CITGO Petroleum Corporation

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CERTIFIED MAIL RETURN RECEIPT REQUESTED
7005 0390 0005 3108 3057

March 24, 2006

Chief
Environmental Enforcement Section
Environment and Natural Resources Division
U.S. Department of Justice
P.O. Box 7611, Ben Franklin Station
Washington, DC 20044-7611
Reference Case No. 90-5-2-1-07277

Re:

Alternative Monitoring Plans, Appendix E and F
Corpus Christi East Refinery and Corpus Christi West Refinery
CITGO Petroleum Corporation
Civil Action Number H-04-3883
Southern District of Texas, Consent Decree entered January 26, 2005

Dear Chief:

CITGO submitted on July 26, 2005, pursuant to Section V.G., Paragraph 64.c. of the referenced Consent Decree, requests for Alternative Monitoring Plans (AMP) for NSPS Subpart J refinery fuel gas streams and fuel gas combustion devices at the Corpus Christi East Refinery and the Corpus Christi West Refinery. CITGO received a denial letter dated February 22, 2006 for one of the AMPs submitted. Therefore, CITGO has revised the AMPs and requests that the enclosed AMPs replace the July 26, 2005 submittals described in Enclosure 1. The AMP requests for fuel gas streams listed in Appendix E and fuel gas combustion devices listed in Appendix F are included as Enclosures 2 - 10.

Copies are being provided to EPA Headquarters and the Applicable EPA Region as described in Section XVII.

If there are questions, or additional information is required, please contact Janice DeVelasco at 832-486-1521.

Sincerely,

Janice DeVelasco

Allen Greene
Manager Environmental Protection

Enclosures

ENCLOSURE 8

ALTERNATIVE MONITORING PLAN
CITGO Petroleum Corporation
Corpus Christi West Refinery
Appendix E

ALTERNATIVE MONITORING PLAN
CITGO Petroleum Corporation
Corpus Christi West Refinery
Merox Disulfide Separator Spent Air Vent

Introduction

The following Alternative Monitoring Plan (AMP) has been developed in accordance with USEPA's guidance issued in *Alternative Monitoring Plan for NSPS Subpart J Refinery Fuel Gas: Conditions for Approval of the Alternative Monitoring Plan for Miscellaneous Refinery Fuel Gas Streams (RFG Guidance).* The RFG Guidance specifies information that must be included to allow for a determination of appropriateness of the AMP. The following information is submitted, per the RFG Guidance, for approval of the use of described recordkeeping and reporting requirements as an alternative to the monitoring described in NSPS Part 60, Subpart J. This request is being made for the Merox Disulfide Separator Spent Air Vent.

Process Description

The Merox process is used to convert mercaptan sulfur to disulfide sulfur from coker LPG and coker gasoline by using a selective oxidation catalyst. The two main applications of the process are extraction and sweetening. Extraction is the removal of mercaptan sulfur, while sweetening is the conversion of mercaptan sulfur to disulfide.

The mercaptan-rich hydrocarbon stream is contacted with a strong aqueous alkali solvent in order to extract mercaptan sulfur from the hydrocarbon. The mercaptan-rich alkali solvent then goes through a regeneration section where air is injected into the solvent and the mercaptan is oxidized to disulfide in an oxidizer. The disulfide is then separated from the solvent in a disulfide separator by coalescing, gravity settling, and decanting. The separated solvent is used again by being recycled to the extractor.

Process Flow (Refer to Figure 1)

Coker LPG enters an absorber where the majority of hydrogen sulfide (H_2S) is absorbed by counter-flowing amine. The LPG then flows through a pre-wash column where caustic (NaOH) is used to remove any remaining H_2S present. The LPG is then sent to a liquid-liquid extractor, where caustic that contains a cobalt based catalyst is used to extract mercaptan from the LPG. Treated LPG goes overhead, while mercaptan-rich caustic solvent exits out the bottom.

