

## INFLUENCE OF CATALYST ON SULFUR DISTRIBUTION IN FCC GASOLINE

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In an effort to learn more about the role of the catalyst on the sulfur content and distribution in FCC gasoline, several catalysts have been tested, and the resulting gasoline range sulfur species examined in detail. In addition, model compound studies have been conducted to examine the cracking of thiophene over the same catalysts. It has been found that catalysts which produce widely different hydrocarbon distributions during FCC produce only marginally different sulfur distributions in the gasoline range. In addition, catalysts which have significant hydrogen-transfer activity more effectively convert thiophene to H<sub>2</sub>S than those with low hydrogen-transfer activity. These findings show that the FCC catalyst may have a role to play in the production of low-sulfur reformulated gasoline.

### Introduction

The reformulated gasoline regulations mandated by the Clean Air Act Amendment of 1990 have set new limits on the composition of gasoline to be sold in many parts of the U.S.<sup>1</sup>. Meeting the requirements of the Act (as specified by the EPA) will present a considerable challenge to the refining industry over the course of the next decade<sup>2</sup>. Besides setting limits on the levels of oxygenates and aromatics (particularly benzene) in reformulated gasoline, it is anticipated that the EPA will set an additional limit on the level of gasoline sulfur<sup>2,3</sup>. A recent report from the Auto/Oil Air Quality Improvement Research Program clearly showed that reduction in the gasoline sulfur level from 500 ppm to 50 ppm had a significant favorable impact on tailpipe emissions<sup>4,5</sup>. The reason is that sulfur emissions poison the active noble metal in emission control catalysts, thus, lower sulfur results in a more effective catalytic converter.

FCC naphtha contributes the largest fraction of sulfur to the total gasoline pool. In fact, 75% to 90% of pool sulfur can be traced to the FCC unit, while only 35% to 40% of the pool volume is FCC gasoline<sup>6,7</sup>. Thus, any move to reduce gasoline sulfur content will invariably impact the FCC unit in some way. Of the possible options, hydrotreating either the FCC feedstock or the FCC naphtha is the most obvious. However, with the concomitant need to reduce the aromatic content of the reformulated gasoline pool, reformer severity will probably be reduced which will limit the refinery's hydrogen supply. In addition, in order to reduce the gasoline sulfur content to the proposed levels (30-50 ppm), "deep" hydrotreating will most likely be required.

A potentially less expensive option is the catalytic removal of sulfur compounds in the FCC unit. In order to examine this alternative, we have studied the impact of the FCC catalyst on the gasoline sulfur content. Previous workers have examined the sulfur distributions resulting from thermal cracking of gas oils<sup>8</sup>, while others have focussed on the effect of the feedstock and operating conditions on the final sulfur distribution<sup>9-12</sup>. However, to date, no study of the effect of the FCC catalyst on gasoline sulfur content has been reported.

In this study, we explored the impact of variations in FCC catalyst properties on the concentration and distribution of gasoline range sulfur compounds in FCC naphtha. In addition, we examined the conversion of thiophene in a thiophene/hexadecane mixture over the same catalysts in order to determine the extent and importance of secondary cracking reactions, i.e. overcracking<sup>13</sup>, on the final sulfur distribution.

### Experimental

The catalysts used for this study are typical of the types of faujasite-based materials which are commercially available, and were chosen to provide a wide variation of hydrogen-transfer (H-T) activity<sup>14-16</sup>. Catalyst properties are given in Table I. The REY catalyst showed the highest steamed unit cell size, and was expected to have the highest H-T activity. In contrast, the USY/Matrix and USY-G catalysts had the lowest steamed unit cell size and thus, the lowest H-T activity. The REUSY catalyst showed properties intermediate between the REY and USY's. All of the catalysts were steam-deactivated for 4 hours at 1500°F prior to testing.

