

EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.8: CARBON DIOXIDE STRIPPING FROM METHYLDIETHANOLAMINE AT MEDIUM PRESSURE

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Contributors: Jimmy O. Y. Ong
Michael K. Porter
Lalit Shah
Kalapi Sheth
Danny A. Woodall
Earl Berry
Charles H. Schrader
John Anderson

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Texaco Energy Systems Inc.
3901 Briarpark Drive
Houston, Texas 77042

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ABSTRACT

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are TESI (a subsidiary of ChevronTexaco), GE, Praxair, and KBR in addition to the DOE. TESI is providing gasification technology and Fischer-Tropsch technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology and KBR is providing engineering.

The EECP converts petroleum coke into synthesis gas in the Gasification section. The synthesis gas is cleaned in Acid Gas Removal (AGR) unit, Sulfur Recovery Unit (SRU), and Tail Gas Treating Unit (TGTU) where acidic gas from synthesis gas is removed and converted into elemental sulfur. The EECP utilizes proven AGR, SRU and TGTU technologies. However, a concept was proposed for stripping carbon dioxide (CO₂) from methyldiethanolamine (MDEA) in the AGR section using available Air Separation Unit (ASU) nitrogen at pressures higher than conventionally practiced. The successful implementation of this concept would result in lower overall capital costs for the EECP. Phase I identified this nitrogen stripping operation as a technical risk for mitigation. An RD&T program was identified to validate design assumptions and performance projections used for the Phase I conceptual design. The RD&T program was executed in Phase II. This topical report summarizes the results of this task of the RD&T program.

To aid in the commercial design, equilibrium data for various loadings of CO₂/hydrogen sulfide (H₂S) in a 45 weight percent (wt %) MDEA solution with nitrogen at 2,413 kilopascals (kPa) (350 pounds per square inch absolute (psia)) and rich MDEA temperatures ranging from 355 K (180 °F) to 378 K (220 °F) were experimentally obtained. Experiments were conducted at DB Robinson & Associates Ltd. (DBR). The equilibrium data were compared to data generated by a commercially available computer simulation package for similar acid gas loadings in a 45 wt% MDEA solution. The results indicated that the equilibrium data generated by computer simulation were in good agreement with the DBR experimental data over the range considered for the EECP design point. Therefore computer simulation could be used to design the commercial unit with reasonable confidence. EECP Phase II RD&T program confirmed the design assumptions and performance projections used for the Phase I conceptual design. However, in Phase III the final design should include the consideration of additional design margin to handle the possibility of increased rich MDEA acid gas loads in specific areas that may be exposed to mass loads above what has been simulated in Phase I.

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Note: Unless specified otherwise, all quarters/years are calendar quarters/years.

II. Executive Summary

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

The EECP converts petroleum coke into synthesis gas in the Gasification section. The synthesis gas is cleaned in the Acid Gas Removal (AGR) unit where acidic gases (CO_2 and H_2S) are removed. The use of amines for acid gas removal of gasifier syngas is well practiced in the industry. The standard process configuration for these applications as well as hundreds of refinery amine units has been a high-pressure absorber with a low-pressure steam reboiled stripper. This simple configuration contributes to the low cost advantage often associated with amine AGRs.

One problem encountered with the standard process configuration has been in syngas applications with high CO_2 content relative to H_2S . Often, removing most of the H_2S causes more CO_2 to be absorbed than desired. The H_2S concentration of the stripper acid gas fed to a downstream Sulfur Recovery Unit (SRU) becomes significantly lower than desired. Additionally, there are problems such as SRU flame stability, incomplete combustion and destruction of trace contaminants in the SRU, and excessive hydraulic pressure drop problems from extra CO_2 gas acting as an inert through the SRU.

The use of available nitrogen from the ASU to strip extra CO_2 from the rich amine in a separate unit operation prior to charging the stripper offers the following advantages:

- H_2S concentration of the AGR acid gas may be increased significantly resulting in improved SRU operations and lower SRU costs.
- Stripped gas containing CO_2 and N_2 is used to generate additional power in the CT. Thus, the extra CO_2 is a benefit and not a liability.
- By adjusting stripping operations, there is an additional control mechanism to adjust the split and routing of CO_2 in the syngas to either the CT or the SRU.

The use of a stripping gas to regenerate the amine is proven industrially at low pressures; indeed, the flashed water vapor in the low-pressure steam reboiled stripper is a prime example. However, this stripping operation at slightly above CT operating pressure has not been commercially demonstrated.

