CITGO Petroleum Corporation

P.O. Box 4689
Houston, TX 77210-4689

CERTIFIED MAIL RETURN RECEIPT REQUESTED
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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 6

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

ALTERNATIVE MONITORING PLAN
CITGO Petroleum Corporation
Corpus Christi East Refinery
Hydrar Degassing Drum Off Gas

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 Hydrar Degassing Drum Off Gas.

Process Description

The Hydrar process hydrogenates benzene to produce high purity cyclohexane. The process employs a platinum catalyst which requires a very low level of contaminates such as H_2S and CO to prevent poisoning. Consequently, hydrogen to and within the unit is processed by absorption, caustic scrubbing, and water washing to preserve catalyst integrity. Benzene charged to the unit must be very pure since the reaction hydrogenates aromatics to extinction while leaving saturated compounds unreacted (potential product impurities). The Hydrar Unit is equipped with a four vessel reactor system along with heat recovery/removal equipment to remove the heat generated by the exothermic reaction. Reaction environment runs approximately 475 psig with temperatures of 350 to 675 degrees Fahrenheit. The Unit is equipped with both hydrogen makeup and recycle compressors to accommodate hydrogen requirements. Final product purification is made in a fractionator by stripping light boiling materials from the Cyclohexane product.

Process Flow (Refer to Figure 1)

Makeup hydrogen to the Hydrar is compressed to system pressure and contacted with lean oil in a two stage countercurrent absorber which functions to remove any heavier components such as propane and also some H_2S. Lean oils utilized are a C9+ aromatic mix in the first stage followed by benzene lean oil in the second stage. Lean hydrogen exiting the absorber is charged along with a portion of the recycle hydrogen to a caustic scrubber for removal of remaining acidic compounds including H_2S. Lean gas from the scrubber is water washed to remove trace amounts of caustic carried over from the scrubber. Rich oil from the absorber is stripped of any H_2S and heavier components in a reboiled stripper. Stripped gases are utilized along with natural gas to fire both the Stripper and Stabilizer Reboiler heaters. Stripped light ends which are condensable (primarily benzene boiling compounds) are purged from the Hydrar to another process for benzene recovery/purification. Purified hydrogen from the water wash column is combined with additional recycle hydrogen, a portion of the benzene charge, and a cyclohexane diluent. This combined stream is then preheated to ~380 deg by exchanging

heat with effluent from the last reactor before the combined stream is charged to the No. 1 Reactor. The exotherm resulting from hydrogenation of the reactant benzene across the platinum catalyst in the first reactor is about 300 degrees. Cyclohexane recycle in the feed is utilized as a heat sink to help control the temperature rise. Effluent from No. 1 Reactor receives some additional feed benzene and exchanges heat with condensate in a 250 psig steam generator. This reduces the effluent temperature down to ~375 degrees before charging to the second reactor. The exotherm across the second reactor is ~300 degrees with both benzene addition to the effluent and steam generation utilized to remove the exotherm. A temperature of ~400 degrees is attained for charging to the No. 3 Reactor. The hydrogenation reaction is basically completed across this reactor with the exotherm causing a 150 degree temperature rise. Effluent from the third reactor is cooled in an air cooled exchanger to ~455 degrees before being charged to the last reactor, No. 4. The purpose of the last reactor is to bring any remaining benzene (minute amount) to equilibrium with the cyclohexane product. The temperature rise across the No. 4 Reactor is typically 1 to 2 degrees. Reactor effluent is used to preheat fresh charge to the first reactor before being cooled by both an air cooled exchanger and a water cooled exchanger. The effluent is then charged to a vapor-liquid separator. The purpose of the separator is to allow separation of the liquid from the excess hydrogen so that the hydrogen can be purified/recycled back to the process while the liquid can be further processed by stabilization. Hydrogen reagent purity is maintained by both a required makeup stream to replace consumed hydrogen and a vent of hydrogen from the separator to fuel gas to prevent the buildup of light inert components such as methane. Liquid from the Separator is charged to the Hydrar Stabilizer for removal of any soluble light ends from the cyclohexane product. The Stabilizer overhead product is a noncondensible Off Gas which is routed to the Refinery Fuel Gas System downstream of any treatment facilities. The bottoms product from the Stabilizer is high purity cyclohexane product. Water from the Separator, Stabilizer OH Receiver, and the water wash flow under pressure to a Water Degassing Drum. The purpose of this drum is to allow removal of any hydrocarbon gases from the waste water before the water is put to the hydrocarbon sewer. This is accomplished by a reduction in pressure which allows the light combustible gases to come out of solution. Gases from the degassing drum are combusted in a burner of the gas fired Stripper Reboiler.