Gas oil cracking experiments were run in the Davison Circulating Riser (DCR<sup>17</sup>) which was run in the adiabatic mode with a riser outlet temperature of 970°F. The feed used in the DCR was a sour heavy gas oil which contained 2.67 wt% sulfur<sup>18</sup>. H<sub>2</sub>S in the light gas fraction was determined by GC analysis. Feed and liquid-product sulfur contents were measured using a LECO sulfur analyzer. Sulfur on coke was determined by measuring SO<sub>2</sub> content of the regenerator flue gas. Sulfur material balances between 99% and 102% were consistently obtained.

Detailed identification of the gasoline range sulfur compounds was obtained using a HP 5890 GC equipped with a PONA capillary column and an Atomic Emission Detector (GCAED). In this system, the separated compounds from the column exit are broken down into constituent elements and excited in a plasma. The various atoms then emit light at characteristic wavelengths and quantitative element-specific information is obtained by monitoring the wavelength(s) characteristic of a specific element. Individual sulfur compound identifications were made using a combination of GCAED and GC-MS. A typical chromatogram is shown in Figure 1.

The hexadecane and thiophene used in the model compound experiments were 99+ % purity gold label Aldrich products. Hexadecane conversion was determined by GC analysis (HP 5890 equipped with a 19091S-001 50 m Fused Silica Capillary column). The reactor system had a standard fixed-bed configuration and the liquid mixture was pumped into the reaction chamber with a syringe infusion pump at the rate of .6 g/min. Nitrogen was co-fed with the hydrocarbons at the rate of 10 cc/min. Contact time was fixed at 3 minutes, and weight hourly space velocity (WHSV) was varied by changing the amount of catalyst in the reactor tube. To maintain constant reactor heat capacity the catalyst was diluted with alundum (EM Science, calcined for 2 hrs. at 1300 °F) to a constant bed volume of 4 ml. Alundum alone shows less than 1 % conversion for this pseudocomponent mixture.

Liquid products were collected in an ice bath and then analyzed by GC. The volume

of the gas products was determined by water displacement. The gas products were analyzed by FID and TCD on a Varian Vista 6000 Gas Chromatograph equipped with a 50 m Chrompack Fused Silica column 7515. Coke levels were determined by mass difference between the catalyst after 100 °C calcination and 540 °C calcination for 1 hour. Only mass balances above 97% are reported in this study.

### Results and Discussion

Table I contains a constant (70 wt%) conversion comparison of the four catalysts tested in the Davison Circulating Riser (DCR). A more detailed analysis of the DCR data is given in a previous paper<sup>18</sup>. From the data, it appears that all of the catalysts are equally efficient at converting feed sulfur from LCO/HCO into lighter products, with the exception of USY-G which shows somewhat lower sulfur conversion activity. No significant differences in product yields are observed: The majority (about 40%) of the feed sulfur is converted into H<sub>2</sub>S, about 3% is converted into coke, while roughly 2% ends up in the gasoline fraction. However, on closer analysis of the sulfur distribution in the gasoline fraction, some differences are observed. For all catalysts, the majority of the gasoline range sulfur compounds are thiophene derivatives. However, the catalysts with high hydrogen-transfer activity (REY, REUSY) produced about 8% less gasoline sulfur than those with low hydrogen-transfer activity (USY, USY-G). This result was unexpected, since thiophene is aromatic and hydrogen-transfer over FCC catalysts typically results in the formation, not the destruction, of aromatic molecules<sup>14-16</sup>. Another difference between the two catalyst types is the molecular weight distribution of the gasoline range sulfur products. While the amounts of lighter products (mercaptans, thiophene, tetrahydrothiophene) is similar for all four, the low H-T catalysts produced larger amounts of the heavier species (propylthiophenes, butylthiophenes, benzothiophene).

