 nozzle
Uncalcined chamber product D <sub>50</sub> (μm)	63	113
Chamber yield (%)	50	87

Although the fines produced with the use of a rotary atomizer could easily be reslurried and spray dried, these additional steps would add unnecessary cost to the final sorbent preparation. From these large batch preparations, the preferred sorbent production method would use spray nozzles rather than atomizers. The physical properties of scaled-up RTI-4 produced with spray nozzles are shown in Table 3-7.

**Table 3-7. Physical Properties of RTI-4**

Surface Area (m <sup>2</sup> /g)	84.7
Bulk Density (g/cm <sup>3</sup> )	1.46
Pore Volume (cm <sup>3</sup> /g)	0.138
DI*	10.0

\*Davison Attrition Index. Typical AI for FCC catalyst is 24.0

### 3.4 SUMMARY

This sorbent development program successfully:

- Identified a mixture of active sulfur removal compounds and suitable support material.
- Developed a scalable sorbent production that produced a sorbent with high activity and attrition resistance for transport reactor applications.
- Demonstrated large-scale production by having SCI produce multiple 100 lb batches of this material with similar or better properties than the samples prepared in RTI's preparation facilities.



## **CHAPTER 4**

### **RTI'S TEST PROGRAM**

The experimental results collected from both RTI's microreactor and PTR systems were the primary guiding force for material screening, sorbent formulation and development, and process development.

The screening tests performed in the microreactor system allowed rapid identification of the materials and composition active for removing thiophenic derivatives. During sorbent development and scale-up efforts, the microreactor was an invaluable tool to rapidly and effectively evaluate the activity of different sorbent preparation. The microreactor system was also useful for gross optimization of process conditions and testing additional hydrocarbon feedstocks.

The PTR system served as the workhouse for process development. In this capacity, the PTR system provided valuable information on desulfurization performance, product quality changes before and after the process, regeneration performance, and regeneration products. The principal use of this information was to facilitate successful process scale up to pilot plant testing in a transport reactor system.

#### **4.1 MATERIAL SCREENING**

Because of the complexity of testing the desulfurization from a hydrocarbon matrix typical of an FCC naphtha or diesel, the initial screening tests used gas phase mixtures of mercaptans and thiophene or ethyl-thiophene in nitrogen. The objective was to identify materials, supports and promoters that showed a high activity for the removal of thiophene. In addition to the ability to remove thiophene, the material needed to be regenerable with mixtures containing oxygen allowing the material to be used multiple times to remove sulfur. Activation treatments with hydrogen and oxygen were also tested. These screening tests were performed in the microreactor system described in Section 2.1.

Initial catalyst screening focused on readily available catalyst materials ranging from ZnO to zinc titanate. Alternative sulfur getters, like iron and copper, along with promoters, like platinum and palladium, were added to the most promising catalyst materials to evaluate potential benefits. The results from this initial testing guided the preparation of laboratory formulations by dry mixing and impregnation as described in detail in Section 3. Based on the results of these screening tests, a promising sorbent formulation, designated as NWA, was identified. Figure 4-1 shows a comparison of an early ZnO formulation and the NWA sorbent for removal of thiophene at 800°F. As can be seen, the thiophene desulfurization performance for NWA is significantly better.

Subsequent sorbent optimization testing was expanded to study sorbent performance issues other than just desulfurization. These issues included sorbent regeneration, multicycle sulfur capacity, deactivation and pretreatment/activation effects and adapting catalyst preparation techniques to facilitate scale-up to commercial production of catalyst. A number of different multicycle tests were conducted to demonstrate the ability of the catalyst to be regenerated and used for desulfurization multiple times. The results from some of this testing are provided in Figures 4-2 and 4-3. Figure 4-2 shows that the sulfur capacity for thiophene remains roughly

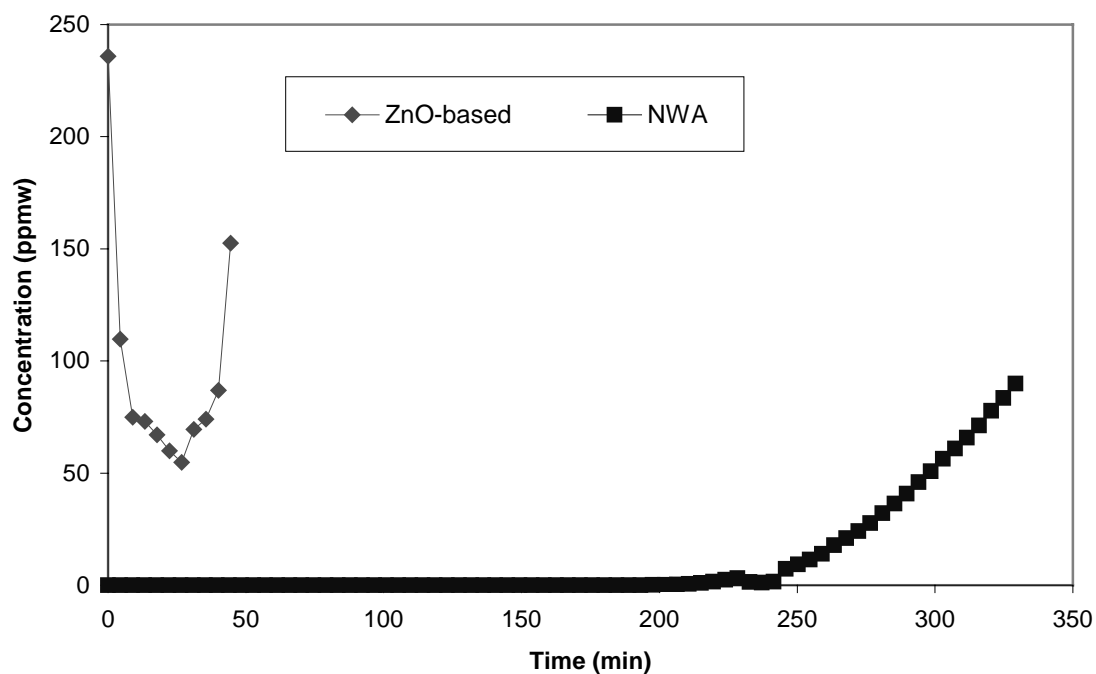


Figure 4-1. Comparison of desulfurization performance.

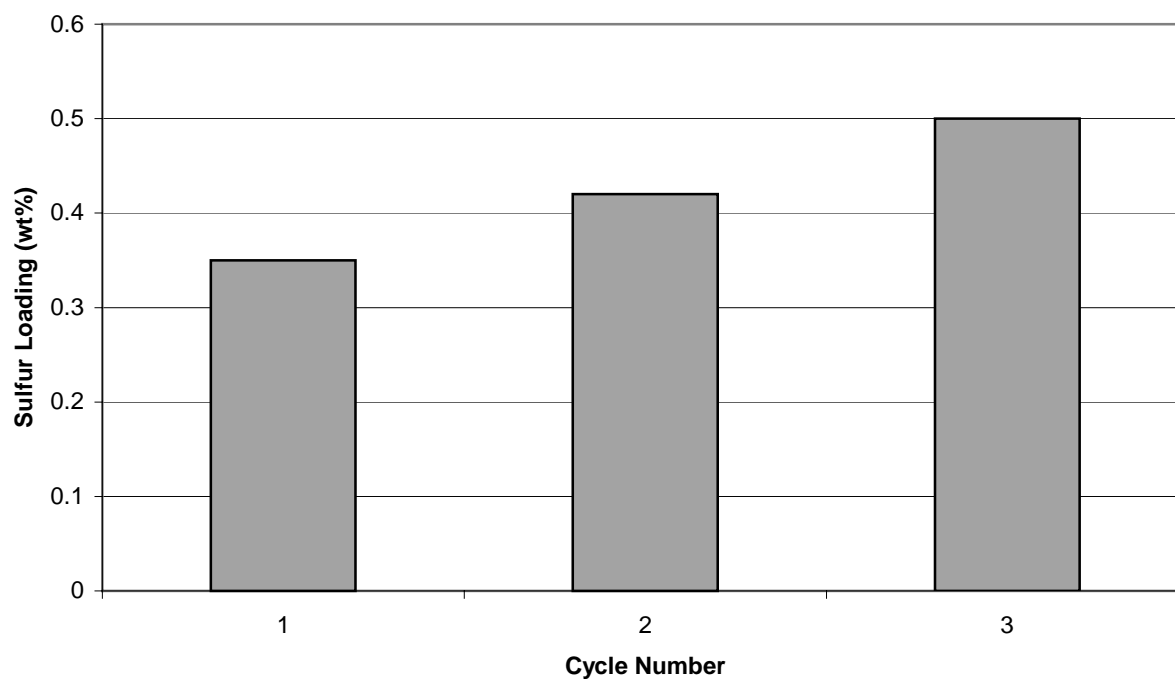
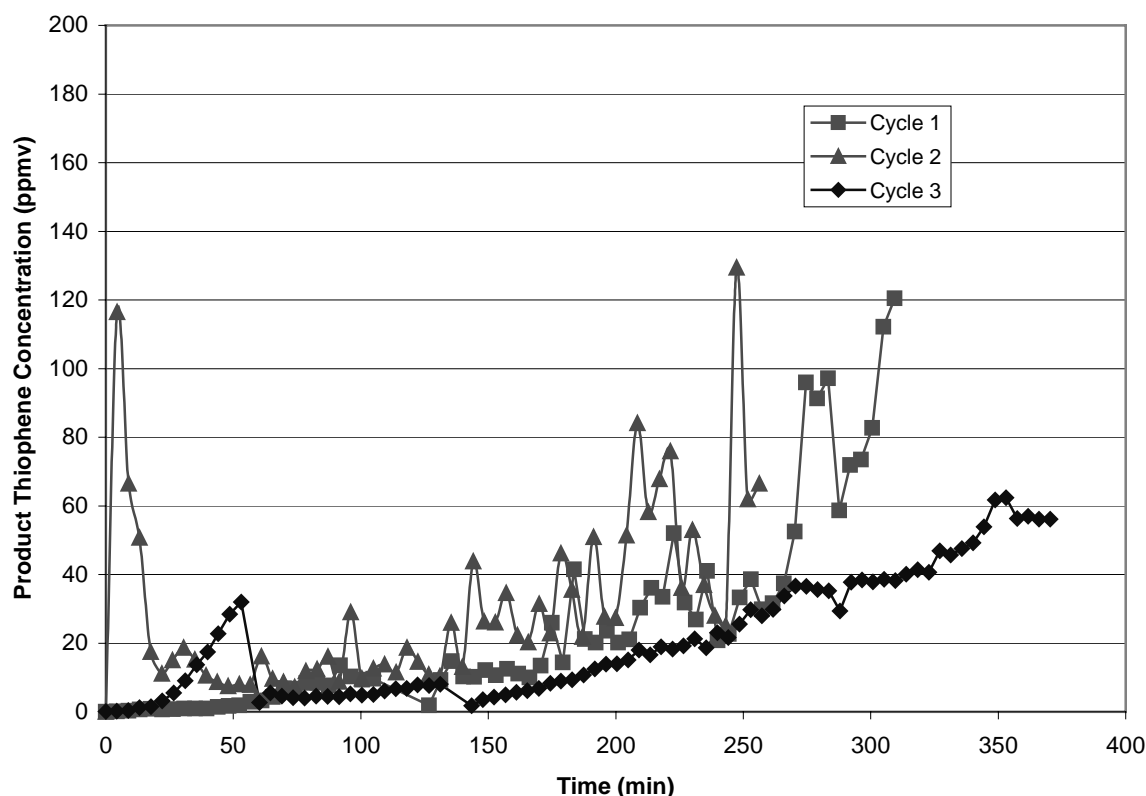


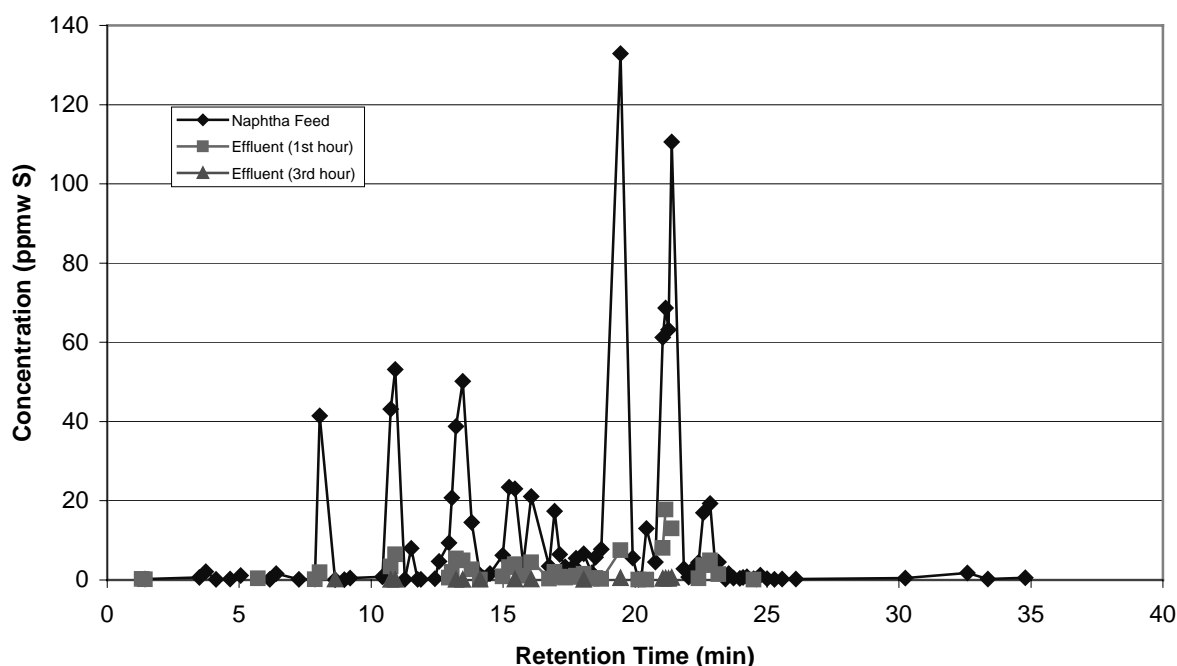
Figure 4-2. Sulfur loading for three sequential cycles.



**Figure 4-3. Thiophene breakthrough profile for three consecutive cycles.**

constant or increases slightly over the first several cycles. Figure 4-3 shows that the sorbent is able to consistently reduce the thiophene concentration from 2,000 ppmv in the feed to below 40 ppmv during cyclic operation. Pretreatment studies show the most promising sorbent formulation developed in this program is more active after an oxidative treatment than a reductive pretreatment. This sorbent behavior clearly differentiates RTI's process from Phillips' S Zorb process.

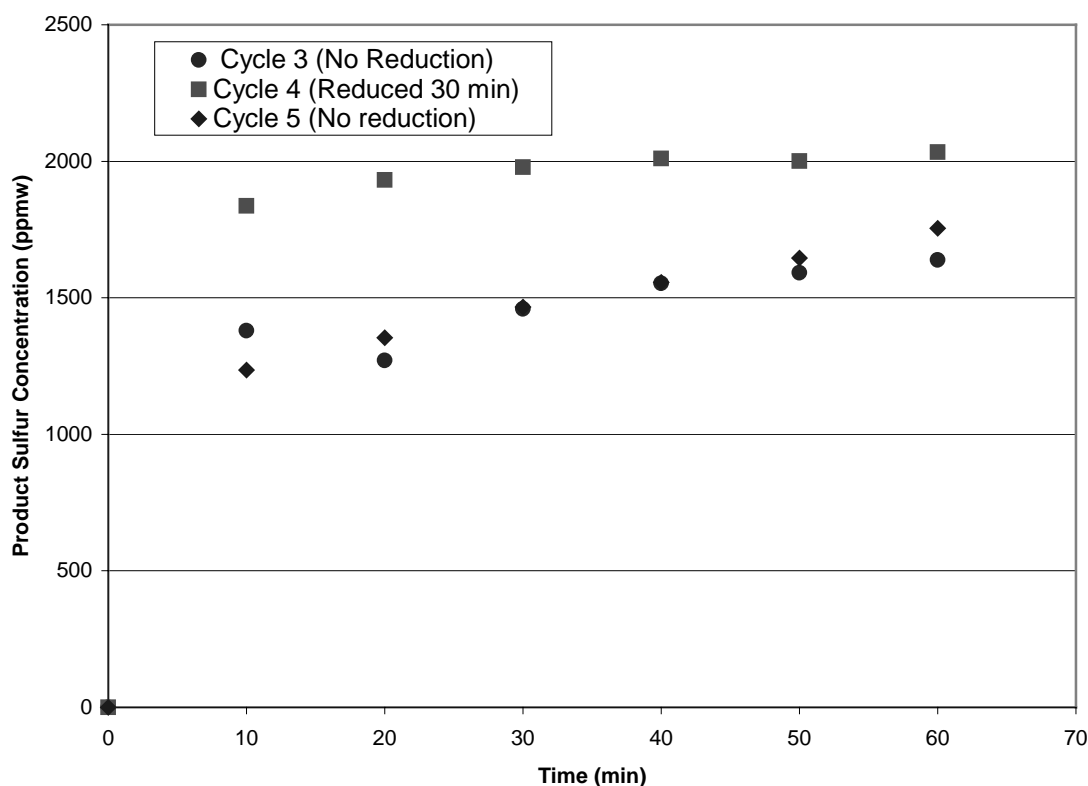
Testing conducted with the NWA sorbent in the microreactor system with FCC naphtha indicated that sulfur concentration of this naphtha sample could be reduced from 2300 to 14 ppmw. This naphtha sample was obtained from Frontier Refinery in Cheyenne, WY. Sulfur speciation (using a sulfur chemiluminescence detector) of feed and product samples obtained from this testing indicated that sulfur removal from the feed was nearly uniform throughout the entire boiling point range, as shown in Figure 4-4, indicating that sorbent has sufficient activity for removal of refractory cyclic sulfur compounds (in addition to straight chain compounds like mercaptans and disulfides) in the short residence time (2 to 5 sec) provided in the reactor. These results provided a clear proof-of-concept for the RTI process for desulfurization of FCC naphtha.



**Figure 4-4. Sulfur speciation of feed and product naphtha samples.**

After initial shakedown testing of the PTR system with EX-S03, a multicycle test with the NWA sorbent was conducted. Multicycle testing involved both a sulfur removal sequence followed by a regeneration sequence to essentially restore the sorbent to its original sulfur removal potential. Prior to initiating Cycle 4, an additional reduction step was introduced to evaluate the desulfurization performance of the reduced form of the sorbent. Figure 4-5 shows that the desulfurization performance for Cycles 3 and 5 were significantly better than Cycle 4, for which essentially no desulfurization activity was observed. Because the sorbent in Cycles 3 and 5 had undergone an oxidation process, whereas the sorbent in Cycle 4 had been reduced, these results confirm earlier findings that the active material for the NWA sorbent was in an oxidized state rather than in a reduced state. These results also confirm that a suitable oxidation step can restore the sorbent's desulfurization performance.

In a second multicycle test with lower FCC naphtha feed rates, the feed and effluent products were analyzed for sulfur compounds. The chromatograms for these samples are provided in Figure 4-6. Comparison of the sulfur species in the FCC naphtha feed and the reactor effluent in Figure 4-6 shows that the NWA did remove sulfur species. Figure 4-6 also shows that the desulfurization activity did not show a particular preference for any specific sulfur species or group of sulfur species. This is very different behavior than is observed with hydrotreating catalysts for which the removal decreases as the sulfur species increases in size, complexity and steric hindrance.



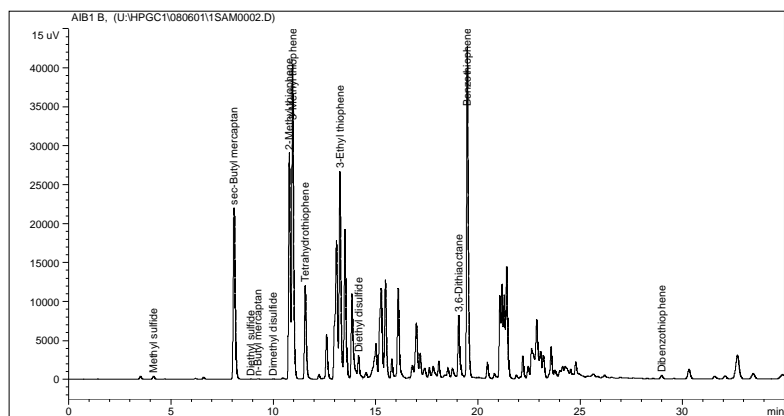
**Figure 4-5. Effects of hydrogen pretreatment on desulfurization performance of NWA.**

## 4.2 SORBENT DEVELOPMENT

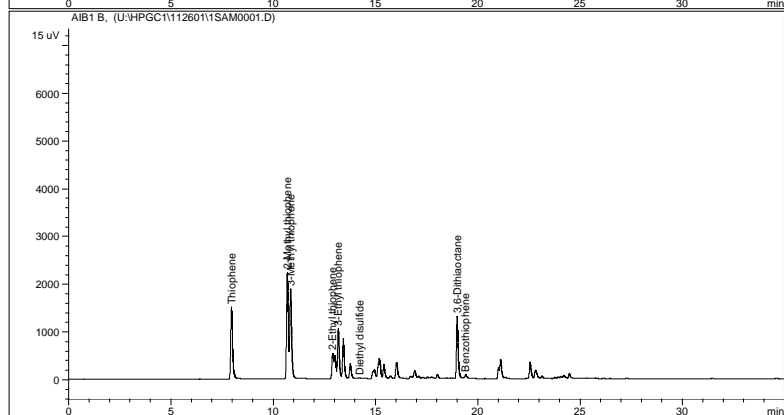
Although the NWA sorbent formulation had been demonstrated to effectively remove thiophene from gas phase, other criteria necessary for the successful commercialization of a regenerable sorbent-based desulfurization process included a simple inexpensive commercial production process for the sorbent and a sorbent with sufficient activity and attrition resistance to be suitable for transport reactor application. This marked the beginning of screening tests aimed at optimization of the sorbent production and composition. The details of the sorbent method development preparation are described previously in Section 3.2. The strong influence of physical properties (like attrition resistance, size, and surface area) on sorbent performance made analytical techniques measuring surface area, pore size distribution, XRD phases, particle size analysis and attrition resistance an essential component of sorbent screening during this phase of sorbent development. Because the actual performance of the sorbent in an appropriate hydrocarbon matrix was important, both the microreactor and PTR systems were actively used in this screening process.