This area represents a low level overall and technical risk to the proposed EECP. Since the AGR block represents approximately 15% of the EECP capital cost, N_2 stripping of CO_2 from MDEA at medium pressures represents a medium level economic risk.

An RD&T task was identified to validate design assumptions and performance projections used for the Phase I conceptual design of stripping CO₂ from MDEA with N₂. This RD&T task was executed in Phase II and results are reported herein.

Four possible options were considered for developing data necessary to design a commercial CO₂ stripper. The first three options (grassroots pilot plant at an operating gasification unit or pilot plants at Southwest Research Institute (SwRI) or Gas Technologies Institute (GTI)) involved the design and operation of a pilot plant to obtain fractionation and packing efficiency data. The fourth option involved development of equilibrium data at various hydrogen sulfide (H₂S) and CO₂ loadings in MDEA using N₂ to maintain system pressure. The equilibrium data option presented the most value since it would validate the commercially available computer simulator used for EECF Phase I conceptual design.

DB Robinson & Associates Ltd. (DBR) was contracted to develop equilibrium data for various acid gas loadings in a 45-weight percent (wt%) MDEA solution under a nitrogen pressure of 2,413 kilopascals (kPa) (350 pounds per square inch absolute (psia)). To determine the effect of the rich MDEA feed temperature, the temperature of the rich MDEA ranged from 355 K (180 °F) to 378 K (220 °F).

A comparison of the DBR data to a commercially available computer simulation package showed that the simulator over predicted the partial pressures of the acid gas at high acid gas loading of the rich MDEA and under predicted the partial pressures at low acid gas loading of the rich MDEA. This trend was observed separately for both H₂S and CO₂. The design points for the proposed EECF concept of 0.17 mole H₂S / mole pure MDEA and 0.43 mole CO₂ / mole pure MDEA are within a region where the simulation and DBR data are in close agreement. The proposed feed temperature of 367 K (200 °F) is appropriate for liberating large amounts of CO₂ from the rich MDEA while retaining the H₂S.

In summary, the difference between the DBR equilibrium data and the computer simulation estimate is judged acceptable, and the AGR design developed in Phase I is considered reasonable. In Phase III appropriate engineering judgment will be applied to account for acid gas distribution between the vapor and liquid phases according to the differences observed between the experimental work and what has been simulated during concept development .