In addition to sulfur content, future reformulated gasoline regulations will also include T90 (the distillation temperature at which 90% of the fuel has boiled away) as a variable in the "complex model" to be used for gasoline certification. Lowering T90 reduces the average molecular weight of gasoline which allows for better vaporization and cleaner combustion in automobile engines. In our study, reduction of T90 from the current level of 380°F (430°F endpoint) to the proposed level of 300°F (340°F endpoint) has the effect of removing the heavy sulfur compounds from the resulting gasoline. All of the benzothiophene and butylthiophenes and some of the propylthiophenes are removed by this change in T90. This effectively eliminates the differences in gasoline sulfur distribution shown by the four catalyst systems<sup>18</sup>.

In an attempt to determine the extent and importance of secondary cracking reactions on the final sulfur distribution, model compound cracking experiments were run for three of the catalysts. Thiophene was tested as a mixture with hexadecane in an effort to mimic a typical hydrocarbon environment during the cracking reactions. The mixture contained 0.5 wt% (5000 ppm) sulfur. Results from this set of experiments are shown in Figures 2 and 3 and Table II.

The data show that, for all catalysts, the conversion of thiophene is low and independent of the conversion of hexadecane (which ranged in conversion from 20-80%). For our data, there is a linear relationship between  $-\ln(1-\text{thiophene conversion})$  and the reciprocal of space velocity (1/WHSV). The linear yield curves, shown for the REY catalyst in Figure 2, further demonstrate that the product selectivity of the thiophene is unaffected by the changes in hexadecane product distribution over this range of conversion. Although we expect the alkylthiophenes to be direct reaction products of thiophene with hexadecane product precursors, these species must be in

great excess with respect to the thiophene if they do not affect either the conversion or the selectivity of the thiophene.

To determine the relative cracking rates of hexadecane and thiophene, we used a technique for the cracking kinetics of model compound mixtures which is described in detail elsewhere<sup>19</sup>. The cracking of the mixture can be represented by two coupled nonlinear equations:

$$\frac{dC_H}{dt} = \frac{K_H \sum_j k_{Hj} C_H [1+G\tau]^{-N}/[VE]}{1 + [K_H C_H + K_T C_T + \sum_j [C_{H0} - C_H] K_{Hj} n_{Hj} + \sum_j [C_{T0} - C_T] K_{Tj} n_{Tj}]/[VE]}, \quad (1)$$

$$\frac{dC_T}{dt} = \frac{K_T \sum_j k_{Tj} C_T [1+G\tau]^{-N}/[VE]}{1 + [K_H C_H + K_T C_T + \sum_j [C_{H0} - C_H] K_{Hj} n_{Hj} + \sum_j [C_{T0} - C_T] K_{Tj} n_{Tj}]/[VE]}, \quad (2)$$

where subscripts H and T represent Hexadecane and Thiophene respectively, C is the concentration, K is the Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption constant,  $k_j$  is the first order reaction through the  $j$ th reaction pathway, G and N are the decay parameters for time on stream  $\tau$ ,  $C_0$  is the initial concentration in the reaction mixture,  $K_j$  is the adsorption constant of the products through reaction pathway  $j$ ,  $n_j$  is the stoichiometry of reaction pathway  $j$ , and [VE] represents the volume expansion of the mixture. Equations 1 and 2 can be simplified by solving for  $dC_H/dC_T$  to obtain:

$$\left( \frac{C_H}{C_{H0}} \right) = \left( \frac{C_T}{C_{T0}} \right)^{\frac{K'_H}{K'_T}} \quad (3)$$

By using equation (3) to examine the relative conversions of hexadecane and thiophene, we can obtain a ratio of effective rate constants  $K'$  that is independent of the catalyst deactivation rate, most competitive sorption terms, and the volume expansion of the mixture. In Figure 2 we plot  $C_H$  vs.  $C_T$  for the REY (high H-T) and USY (low H-T) catalysts along with the curve fitted to equation (3). The data show that hexadecane cracks approximately 10.4 times faster than thiophene under these conditions. No difference is observed between the two faujasite types, which indicates that the increased hydrogen-transfer kinetics of the REY does not alter the relative cracking rates of the thiophene and the hexadecane.