An additional complication was that the market analysis, discussed in detail in Section 8.1, indicated that the opportunities to successfully attract a demonstration partner for just sulfur removal to meet the new gasoline sulfur limits were rapidly dwindling. However, by expanding the program to include diesel, the number of potential partners for hosting a demonstration unit and the potential to test RTI's TReND desulfurization process increased. Thus, RTI petitioned and was granted technical redirection for this project expanding the scope to include diesel desulfurization, as discussed previously in Section 1.4. Consequently, both the sorbent and process development work shifted towards diesel desulfurization.

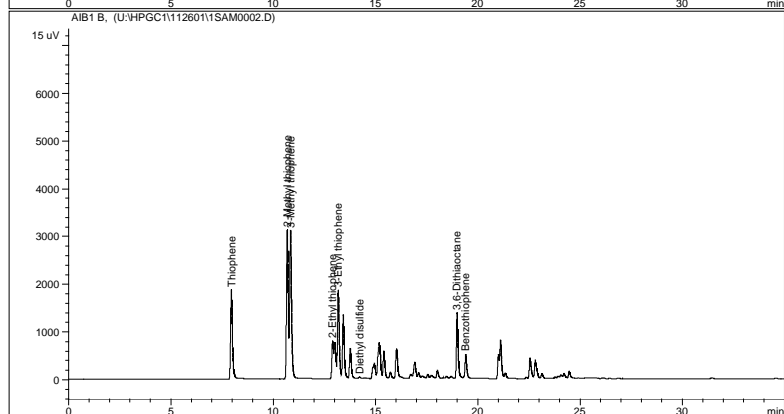
(a) Feed



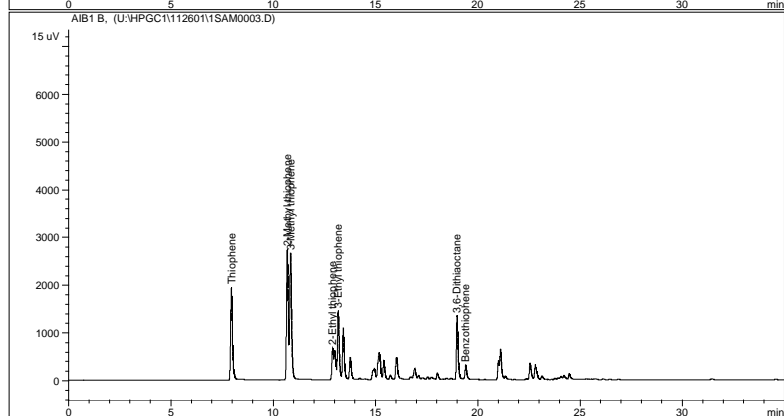
(b) Cycle 1 Product



(c) Cycle 2 Product

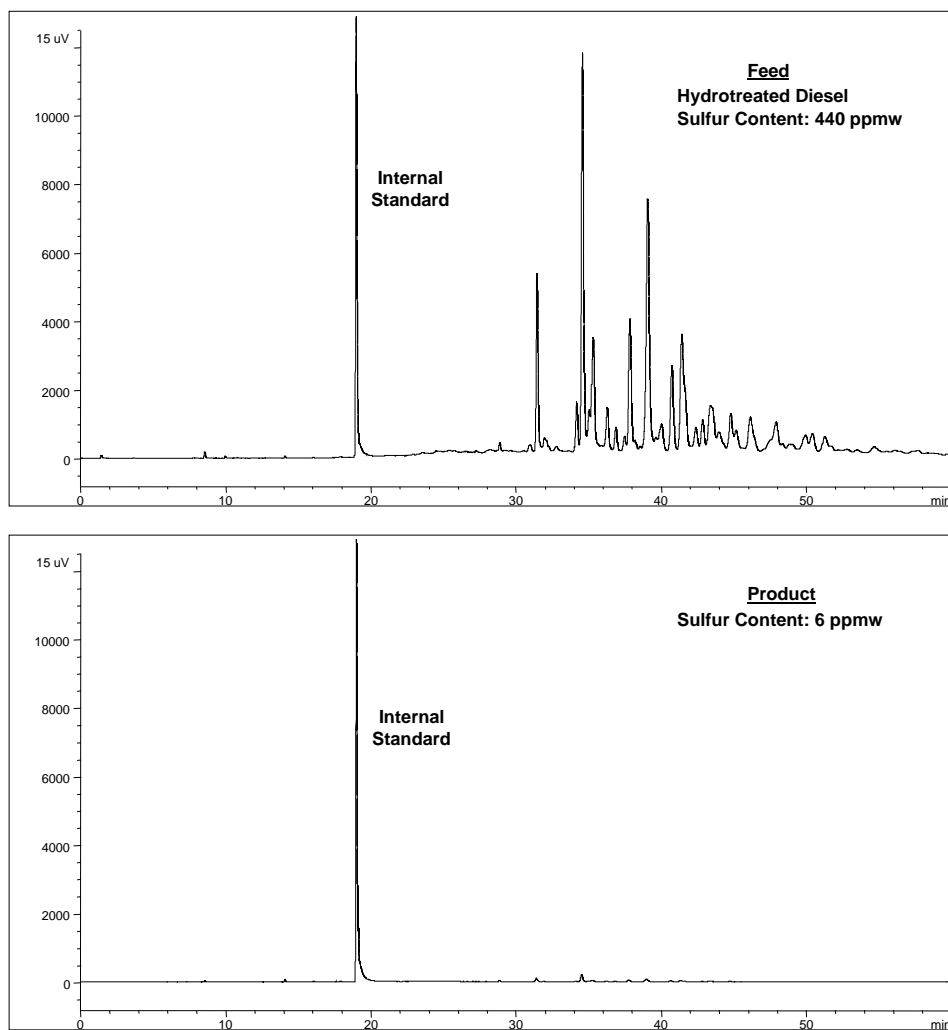


(d) Cycle 3 Product



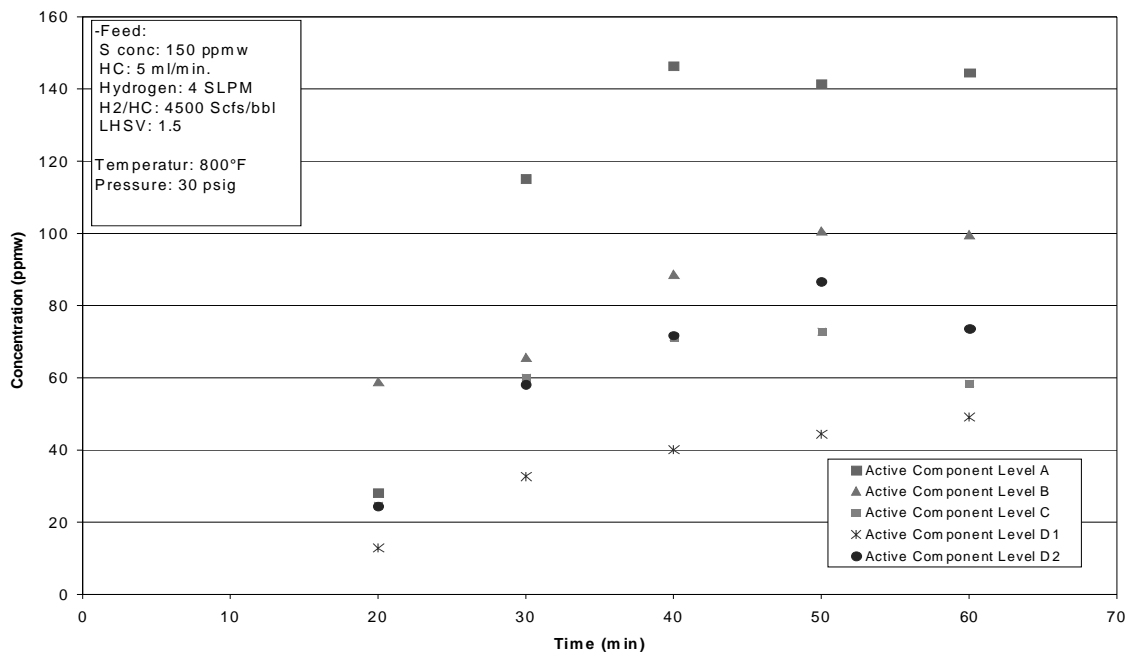
**Figure 4-6. GC chromatograms of the feed and product samples for FCC naphtha multicycle testing in PTR system.**

Consistent with this shift in the project, testing of sorbent samples with hydrotreated diesel began in the microreactor system. The chromatograms of the sulfur distribution in the hydrotreated diesel feed and the product effluent are shown in Figure 4-7. An important feature to recognize with the hydrotreated diesel is the hydrotreating process has removed all the sulfur species that can easily and readily be removed by hydrotreating. These remaining sulfur species, which begin with dibenzothiophene, are effectively removed with sorbents being developed in the sorbent development program.



**Figure 4-7. Chromatograms of hydrotreated diesel feed and product effluent with RTI's coprecipitated spray dried sorbents.**

During development of the sorbent production method, parametric testing of sorbent composition was conducted as described in Section 3.2, to optimize the production method and sorbent performance. Naturally, the amount of active component in the sorbent was tested in the microreactor and PTR systems. The total sulfur concentration in the liquid product collected from the fifth cycle of tests with sorbent formulations with different levels of active components is provided in Figure 4-8.



**Figure 4-8 Liquid product sulfur concentrations during parametric testing of active component content.**

The results in Figure 4-8 indicate a window of active material content in the sorbent provides satisfactory removal of sulfur from hydrotreated diesel.

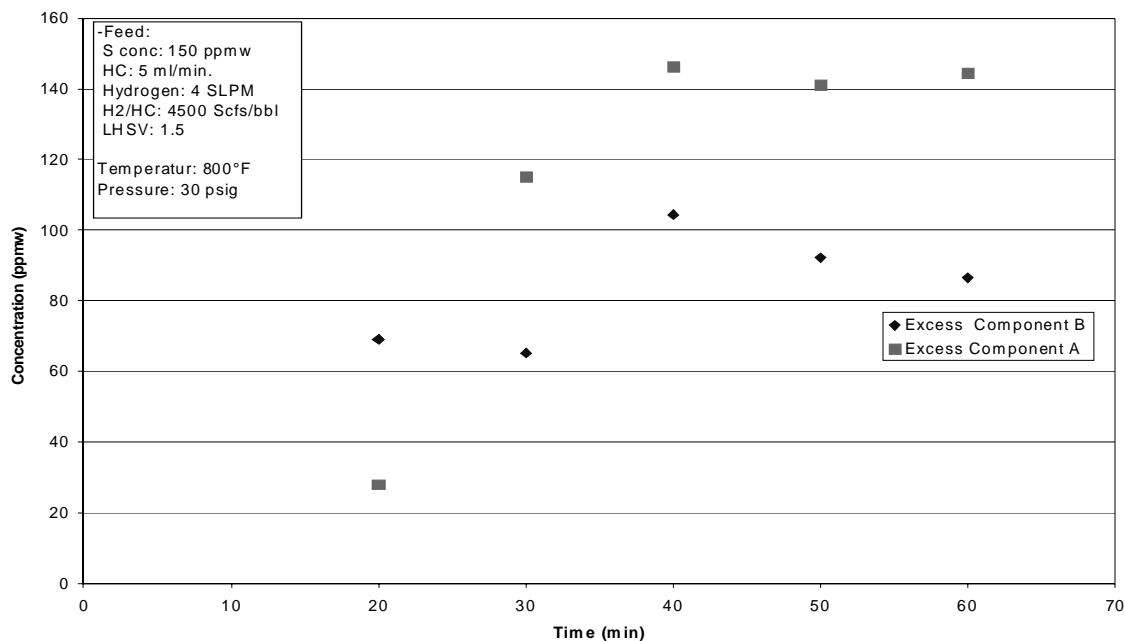
Multiple preparations with different amounts of the support components were also prepared. Figure 4-9 contains the total sulfur concentration in the product from the fifth cycle of multicycle testing with these materials. Figure 4-9 shows that the sample with excess component A is able to reduce the sulfur down to very low effluent concentrations, but has a very limited capacity. The sample with excess Component B did not reduce the effluent sulfur concentrations to extremely low values, but does seem to enhance the sulfur capacity of the material.

These results, along with the physical characterization data, were used to identify the sorbent composition and production method with both the appropriate chemical activity and attrition resistance for the TReND process. As mentioned in Section 3.2, this composition was designated as RTI-4.

### 4.3 PROCESS DEVELOPMENT

Because part of the research for production method development involved sorbent composition, one sorbent composition was selected for the initial research relating to process development. RTI-2 was selected for this duty, because it was the product of a method based on coprecipitation and spray drying with good attrition resistance and activity for FCC naphtha desulfurization. RTI-2 was eventually replaced with RTI-4 for process development research when the production method for RTI-4 was firmly established for desulfurization of diesel.

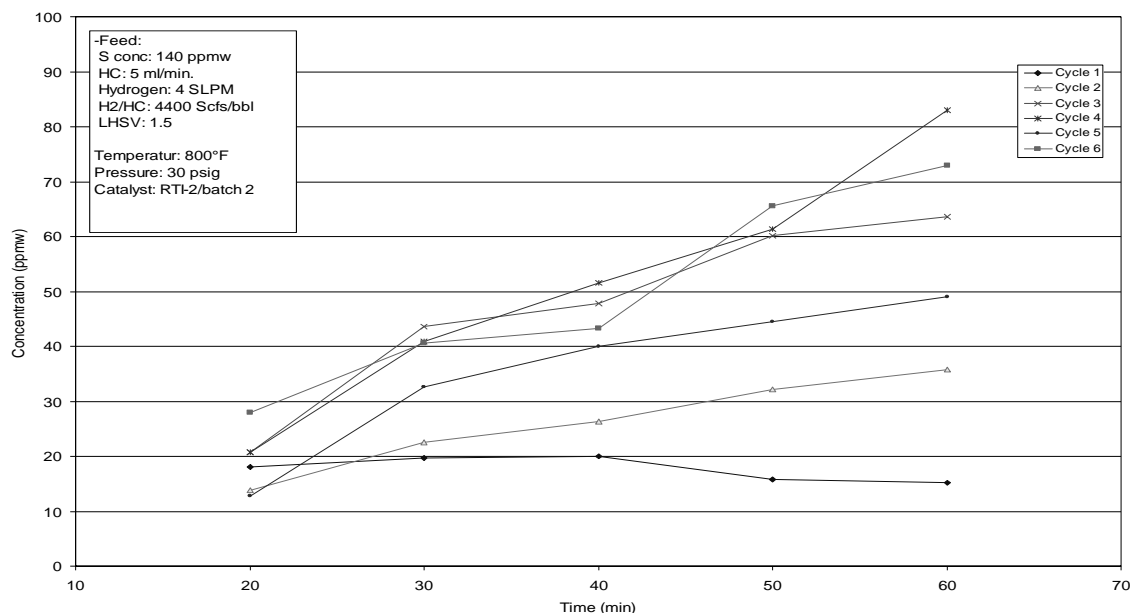




**Figure 4-9. Liquid product sulfur concentrations for parametric testing of sorbent support composition.**

Figure 4-10 contains the total sulfur content of the liquid product from one of the multicycle tests for the RTI-2 sorbent in the PTR. These results show that with increased exposure time, the sulfur concentration in the effluent increases. This gradual increase in the effluent sulfur species resembles the standard breakthrough profile for sorbent materials as the adsorption capacity of the sorbent is used up. Although this indicates that the capacity for sulfur species of RTI-2 is relatively limited, the proposed transport reactor system uses a riser reactor with residence time of < 10 seconds for sulfur removal prior to regeneration of the sorbent. If even after 20 min of exposure, the effluent sulfur concentration is < 30 ppmw, RTI-2 should readily maintain the effluent concentration below the 15 ppmw limit for the typical 10 second residence time in a transport reactor.

Figure 4-10 also demonstrates that the desulfurization performance of RTI-2 does decrease during the first few cycles, but eventually stabilizes and remains relatively constant. This demonstrates that the regeneration with oxygen is effective for restoring the sulfur removal capacity.



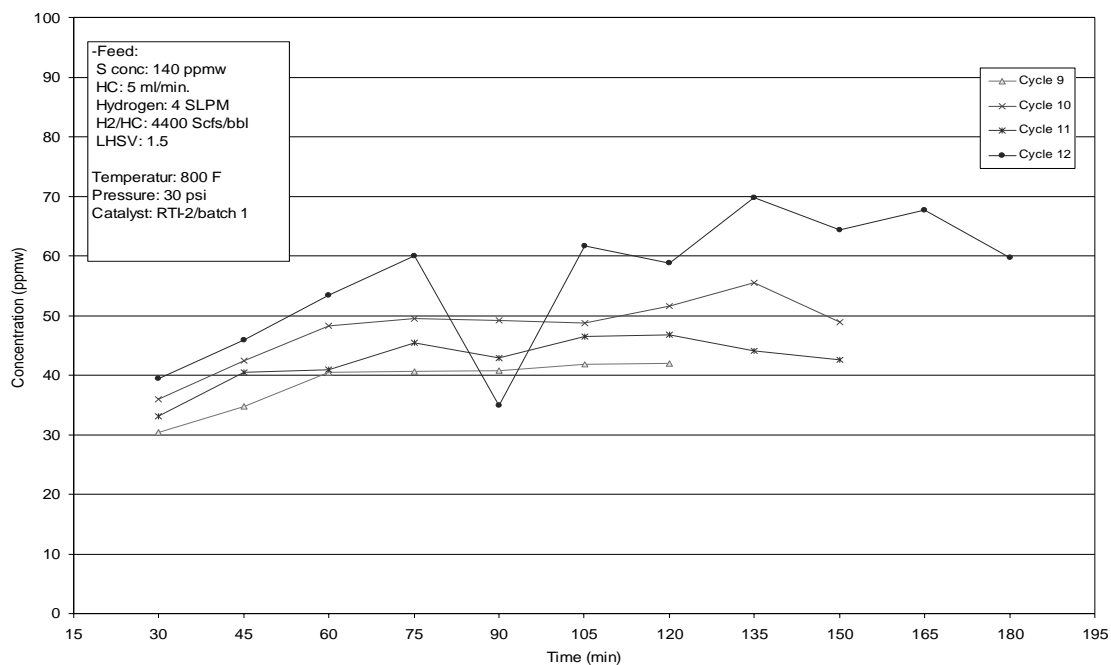
**Figure 4-10. Liquid sulfur product concentrations for multicycle test with RTI-2.**

These results were very encouraging and prompted a multicycle test to accumulate sufficient liquid product to measure such standard diesel specifications as density, boiling point, pour point, cold filter plug flow, cetane number, cetane index, and color. The conditions for this test are provided in Table 4-1. The effluent sulfur content of the product during the multicycle test from which this product sample was collected is shown in Figure 4-11.

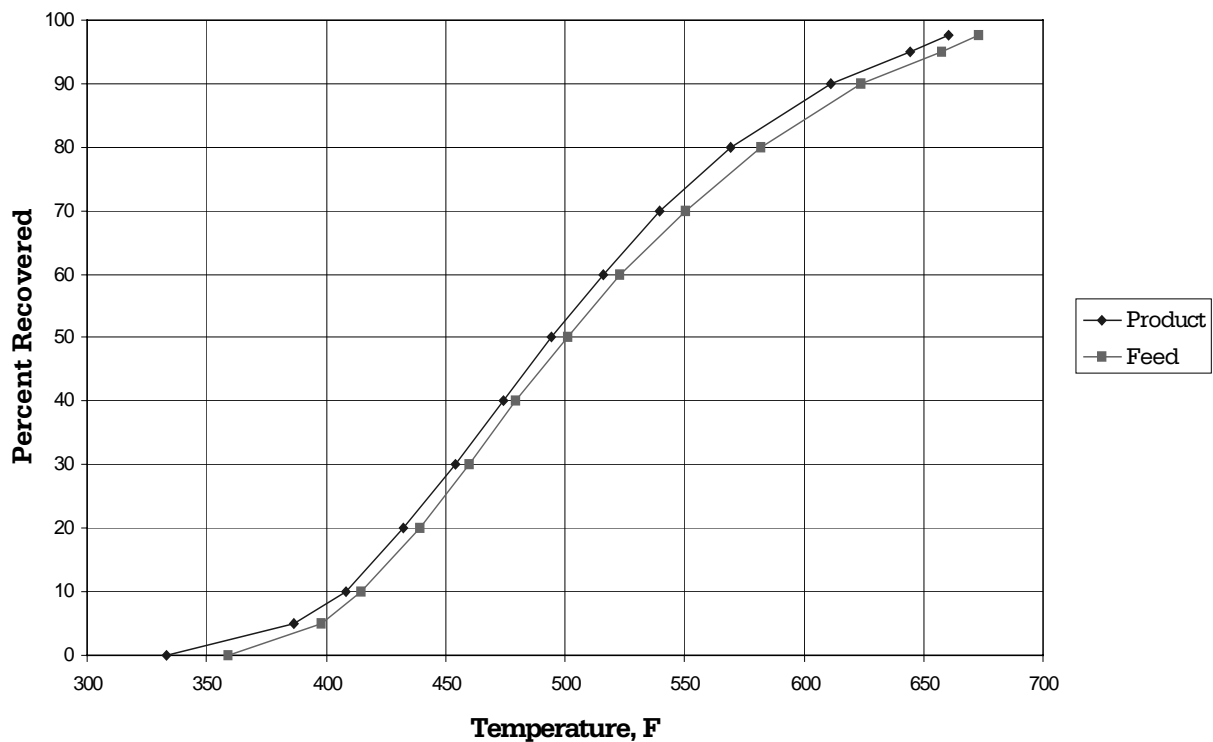
**Table 4-1. Process Conditions for Product Specification Analysis**

Condition	Sulfidation	Regeneration
Pressure (psig)	30	30
Temperature (°F)	800	800
Flow (slpm)	4.52	10
Sulfur in Diesel (ppmw)	140	
Composition (vol%)		
Diesel	11.7	
Hydrogen	88.3	
Nitrogen		98
Oxygen		2

The distillation curves for the hydrotreated diesel feed and cumulative product sample are provided in Figure 4-12. The remaining analytical results are shown in Table 4-2. The information in Table 4-2 shows both positive and negative results. The positive results include the substantially reduced sulfur concentration; the decrease in the nitrogen concentration; and small decrease in the cetane number, cetane index, and density. The negative changes include the large changes observed in color, pour point, cloud point, and cold plugging flow point.



