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Project Summary

Environmental Assessment: Source Test and Evaluation Report - Rectisol Acid Gas Removal

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In June 1982, a Rectisol acid gas removal unit at a Texaco refinery at Wilmington, CA, was tested. The primary goal of the test was to provide a data base for evaluation of Rectisol performance in entrained coal gasification applications. This Rectisol unit processes gases from the partial oxidation (POX) of oil by the Texaco Synthesis Gas Generation Process. A secondary goal of the test was to validate sampling/analytical methods for constituents such as HCN and NH_3 which were expected to be present at very low levels in the Wilmington gas samples.

During the tests, the Rectisol unit handled a feed gas containing about 0.2% H_2S, a few ppmv COS, and >30% CO_2 and generated a product gas containing <0.1 ppmv total sulfur and usually <200 ppmv CO_2. CO_2-rich offgases from the Rectisol unit contained <10 ppmv total sulfur. With regard to minor constituents, the CO_2-rich offgases contained about 400-900 ppmv of methanol (derived from the process solvent), <1 ppmv of hydrocarbons other than methane and ethane, and <1 ppmv each of HCN or NH_3. Due to their absence in the vacuum residual oil feed to the POX unit, no detectable amounts of volatile heavy elements (e.g., Hg, As, Se) were found in Rectisol gases.

Data from the test are evaluated in the report from the standpoint of differences in feed gas composition which would be encountered in coal vs. oil applications and/or where only part of the gas is shifted.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, (IERL—RTP), is responsible for the Agency's environmental assessment activities and for control technology development research relating to substitute fuels from coal. Part of the assessment activities involve generating background data on the characteristics of waste streams generated by coal gasification and associated technologies and evaluation of the performance of control technologies for such waste streams. IERL-RTP assessment programs involve three general areas: (1) collecting and evaluating existing process and environmental data, (2) acquiring supplementary data by sampling and analyzing selected process/waste streams at domestic or foreign facilities, and (3) environmental assessment and necessary process engineering support studies.

The proposed widespread use of Rectisol in U.S. coal gasification facilities and the importance of removed acid gas as potential atmospheric emissions from such facilities prompted EPA to investigate a test program at an existing unit. Currently, the only Rectisol units

operating in coal gasification applications are outside the U.S. However, two units exist in the U.S. which process gases from the Texaco synthesis gas generation process (partial oxidation, or POX) of heavy oil. After exploring both overseas and domestic units, the Rectisol unit at Texaco's Wilmington refinery was selected for testing. Although this unit processes shifted gas from oil (rather than coal gasification), the design is similar to at least one planned for a U. S. coal gasification facility; hence, the data for this unit can be useful for assessing coal-based units.

The goals of the Wilmington Rectisol test were threefold: (1) to evaluate the performance of the specific unit from an environmental standpoint by characterizing both process and waste streams for a variety of species of environmental interest; (2) to establish the applicability of key sampling and analytical techniques as applied to the matrices of Rectisol streams; and (3) to provide test data as a partial basis for estimating the environmental effects of Rectisol units in coal gasification applications.

The Facility

The Rectisol unit at the Texaco refinery in Wilmington, CA, designed and built by Linde A. G. of Munich, Federal Republic of Germany, is part of a hydrogen production train referred to as the hydrogen generation unit (HGU). The HGU, based on gasification of vacuum residual oil to generate synthesis gas, provides part of the hydrogen used in the refinery. The Texaco POX gasifier generates a hot crude gas containing about 43% H_2, 50% CO, 5% CO_2, 0.5% H_2S plus COS, and entrained soot consisting primarily of ungasified carbon. The soot is removed by water washing in a carbon scrubber which also cools the gas and recovers heat. Dust-free cooled gas is fed to a sour (sulfur tolerant) shift conversion unit. Shifted gas is cooled in stages with steam production and condensate recovery. Cooled condensates are either recycled to the shift reactor or to the carbon scrubber or discharged to wastewater treatment. Cooled shifted gas is fed to the Rectisol unit for removal of H_2S and CO_2. For trace CO removal, a copper liquor wash step follows the Rectisol unit.

The Wilmington Rectisol unit utilizes high-pressure acid gas removal with a design capacity of 4000 kmoles/hr of throughput. The process utilizes cold methanol as a solvent to remove acid gases by physical absorption under pressure, with solvent regeneration by a combination of pressure reduction, stripping with inert gas (N_2), and heating. The wash process was designed to remove H_2S + COS to <1 ppm and CO_2 to 10 ppm and to supply an H_2S stream with at least 10% H_2S and a CO_2 tailgas with 5 ppm maximum H_2S.