While analysis of the kinetic data show no difference between the rates of thiophene cracking over the high and low H-T catalysts, there is a difference between the product selectivities of the catalysts. Table II shows the product distributions for the four catalysts interpolated to a constant 4 mol% conversion. At this low conversion, only primary products are expected to form. The product selectivity varies smoothly with the hydrogen-transfer activity of the catalysts. With REY, tetrahydrothiophene is the most abundant product, while ethylthiophene is the major product over USY. REUSY shows behavior intermediate between the other two. This is consistent with the riser data (Table I) which showed increased levels of the heavier thiophene derivatives for the low H-T catalysts. It is also interesting to note that there is some formation of  $H_2S$ , a secondary reaction product, over the REY and REUSY catalysts, even at this low conversion level.

There appear to be two different mechanisms for the conversion of thiophene over faujasite-based FCC catalysts. The dominant mechanism over the high H-T catalysts is the hydrogenation of thiophene to tetrahydrothiophene, followed by the cracking of this product to form H<sub>2</sub>S. Conversely, the dominant mechanism over the low H-T catalysts is the alkylation of thiophene to methyl, ethyl and propyl thiophene. Thus, the lower the H-T activity, the higher the average molecular weight of the sulfur products. Also, it appears that the relative importance of the two reaction pathways varies smoothly with H-T activity, since the REUSY shows behavior intermediate between the other catalysts.

### Conclusions

Examination of the role of catalyst properties on the distribution of sulfur compounds present in FCC gasoline has shown that only small differences exist between catalyst types, and the primary impact of the catalyst is on the molecular weight distribution of the thiophene derivatives which are produced. Model compound experiments have shown that thiophene can be either alkylated or hydrogenated over FCC catalysts under cracking conditions, albeit at an extremely low rate. Catalysts with high site-density and therefore high hydrogen-transfer activity preferentially hydrogenate thiophene to tetrahydrothiophene which can then be cracked to H<sub>2</sub>S. In contrast, catalysts with low site density and low hydrogen-transfer activity favor alkylation of thiophene to higher molecular weight products. However, the small differences between catalyst types indicate that alternative materials will be required to significantly affect the sulfur content of FCC gasoline.

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Table I.  
Distribution of Sulfur Products from  
DCR Cracking of Gas Oil over FCC Catalysts

Liquid Conversion = 70 wt%

Catalyst Properties	REY	REUSY	USY/MATRIX	USY-G
Re <sub>2</sub> O <sub>3</sub> , wt%	4.73	2.79	0.02	0.04
Unit Cell*, Å	24.49	24.30	24.19	24.24
Zeolite SA, m <sup>2</sup> /g	38	131	81	196
Matrix SA, m <sup>2</sup> /g	24	23	55	25
Sulfur Conversion (wt%)	45.5	44.5	45.0	42.5
Product Yields (wt%)				
H <sub>2</sub> S	40.1	39.1	40.1	36.7
Gasoline	2.0	2.0	2.0	2.2
LCO/HCO	54.5	55.5	55.0	57.5
Coke	3.3	3.3	3.0	3.7
Gasoline Sulfur (ppm S)	1175	1175	1280	1280
mercaptans	169	61	169	167
thiophene	62	168	59	59
tetrahydrothiophene	17	17	17	17
methylthiophenes	150	148	160	158
ethylthiophenes	171	169	176	174
propylthiophenes	120	119	145	144
butylthiophenes	133	142	164	174
benzothiophene	353	351	389	385

\* After 4 hr, 1500°F steam deactivation

Table II.