**Figure 4-11. Effluent sulfur concentration during product collection for product specification analysis.**



**Figure 4-12. ASTM D86 distillation curves for hydrotreated diesel feed and product.**

**Table 4-2. Results from Feed and Product Specification Analysis**

Property	Feed	Product
Cetane Index	44.0	43.1
Cetane Number	39.9	38.4
Density (g/ml @ 60°F)	0.8548	0.8548
Cloud Point (°F)	+4	-2
Cold Filter Plugging Point (°C)	-24	-29
Pour Point (°F)	-15	-25
Color	1.5	5.0
Total Nitrogen (ppmv)	17	13
Total Sulfur (ppmv)	140	38

The shift in the boiling point curve of the product towards lower temperature is also not particularly positive. Some of this result could arise because the PTR performs both the adsorption and regeneration process in the same reactors. Thus, any degradation during regeneration of hydrocarbons trapped in the system could contaminate product sample in the subsequent adsorption cycle.

Subsequent testing indicated that the product color was seriously affected by contamination of a particle filter in the reactor effluent line and final regeneration temperature. Both of these features point to the potential that performing both the adsorption and regeneration in the same reactor vessel results in some cross contamination of the product. Color analysis of the samples from the pilot plant tests in KBR's Transport Reactor Test Unit (see Section 5.3) did not show any difference in the color number for the product samples and the hydrotreated diesel feed. This confirms that cross contamination between adsorption and regeneration results in the significant color change observed in Table 4-3. Unfortunately, the limited amount of sample available from the TRTU testing permitted only limited analysis. There was not enough sample for cloud point, pour point and cold filter plugging point. Thus, the possibility of cross contamination of the liquid product could have also cause the significant deviations observed in cloud point, pour point and cold filter plugging point similar to what was observed for color.

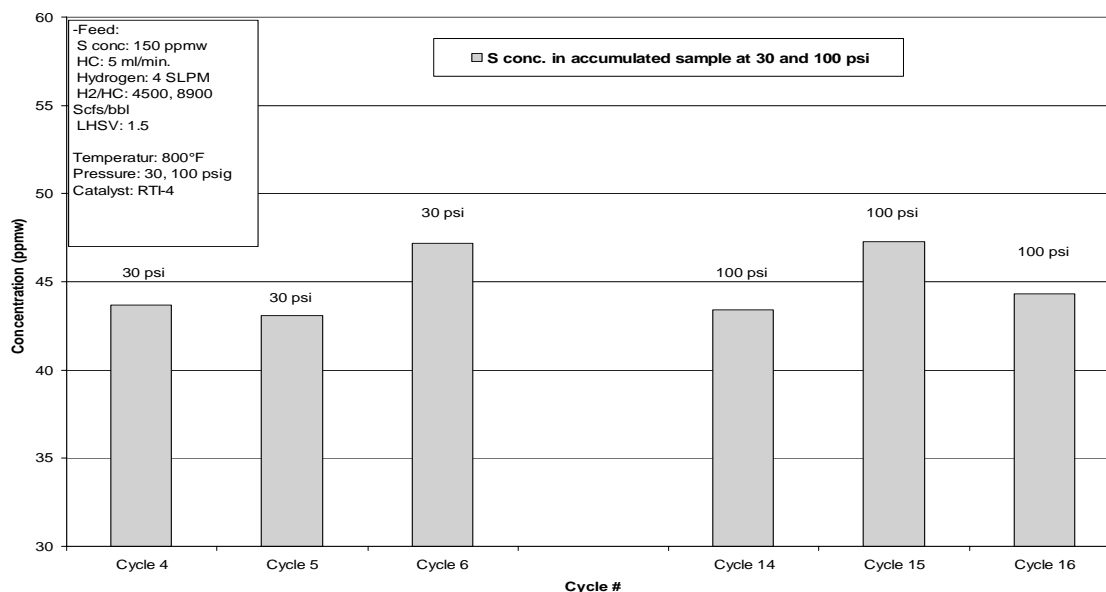
Because the marketing analysis (see Section 8.1) indicated refineries could potentially use RTI's TReND process as a primary desulfurization system and/or as a polishing desulfurization system with high pressure hydrotreating processes, multicycle testing with RTI-4 was conducted both at 30 psig and 100 psig. The cumulative sulfur liquid product sulfur concentrations for these tests are provided in Figure 4-13.

Figure 4-13 does not show any significant difference in the sulfur removal of RTI-4 at 30 and 100 psig. This suggests that total system pressure does not affect sulfur removal.

**Table 4-3. Operating Conditions during Parametric Testing in PTR System to Study Coke Formation**

	Cycle #						
	1-5*, 10, 14, 15	6, 13	7	8	9	11	12
Sulfidation							
Pressure (psig)	30	30	30	30	30	30	30
Temperature (°F)	800	850	800	850	850	850	850
Flow Rate (SLPM)	4.45	4.45	4.45	4.45	4.45	4.90	4.90
Feed Sulfur (ppmw)	140	140	140	140	140	140	140
Composition (vol%)							
Diesel	10	10	10	10	10	18.4	18.4
Hydrogen	90		22.5	45	22.5	81.6	20.4
Nitrogen		90	67.5	45	67.5		61.2
Regeneration							
Pressure (psig)	30	30	30	30	30	30	30
Temperature (°F)	800,1200	800	800, 1200	800	800	800, 1200	800, 1200
Flow Rate (SLPM)	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Composition (vol%)							
Nitrogen	98	98	98	98	98	98	98
Oxygen	2	2	2	2	2	2	2

\* During Cycle 5, the sulfur removal at 850°F was preceded by a reducing pretreatment.



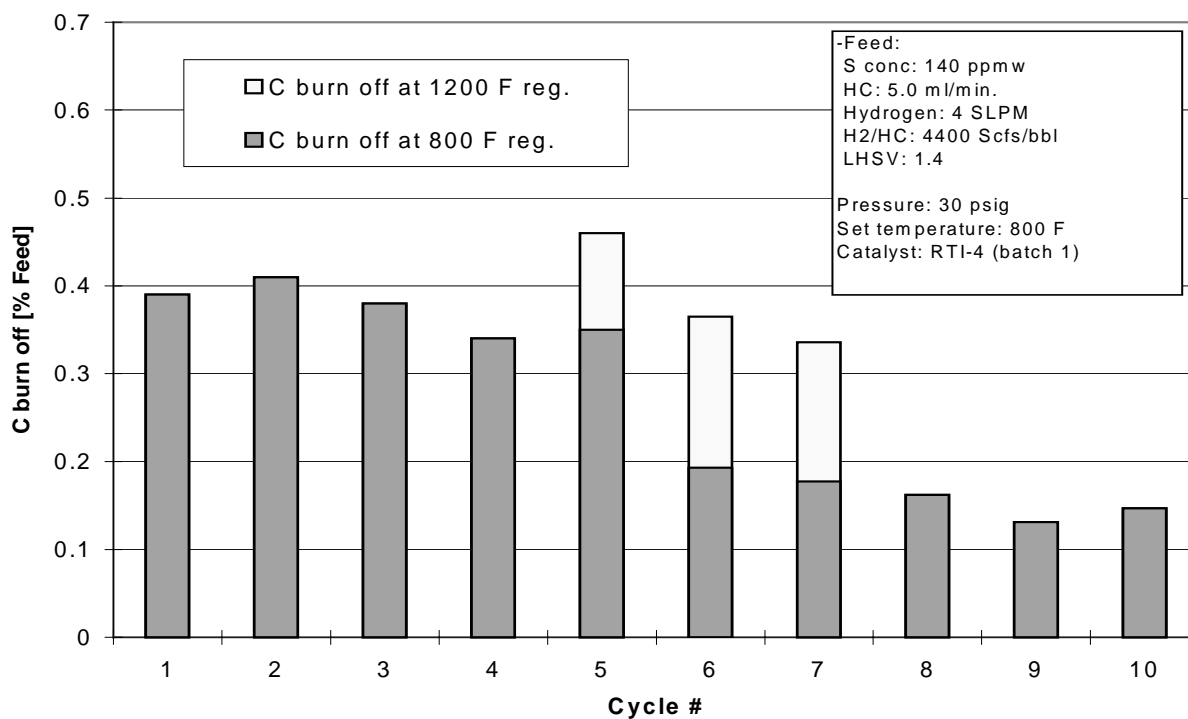
**Figure 4-13. Sulfur concentration for cumulative liquid product during multicycle testing at 30 and 100 psig.**

From the beginning of testing with actual liquid fuels, the necessity of introducing hydrogen with the hydrocarbon vapor was known as a means of suppressing the decomposition of the hydrocarbon at operating temperatures. Because of the continual presence of hydrogen, no

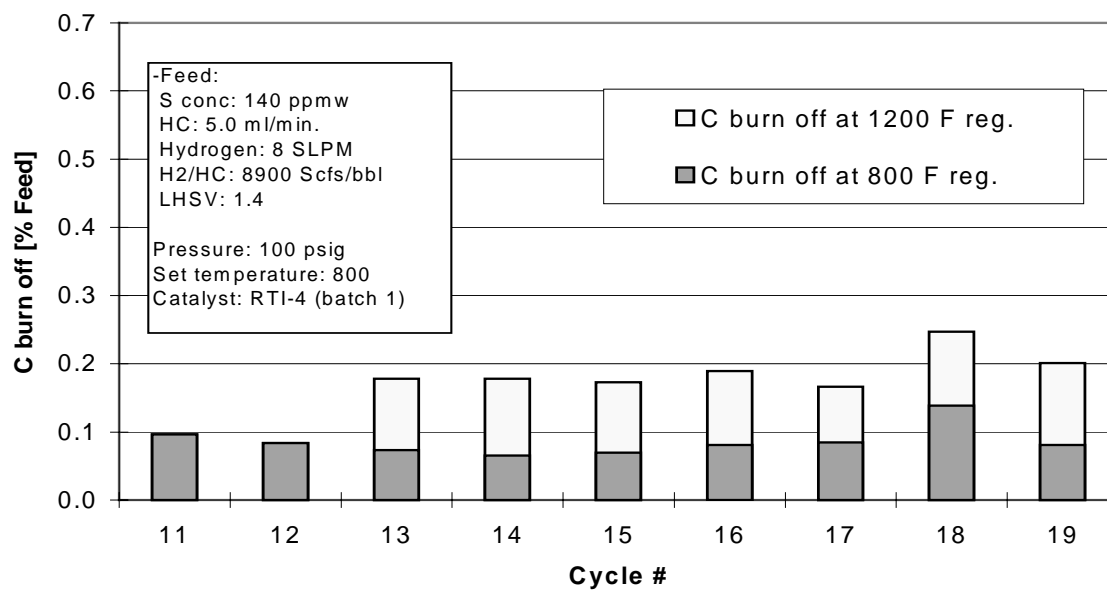
accurate understanding of the amount of hydrogen consumed by the sulfur removal mechanism could be determined. Using argon and hydrogen and helium and hydrogen mixtures, a more accurate estimate of the hydrogen consumption during the sulfur removal process was investigated. The intention was to use either the argon or helium as an inert of known concentration. Unfortunately, the need to extensively purge the system with nitrogen between adsorption and regeneration steps for safety resulted in a significant amount of nitrogen being present in the process gas samples collected. This, coupled with standard variances that are associated with gas sampling and GC analysis, introduced sufficient variance such that reliable results for hydrogen consumption could not be determined. Because this problem remained even after several attempts to minimize variances associated with sampling and analysis, this effort was abandoned with the understanding that more accurate estimates of hydrogen consumption could be obtained in continuous transport reactor pilot plant testing. However, during the transport reactor pilot plant testing other pressing issues dominated and estimates of the hydrogen consumption during sulfur removal for RTI's TReND process could not be evaluated.

Reactor effluent was also monitored during regeneration. One of the primary components monitored for by continuous analyzers was  $\text{SO}_2$ . The intention behind this action was to demonstrate the fate of the sulfur removed from the hydrocarbon fuel. The low initial concentration of the sulfur in the fuels combined with the limited sulfur capacity of the sorbent for these recalcitrant sulfur species meant that the  $\text{SO}_2$  concentration during regeneration would be small. Although the  $\text{SO}_2$  analyzer used did have the capability to measure  $\text{SO}_2$  concentrations down to 10 ppmv, accurate measurement of the  $\text{SO}_2$  generated during regeneration could not be measured. During conceptualization of the RTI TReND process, the high sulfur capacity of the sorbent was conceived as a means to concentrate sulfur from the hydrocarbon feed in the regeneration effluent for ultimate disposal. Although some attempts were made during the shakedown testing in the transport reactor pilot plant testing to complete the process sulfur balance, these were not successful. Actual transport reactor pilot plant testing focused on other issues than the sulfur balance.

The regeneration effluent gas was also monitored for CO and  $\text{CO}_2$ . This provided an accurate means to monitor the coke formation during the sulfur removal process. The results presenting the estimated amount of carbon removed during regeneration for multiple cycles at system operating pressures of 30 psig and 100 psig are displayed in Figure 4-14 and 4-15, respectively. The results in Figures 4-14 and 4-15 show that the coke formation during the sulfur removal process for testing in RTI's PTR system is < 0.5 wt%. Furthermore, the results in Figures 4-14 and 4-15 also show that the coke formation is systematically less at an operating pressure of 100 psig than 30 psig.



**Figure 4-14. Estimated carbon removed during regeneration after sulfur removal at 30 psig.**

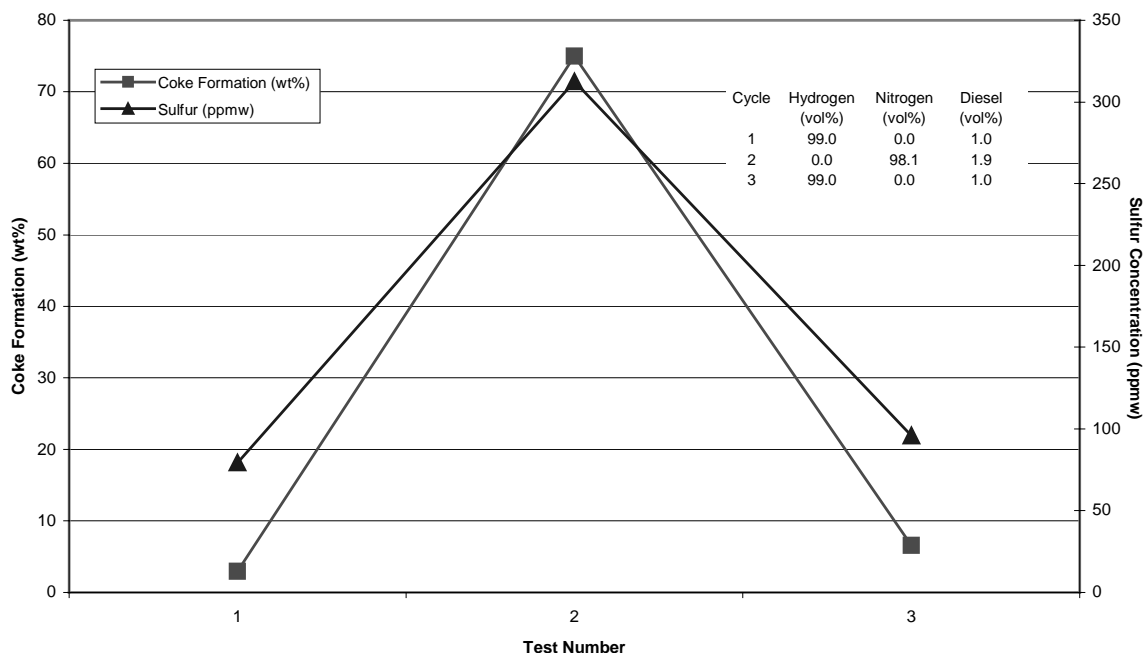


**Figure 4-15. Estimated carbon removed during regeneration after sulfur removal at 100 psig.**

From these results, coke formation during sulfur removal was not viewed as a potential problem for commercial operation of the TRenD process. However, the results from pilot plant testing in KBR's FCC pilot plant unit (see Section 5.2) showed coke concentrations of between 9 and 13 wt%. This level of coke formation was clearly unacceptable. Because one of the limitations of the FCC pilot plant was the need for nitrogen to transfer sorbent from the standpipe after the regenerator to the riser reactor, the reaction gas in the riser had a concentration of nitrogen > 47 vol%. Prior to the testing in the FCC pilot unit at KBR, nitrogen was perceived as an inert that would not affect the reactions in the riser. To investigate the potential that the introduction of nitrogen into the feed gas during sulfur removal could affect coke formation, a multicycle test with RTI-4 with either hydrogen or nitrogen as the primary reactive gas component was conducted in the microreactor system. The results from this multicycle test are presented in Figure 4-16.

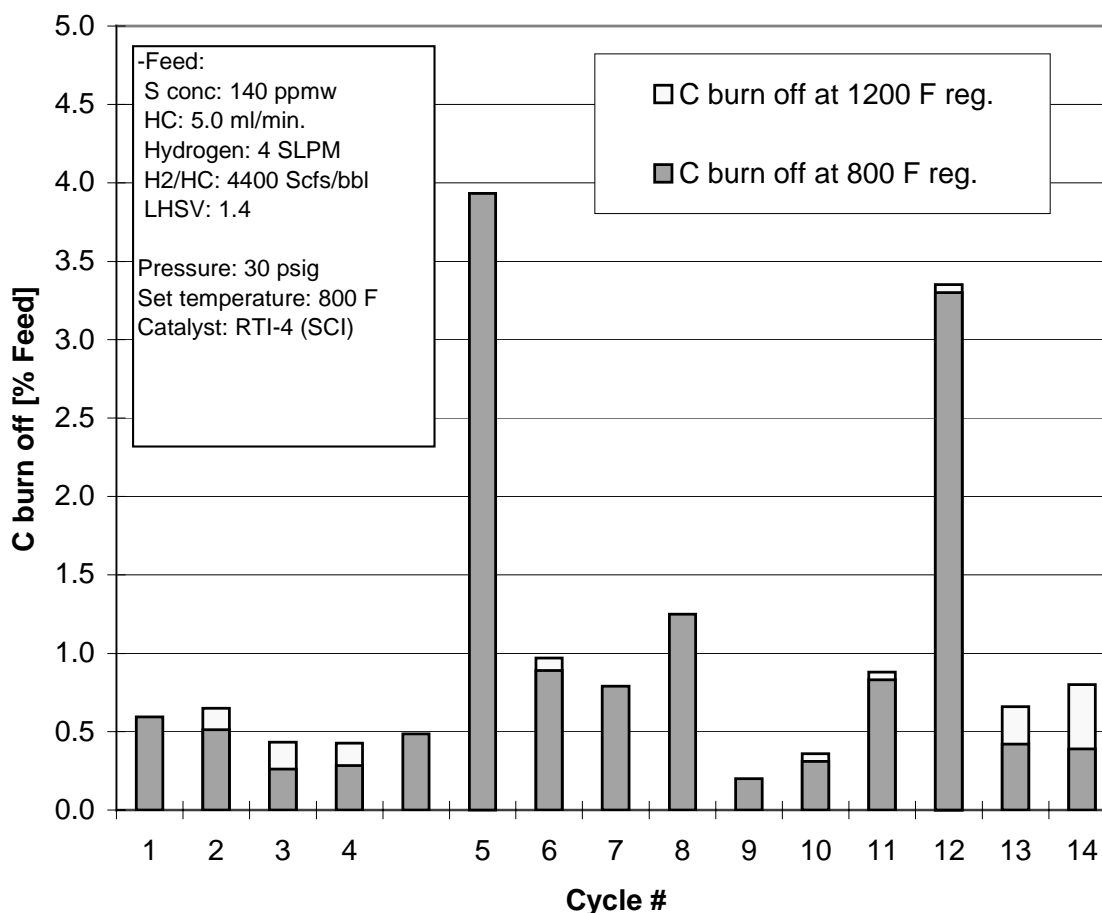
Figure 4-16 shows that when the hydrogen component of the reactive gas mixture is replaced with nitrogen, both the coke formation and effluent sulfur concentration increased. This would suggest that hydrogen is essential for preventing coke formation. These results also suggest that coke formation on the sorbent poisons sites that are active for the removal of sulfur.

Similar testing was performed with RTI-4 in RTI's PTR system. For the first four cycles of this multicycle test, the operating conditions were identical to operating conditions used in previous PTR testing for which low coke formation had been recorded. After these four initial cycles, a number of different hydrogen and nitrogen reactive gas mixtures were tested. The details of the operating conditions are provided in Table 4-3. The estimated carbon released during regeneration for this multicycle test is shown in Figure 4-17.