The Wilmington Rectisol unit is designed for completely selective removal of H_2S + COS and of CO_2. While results from this unit are relevant to current designs from an environmental point of view, the economics of the Wilmington unit are no longer typical. Modern plants have lower specific energy requirements and the tendency is towards higher operating pressures, higher concentrations of H_2S + COS in the sulfur-rich off-gas, and larger capacities.

Figure 1 is a simplified flow diagram of the process indicating streams of interest for environmental testing. The feed gas (Stream 1) is cooled against cold separation products. After separation of the condensate, H_2S and COS are removed from the gas in the bottom section of the wash tower with CO_2-loaded methanol. The sulfur-free gas is washed in the top section of the tower to remove CO_2. The gas leaving the top of the wash tower (Stream 2) is delivered to the copper liquor plant where CO is removed to ppm levels.

The methanol leaving the bottom of the H_2S absorption section of the tower contains all of the H_2S and also CO_2 and H_2 in amounts corresponding to their partial pressures and solubilities. Hydrogen recovery is increased by flashing the loaded methanol to an intermediate pressure and recycling the flash gas back to the feed gas via a small recycle compressor.

The flashed methanol still contains too much CO_2 to achieve the necessary H_2S concentration and must be further flashed and stripped with inert gas in the bottom section of the H_2S enrichment column. The stripping gas (Stream 6) is nitrogen obtained from the oxygen plant which supplies oxygen to the POX units.

The CO_2-rich offgas (Stream 3b) from the top of the H_2S-enrichment column is discharged to the atmosphere. From the loaded methanol from the bottom of the H_2S-enrichment column, the absorbed H_2S and CO_2 are stripped in the warm stripper column with reboiled methanol vapor. The stripped gases (Stream 4) are sent to the Claus plant for sulfur recovery.

The main stream of CO_2-loaded methanol leaving the CO_2-absorption section of the wash column, after H_2-recovery by flashing, is let down and stripped with nitrogen in the cold stripper to remove much of the dissolved CO_2. The column overhead (Stream 3a) is discharged to the atmosphere. The cold, partly stripped methanol is returned to an intermediate tray of the CO_2 absorber.

The methanol/water mixture condensed from the feed gas is separated in a still which produces pure methanol overhead and wastewater (Stream 5) in the sump. This keeps the water content of the circulating methanol at a low level.

Test Description

Gas sampling ports are located in pressurized gas recycle loops through which a slipstream of the process gas may be passed. The recycle configurations and valving are such that all samples could be taken at ground level. Samples of the still bottoms were also available from a ground level tap. Sample loop configurations did not permit the use of probes for flow rate measurements, and all flow rate, temperature, and pressure data were provided by Texaco from existing in-line equipment. The sample loops were modified and the in-line flow measurement equipment was calibrated by Texaco during a scheduled plant downtime for maintenance.

In most cases, sampling lines were several meters long. This was of some concern relative to obtaining representative samples, particularly of the Rectisol feed gas which contains both moisture and water-soluble species (e.g., NH_3). The possible biases due to the loss of water-soluble species from the feed gas and of methanol contamination are addressed.

The test period was from June 6 through 17, 1982. The shift and Rectisol units had been operating continuously for over a week so that steady operation existed at the start of the test. Six streams were sampled during the tests: Stream 1 - Rectisol feed gas, Stream 2 - product gas, Stream 3a - cold stripper offgas, Stream 3b - H_2S-enrichment column offgas, Stream 4 - H_2S-rich offgas, and Stream 5 - methanol still bottoms.