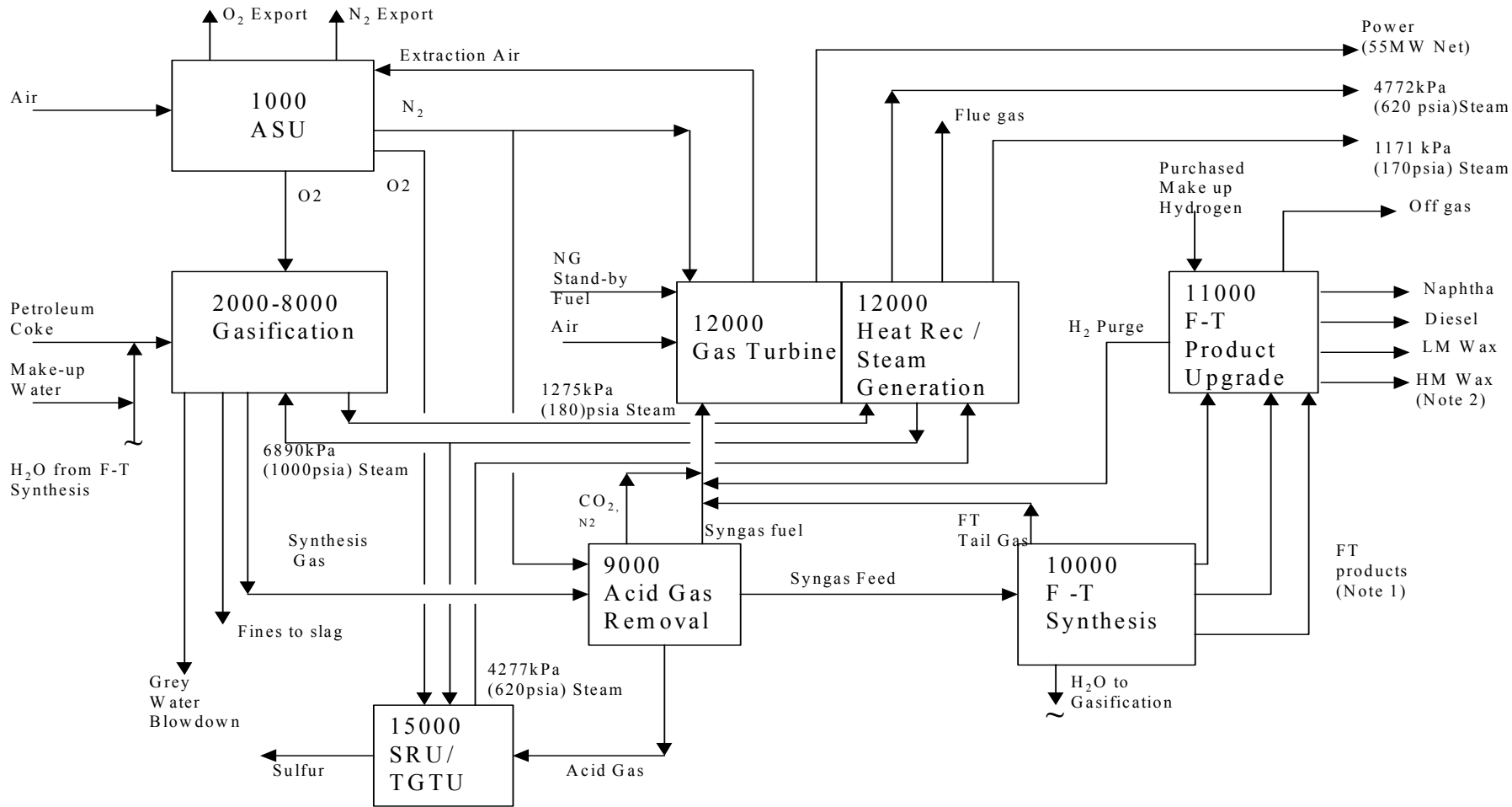
III. Background

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and will consume approximately 1,235 short tons per day of petroleum coke. The EECP Concept is illustrated in Schematic 1.

Petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen, carbon monoxide, water vapor, and carbon dioxide with small amounts of hydrogen sulfide, methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. One portion of the stream is treated in the AGR to remove CO₂ and H₂S and then forwarded to the F-T Synthesis Unit. The other portion is treated in the AGR to remove the bulk of H₂S with minimal CO₂ removal and then forwarded as fuel to the General Electric frame 6FA gas turbine. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO₂. The resulting CO₂ and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides emissions. The bulk of the nitrogen from the air separation unit is also sent to the gas turbine as a separate stream, where its mass flow also helps increase the power production and reduce nitrogen oxide emissions.

Overall, approximately 75% of the sweetened syngas is sent to the gas turbine as fuel. The remaining 25% is first passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur and then forwarded to the Fischer-Tropsch Synthesis Unit. In the F-T reactor,



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NOTES:

1. Includes Light, Medium and Heavy FT Liquid product streams
2. LM = Low Melt
HM = High Melt

**DOE EARLY ENTRANCE COPRODUCTION PLANT
 PORT ARTHUR REFINERY**

OVERALL BLOCK FLOW DIAGRAM

DRAWN JSA	DATE 10/10/00	DOE AWARD NUMBER: DE-FC-99FT40658	REV.
DESIGNER	DATE	SUBCONTRACTOR PROJECT NO: 9202	0
CHECKED	DATE	TASK NO: 4.1.2	
APPROVED	DATE	DRAWING NO: KBR-P-BFD-0001	

Schematic 1 - EECOP Concept

carbon monoxide and hydrogen react, aided by an iron-based catalyst, to form mainly heavy straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid, and light F-T liquid are sent to the F-T product upgrading unit while F-T water, a reaction byproduct, is returned to the Gasification Unit and injected into the gasifier. The F-T tail gas and AGR off gas are fed to the gas turbine and mixed with syngas. This increases electrical power production by 11%.

In the F-T Product Upgrading Unit (F-TPU), the three F-T liquids are combined and processed as a single feed. In the presence of a hydrotreating catalyst, hydrogen reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracked light ends. The resulting four liquid product streams are naphtha, diesel, low melt wax, and high melt wax that leave the EECP facility via tank truck.

The power block consists of a GE PG6101 (FA) 60 Hz heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas as start-up and backup fuel, and primary fuel as a mixture of syngas from the gasifier, offgas from the AGR Unit, and tail gas from the F-T Synthesis Unit. Nitrogen gas for injection is supplied by the ASU for NO_x abatement, power augmentation, and the fuel purge system.