**Figure 4-16. Multicyle test with hydrogen and nitrogen as the primary reactive gas component.**





**Figure 4-17. Estimated carbon removal during regeneration during parametric testing for coke formation.**

Figure 4-17 shows that coke formation for hydrogen concentrations of  $\geq 80$  vol% resulted in typical coke formation of 0.5 wt%. However, at lower hydrogen concentrations, the coke formation increased. The worst coke formation was observed in the complete absence of hydrogen. These results confirm the results obtained in the microreactor system.

Because KBR's FCC pilot plant unit needs a significant amount of nitrogen to safely transport the sorbent from the regenerator to the riser, an additional test in KBR's TRTU was completed as described in Section 5.3 for which operating at high hydrogen concentrations and/or pressure was not a problem.

#### 4.4 ACIDITY MEASUREMENTS

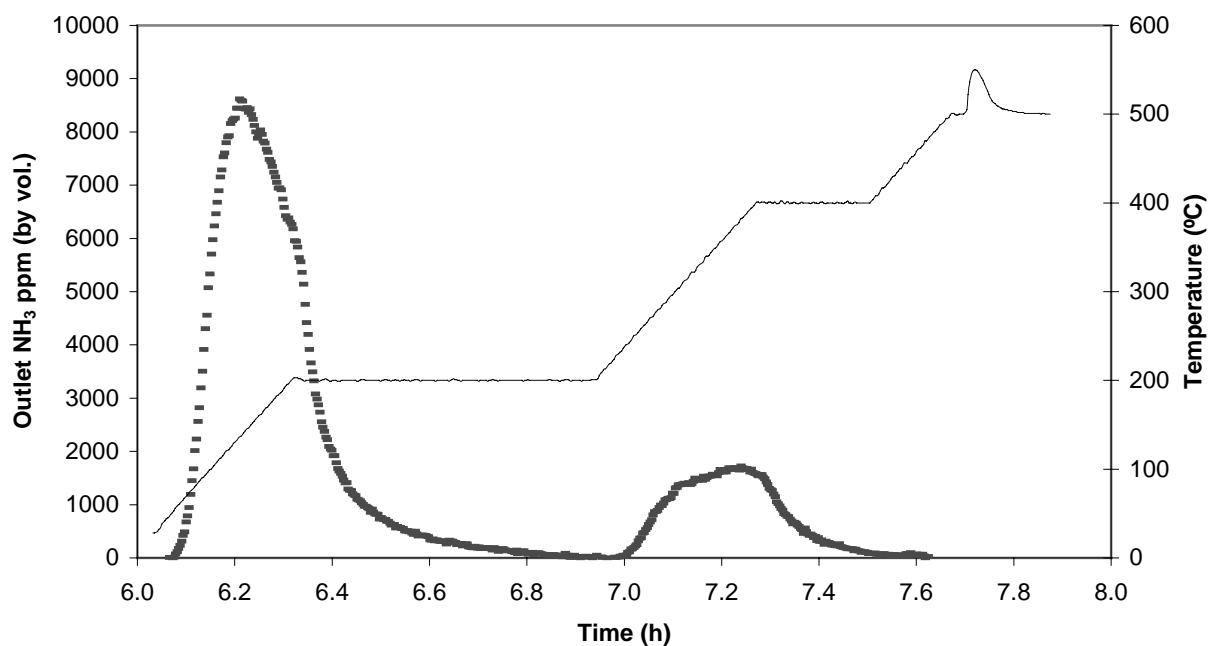
An alternative hypothesis to the lack of hydrogen concentration causing the high coke formation during testing in KBR's FCC pilot plant unit was the coke formation was catalyzed at acidic sites on the sorbent. Acidic sites catalyze coke formation and a number of other reactions listed in Table 4-4. Furthermore, coke formation is generally associated with the strongest acid sites. If the sorbent's acidity is strong enough to catalyze coke formation, the acidity of the sorbent could

**Table 4-4. List of Reactions Catalyzed by Acidic Sites**

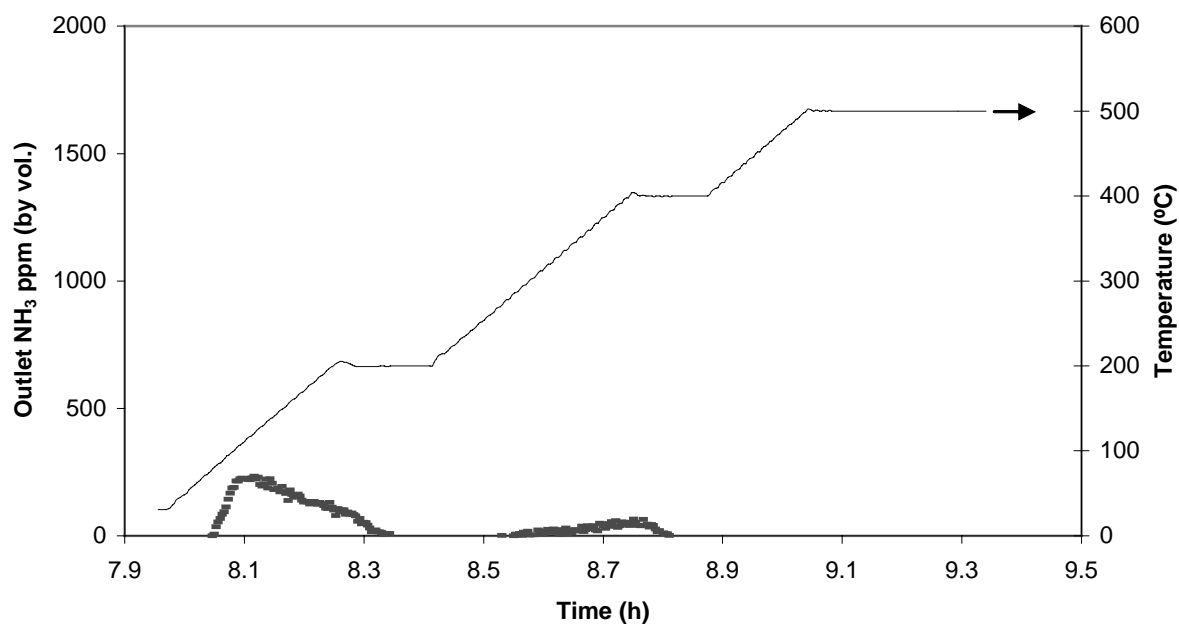
Reactions	Cracking Reactions
Cracking of C-C bonds	+
Alkyl group isomerization	+
Double bond isomerization	+
Dealkylation	
Dehydroxylation	
Dehydrogenation	+
Polymerization	
Oligomerization	
Cyclization	+
Alkylatiuon	+
"Coke" formation	+

catalyze other hydrocarbon reactions that would change the chemical and physical properties of the product. This product degradation, if severe enough, could render the process unacceptable for commercial fuel desulfurization. Therefore, the acidity of the RTI-4 sorbent was measured.

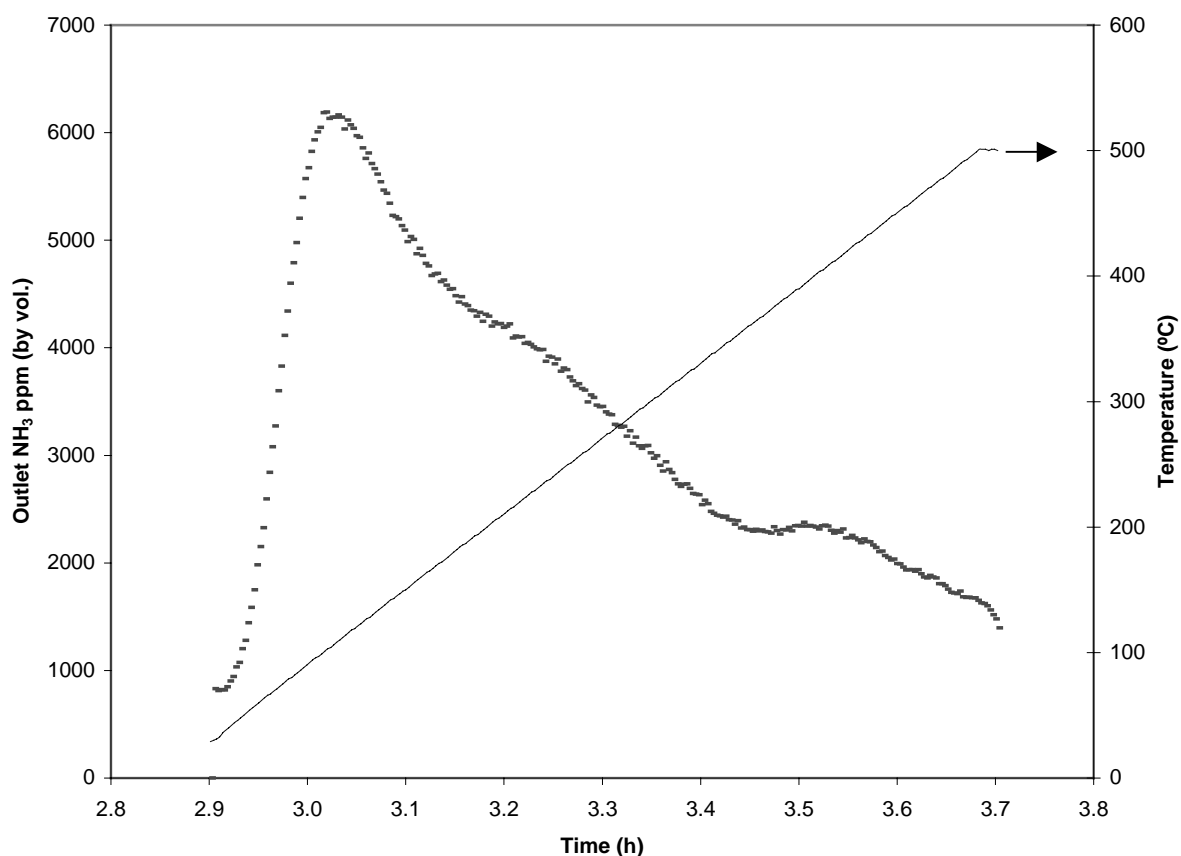
Acidity determinations are difficult, because the type of acidity (Bronstead or Lewis), acid strength, and distribution of acid strength all influence the acidity of a catalyst. Two methods of measuring acidity include non-aqueous titration and base chemisorption. For testing RTI-4, base chemisorption with ammonia was used. In this test, ammonia is used to saturate any acidic sites on the catalyst. The sample is then heated in a systematic manner to desorb the ammonia. The advantage of this method is it provides both an estimate of acid strength and relative amount of acidic sites of a particular acid strength. Unfortunately, the method is qualitative rather than quantitative, and interpretation of the test results is best done on samples tested with the same instrument. In the first round of testing, the acidity testing was arranged for an FCC catalyst, EX-S03 and RTI-4. The results are presented in Figures 4-18 to 4-20. In these figures, the dashed line corresponds to ammonia desorption and the solid line the temperature profile. Except for the different temperature ramping profiles for each catalyst, these ammonia chemisorption tests were performed identically.



**Figure 4-18. Temperature programmed desorption of ammonia on FCC catalyst after adsorption at 25°C.**



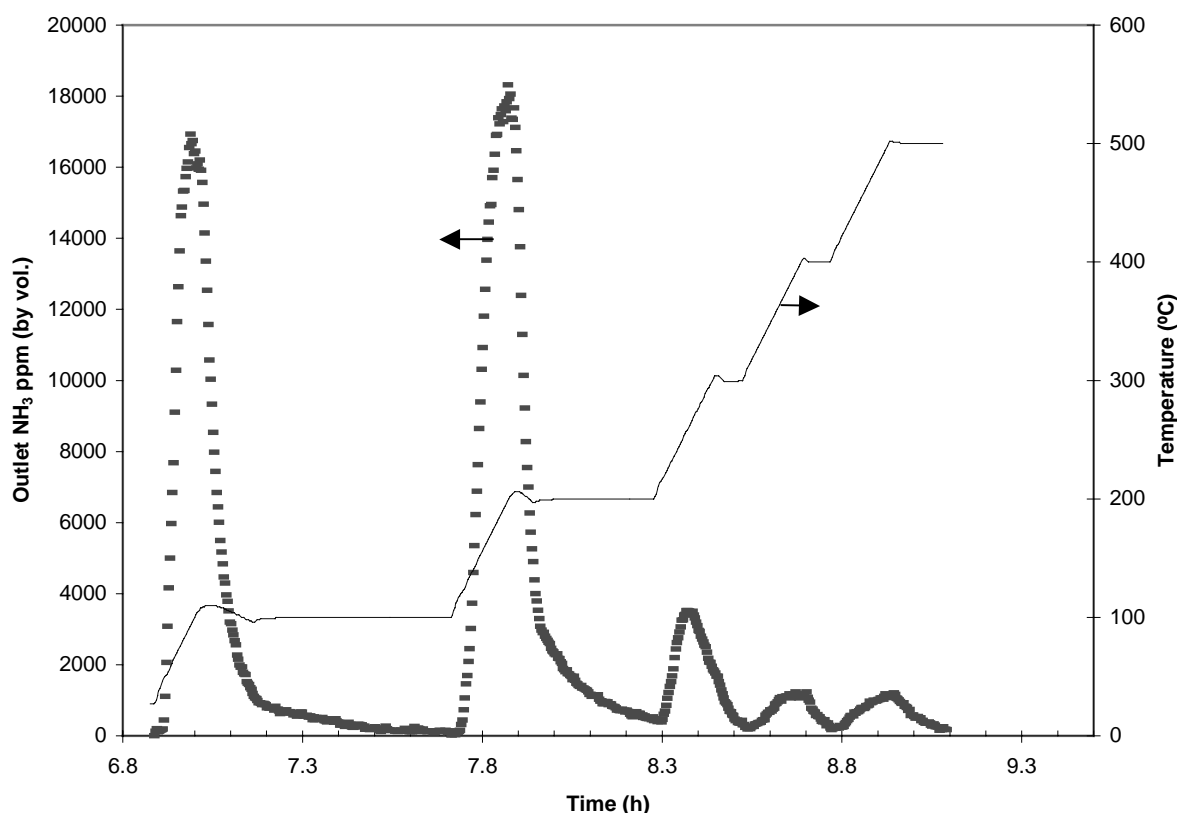
**Figure 4-19. Temperature programmed desorption of ammonia on EX-S03 catalyst after adsorption at 25°C.**



**Figure 4-20. Temperature programmed desorption of ammonia on RTI-4 catalyst after adsorption at 25°C.**

Figures 4-18, 4-19, and 4-20 clearly show that all three samples absorb and desorb some ammonia. For all three materials, the bulk of the ammonia desorption occurs below 200°C. Because temperature represents the thermal energy necessary to break the bonds between the acid sites and ammonia resulting in ammonia desorption, these sites are weaker in nature. All three materials also desorb more ammonia between 200 and 400°C. These are stronger acid sites. For EX-S03 and FCC materials, no ammonia desorption was observed above 400°C. Figure 4-19 does show desorption of ammonia for RTI-4 at above 400°C indicating extremely strong acidic sites. Figures 4-18 through 4-20 also show that the relative amount of acidic sites are similar for RTI and FCC catalyst, but much higher than for EX-S03.

Because the operating conditions during which low coke formation was observed were at high temperatures and high hydrogen concentrations, the sorbent's chemical state might be very different than for a sample at room temperature in air. This prompted the RTI-4 sorbent to be retested for ammonia desorption after a hydrogen pretreatment at 300°C. The result of this ammonia desorption test are provided in Figure 4-21.

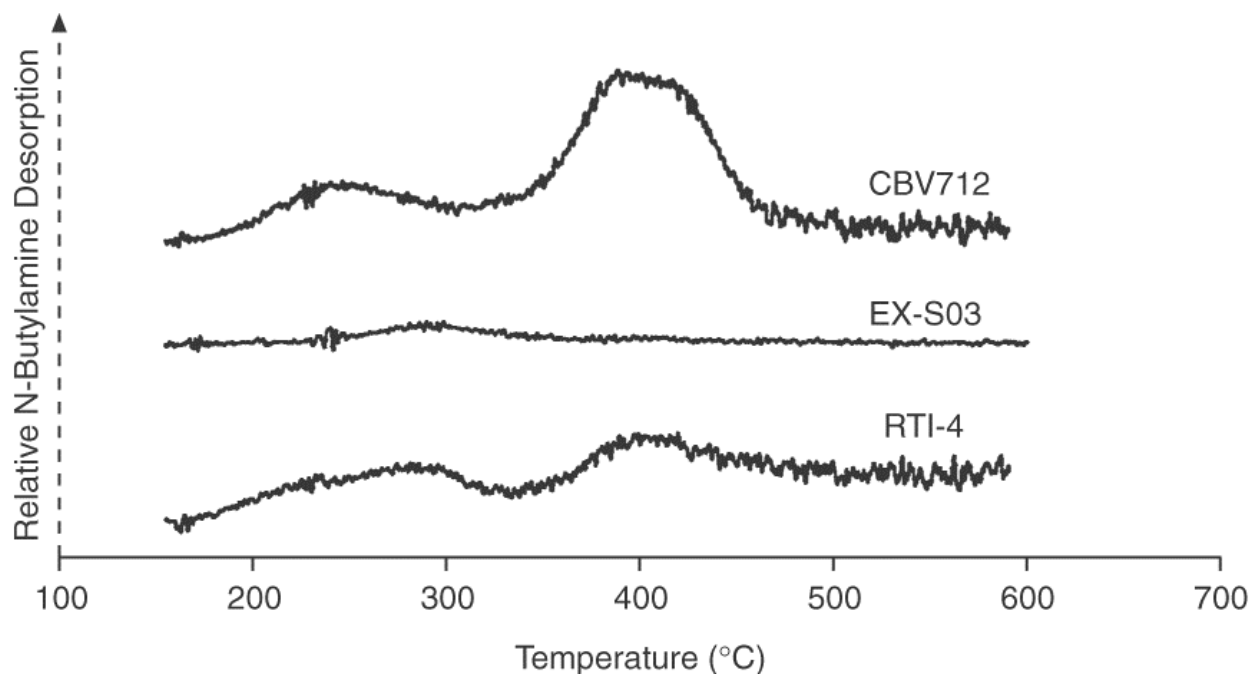


**Figure 4-21. Ammonia desorption results for RTI-4 after hydrogen pretreatment at 300°C.**

Although the temperature profiles are different, the ammonia desorption patterns in Figures 4-20 and 4-21 are very similar. In both cases, the bulk of the acid sites for RTI-4 are weaker acidic sites that desorb ammonia below 200°C. Progressively smaller amounts of ammonia are desorbed at higher temperatures. Thus, the hydrogen pretreatment at 300°C does not affect the acidity of the RTI-4 sorbent.

Because the active component is an oxidizing agent and ammonia is a suitable reducing agent, there is the potential that the ammonia is interacting with the sorbent not as just an acid, but also as an oxidizing agent. For ammonia, separating these two effects would be very difficult. To confirm the acidity results observed with ammonia, desorption testing was repeated for a FCC zeolite catalyst, EX-S03 and RTI-4 with n-butylamine instead of ammonia. Figure 4-22 shows the test results from this n-butylamine desorption testing.

The results in Figure 4-22 confirm that EX-S03 has only a few extremely weak acid sites. RTI-4 is more acidic than EX-S03, but less acidic than the FCC zeolite catalyst. RTI-4's acidity comes from a mixture of weaker acid sites and stronger acid sites. For RTI-4, the relative amount of the stronger acid sites is only slightly greater than the weaker sites. Furthermore, the number and strength of the strong acid sites on RTI-4 are less than observed for the FCC zeolite catalyst. These results show the same trend observed with the ammonia desorption results. EX-S03 is not acidic; RTI-4 is more acidic, but not as acidic as FCC catalyst.



**Figure 4-22. N-Butylamine desorption profiles during temperature programmed desorption testing.**

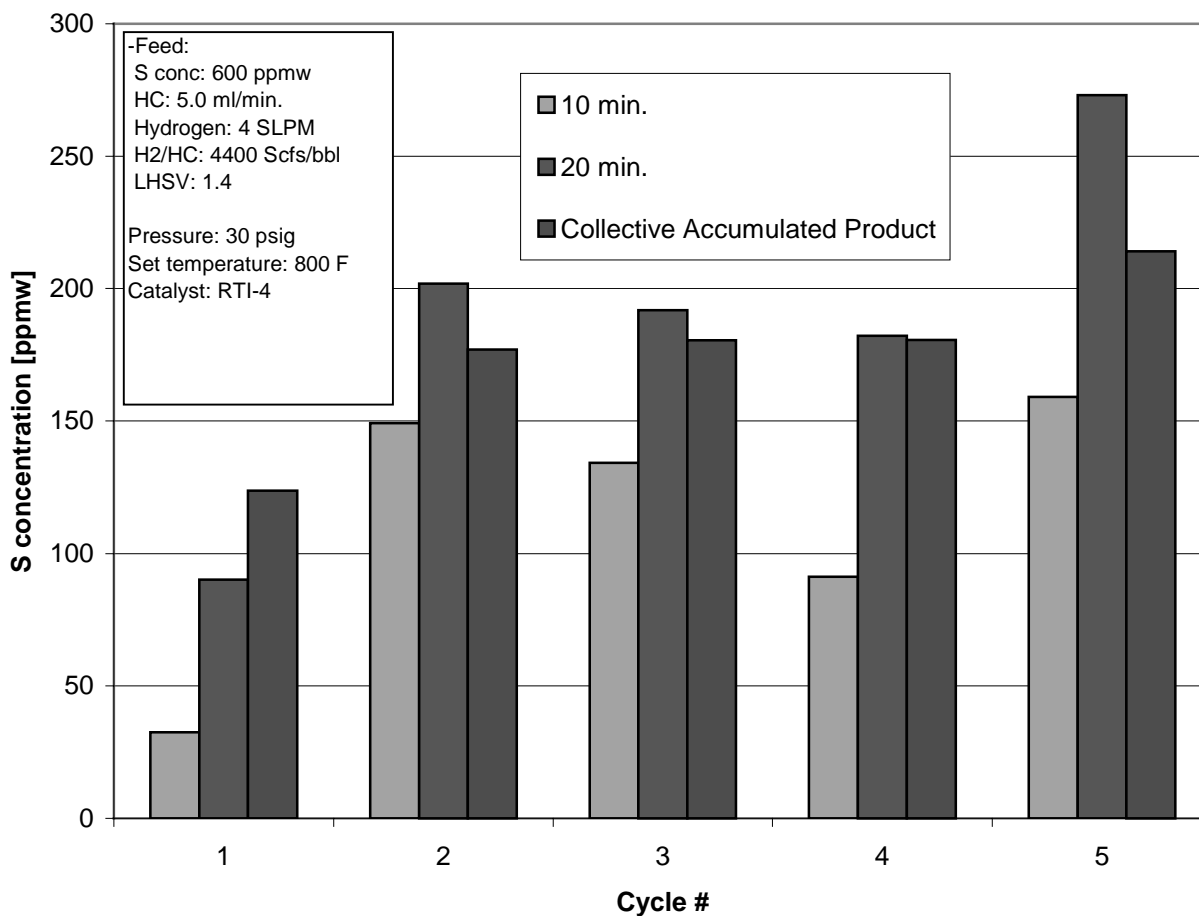
Although this testing does indicate that RTI-4 is acidic, this testing does not confirm that the acidity was the cause for high coke formation observed during testing with RTI-4 observed in KBR's FCC pilot plant. Test results in RTI's microreactor and PTR systems, KBR's TRTU (see Section 5.3) and microactivity (MAT) testing at KBR (see Section 5.1.2) showed that coke formation and production of light gases (C1 to C4 gases) were extremely low at high hydrogen concentrations. Based on these observations, the low hydrogen concentration was one of the causes for the high coke formation observed during the testing in KBR's FCC pilot plant unit. Further testing will be necessary to determine product degradation for the TReND process and the relative contribution of the acidity of the RTI-4 sorbent to product degradation.