The gaseous process/waste stream samples acquired during the test period and analyses performed are identified in the report. Where possible, standard sampling/analytical techniques were employed and details of the procedures are given. The first 3 days were devoted to equipment setup, preliminary sampling and characterization to obtain order of magnitude stream compositions, and evaluation of the adequacy of propose

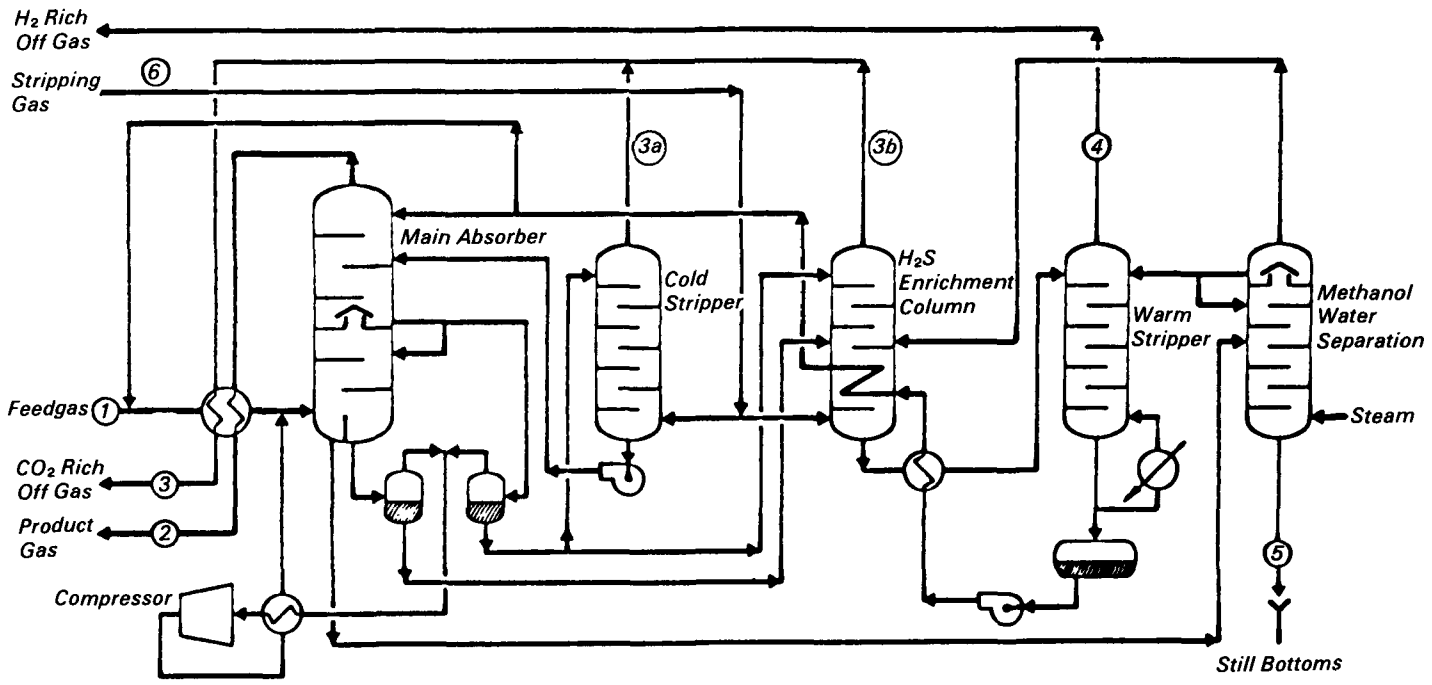

Figure 1. Simplified flow diagram of the Wilmington Rectisol unit.

sampling and analytical methodologies. Material balance data were obtained during the last 5 days of testing.

Test Data Summary and Conclusions

The Wilmington program resulted in the collection of both process and environmental data. Results are briefly and partially summarized here.

- With regard to the characterization of process performance, the most significant parameter to vary in the Rectisol feed was the H_2S concentration, which decreased during the tests. As a result, roughly proportional reductions of H_2S concentration were observed in the H_2S-rich offgas.

- Measured and estimated flow rate data for the Rectisol process/waste streams were substantiated by material/species balance estimates.

- The principal potential pollutant species in the CO_2-rich offgases were H_2S, COS, CO, and methanol. Other inorganic species detected were NH_3, HCN, and Cl. Some portion of both NH_3 and Cl are believed to be attributable to entrained process methanol. Other than methanol, nonmethane organic compounds detected were individually present at concentrations <1.6 ppmv.

- H_2 was present at levels of >1% by volume in the CO_2-rich offgases for the latter part of the test period. This level is considerably higher than that for the plant design and may be related to off-specification operation of the recycle compressor.

- The principal constituents of environmental interest detected in the H_2S-rich offgas were H_2S, COS, and methanol. Organics present in the H_2S-rich offgas consisted almost entirely of methanol; however, ppmv concentrations of C_2 through C_6 hydrocarbons, benzene, and toluene were also detected.