<u>No Crossover or Entry Points for Sour Gas</u>

The Hydrar Degassing Drum Off Gas does not contain any crossover or other entry points for sour gas to be introduced into the gas within the Hydrar Unit battery limits. The Degassing Drum Off Gas is consumed in the Hydrar Stripper Reboiler Heater by injection next to the heater's single burner. Refer to the attached P&ID.

ALTERNATIVE MONITORING PLAN
CITGO Petroleum Corporation
Corpus Christi East Refinery
Hydrar Degassing Drum Off Gas

Low Sulfur Conditions and Requirements

Hydrogen gases consumed in the Hydrar process are required to be nearly free of catalyst poisons. These poisons include both CO and sulfur compounds. Any sulfur bearing compounds that are not removed by feed treatment are converted to H_2S across the Hydrar catalyst and result in a rapid but temporary poisoning which requires removal of the source to rejuvenate the catalyst. Typically, sulfur poisoning results from weak or spent caustic solution and is rapidly corrected by changing out the caustic (<1 hr period required). CO is a temporary poison for which we have no guard treatment. CO poisoning, like sulfur poisoning rapidly deactivates the catalyst, but requires hydrogen stripping (12 to 24 hr stripping period) for catalyst rejuvenation. The sulfur content of the Hydrar Degassing Drum Off Gas is primarily a function of the amount of sulfur left in the caustic scrubbed hydrogen charged to the reactor system. Any appreciable sulfur content rapidly deactivates the catalyst and is observed by a loss in reaction as measured by the temperature rise encountered across the first three reactors. It is emphasized that H_2S is very undesirable in the Hydrar Unit and therefore, aggressive measures are taken to keep sulfur out of the unit.

Monitoring Results Description/Evaluation

CITGO Corpus Christi East Refinery monitored the H_2S (ppm) content of the Hydrar Degassing Drum Off Gas and the reactor temperature rise across each of the first three Hydrar reactors. The data collection period was from 06/07/05 to 06/24/05 and is summarized below. The Degassing Drum Off Gas H_2S monitoring was conducted using GASTEC Detector Tubes (No. 4LT, Hydrogen Sulfide) and all samples were obtained as grab samples.

The average H_2S content in the Degassing Drum Off Gas for the data collection time period was 0 ppm. These results show that the average plus three standard deviations is less than 81ppm and therefore qualifies for an AMP.

Date	Degassing Drum Off Gas H_2S, ppm	Rxr No. 1 Temperature Rise, °F	Rxr No. 2 Temperature Rise, °F	Rxr No. 3 Temperature Rise, °F
6/7/05	0	247	260	158
6/8/05	0	258	260	148
6/9/05	0	258	259	146
6/10/05	Unit Down	---	---	---
6/11/05	0	293	282	166
6/12/05	0	298	286	178
6/13/05	0	301	288	183
6/14/05	0	294	282	180
6/15/05	0	290	294	183

6/16/05	0	276	278	165
6/17/05	0	297	295	151
6/18/05	0	296	285	148
6/19/05	Unit Down	---	---	---
6/20/05	0	284	302	166
6/21/05	Unit Down	---	---	---
6/22/05	0	275	290	148
6/23/05	0	255	241	159
6/24/05	0	261	247	164
Average	0	279	277	163
Average + 3*Standard Deviation	0			

Monitoring Proposal

1. CITGO Corpus Christi East Refinery will monitor the H_2S content of the Hydrar Degassing Drum Off Gas on a daily basis with detector tubes of an appropriate range.