#### 4.5 TESTING WITH OTHER TRANSPORTATION FUELS

Because the sample of hydrotreated diesel had a sulfur concentration of roughly 140 ppmw and the current standard for on-road hydrotreated diesel is 500 ppmw, RTI-4 was tested in RTI's PTR system with a mixture of hydrotreated diesel and LCO. This mixture combined the appropriate amount of hydrotreated diesel with 140 ppmw sulfur and LCO with 2.4 wt% sulfur to get a mixture that had roughly 600 ppmw sulfur. Figure 4-23 shows the total sulfur for the time dependent sample at 10 and 20 minutes and collective accumulated product during a five-cycle test.

Figure 4-23 shows that RTI-4 does remove a significant amount of sulfur from the hydrotreated diesel spiked with LCO. Although the LCO content in the mixture in this test was small, these results suggest that RTI-4 could be used to remove sulfur from LCO. Because this test was not optimized either for process conditions or for sorbent composition, there is the potential that the sulfur removal for LCO could also be improved.

In addition to LCO, several multicycle tests with Jet A fuel were conducted in the microreactor system. The total sulfur concentration in the product from these two tests are provided in Tables 4-5 and 4-6



**Figure 4-23. Total product sulfur concentrations for multicycle test with hydrotreated diesel spiked with light cycle oil.**

**Table 4-5. Product Sulfur Concentrations for Multicycle Testing with Jet A Fuel at 6 ml/h**

Cycle #	Sulfur (ppmw)	
	Feed	Product
1	875	25
2	875	23
3	875	41

**Table 4-6. Total Sulfur Concentrations in the Product from Testing with Jet A Fuel at 12 ml/h**

Cycle #	Sulfur (ppmw)	
	Feed	Product
1	875	20
2	875	45
3	875	63
4	875	84
5	875	91

As with the hydrotreated diesel spiked with LCO, these results indicate that RTI-4 has the potential to remove sulfur from Jet A fuel. The potential of RTI-4 to remove sulfur from FCC naphtha, hydrotreated diesel, hydrotreated diesel spiked with LCO, and Jet A fuel shows that sorbent screening process has identified a winning composition for sulfur removal from transportation fuels. Furthermore, the sorbent development program effectively scaled up the production of this sorbent to produce a highly active and attrition resistant sorbent that can be used with multiple transportation fuels.



## CHAPTER 5

### KBR'S TEST PROGRAM

#### 5.1 MAT TESTING

##### 5.1.1 Material Evaluation as FCC Additive

During the concept development stage of this technology, one application considered was that this material could be added like an additive to the FCC catalyst. This technology has some strong advantages, including limited or no capital equipment investment. To investigate this potential application, MAT tests were conducted to evaluate the feasibility of using RTI's desulfurization sorbent as an FCC additive. A total of four samples were prepared. A list of these samples is shown in Table 5-1. The two materials added as sorbent/additives for this testing were EX-S03 and NWA. The EX-S03 was a commercial syngas polishing sorbent developed by RTI that had shown some desulfurization activity for sulfides, disulfides and thiophenes during initial testing of the potential for regenerable sorbents for desulfurization of naphtha and diesel. The NWA material was a laboratory formulation that had shown considerable promise during microreactor screening tests (see Section 3.1).

The first set of MAT tests was performed in KBR's fixed-bed reactor system. The conditions for this series of tests are provided in Table 5-2. The conditions were selected to represent typical operations for an FCC unit. A second series of MAT tests was performed in KBR's fluidized bed reactor system. The conditions for these tests are shown in Table 5-3 and are basically identical to the conditions for the fixed-bed tests.

**Table 5-1. Test Samples for FCC Additive Testing**

Material	Composition		
	E-Cat	EX-S03	NWA
	(wt%)	(wt%)	(wt%)
E-Cat	100		
Mix-A	90	10	
Mix-B	90		10
Mix-C	95		5

**Table 5-2. Test Conditions for Fixed-bed MAT Tests**

Condition	E-Cat	Mix-A	Mix-B	Mix-C
Catalyst Charge (g)	5.10	5.10	5.10	5.10
Feed Charge (g)	1.00	1.00	1.00	1.00
Catalyst/Oil Ratio	5.2	5.1	5.1	5.1
Preheat Temperature (°F)	1010	1010	1010	1010
Bed Temperature (°F)	980	980	980	980
Oil Inject Time (seconds)	30	30	30	30

**Table 5-3. Test Conditions for Fluidized-bed MAT Tests**

Condition	E-Cat	Mix-B	Mix-C
Catalyst Charge (g)	5.00	5.10	5.00
Feed Charge (g)	0.99	1.00	1.00
Catalyst/Oil Ratio	5.1	5.0	5.0
Preheat Temperature (°F)	1010	1010	1010
Bed Temperature (°F)	980	980	980
Oil Inject Time (seconds)	30	30	30

The results for the fixed-bed MAT testing are presented in Table 5-4. The results in Table 5-4 show no essential change in the boiling point distribution for the hydrocarbon products. The only two items in Table 5-4 that do indicate a difference between the samples with and without RTI's sorbent are the amount of H<sub>2</sub>S in the product stream and the amount of coke formation observed. The decrease in the effluent H<sub>2</sub>S concentration was anticipated, as both EX-S03 and NWA are desulfurization sorbents with activity for H<sub>2</sub>S as well as other sulfur compounds. The slight increase in coke formation was not anticipated, but possibly based on the sorbent's composition.

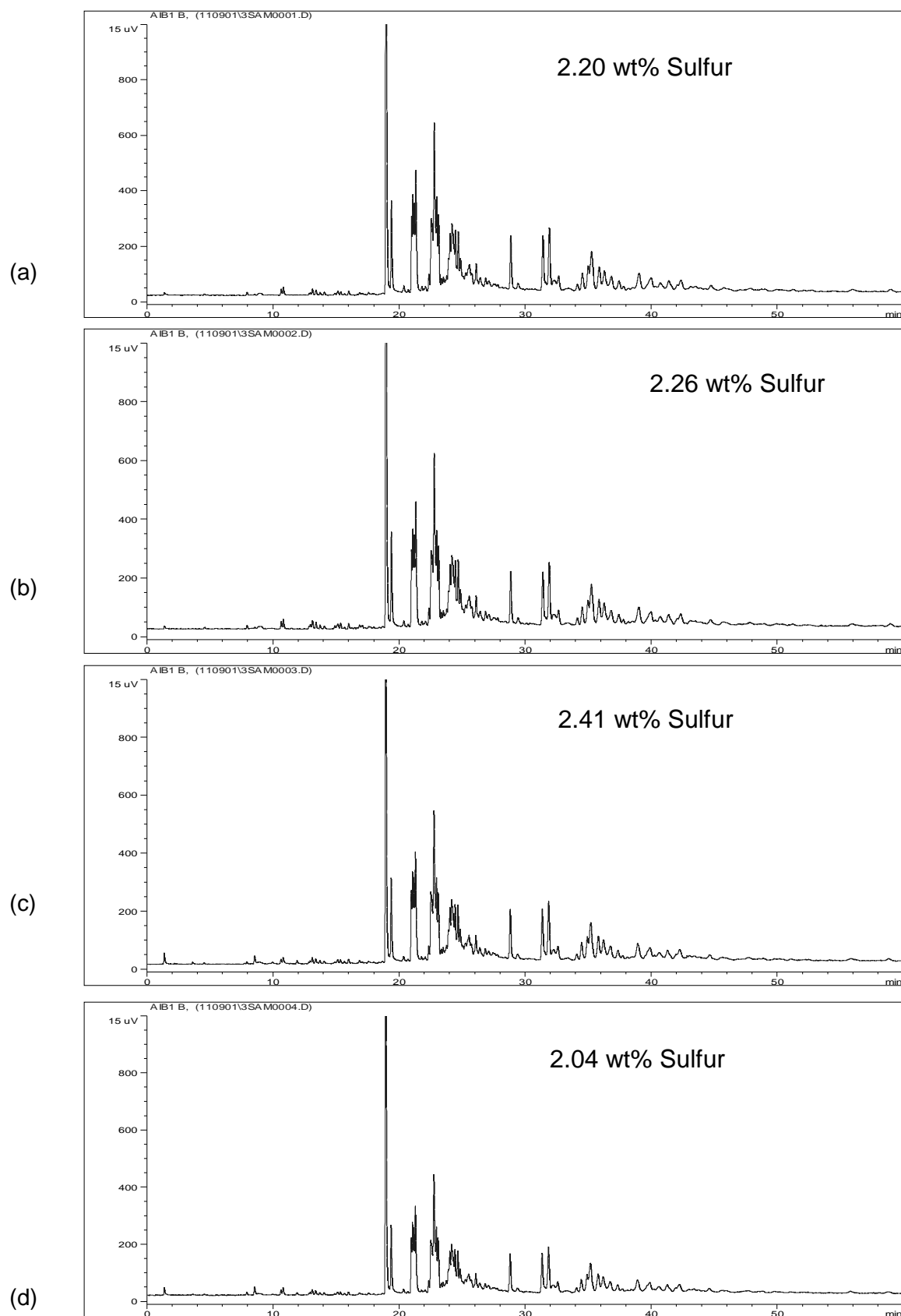
**Table 5-4. Results from Fixed-bed MAT Tests**

	E-Cat	Mix-A	Mix-B	Mix-C
Conversion [%]	72.23	72.40	72.93	72.54
H <sub>2</sub> S [vol%]	1.73	0.48	0.33	0.87
Light Gas (C1 to C4) [%]	18.27	18.23	18.04	18.11
C5-430°F (Gasoline) [%]	47.78	47.80	47.08	47.11
430°F-650°F (Diesel) [%]	19.63	19.70	19.59	19.52
650°F-800°F (HCO) [%]	5.65	6.11	5.71	5.85
800°F+ (Bottoms) [%]	1.50	1.79	1.85	2.09
Coke Deposited [%]	5.45	5.89	7.49	6.46

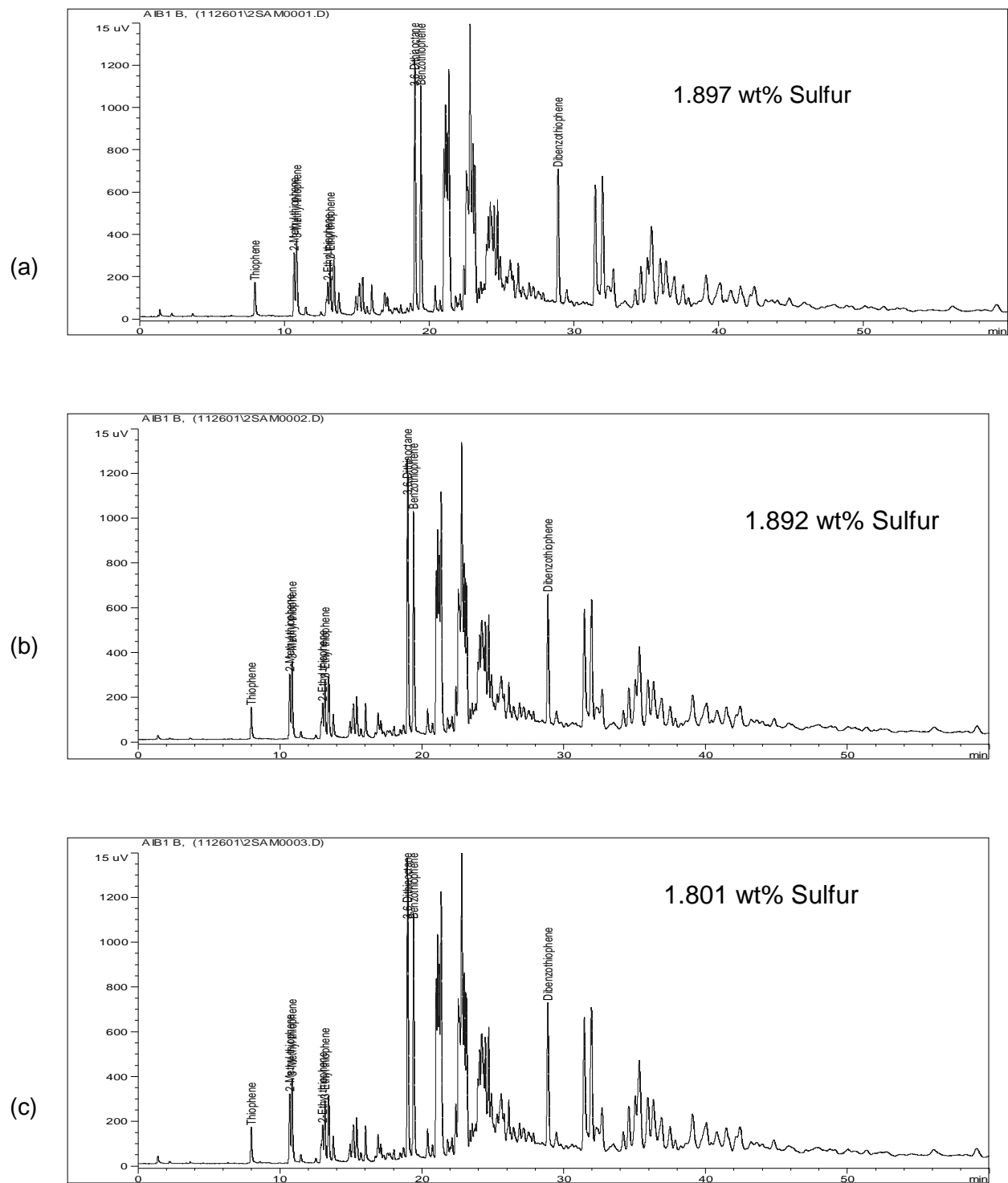
The hydrocarbon product was also analyzed for parafins, olefins, naphthenes, and aromatics (PONA) and sulfur species distribution by means of a Hewlett-Packard GC equipped with an SCD. The results from the PONA testing, shown in Table 5-5, confirm the observation that the additive did not affect the cracking activity or product distribution of the FCC catalyst. The chromatograms in Figure 5-1 show that the predominated sulfur species present in the product ranged from benzothiophene and alkyl substituted benzothiophenes through dibenzothiophene and alkyl substituted dibenzothiophenes. The sorbent/additive NWA did not alter the sulfur species distribution observed in the product, but was responsible for an observable decrease in all the sulfur species in the effluent product.

**Table 5-5. PONA Results from Fixed-bed MAT Tests**

	E-Cat	Mix-B	Mix-C
Aromatics (%)	38.95	40.42	39.32
I-Paraffins (%)	17.01	15.89	17.68
Naphthalenes(%)	7.26	6.92	6.32
Olefins (%)	31.78	32.04	32.34
Paraffin (%)	2.23	2.80	3.02
Oxygenates (%)			
Unidentified (%)	2.77	1.93	1.33



**Figure 5-1. Chromatograms of liquid product from fixed-bed MAT testing (a) baseline with only FCC catalyst, (b) Mix-A, (c) Mix-B, and (d) Mix-C.**



**Figure 5-2. Chromatograms from fluidized-bed MAT testing of NWA sorbent as possible FCC additive (a) base case with only FCC Catalyst, (b) Mix-B, and (c) Mix-C.**

The results for the fluidized-bed MAT tests are provided in Table 5-6. The same decrease in the H<sub>2</sub>S concentration in the effluent product that was observed in the fixed-bed MAT testing was also observed in this fluidized-bed testing. However, the coke formation in these fluidized-bed MAT tests did not show a significant difference from the control tests with just FCC catalyst.

**Table 5-6. Results from Fluidized-bed MAT Tests**

	<b>E-Cat</b>	<b>Mix-B</b>	<b>Mix-C</b>
Conversion [%]	65.25	72.93	72.54
H <sub>2</sub> S [vol%]	1.40	0.33	0.67
Light Gas (C1 to C4) [%]	18.07	17.04	16.89
C5-430°F (Gasoline) [%]	40.85	40.83	40.77
430°F-650°F (Diesel) [%]	20.59	21.02	21.44
650°F-800°F (HCO) [%]	10.13	10.71	10.68
800°F+ (Bottoms) [%]	4.03	4.09	4.21
Coke Deposited [%]	4.93	5.98	5.34

As in the fixed-bed MAT tests, the hydrocarbon product was analyzed for PONA and sulfur species. The PONA analysis provided in Table 5-7 show that the sorbent /additive did not affect the chemical composition or distribution of the hydrocarbon effluent. The chromatographs shown in Figure 5-2 show the sulfur species distribution for fluidized-bed MAT tests with comparison to the results with an FCC catalyst. For the most part, the same distribution of the sulfur species is present in both the feed and the product. However, in results for sorbent/additive NWA there is a significant decrease in the amount of all the sulfur species in the product. Upon further observation, the amount of removal does not seem to change as the sulfur species becomes more difficult to remove by means of hydrotreating.

**Table 5-7. PONA Results from Fluidized-bed MAT Tests**

	<b>E-Cat</b>	<b>Mix-B</b>	<b>Mix-C</b>
Aromatics (%)	47.05	40.42	47.20
I-Paraffins (%)	11.54	10.58	10.88
Naphthalenes(%)	4.62	5.46	5.19
Olefins (%)	31.71	31.10	31.21
Paraffin (%)	2.74	2.50	2.53
Oxygenates (%)	0.13	0.10	0.11
Unidentified (%)	2.21	2.70	2.88

The conclusion from this sequence of MAT testing is the active component identified in NWA does indeed possess the ability to remove sulfur species during FCC operation. The non-optimal material, NWA, showed desulfurization activity for sulfur species from benzothiophene through alkyl-substituted dibenzothiophenes and more recalcitrant and complex sulfur species. In addition, the results seem to indicate that the sorbents desulfurization activity is similar for the typical distribution of sulfur species found in FCC hydrocarbon product streams. This result differs considerably from commercial hydrotreating results, where more aggressive operating conditions and catalysts are necessary as the sulfur species changes from benzothiophene to dibenzothiophene and on to more complex sulfur species.

Although the results did show potential of the materials being developed as additives for FCC application, further testing for this application was postponed to permit focusing more research effort on the development and optimization of a desulfurization sorbent. The test results from

microreactor and PTR systems also showed more impressive desulfurization performance than observed during the MAT testing.

### 5.1.2 Hydrotreated Diesel Testing

During the course of testing desulfurization sorbents in KBR's FCC pilot plant described in the subsequent sections, MAT testing was recommended as a rapid cost effective means of testing the effects of hydrogen on coking and cracking reactivity of RTI-4. A total of six MAT tests were performed at similar test conditions to fulfill this testing requirement. The testing focused on three materials: a typical FCC catalyst, RTI-4, and glass coils. The tests with these sample materials were conducted in KBR's fixed-bed MAT testing system with nitrogen as the diluent gas for one test and hydrogen in a second test. The results for this testing are summarized in Tables 5-8 through 5-10.

**Table 5-8. MAT Testing Results for RTI-4**

<b>Fraction (wt%)</b>	<b>100% Hydrogen</b>	<b>100% Nitrogen</b>
Hydrogen	1.15	0.00
C1- C4 (gas)	0.2	0.07
C5-430°F	22.24	21.35
430°F-650°F	65.08	61.12
650°F-800°F	6.54	7.50
800°F+	0.00	0.00
Coke	4.81	9.95
Material Balance	105.1	107.5

Table 5-8 shows that coke formation in nitrogen was almost twice as large as the coke formation in hydrogen with RTI-4. Further examination of the results in Table 5-8 shows essentially no C1 to C4 hydrocarbons in the products from either test with RTI-4. These results suggest that different reaction mechanisms are responsible for coke formation and production of C1 to C4 hydrocarbons for RTI-4. In addition, the coking mechanism is much more active and is significantly hindered by the presence of hydrogen.

Table 5-9 shows the MAT results obtained with the glass helices. Because the combustion process typically used to determine the coke content of the sample exceeds the melting point of the glass helices, this procedure was not performed and coke formation was not determined. The primary reason for testing glass helices was they were assumed to be inert with respect to reaction with hydrocarbons. From the analysis of the various component fractions, there was no significant difference between the test results with hydrogen or nitrogen. These results suggest that thermal cracking and most probably coking are very slow at temperatures up to 700°F.