Adequacy of Sampling and Analytical Techniques

The tests provided the opportunity to validate certain methods for the levels of target species and matrices involved and to identify a number of limitations to methods which have been used in other types of tests. For sources involving fuel combustion, incineration, or sulfur recovery in refineries and coke plants, the gas matrices generally contain only a few percent of CO_2. In coal and oil gasification, most waste gases contain much higher levels of CO_2. Also, Rectisol gas streams constitute a much more reducing environment than do combustion gases so that collecting media designed for combustion sources are not necessarily applicable to Rectisol testing. The following are some of the findings related to test methods. The findings should be generally relevant to testing of acid gas removal and sulfur control units in coal gasification facilities.

- H_2S and COS were readily quantifiable by gas chromatography (GC), as used at Wilmington, in the range of 1 ppmv to about 1%. The relatively poor results obtained with thermal conductivity GC for high level H_2S samples (H_2S-rich offgas or Claus feed gas) are thought to relate to column saturation problems indicated by tailing peaks.

- H_2S can be readily quantified at percent levels using a wet chemical procedure adapted from EPA methods 7 and 11. The method proved to be quite reproducible at Wilmington when compared to thermal conductivity GC data for H_2S at percent levels. Good H_2S material closure around the Rectisol unit was obtained when these grab sample

data were used, suggesting that the method has no obvious bias.

- High levels of CO_2 in gases present limitations with the use of alkaline impinger solutions for collection of HCN, since CO_2 tends to neutralize the solutions with consequent loss of HCN collection efficiency. An alternative collection technique using H_2SO_4 was verified prior to the Wilmington test and utilized in the field.

- When levels of H_2S exceed a few percent in the sample gas, the H_2SO_4 technique cannot be used unless high levels of HCN are also encountered. With high HCN levels, only small sample volumes need be taken for sufficient HCN collection for subsequent analysis. In such cases the sulfur interference can be tolerated.

- Ammonia could be collected in acid impinger solutions from the high CO_2 gases at Wilmington. Blank levels in dilute HCl tend to be much lower than in dilute H_2SO_4, and the detection limit with HCl is about 0.1 ppmv.

- Na_2CO_3 solutions were used in impingers to collect HCOOH, HCl, and HF from gas streams. The efficiency of collection of these species is not known since their concentrations were very low.

- The collection efficiency of the heavy element oxidative impinger train for high CO_2 streams at Wilmington is believed to be similar to that observed in sampling of combustion gases. In the case of the H_2S-rich offgas, the high H_2S levels quickly exhaust the H_2O_2 in the first impinger. Thus, an alternative technique is required for collection of volatile heavy elements in streams containing high levels of reduced sulfur species.

- XAD-2 resin trap samples were taken of the Rectisol feed gas and CO_2 offgases. Although the C_6 through C_8 aromatics were present near or below detection limits, the XAD data and on-site GC data are at least reasonably consistent for C_7 and C_8 aromatics.

Wilmington Rectisol Differences Related to Coal Gasification Applications

Several basic features of the Wilmington Rectisol unit would be found in essentially all Rectisol units, regardless of the type of service. However, feed gases which differ greatly in composition from those at Wilmington will involve somewhat different designs. Also, the requirements for product gas purity and offgas pollutant loadings will impact Rectisol design. Since the results of the subject test cannot be utilized for other units without a consideration of design differences, some of the factors which influence Rectisol design and how they relate to test results are discussed in the report. In the discussion of other Rectisol applications, the emphasis is on how the data from or features of the Wilmington Rectisol relate to these applications.

The characteristics of Rectisol feed gases are determined by (1) the specific gasification process, (2) the gasifier feed characteristics, (3) the position of shift relative to sulfur removal, (4) the end use of the gas which influences the extent of shift required, and (5) the final washing or moisture removal step(s) preceding Rectisol. The report discusses the impacts of each of these factors on Rectisol feed gas characteristics. Although the major focus is on entrained coal gasification applications, some comments regarding other applications are also included. Two examples of Rectisol designs are examined to illustrate the influence of feed gas characteristics, product specifications, and environmental requirements on design.

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The complete report, entitled "Environmental Assessment: Source Test and Evaluation Report—Rectisol Acid Gas Removal," (Order No. PB 84-153 238; Cost: $16.00, subject to change) will be available only from:
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