2. Though not expected, if at any time the Hydrar Degassing Drum Off Gas stream average detector tube result plus 3 standard deviations for the seven most recent samples is greater than 81 ppm H_2S, 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 daily 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 readings will be maintained for a period of two (2) years.

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Corpus Christi East Refinery
Hydrar Degassing Drum Off Gas
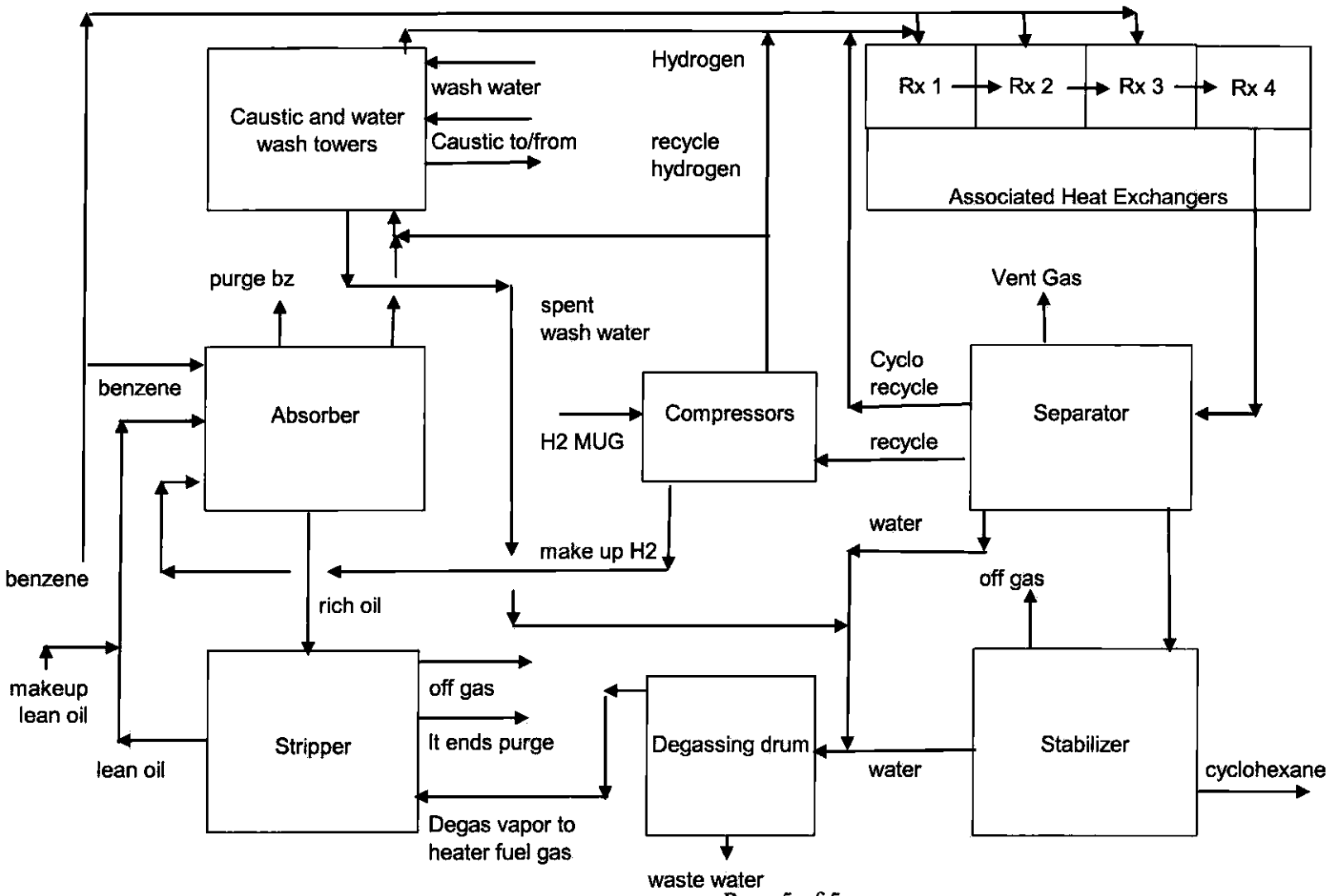
Figure I
Hydrar Unit - Cyclohexane