Because the fractions for C1 to C4, C5-430°F, and 430°F-650°F were approximately the same size for both the glass helices and RTI-4, RTI-4's reactive towards the hydrotreated diesel is similar to that of glass helices that have been assumed to be inert for all practical purposes. RTI-4 does show a decrease in the 650°F-800°F fraction compared to the results obtained for the glass helices. RTI-4 also showed a significant amount of coke formation. Conversion of higher-boiling refractory compounds to coke is known to produce carbon residue coke. This would suggest that RTI-4 generates carbon residue coke from the 650°F-800°F fraction.

**Table 5-9. MAT Test Results with Glass Helices**

<b>Fraction (wt%)</b>	<b>100% Hydrogen</b>	<b>100% Nitrogen</b>
Hydrogen	0.04	0.00
C1- C4 (gas)	0.97	0.23
C5-430°F	22.40	22.45
430°F-650°F	65.47	66.43
650°F-800°F	11.12	10.86
800°F+	0.00	0.00
Coke	ND	ND
Material Balance	99.50	95.3
Coke Formation (Inferred)	0.5	4.7

These MAT results for the FCC catalyst in Table 5-10 are different from the results observed for RTI-4 and glass helices. The first difference is the concentration of hydrogen in the feed does not have any affect on the coke formation as was observed with RTI-4. With the FCC catalyst, a large portion of the 430°F-650°F fraction of the feed has been broken down into lower boiling compounds in the C5- 430°F and C1 to C4 fractions. Hydrogen does seem to increase the C1 to C4 fraction in the presence of FCC catalyst. A large portion of the 650°F–800°F fraction is also broken into lighter boiling compounds. However, with the FCC catalyst, there is also a small formation of heavier boiling compounds as demonstrated by the amount of 800°F+ fraction and coke. As the cracking functionality for FCC catalysts can be assumed to have been maximized, the shifts observed in the various fractions during the MAT testing with the FCC catalyst must be the result of the various cracking reaction mechanisms. However, the results from MAT testing with RTI-4 are almost identical to the results with the inert glass helices except for the coke formation. This would suggest that the cracking activity of RTI-4 is very limited.

**Table 5-10. MAT Tests results with FCC Catalysts**

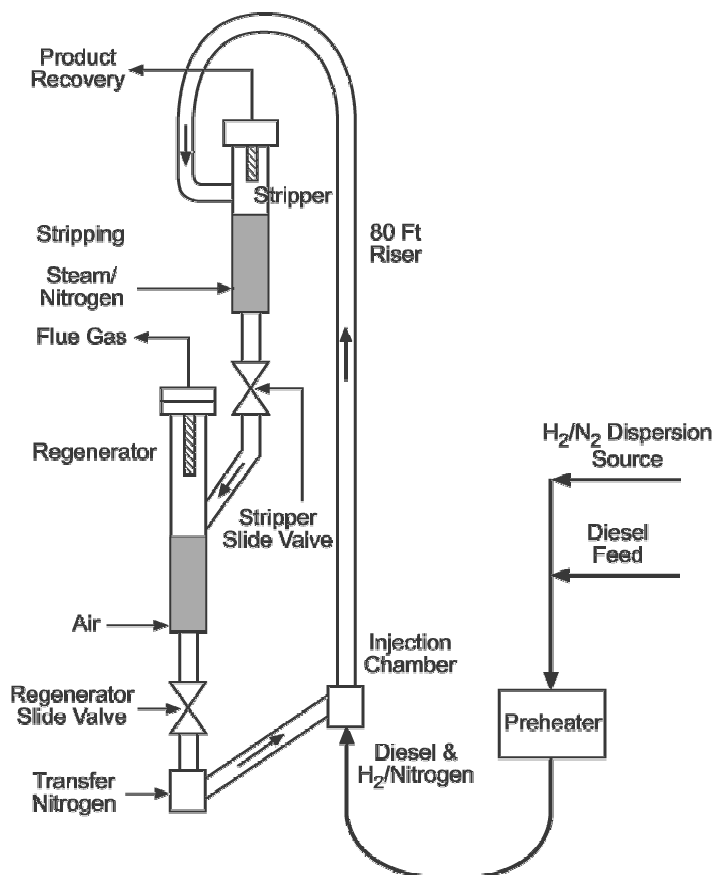
<b>Fraction (wt%)</b>	<b>100% Hydrogen</b>	<b>100% Nitrogen</b>
Hydrogen	0.24	0.14
C1- C4 (gas)	6.06	3.43
C5-430°F	51.19	53.21
430°F-650°F	37.04	37.99
650°F-800°F	1.56	1.40
800°F+	1.55	1.22
Coke	2.59	2.58
Material Balance	99.0	104.9

The conclusions that can be drawn from these MAT tests indicate that reactivity of RTI-4 towards hydrotreated diesel is closer to that of glass helices than FCC catalyst. As glass helices were assumed to be inert for these MAT tests, RTI-4 has little or no cracking activity. However, RTI-4 did demonstrate a high activity for coke formation that could be significantly reduced by the presence of hydrogen.

## **5.2 FCC PILOT PLANT TESTING**

Although RTI's PTR system provided an effective means to test sorbent formulations at realistic operating conditions, this system could not adequately simulate continuous transport reactor operation. For this type of testing, RTI worked with KBR, which possesses two pilot transport reactor systems. The first system is an FCC pilot plant test system. A simplified schematic of

this system is shown in Figure 5-3. This system has a transport adsorption reactor with enough height to accommodate an 8 s residence time at a gas flow velocity of 10 ft/s. However, the maximum operating pressure for this FCC pilot plant system was 50 psig. In addition, sorbent transfer from the standpipe below the regenerator to the transport reactor was accomplished with nitrogen, which results in a significant nitrogen concentration in the reaction gas. Nitrogen is used because slip of nitrogen back into the regenerator would not result in a safety or explosion hazard.

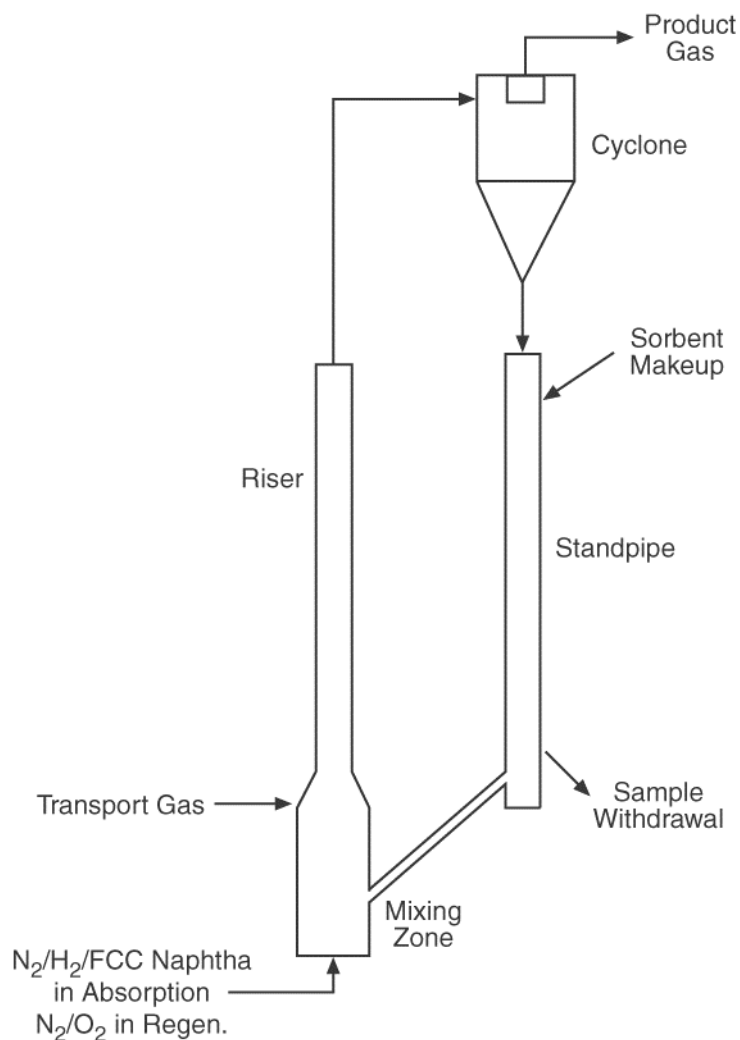


**Figure 5-3. Schematic of KBR's FCC pilot plant unit.**

The second transport reactor available at KBR is the TRTU. Unlike KBR's FCC system, the TRTU system, shown in Figure 5-4, is a single loop system and cannot simulate both adsorption and regeneration simultaneously. The TRTU can be run at pressures up to 150 psig and operated with reaction gas that does not contain large amounts of nitrogen. RTI has used the TRTU system in the past to test attrition resistance desulfurization sorbents for syngas application, most notably EX-S03.

At the most fundamental level, any pilot plant testing at KBR was expected to demonstrate the feasibility of regenerable desulfurization sorbents for naphtha/diesel in a transport reactor at pilot plant scale. Additional objectives for pilot plant testing included sufficient testing to permit optimization of operating parameters; evaluating sorbent performance issues particularly relating to extended operation, deactivation and attrition resistance; and development of a detailed engineering package for a demonstration unit.





**Figure 5-4. Schematic of KBR's TRTU system.**

Because of these objectives, the FCC system was selected for initial pilot plant testing as a closer approximation of the commercial embodiment of RTI's naphtha/diesel desulfurization technology. The low pressure limitation and the nitrogen dilution necessary for sorbent transfer were not envisioned to have a significant effect on achieving the desired objectives. Desulfurization performance was not expected to be affected by a high nitrogen content of the reaction gas, because nitrogen was considered to be inert. Although the commercial embodiment would operate at higher pressures, testing in RTI's PTR had not shown desulfurization performance to be significantly influenced by pressure.

### 5.2.1 FCC System Shakedown

Because the FCC pilot plant did require both operational and hardware modifications for performing the required naphtha/diesel desulfurization testing, the system was initially tested with hydrotreated diesel and EX-S03. A 55-gal drum of hydrotreated diesel was sent to KBR for this testing. Key operating parameters for these tests are provided in Table 5-11. The standard testing procedure was to establish circulation of the sorbent with the total flow rate to be used in the test. The regenerator oxygen flow was started replacing the nitrogen flow. The

hydrotreated diesel flow was started replacing a portion of the nitrogen flow in the adsorption reactor. When stable operating conditions were achieved, sample collection was started. Mass balance analysis was performed each hour. If the mass balance was within the allowable tolerance limit, the results were accepted. The test was continued until 4 hours of reliable mass balance results were collected.

A total of three tests were completed with EX-S03. The results for these tests are summarized in Table 5-12. From the results in Table 5-12, EX-S03 does have some desulfurization activity removing approximately 21% of the sulfur in the hydrotreated diesel. Although several attempts were made to quantify the amount of SO<sub>2</sub> present in the regeneration tailgas stream, an accurate measure of this concentration was not possible. During the first two tests, a continuous SO<sub>2</sub> analyzer was used. The detection limit for this instrument was roughly 200 ppmv. In the third test, an impinger filled with an appropriate base was used to collect the SO<sub>2</sub> in the tailgas, but the concentration of SO<sub>2</sub> was still not sufficient to be adequately measured. Therefore, the sulfur balance could not be completed for any of the shakedown tests. The shakedown tests did confirm that the SO<sub>2</sub> concentration in the regenerator effluent is extremely low. This suggests that the SO<sub>2</sub> will probably have to be separated and concentrated to generate a useful byproduct or disposable suitable form.

**Table 5-11. Key Operating Parameter for FCC Pilot Plant Testing**

	<b>Shake 1</b>	<b>Shake 2</b>	<b>Shake 3</b>	<b>Test 1</b>	<b>Test 2</b>
Solids Circulation (lb/h)	35.5	50	50	26	44
Gas Flow (scfh)					
Nitrogen	19.3	19.3	19.3	14	14
Hydrogen	9.3	9.3	9.3	11	
Diesel	9.6	9.6	9.6	5	
Cat/Oil	7.3	9.7	10	10.2	8.6
Mixing Zone					
Solids Temperature (°F)	830	800		850	925
Diesel Temperature (°F)	100	267	151	605	256
Riser Temperature (°F)	782	785	777	782	790
Residence Time (s)	8	8	8	10	8
Regenerator Temperature (°F)	1050	1050	1050	1270	1285
Regenerator Flow (scfh)	78	77	77	85	77
Excess Oxygen (mole%)	16	8	7	3	9

In addition to minor desulfurization activity for the sulfur species in hydrotreated diesel, EX-S03 has demonstrated superior attrition resistance for transport reactor applications and is non-reactive with CO and H<sub>2</sub> gases and should have very low reactivity with hydrocarbons. However, the results from the carbon balance in Table 5-12, showed that EX-S03 did promote the formation of about 2 wt% of coke and about 10 wt% light hydrocarbon gases. These results seem to indicate a significant amount of coking and light hydrocarbon gas formation that typically results from cracking reactions. Thus, potential explanations for this observation are moderate catalytic cracking ability of EX-S03, the FCC system, or some combination of these two results. The acidity testing of EX-S03 (see Section 4.4) typically showed extremely low acidity that would suggest that EX-S03's catalytic cracking ability would be very small. This would tend to suggest that the FCC pilot plant has a measurable natural coking and light hydrocarbon formation activity.

**Table 5-12. EX-S03 Shakedown Test Results for FCC Pilot Plant Testing**

<b>Mass Balance (wt%)</b>	<b>Shake 1</b>	<b>Shake 2</b>	<b>Shake 3</b>
Total	101	98	101
Carbon	98.3	98.9	99.0
Hydrogen	98.0	99.9	101.0
Sulfur	80.0	78.0	
Product (wt%)			
Coke	1.68	1.84	2.35
Gas	9.81	7.01	6.2
Liquid	88.5	91.1	91.5

### 5.2.2 RTI-4 Testing

After the shakedown testing with EX-S03 was completed, a sample from a large batch of RTI-4 prepared in commercial equipment by SCI was loaded into the FCC pilot test reactor. During the first several days of this test, the sorbent circulation properties were tested to determine the suitable flow regimes to transport and circulate the particles with different ratios of nitrogen and hydrogen. To ensure that a majority of the hydrotreated diesel sample was vaporized upon being mixed with the sorbent in the mixing zone of the transport reactor, the temperature setting of the preheating section was increased to 600°F.

Examination of the results shown in Table 5-13 for this test indicates that RTI-4 did remove roughly  $\geq 60\%$  of the sulfur. Unfortunately, the coke formation for this test was  $\geq 13$  wt%. This was significantly higher than the results observed for EX-S03 testing in the FCC pilot plant system and any of the results from testing of RTI-4 in RTI's PTR system.

**Table 5-13. RTI-4 FCC Pilot Plant Results**

	<b>Test 1</b>	<b>Test 2</b>
Total Mass Balance (wt%)	101	99
Product (wt%)		
Coke	13	9
Gas	11	6
Liquid	76	85

The initial assumption was that these results were related to increasing the preheater temperature to ensure vaporization of the hydrotreated diesel. Thus, a second test was run with the same catalyst sample with similar conditions to the tests with EX-S03.

The results from this test show a lower desulfurization effectiveness of 36% and a coke formation rate of about 8 wt%. The large coke formation observed with RTI-4 during these two tests was considered to be unacceptable for commercial operation. As these results were very different from previous test results in RTI's microreactor and PTR, additional testing was conducted to evaluate the cause of this coke formation. These tests included performing MAT tests at KBR (see Section 5.1.2), additional testing with hydrogen and nitrogen mixtures in RTI's PTR and microreactor systems (see Section 4.3) and acidity measurements (see Section 4.4).

The results from these various tests are described in other sections of this report. However, the net results from this testing indicated that the hydrogen partial pressure had a significant effect on the coke formation. Because KBR's FCC pilot plant system requires a significant flow of

nitrogen to transfer the sorbent from the regenerator to transport reactor, KBR's FCC pilot plant was not appropriate for additional testing of RTI-4.

### 5.3 TRTU TESTING

Although KBR's FCC pilot plant system could not achieve both a high operating pressure and high hydrogen partial pressure, KBR's TRTU system could achieve an operating pressure of 100 psig with essentially 100% H<sub>2</sub>. Thus, one final test was arranged in the TRTU. The conditions for this test are provided in Table 5-14.

**Table 5-14. Operating Conditions for TRTU Testing**

	<b>Test 3</b>
Solids Circulation (lb/h)	1100+
Hydrogen Flow (scfh)	975
Diesel Flow (ml/h)	4000
Riser Temperature (°F)	710
Residence Time (s)	2-3

The test results are summarized in Table 5-15. The test results clearly indicate a coke formation of around 0.6 wt% that is in very good agreement with the earlier results obtained with RTI-4. This also confirms that hydrogen partial pressure has a significant impact on coke formation and decomposition of the liquid product resulting in light hydrocarbon formation. The desulfurization activity of RTI-4 was only able to reduce the effluent sulfur concentration in the liquid product to about 70 ppmw. This represents a sulfur removal of 48%. Although this is not enough to meet the design of 15 ppmw, the residence time was only 2 to 3 seconds, because of the high hydrogen flow rate necessary to transport the particles. This is roughly one quarter to one third the residence time used in the FCC pilot plant test with about the same sulfur removal. If the residence time could be increased to from 6 to 8 seconds, it has been estimated that the effluent sulfur concentration would be roughly 7 ppmw.

**Table 5-15. TRTU Test Results**

Product Sulfur (ppmw)	120	102	85	72	73
Sorbent Carbon (wt%)	0.56 to 0.58*				
Light Gas (vol%)	ND**				

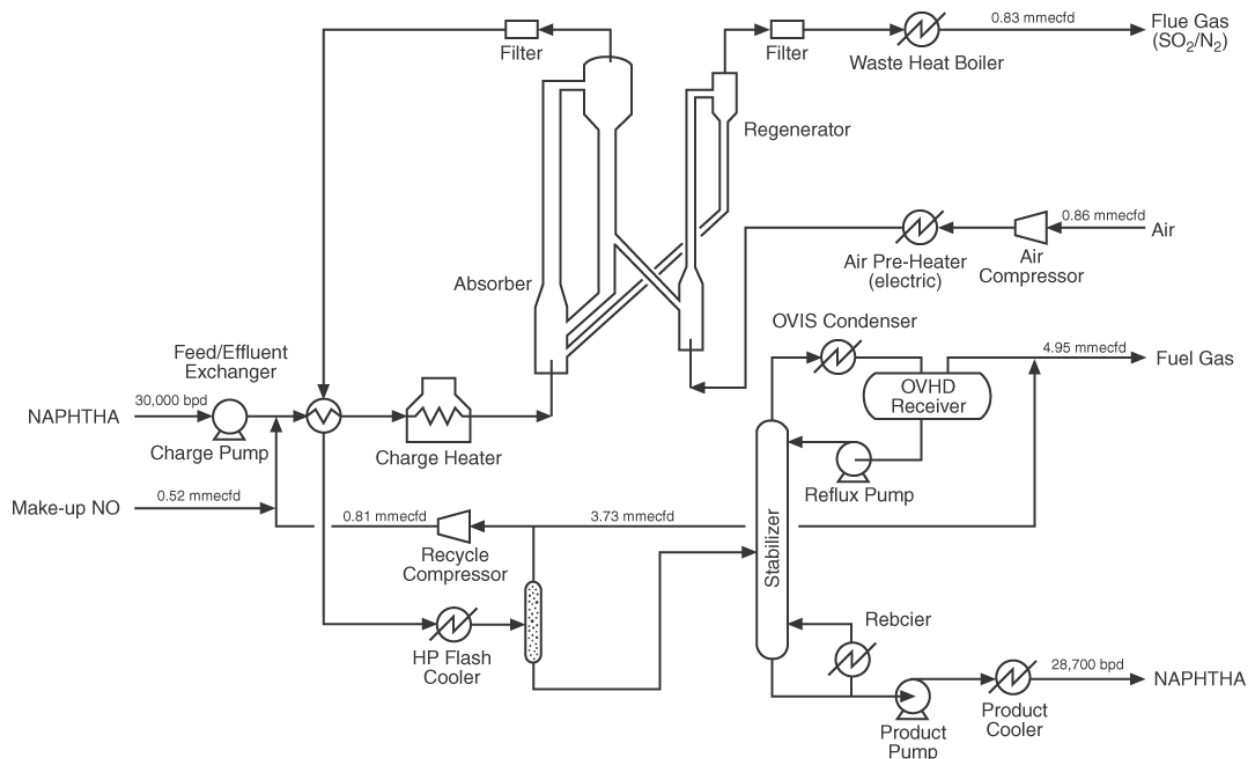
\*Carbon content of fresh sorbent was 0.01 to 0.04 wt%

\*\* Not Detected

## CHAPTER 6

### TECHNICAL AND ECONOMIC FEASIBILITY

The first step in an economic evaluation of the RTI's desulfurization technology was to obtain capital costs and operating expenses. Because no commercial units have been constructed and limited pilot plant results are available, estimates and approximations were made to develop reasonable predictions for capital cost and operating expenses. A simplified process flow diagram (PFD) for RTI's transport reactor desulfurization process can be seen in Figure 6-1. Based on this PFD, Design II process simulator software was used to model the absorber and regenerator. The output from this software included adsorber and regenerator sizes, sorbent circulation rates, sorbent inventory and losses, and energy balances. The key design criteria for this simulation are provided in Table 6-1.