The Merox unit also treats coker gasoline similarly. Coker gasoline is first treated with caustic in a pre-wash column to remove any dissolved H_2S. The gasoline then flows through an extractor, where catalyst rich caustic is used to extract mercaptan from the gasoline. The gasoline is then injected with air and a small amount of low concentration caustic just prior to the MINALK reactor. The reactor is filled with catalyst-impregnated activated carbon that allows a large surface area where mercaptans, caustic, and oxygen may come in contact to complete the sweetening reaction. The rich caustic from the

coker gasoline extractor merges with rich caustic from the LPG extractor for regeneration.

The merged mercaptan-rich caustic is heated in an exchanger by 65 psig steam. Air is then injected into the stream along with a small amount of wash naphtha. The mercaptan reacts with oxygen in the air and forms disulfide in the oxidizer. The disulfide oil, wash naphtha, and spent air flow to the disulfide separator where separation occurs. The spent air vents overhead to the mid-distillate hydrotreater (MDHT) fractionator reboiler, and the disulfide/wash naphtha and caustic solvent separate in the separator. The regenerated caustic is recycled back to the extractors, and the disulfide oil and naphtha are sent to the MDHT for hydrotreating.

No Crossover or Entry Points for Sour Gas

The Merox Disulfide Separator Spent Air Vent does not contain any crossover or other entry points for sour gas to be introduced into the vent gas. The spent air vent does combine with the overhead gas from the water balance column downstream, but the water balance column composition only contains treated fuel gas and water. The treated fuel gas is from the mixed fuel gas drum, which is monitored according to NSPS Part 60, Subpart J. Refer to attached P&ID's.

Low Sulfur Conditions and Requirements

In order to reduce acid consumption in the alkylation unit, sulfur compounds are removed from the coker LPG. Sulfur compounds are also removed from coker gasoline in order to meet gasoline product specifications.

The Merox Disulfide Separator Spent Air Vent contains no H_2S and very low amounts of other sulfur compounds in the gas stream at all times. H_2S is indicated by monitoring caustic strength in the pre-wash columns and the circulating regenerated caustic. Therefore, the caustic is monitored and changed out when the caustic in the pre-wash columns are over 50% spent. The regenerated/circulating caustic is changed out when the caustic is over 20% spent.

Monitoring Results Description/Evaluation

Two weeks of daily sampling was obtained on the Merox Disulfide Separator Spent Air Vent, LPG pre-wash caustic, gasoline pre-wash caustic, and regenerated/recirculating caustic. Detector tubes were used in order to measure the concentration of H_2S in the spent air vent, and results show that H_2S was not present in any of the14 samples. In conjunction with the daily detector tube readings, routine lab tests were conducted on the three caustic samples to measure the percentage the caustic was spent. Refer to Table 1 for a summary of the results. These results indicate that Merox Disulfide Separator Spent

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Air Vent H_2S concentration is well within the allowable limits for an alternate monitoring plan.

Monitoring Proposal

1. CITGO Corpus Christi West Refinery will monitor the H_2S content of the Merox Disulfide Separator Spent Air Vent on a once/day frequency with detector tubes of an appropriate range. .

2. Though not expected, if at any time the H_2S average detector tube result plus 3 standard deviations for the seven most recent samples is greater than 81 ppm, CITGO shall notify the agency of those results before the end of the next business day following the last sample day. Sampling will continue on a once/day basis until the agency approves a revised sampling schedule or makes a determination to withdraw approval of the gas stream/system from the AMP.

Records of the H_2S detector tube results will be maintained for a period of two (2) years.

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Table 1
Spent Air Vent & Spent Caustic Sampling Results

Sample	Date	H_2S (ppm)	LPG Pre-wash Spent Caustic %	Gasoline Pre-wash Spent Caustic %	Regen/Recirculating Spent Caustic %
1	May 23, 2005	0	25	34.5	18.8
2	May 24, 2005	0	25.3	41.8	19.9
3	May 25, 2005	0	22.5	45.3	19.2
4	May 26, 2005	0	24.3	37	18.7
5	May 27, 2005	0	23.1	33.9	24.4
6	May 28, 2005	0	24.8	36.1	20.5
7	May 29, 2005	0	25.4	43.5	20.9
8	May 30, 2005	0	25.5	44.1	20.5
9	May 31, 2005	0	26.2	41.6	21.7
10	June 1, 2005	0	25	42.2	19.2
11	June 2, 2005	0	24.4	42.4	21.4
12	June 3, 2005	0	25.6	40.5	19
13	June 4, 2005	0	25.3	49	15.5
14	June 5, 2005	0	26.4	45.2	16.9