Sulfur Product Yields from Cracking of Thiophene in Hexadecane, Interpolated to 4 vol% Thiophene Conversion

Operating Conditions: 500°C, 1 atm

Product Yields	<u>REY</u>	<u>REUSY</u>	<u>USY-G</u>
Tetrahydrothiophene	1.7	1.5	1.0
Alkylthiophenes	2.2	2.4	3.0
Methylthiophene	1.2	1.3	1.4
Ethylthiophene	1.0	1.1	1.6
Hydrogen Sulfide	0.1	0.1	0.0

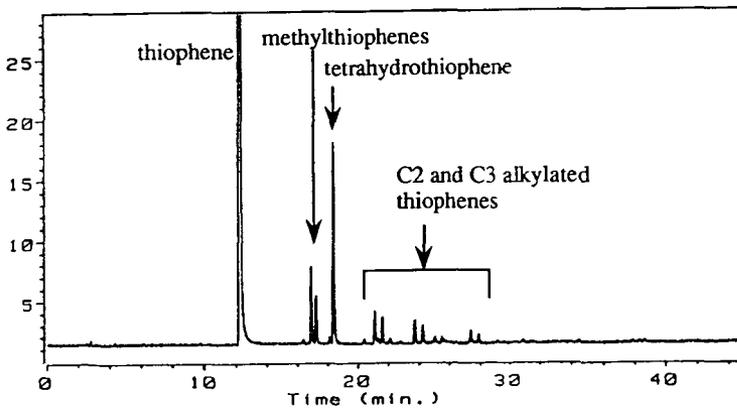


Figure 1 Sulfur GCAES Chromatogram from Cracking of Thiophene in Hexadecane

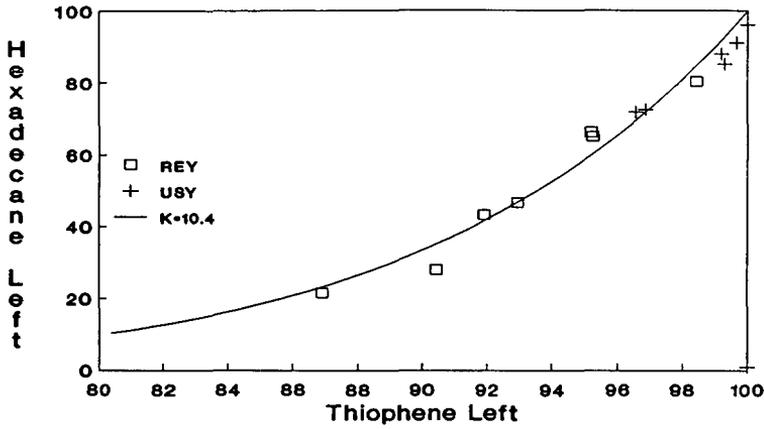


Figure 2 Product Yields from Cracking of Thiophene in Hexadecane over REY Catalyst

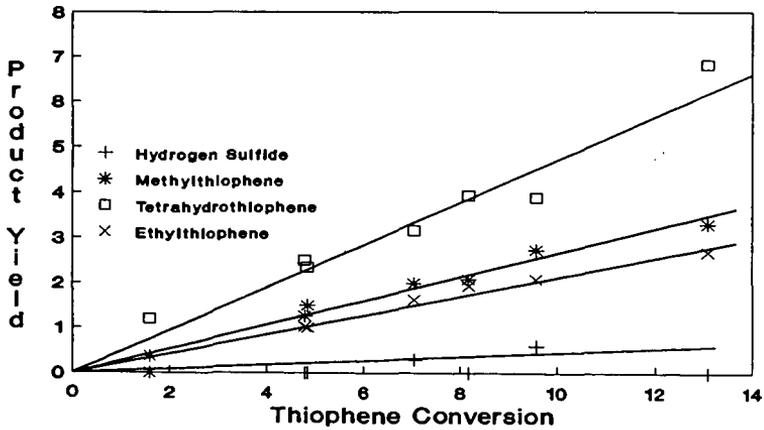


Figure 3 Relative Conversion of Thiophene and Hexadecane from Cracking of Mixture