**Figure 6-1. Simplified process flow diagram of TReND process for naphtha desulfurization.**

**Table 6-1. Key Design Parameters**

	<b>Target</b>
Absorber Temperature (°F)	700
Regeneration Feed Air Temperature (°F)	800
System Pressure (psig)	150
Hydrogen Consumption (scf/bbl)	20
H <sub>2</sub> Recycle Rate (scf/bbl)	50
Recycle H <sub>2</sub> Purity (mol%)	50
Sulfur in Feed (ppmw)	2000
Sulfur in Product (ppmw)	20

Construction and capital costs obtained from KBR for the polishing transport desulfurization system built for the Clean Coal Demonstration plant at Pinon Pine provided realistic estimates for costing. In addition, Est\$Pro and Design II simulator software provided factored estimates and installed costs. The specific items included and not included in these estimates are provided in Table 6-2.

**Table 6-2. Cost Estimate Details**

	<b>Estimate includes</b>
DCS	Yes
Underground Sewer	Yes
Fresh and Spent Sorbent Storage	Yes
Offsites	No
Tankage	No
Unit Paving	No
Interconnecting Pipe	No
Contingency	Yes (15%)

The capital cost estimates for RTI's desulfurization and other sulfur removal technologies including conventional hydrotreating, Phillips S-Zorb, and CD tech are shown in Figure 6-2.

The operating costs were also estimated based on historical averaged prices for utilities, in-house generation costs for hydrogen production, cooling water, and steam. These operating costs did take into account sorbent consumption, but do not include maintenance, operating, and other overhead costs. A yield penalty was also calculated valuing FCC gasoline at unleaded regular prices. The results of these estimates are provided in Tables 6-3 and 6-4.

The conclusions that can be drawn from these estimates are that RTI's desulfurization process appears to have a significant cost advantage over other available sulfur removal technologies, both for capital costs and operating expenses. Based on DOE projections, the best estimates on the impact of the cost of diesel indicate a 6 to 7¢/gal increase (Energy Information Administration, 2001). Similar estimates for Phillip's S Zorb and RTI's TReND processes are provided in Table 6-5.

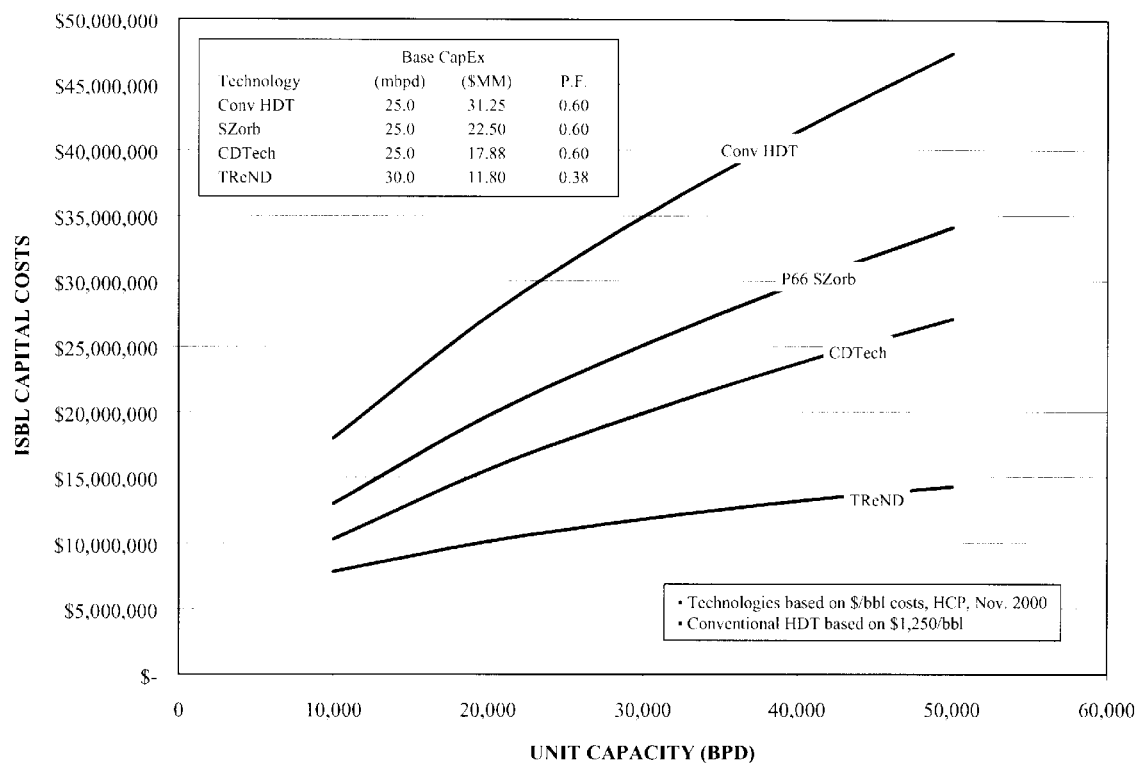


Figure 6-2. Technology capex comparison.

Table 6-3. Operating Costs for RTI's Desulfurization Process

Operating Expense	Cost
	(\$/bbl)
Power	0.007
Steam	0.069
Cooling Water	0.007
Fuel (consumed)	0.082
Hydrogen	0.022
Catalyst	0.010
<b>Total</b>	<b>0.197</b>

Table 6-4. Yield Penalty Estimates

Category	Yield Penalty
	(\$/bbl)
Fuel (yielded)	0.79
Gasoline (loss)	(1.44)
<b>Total Penalty</b>	<b>(0.65)</b>

**Table 6-5. Diesel Cost Impact for Various Technologies**

	<b>Hydrotreating</b>	<b>S Zorb</b>	<b>TReND</b>
Capital Costs (\$/bbl)	1,200-1,800	800-1,200	500-700
H <sub>2</sub> Consumption (scf/bbl)	1,000	400	20-100
Cost Impact (¢/gal)	6-10	4-8	2-4

Although RTI's TReND process has a clear economic advantage over conventional and other similar emerging sulfur removal technologies, effective efforts to penetrate this market will require assistance to demonstrate this technology and its advantages. This assistance includes both identifying a host site for a demonstration unit and testing and securing financial support for this demonstration. To effectively recruit a refinery host site, an effort was made to evaluate the market and identify a short list of candidates that would be most receptive to RTI's plans and objectives.

## **6.1 MARKET ASSESSMENT**

Refiners have demonstrated expertise in both the technical and economic evaluation of technologies. Developing these traits has been a necessity. Over the last 20 years, refiners have typically seen only a 5% return on their capital investments. Refiners have also been required to meet many emission and product specifications to comply with environmental regulations. Product sulfur limits just happen to be one of many regulatory requirements that refiners are actively working to meet. Because the profit margins on the products a refiner produces are extremely small, refiners are extremely cost conscious in evaluating new technologies.

To generate profit from a product slate with extremely low profit margin, refiners are focused on maximizing their production particularly for products with the highest profit margin, such as gasoline and diesel. This translates into extracting the maximum efficiency and capacity possible from available equipment, but also selecting robust technology that maintain extremely high on-stream availability. Therefore refiners are not only looking for technologies that are effective and inexpensive, but for technologies that also increase or at least maintain product yield and are extremely robust with extensive commercial operating experience.

Thus, refiners are typically not interested in new technologies particularly for applications necessary for regulatory compliance. However, their desire to implement the lowest cost technology does provide opportunity for new technologies provided a significant cost incentive does exist, like for RTI's TReND process.

In addition to expediting the research and development process towards pilot plant testing, RTI also allotted resources to market analysis. This market analysis provided detailed information about the potential market for RTI's TReND process and identified a potential short list of refiners that might be interested in hosting a demonstration unit.

### **6.1.1 Methodology**

Because the purpose of this market assessment was not to determine the market exactly, but to obtain a relatively accurate estimate of the market and identify a list of potential candidates for hosting a demonstration unit, detailed analysis of the processing scheme of different refiners was not analyzed with a linear program model or similar tool. Instead, a screening technique employing a set of decision rules was used to identify potential refineries that might utilize the



advantages of RTI's technology. The decision rules were based on the processing configuration at a particular refinery.

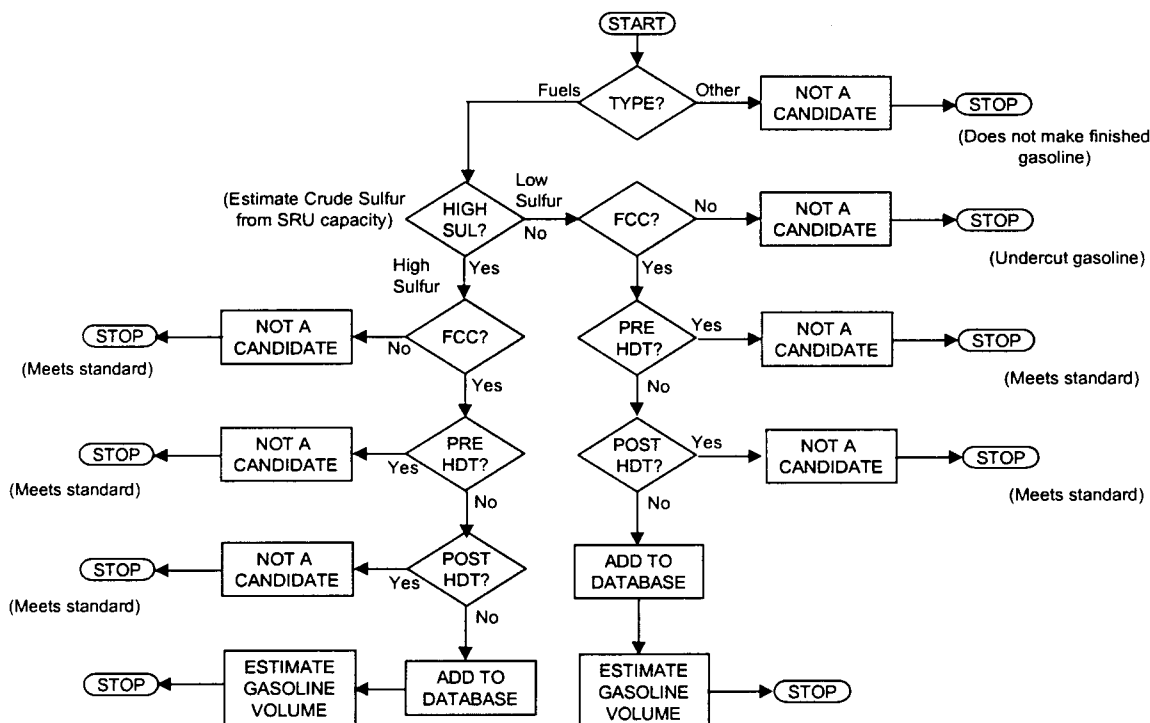
The "Worldwide Refining Capacity" survey assembled and published in the *Oil & Gas Journal* (Worldwide Refining Capacity, 2000) served as the main means to identify the process configuration at the 152 U.S. refineries listed in this survey. By chance, this survey subdivided hydrotreating units into 13 categories, which greatly improves the potential of the methodology being applied. Although similar methodologies could be applied to both gasoline and diesel, each had special features that are described below.

### **6.1.2 Gasoline Methodology**

The primary goal of this methodology was to identify candidate refineries that will need to implement desulfurization technology. However, this exercise also attempts to evaluate the overall gasoline pool sulfur prior to installation of the desulfurization units. This step is important because the regulations allow different phase-in periods for small refiners and Geographical Phase-in Area (GPA).

The specific screening steps are depicted graphically in a decision tree in Figure 6-3 and described below:

- Determine if a refinery is a fuel or specialty refinery—This determination is made based on the overall processing configuration. For example, if the refinery has only a crude distillation unit and an asphalt plant, it is deemed a specialty refinery and is excluded.
- Estimate sulfur content of the crude oil—The sulfur content of the crude run at the refinery is approximated from the sulfur plant capacity and the crude distillation unit capacity. If the refinery has no sulfur plant, it is assumed to process sweet crude oil.
- Estimate sulfur content of intermediate streams—Based on the level of sulfur in the crude, the refinery is designated as a high-sulfur or low-sulfur refinery. This designation is used to distribute the sulfur in the crude to intermediate streams based on the distribution in West Texas Sour (high sulfur) and West Texas Intermediate (low sulfur).
- Develop overall gasoline pool sulfur—This number is calculated from the estimated sulfur in intermediate streams and the individual unit processing capacity.
- Apply decision rules for individual units—This step is intended to eliminate refineries that have capacity to meet target today. It simply examines the processing units available at each refinery and makes a determination whether the refiner can meet the required sulfur level.
- Eliminate refineries that have technology alliances—As a practical matter, these refineries include BP, Chevron, ExxonMobil, Shell and Phillips-Tosco.



**Figure 6-3. Decision tree used to select candidate refineries gasoline sulfur regulation.**

This methodology yielded a list of refineries that would need to actively select a desulfurization technology to meet the new fuel quality regulations. These refineries represent the potential market for RTI's TReND process. Finally, small refineries and refineries with hardship waivers were highlighted because of their special status.

### 6.1.3 Diesel Methodology

The methodology for diesel is similar in many aspects to that used for gasoline. The primary complication is that distillate streams in a refinery can have other uses than production of diesel, particularly on-road diesel. For this analysis, only refiners currently manufacturing diesel, will continue this activity in the future. Only refineries with hydrocracking capacity, diesel or distillate hydrotreating capacity, and/or aromatic saturation capacity are assumed to be producing on-road diesel currently. Refineries with no diesel desulfurization capacity are assumed to produce only heating oil.

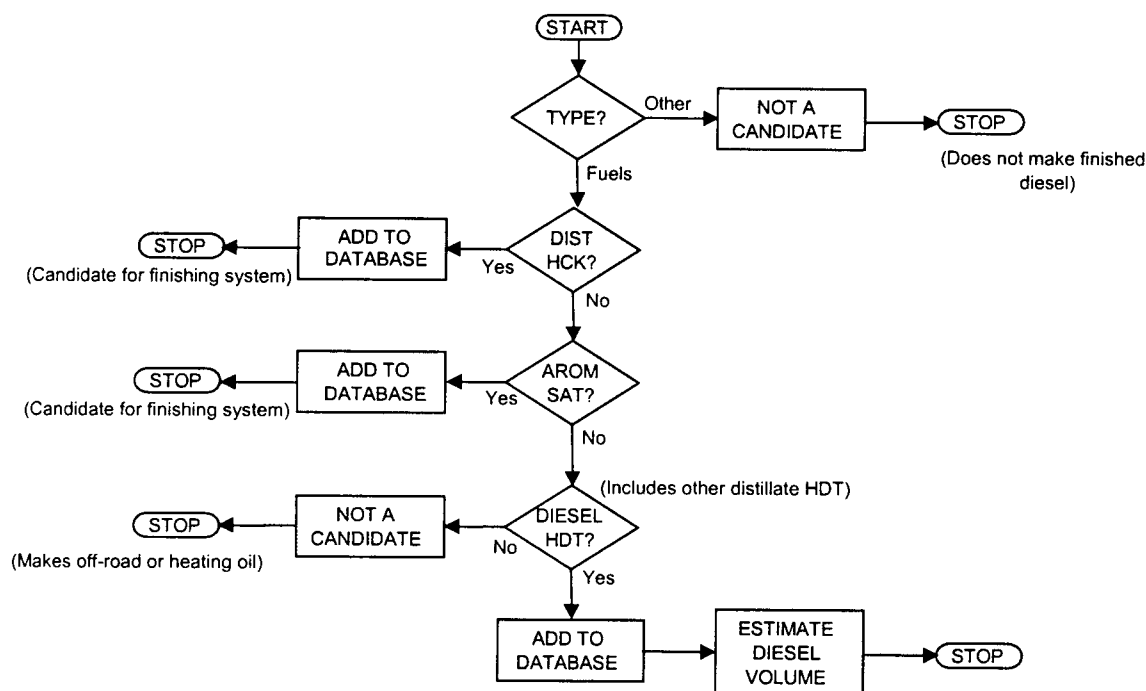
Unlike the gasoline analysis, estimation of the diesel pool sulfur is not necessary because the regulations for diesel do not include any special provisions based on pool sulfur levels.

The specific steps for the diesel methodology are shown in Figure 6-4 and described below:

- Determine if the refinery is a fuels or specialty refinery—This step is conducted in the same manner as for the gasoline analysis.
- Apply decision rules for individual units—This step is intended to eliminate refineries that have the capacity to meet the target today. It simply examines the processing units

available at each refinery and makes a determination of whether or not the refinery is a candidate based on configuration.

- Estimate the volume of on-road diesel—This calculation is based on the capacity of diesel hydrotreaters, aromatic saturation units, and distillate hydrocrackers.
- Eliminate refineries that have technology alliances—these refineries include BP, Chevron, ExxonMobil, Shell and Phillips-Tosco.



**Figure 6-4. Decision tree used to select candidate refineries diesel sulfur regulation.**

The refineries identified by this methodology are the primary candidates for RTI's TReND process as a stand-alone unit. Potential candidates for polishing units can be culled from the refineries that possess either hydrocracking or aromatic saturation capacity. This capacity may be capable of meeting the current regulatory requirements, but some additional capacity may be necessary to meet the new regulatory specifications.

#### 6.1.4 Projected U.S. Desulfurization Market

Using the methodologies for gasoline and diesel described above, the predictions for the market assessment for RTI's TReND process are presented below.

##### 6.1.4.1 Gasoline

Out of the 152 refineries for which information was available through the *Oil & Gas Journal*, 90 refineries were determined not to need RTI's TReND process for the reasons listed in Table 6-6.

**Table 6-6. Breakdown Explanation for Refineries Not Requiring Desulfurization Technology for Gasoline Production**

Reason	Number
Specialty Refinery (No Fuel Production)	36
No FCC Unit (No Gasoline Production)	13
Adequate FCC Sulfur Pretreatment	14
Adequate FCC Sulfur Post treatment	4
Established Technology Alliance	23
Total	90

For the remaining refineries, an approximate schedule for the technology selection including the provisions for GPA and hardship allowances is provided in Table 6-7.

**Table 6-7. Time Schedule for Desulfurization Technology Selection for Gasoline Refiners**

Category	Number	Selection Schedule
Sulfur Pool $\geq$ 300 ppmw	23	Complete*
Sulfur Pool < 300 ppmw	29	2001-2002
GPA	8	2003-2004
Hardship Allowances	2	2005-2006

\* On-line operation scheduled for January 1, 2004.

The obvious conclusion from Table 6-6 is that the potential market dramatically decreases after 2002. The primary reason is selection, design, and construction of the necessary desulfurization system must be completed in time to meet the regulatory deadline. Although there are a number of refineries that can delay their decisions beyond 2002, the potential and willingness of these refineries to host and/or finance a demonstration unit is questionable. Because of their size and financial situation, these refineries may be averse to the risk associated with demonstrating a new technology.

An alternative approach would be to consider the market for polishing units. Analysis shows that 27 refineries would potentially be in the market for polishing desulfurization technology to meet the regulatory limits. This approach has the definite advantage that the desulfurization unit would be smaller and have less impact on total product slate. However, refiners in this category may still be averse to assisting in a demonstration of new technology with the given deadlines, if the technology has not already established a satisfactory level of bench-scale and pilot plant testing.

This analysis does not portray a promising picture for emerging sulfur removal technology. For any technology trying to take advantage of the market demand created by the implementation of the new regulations, this technology must complete a successful demonstration between the end of 2001 and beginning of 2002. Because RTI's TReND process did not achieve this milestone, attempts to find a demonstration partner and commercialize this technology for gasoline desulfurization did not seem very promising.

#### **6.1.4.2 Diesel**

The estimated number of refineries that would not require any desulfurization technology to meet the regulatory requirements for diesel is 87. The breakdown analysis for eliminating these refineries from the estimated market for new desulfurization technology is provided in Table 6-8.

**Table 6-8. Estimated Number of Refineries Not Requiring Desulfurization Technology for On-Road Diesel Production**

<b>Reason</b>	<b>Number of refineries</b>
Specialty Refinery (No Diesel Production)	36
No On-road Diesel Production	24
Established Technology Alliance	27
Total	87

Of the 152 U.S. refineries initially included in the evaluation for potential market requirements for novel diesel desulfurization technology, 65 refineries demonstrated conditions that indicated that a new desulfurization unit, a polishing desulfurization unit or a combination of both new desulfurization and polishing desulfurization units would be necessary to meet the regulatory sulfur limits for diesel. Table 6-9 shows the breakdown of this analysis.

**Table 6-9. Breakdown Analysis for Diesel Desulfurization Requirements from U.S. Refineries**

<b>Type Of Desulfurization Requirement</b>	<b>Number of Refineries</b>	<b>Capacity (Million b/sd)</b>
New Desulfurization Unit	37	0.988
Polishing Desulfurization Unit	15	0.175
New and Polishing Units	13	0.610
Total	65	1.773

Given the June 1, 2006 deadline for compliance with diesel sulfur regulatory requirements and the uncertainty relating to off-road diesel sulfur standard, many refineries are delaying their decision as long as possible, which means that decisions for investment in diesel desulfurization technology must be made by the end of 2003. For refineries that qualify as small refineries, the compliance date can be postponed to June 1, 2010. This effectively extends the decision date for small refineries to late 2007. An estimate of the number of refineries that could apply for this classification is 11 refineries with diesel capacity of roughly 240,400 b/cd.

### **6.1.5 Market Implications**

Although the market analysis described above only accounts for the U.S. desulfurization markets, Europe is implementing similar sulfur limits on both gasoline and diesel with phase in of the technology over a similar period. Typically, the European market has been much more heavily weighted towards diesel, because of the larger portion of diesel passenger vehicles used in Europe. This increases the desulfurization market size, but does not alter the deadline for commercial demonstration of an emerging desulfurization technology.

Thus, both capturing some of the market created by new regulatory sulfur limits in the U.S. and establishing a commercially accepted desulfurization technology require meeting the deadlines facing U.S. refineries. For the gasoline market, the market effectively closed by the end of 2002. Allowing time for marketing, an emerging technology would have had to completed demonstration testing between the end of 2001 and middle of 2002. This was very unfortunate news for development of RTI's TReND process for naphtha desulfurization, because meeting the technical requirements for this deadline were improbable, if not impossible.