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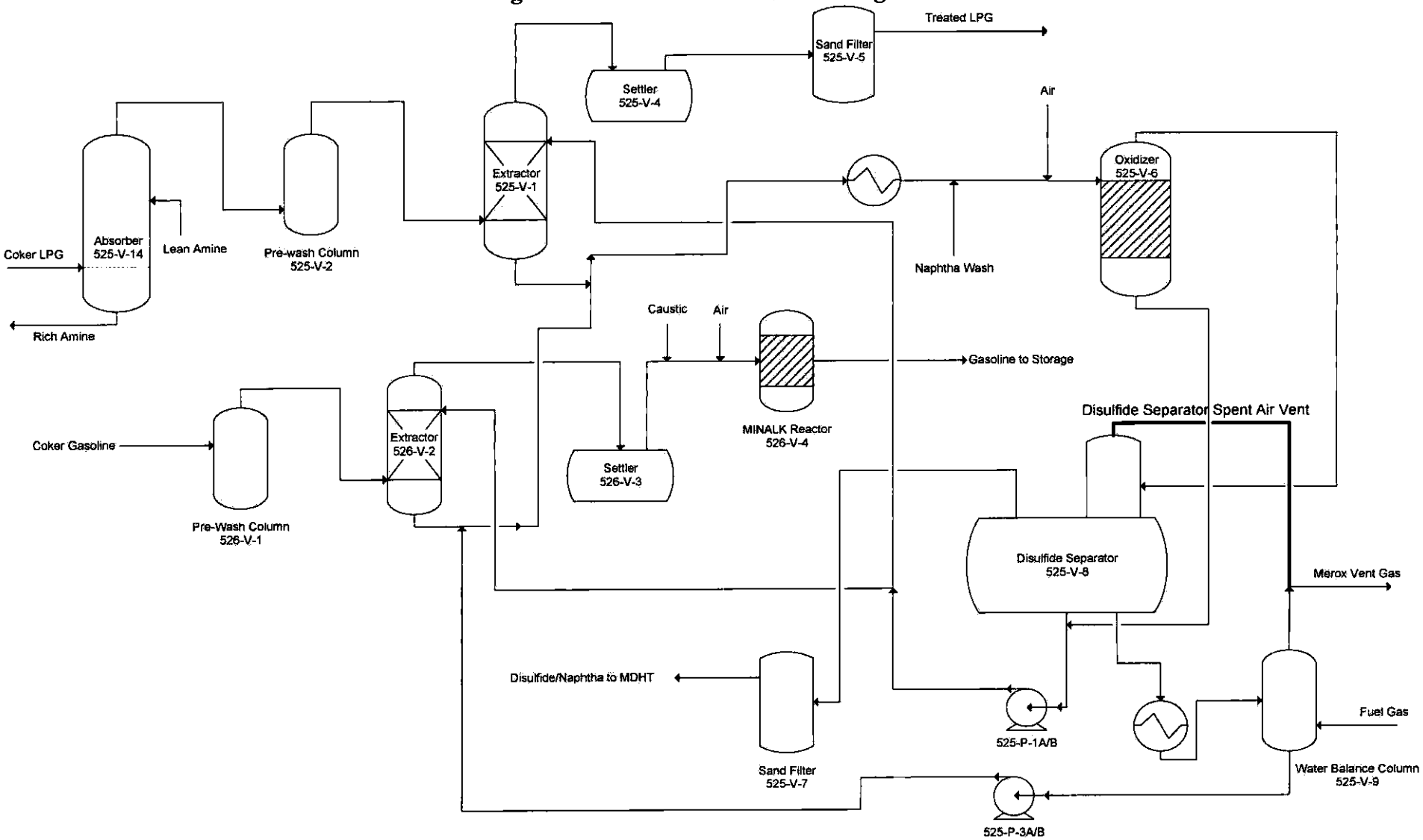
Figure 1 - West Plant Merox Flow Diagram