The market for diesel desulfurization requirements expanded the window of opportunity both for the main group of refineries and for small refineries. For the late 2003 deadline, development of RTI's TReND process could be advanced far enough to be ready with high activity levels and minimal scale up or development setbacks. The potential to meet the 2007 deadline for small refineries was challenging, but more realistic. Based on this analysis, the potential for securing a refinery to host a demonstration unit for diesel desulfurization was much more promising than for gasoline. For these reasons RTI requested and was granted a technical redirection of the project objectives to expand RTI's TReND desulfurization process to diesel.

## **6.2 DEMONSTRATION UNIT CANDIDATES**

Selection of a targeted list of potential refineries that might be interested in hosting a demonstration unit can only use the information assembled in the market assessment as a starting point. Potential candidates must be open to new ideas and willing to take some risk to help demonstrate a potentially better and less expensive technology. Because this trait is particularly rare, and additional technical requirements presented quite a challenge.

Historically, refiners are unwilling to tolerate even the slightest risk. This aversion to risk arises from trying to profit from thin-margined product or slate of products. This goal dictates an operational philosophy that mandates maximizing on-stream operation and an investment philosophy that minimizes capital investments. Most refiners are not interested in participating in technology demonstration, because operating demonstration units increases the frequency of plant shutdowns and the potential of producing unmarketable/lower value product. Small refinery companies and independent refineries are willing to consider new and alternate technologies, but only if the potential benefit outweighs the risk.

Finally, the potential host candidate should process enough distillate and gasoline feedstocks that a relatively robust demonstration of the RTI TReND process can be completed. At minimum, this should include light straight run and FCC naphthas for gasoline range material and hydrotreated diesel, light cycle oil, and coker distillate for the diesel range material.

Therefore, the characteristics identified as important for refineries being considered as candidates for hosting a demonstration of RTI's TReND desulfurization process were:

- Be an independent refinery or belong to a small company
- Be a fuels refinery producing some on-road diesel
- Have no close ties with technology companies offering desulfurization processes
- Have a positive impression/reference/experience with RTI and RTI's technical abilities
- Be willing to participate in process development activities
- Have some resources available to assist in engineering and operating the demonstration unit
- Have the variety of streams needed for operation of the demonstration unit
- Be open to the idea
- Be willing to accept some risk.

In consultation with NEXIDA, RTI compiled the following list of potential refineries for potentially hosting a demonstration of RTI's TReND desulfurization process:

- Frontier Refining, Inc. (Cheyenne, WY)
- Countrymark Cooperative (Mount Vernon, IN)

- Placid Refining (Port Allen, LA)
- Premcor Refining Group (Lime, OH)
- Giant Refining Co. (Bloomfield and Gallup, NM)
- Montana Refining Co. (Great Falls, MO)
- Orion Refining Corp. (Norco, LA).

### 6.3 TECHNICAL ASSESSMENT

As many of the advantages of the TReND process depend on the ability to conduct the sulfur removal process in a transport reactor system, the following section attempts to evaluate the conditions and length of time the sorbent would need to be exposed to the feed for producing a low sulfur product. Because the diesel target is 15 ppmv and lower than the gasoline target (20-25 ppmw), the results in this section focus on a product with 5 ppmw of sulfur.

Observations from testing in various reactor systems have been employed to generate simplified sulfur removal rates and potential limits of application. This information has been extrapolated to predict the residence time necessary for achieving a product with  $\leq 5$  ppmw sulfur. Because the complex chemistry of the desulfurization process is not known, a first order reaction was assumed generating a sulfur expression described by  $N_s = N_{s0}e^{-kt}$ , where  $N_s$  is the moles of sulfur in the liquid product at any given time,  $t$ ,  $N_{s0}$  is the moles of sulfur in the liquid feed, and  $k$  is the rate constant.

For tests with RTI-4 at the conditions provided in Table 6-10, the rate analysis, which represents an average for the cycles list in Table 6-10, is shown in Table 6-11 and 6-12. Tables 6-11 and 6-12 also provide an estimate of the total sulfur loaded on the sorbent and the residence time necessary to reduce the product sulfur concentration to  $\leq 5$  ppmw.

**Table 6-10. Operating Conditions for PTR Test Series**

Condition	Series 1	Series 2
Pressure (psig)	30	100
Temperature (°F)	700	700
Hydrogen (slpm)	4	8
Diesel (ml/min)	5	5
Residence Time (s)	2.94	2.97
Cycles	3,5, and 9	13,15, and 19

**Table 6-11. Results from PTR Testing at 30 psig**

Time	Effluent sulfur	Rate Constant	Sulfur Loading	Required Residence Time*
(min)	(ppmw)	(s <sup>-1</sup> )	(mg S/kg Sorbent)	(s)
20	22	0.507	54	6.7
30	61	0.441	73	7.7
40	75	0.232	89	14.7
50	75	0.213	105	15.9
60	66	0.209	123	16.3

\* This represents the residence time necessary to achieve an effluent concentration of  $\leq 5$  ppmw at the observed removal rate.

**Table 6-12. Results from PTR Testing at 100 psig**

<b>Time</b> (min)	<b>Effluent sulfur</b> (ppmw)	<b>Rate Constant</b> (s <sup>-1</sup> )	<b>Sulfur Loading</b> (mg S/kg Sorbent)	<b>Required Residence Time*</b> (s)
20	30	0.651	51	5.2
30	36	0.303	75	11.2
40	68	0.232	92	14.7
50	72	0.231	109	14.7
60	73	0.274	125	12.4

\* This represents the residence time necessary to achieve an effluent concentration of  $\leq 5$  ppmw at the observed removal rate.

The rate constants shown in Tables 6-11 and 6-12 are similar both in magnitude and because the rate appears to decrease with increased exposure time. Because of the similarities between the two sets of results, the effect of hydrogen pressure does not appear to be a significant factor affecting the rate of sulfur removal. Although the hydrogen partial pressure does not affect the sulfur removal rate, exposure time does. One of the potential explanations for this behavior is that, as sulfur is adsorbed onto the sorbent, the sorbent's available sulfur capacity decreases reducing the removal rate. Another potential explanation is active sites for sulfur removal are deactivated by coke formation, which increases as exposure time increases. Based on the amount of CO<sub>2</sub> generated during regeneration, the coke content of the sorbents for these tests was about 0.5 wt%.

In another series of tests in the PTR, the sorbent was exposed to a hydrotreated diesel sample spiked with LCO to increase the sulfur concentration to 600 ppmw. The conditions for this test were 30 psig, 800°F, 4 slpm hydrogen and 5 ml/min of spiked hydrotreated diesel. The results from rate analysis for the samples collected at 20 min for Cycles 1 through 5 are presented in Table 6-13.

**Table 6-13. PTR Test Results with Hydrotreated Diesel and LCO**

<b>Cycle</b>	<b>Effluent Sulfur Concentration</b> (ppmw)	<b>Rate Constant</b> (s <sup>-1</sup> )	<b>Sulfur Loading</b> (mg S/kg Sorbent)
1	91	0.767	216
2	202	0.495	169
3	191	0.515	174
4	181	0.532	178
5	272	0.395	139

The results from Table 6-13 shows that rate constants for this test with LCO spiked hydrotreated diesel are approximately the same order of magnitude as the rate constants obtained for the test series with 30 psig and 100 psig and hydrotreated diesel. However, for the test with the LCO spiked hydrotreated diesel, the sulfur loadings are two to four times larger than in the 30 psig and 100 psig test series with hydrotreated diesel. From the regeneration results, the coke formation during this test with LCO spiked hydrotreated diesel the coke formation was approximately 0.5 wt%. This is the same as was observed in the tests at 30 and 100 psig with hydrotreated diesel. These results would suggest that coke formation affects the sulfur removal rate and not sulfur loading at least for sulfur loadings less than 150 mg S/kg of sorbent.

Regardless of which factor actually causes the decrease in the rate, the fact remains that the sulfur removal rate increases for shorter exposure time. However, the sulfur removal rate, after



20 minutes of exposure in the PTR, was still large enough to allow complete desulfurization of the hydrotreated diesel to  $\leq 5$  ppmw in a residence time of between 6 and 10 s. One important feature of the proposed transport desulfurization system is that after exposure in the adsorption riser, the sorbent would be regenerated removing any accumulated sulfur and coke. Therefore, the exposure time would be much smaller and sulfur removal rates would be expected to be significantly higher in a transport reactor system.

In the microreactor system, a fixed fluidized bed of the sorbent is exposed to mixture of hydrogen and hydrocarbon vapor at reaction temperature and atmospheric pressure. The atmospheric operating pressure allows use of a syringe pump that can pump the hydrocarbon feed at lower rates than possible in the PTR system. This effectively reduces the exposure time of the sorbent to the hydrocarbon vapor. The results for two tests can be seen in Tables 6-14 and 6-15. The results in Table 6-14 are with a hydrotreated diesel sample with 440 ppmw sulfur at 4.3 ml/h, 700°F, and 1 slpm hydrogen. The results in Table 6-15 are with Jet-A fuel with 875 ppmw sulfur at 6 ml/h, 700°F, and 1 slpm of hydrogen.

**Table 6-14. Microreactor Test Results with Hydrotreated Diesel**

Effluent Concentration (ppmw)	Residence Time (s)	Rate Constant (s <sup>-1</sup> )	Sulfur Loading (mg S/kg Sorbent)
23	0.96	3.09	91
22	0.96	3.11	92

**Table 6-15. Microreactor Test results with Jet A Fuel**

Effluent Sulfur Concentration (ppmw)	Rate Constant (s <sup>-1</sup> )	Sulfur Loading (mg S/kg Sorbent)
25	3.71	260
23	3.77	261
41	3.17	255

The results in Tables 6-14 and 6-15 demonstrate that by effectively reducing the exposure time to the hydrocarbon vapor, the sulfur removal rates increase significantly. The results in Table 6-15 confirm results obtained in the PTR system that showed similar sulfur removal rates at both lower and higher sulfur loadings suggesting that coke formation was the cause of decreased sulfur removal rate with increased exposure time.

Using the microreactor system, a series of tests were conducted attempting to reduce the effective exposure time sufficiently to produce a product with  $\leq 7$  ppmw sulfur. These tests were conducted at 700°F, 4.3 ml/h of hydrotreated diesel, and 1 to 2 slpm of hydrogen. The hydrotreated diesel samples had either a sulfur concentration of 132 ppmw or 440 ppmw. The analysis of these results is shown in Table 6-16.

**Table 6-16. Microreactor Test Results Producing Diesel with  $\leq 7$  ppmv**

Feed Concentration (ppmw)	Effluent Concentration (ppmw)	Residence Time (s)	Rate Constant (s <sup>-1</sup> )	Sulfur Loading (mg S/kg Sorbent)
132	5	0.96	3.50	28
132	3	0.55	6.73	28
440	2	0.48	11.21	96

The results in Table 6-16 demonstrate that it is possible to produce product with sulfur concentrations of  $\leq 7$  ppmw. Table 6-16 also shows that, at lower effective exposure, the sulfur removal rates increase and residence times of less than 1 s are sufficient to reduce the sulfur concentrations to  $\leq 5$  ppmv. Therefore, the results from the PTR and microreactor systems demonstrate that:

- Sulfur removal rates increase with decreased effective exposure, and
- Residence times of  $\leq 10$  seconds will produce a hydrotreated diesel product with  $\leq 7$  ppmw of sulfur even under the adverse effective exposure conditions in the PTR.

These facts suggest that in a transport reactor system with continuous regeneration, the sulfur removal rate should be sufficiently high to reduce the product sulfur level to  $\leq 7$  ppmw in at least 10 seconds of residence time. This was the primary reason for favoring pilot plant testing in KBR's FCC pilot plant system. Unfortunately, the system configuration needed a significant amount of nitrogen to move the sorbent from the standpipe to the riser. The high nitrogen content has been demonstrated to be one of the causes that resulted in the high coke formation (see Section 4.2). At these high coke concentrations, the sulfur removal rate was extremely low.

Because suitable conditions could not be identified for operating the FCC pilot plant at conditions with lower coke formation, a test was conducted in KBR's TRTU. Unlike KBR's FCC pilot plant system, that has both a riser reactor and a regeneration reactor, the TRTU is only a single loop riser reactor. Therefore, the test in the TRTU would operate as a riser adsorber only. This would be less representative of the ideal transport reactor system, but would allow operating at a higher hydrogen concentration and operating pressure believed necessary to achieve low coke formation.

With an effective residence time in the TRTU of about 3 s, a temperature of 710°F, and a pressure of 100 psig, the conditions were similar to the conditions in RTI's PTR tests. In fact, the test results from the TRTU test, shown in Table 6-17, are essentially identical to the results obtained in RTI's PTR system after 60 min of exposure for both the sulfur removal rate and the amount of coke formation measured. These facts provide additional support that, at lower effective exposure, the sulfur removal rates should be high enough to reduce product sulfur concentrations to  $\leq 7$  ppmw in a transport reactor system.

**Table 6-17. Analysis of Transport Pilot Plant Test Results**

Test	Effluent Sulfur	Residence Time	Sulfur Loading	Coke Formation	Rate Constant
	(ppmw)	(s)	(mg S/ kg Sorbent)	(wt%)	(s <sup>-1</sup> )
TRTU-1	75	2.5	36	0.6	0.196

More research will be necessary to demonstrate the effective range of sulfur removal rates in a transport reactor system in order to effectively design a demonstration or commercial unit. However, the experimental results do provide ample evidence that, as effective exposure time is reduced, sulfur removal rates increase. In the proposed transport reactor system, after exposure of the sorbent in the riser reactor, the sorbent would be regenerated. This would result in an extremely short effective exposure time. Sulfur removal rates at the high exposure conditions observed in RTI's PTR system were sufficient to remove the sulfur in hydrotreated diesel to  $\leq 5$  ppmv in from 6 to 14 s. At the reduced exposure in the microreactor system, the

sulfur removal rates had increased allowing desulfurization of the hydrotreated diesel to  $\leq 5$  ppmv in a residence time of  $\leq 1$  s. Examination of the experimental results suggests that the coke formation is the critical factor determining effective exposure.

## CHAPTER 7

### SUMMARY AND CONCLUSIONS

In retrospect, a great deal of work and learning was accomplished in this project. The initial, and somewhat naïve, understanding of the situation facing refiners created the belief that new and improved desulfurization technologies would be essential to meeting the requirements of EPA's Tier 2 regulations. Greater understanding of the refiner's view of both the regulatory constraints that will be enforced in the near future and their philosophy about capital investment and technology selection did not change the desire for new technology, but did significantly alter the realistic time schedule for technology development. Because our original time schedule was overly optimistic, project activities and targets had to be accelerated to meet commercialization targets.

In spite of accelerating the schedule, a tremendous amount of progress was made in this project. In sorbent development, the accomplishments included:

- Materials screening—Suitable active components and support materials were identified. Rough composition optimization completed.
- Method development—Scaleable coprecipitation and spray drying procedures were identified that produce sorbent with chemical and physical properties appropriate for transport reactor-based TReND process.
- Large batch production—Süd Chemie prepared multiple batches of approximately 100 lbs with commercial catalyst production equipment duplicating or improving the chemical and physical properties obtained at production in RTI's small-scale production facilities.

A matching set of accomplishments for process development included:

- Design and construction of a specialized reactor system devoted to liquid fuel desulfurization.
- Testing of multiple reactor systems supporting sorbent development efforts.
- Testing in multiple reactor systems investigating and optimizing operational parameters for desulfurization, regeneration, hydrogen effects, coking, liquid product specifications and sorbent multicycle performance activity.
- Transport reactor testing of sorbent in two reactor systems.
- Conducting limited testing of the potential of using this sorbent as an FCC additive for removing sulfur during fluidized catalytic cracking.
- Demonstrating sorbent's desulfurization potential for multiple fuels including FCC naphtha, hydrotreated diesel, hydrotreated diesel spiked with LCO, Jet A fuel.

In addition to these technical activities, marketing and commercialization activities included:

- Identification of the relative U.S. market size for both gasoline and diesel desulfurization markets.
- Estimating capital costs and operating expenses for TReND process based on available information.
- Generating a short list of refiners that could be approached as demonstration partners.

- Filing a patent application disclosing both the sorbent composition and process applications.

Therefore, tremendous progress was made in 2 years in a project that began as a conceptualized process based on promising results from several small laboratory scale tests. Unfortunately, progress in this project was not sufficient to accumulate enough transport reactor test results to answer many of the key questions about process performance. Based on contacts with refiners, marketing the TReND process with this performance information would have been challenging. Without this information, making progress towards lining up a demonstration partner has been extremely slow.

The hope of locating a demonstration partner is not completely gone. RTI has received several inquiries that are being pursued with industrial contacts interested in testing and working with this desulfurization technology. The work, particularly in development of a sorbent production method and scale up of sorbent production completed in this project, has also been successfully leveraged for sorbent development for other DOE related projects. Plans also exist to continue leveraging this sorbent development knowledge for other sorbents/catalysts requiring physical and chemical properties suitable for transport reactor applications. Discussions are under way with a large refinery technology developer to advance the development of this technology.

## APPENDIX A

## REPORT ON ACIDITY MEASUREMENTS OF RTI SAMPLES

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**Submitted to RTI by E-mail:**

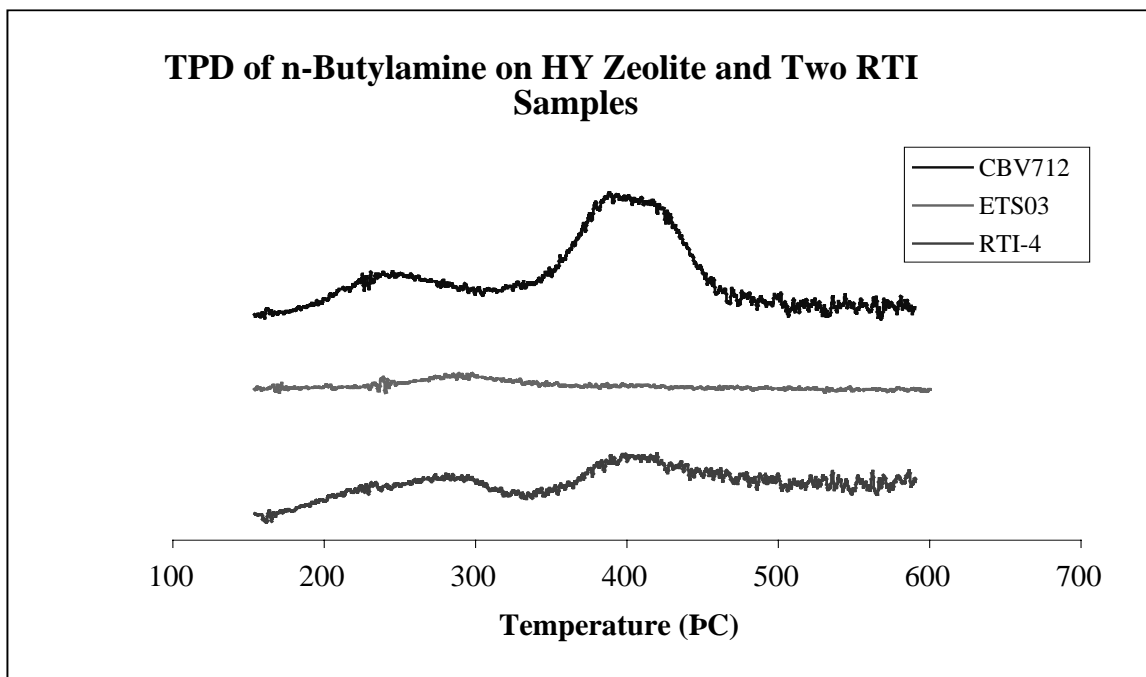
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**January 30, 2003**

This brief report contains the results of acidity measurements using n-butylamine temperature-programmed desorption (TPD) for two RTI samples [ETS0<sub>3</sub>, and RTI-4]. At the request of RTI, we also selected an acidic zeolite (USY, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=12) and performed the measurement using the same instrument by the same procedure in the same time period for comparison purpose.

Figure 1 shows the nBA TPD profiles. It seems that the ETS-3 sample (white) is their raw material, on which they supported some metals to form RTI-4 (black). The ETS-3 is very weak in acidity as compared with the acidic Y zeolite sample. However, the acidity of the modified RTI-4 (reduced in H<sub>2</sub> at 350°C for 1 hour) has higher acidity, but is still less acidic than our USY sample.



**Figure 1. n-Butylamine TPD profiles for RTI samples and an acidic Y zeolite sample.**

Table 1 shows the quantitative acidity data on the three samples. The maximum TPD peak temperatures are also listed in Table 1.

**Table 1. Acidity of RTI samples and an Acidic Y-Zeolite Sample**

Samples	HY (CBV712)		ETS-3		RTI-4	
Peak Temperature (°C)	236 <sup>a</sup>	384 <sup>b</sup> , 416 <sup>c</sup>	299 <sup>a</sup>	N/A	288 <sup>a</sup>	392 <sup>b</sup> , 412 <sup>c</sup>
Acidity (mmol/g)	0.116	0.431	0.049	0	0.141	0.161
Total Acidity (mmol/g)	0.547		0.049		0.302	

- a. Peak at 150-300°C: the desorption of n-butylamine from medium acidic sites;
- b. Peak at 350-450°C: the decomposition of n-butylamine to ammonia from strong acidic sites;
- c. Peak at 400-500°C: the decomposition of n-butylamine to butane from strong acidic sites.

The acidity values in Table 1 are represented as mili-mol per gram of sample. The TPD peaks at below 340°C is considered to be weak and medium acidic sites. The Bronsted acidity is represented by the area of high temperature peak of n-BA TPD, which is in the range of 350-460°C. The integration includes tail up to 500°C.

TPD peaks at further higher temperatures, if any, are not considered to be due to acidic sites, but rather due to surface dehydration (e.g., removal of surface silanol groups, etc.).



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