The Praxair ASU is designed as a single train elevated pressure unit. Its primary duty is to provide oxygen to the gasifier and Sulfur Recovery Unit (SRU), and all of the EECP's requirements for nitrogen and instrument and compressed air. ASU nitrogen product applications within the EECP include its use as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NO_x emissions, and as an inert gas for purging and inerting. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor, hence oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums as they enter the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS off gas, oxygen, and air to a burner. In the thermal reactor, the H₂S, a portion of which has been combusted to sulfur dioxide (SO₂), starts to recombine with the SO₂ to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser where all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H₂S and SO₂ are converted to sulfur. The sulfur is removed in the second pass of the primary sulfur condenser, and the gas goes through a reheat, catalytic reaction, and condensing stage two more times before leaving the SRU as a tail gas. The molten sulfur from all four condensing stages is sent to the sulfur pit, from which sulfur product is transported off site by tank truck.

The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO₂ back to H₂S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along with the condensate from the SRU knockout drums to the SWS. H₂S is removed from the quenched tail gas in an absorber by using lean methyldiethanolamine (MDEA) solvent from the AGR Unit. The tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

The use of amines for acid gas removal of gasifier syngas is relatively widespread. The standard process configuration for these applications as well as hundreds of refinery amine units has been a high-pressure absorber with a low-pressure steam reboiled stripper. This simple configuration contributes to the low cost advantage often associated with amine AGRs.

One problem encountered with the standard process configuration has been in syngas applications with high CO₂ content relative to H₂S. Often, removing most of the H₂S causes more CO₂ to be absorbed than desired. The H₂S concentration of the stripper acid gas fed to a downstream Sulfur Recovery Unit (SRU) is then significantly lower than desired. Additionally, there are problems such as SRU flame stability, incomplete combustion and destruction of trace contaminants in the SRU, and excessive hydraulic pressure drop problems from extra CO₂ gas acting as an inert through the SRU.

The use of available nitrogen from the ASU to strip extra CO₂ from the rich amine in a separate unit operation prior to charging the stripper offers the following advantages:

- H₂S concentration of the AGR acid gas may be increased significantly resulting in improved SRU operations and lower SRU costs.
- Stripped gas containing CO₂ and N₂ is used to generate additional power in the CT.
- By adjusting stripping operations, there is an additional control mechanism to adjust the split and routing of CO₂ in the syngas to either the CT or the SRU.

The use of a stripping gas to regenerate the amine is proven industrially at low pressures; indeed, the flashed water vapor in the low-pressure steam reboiled stripper is a prime example. However, this stripping operation at slightly above CT operating pressure has not been commercially demonstrated. The lack of commercial demonstration represent a low level overall and technical risk to the proposed EECF. Since the AGR block represents approximately 15% of the EECF capital cost, N₂ stripping of CO₂ from MDEA at medium pressures represents a medium level economic risk.

For Phase II, a RD&T task was identified to validate design assumptions and performance projections used for the Phase I conceptual design for N₂ stripping of CO₂ from MDEA.. In Phase II the objective was to develop the data necessary to properly design a commercial stripping column using nitrogen at medium pressure to remove CO₂ from MDEA. Several possible options were considered:

1. Grassroots Pilot Unit Option – This option would include the design and the interface with the engineering contractor to construct a grassroots pilot unit. This option would include the design of all process equipment, design of all control and data acquisition

equipment, and equipment layout for a grassroots pilot plant mounted on a mobile skid. It would also include the integration of the skid mounted pilot unit with an operating commercial facility possibly Tampa Electric Integrated Gasification Combined Cycle (IGCC) or Delaware City Repowering Project (DCRP) IGCC. Operation of the pilot unit at this selected commercial facility would provide information for the commercial design of CO₂ Stripper.

2. Southwest Research Institute Option – Southwest Research Institute (SwRI) proposed using a 152 millimeters (mm) (6 inch (in.)) diameter tower for physical measurements and hiring an outside consultant from Concorde Technologies for computer modeling. SwRI proposed investigating multiple feed zones to the stripper tower, identifying a superior absorbent other than MDEA, and investigating tower pressure drop to determine if foaming would occur in this system.
3. Gas Technologies Institute Option – This option involved renting an existing pilot unit from Gas Technologies Institute (GTI) and modifying the unit to meet the design criteria for a CO₂ Stripper pilot plant operation. These modifications would include design of a stripper of sufficient size to obtain information necessary to determine Height Equivalent to a Theoretical Plate (HETP) and other design criteria of selected packing. The modifications also included installation of the stripper on an existing skid plus installation of new control instrumentation such as mass flow meters, control valves, pressure transmitters, etc. GTI would provide operating personnel onsite for operation of the stripper.
4. DB Robinson & Associates Ltd. (DBR) Option – This option involved DBR collecting equilibrium data to check against an existing commercially available computer simulation model. If required, the new equilibrium data could be incorporated into the computer simulation package.

Option 1 was the highest cost option. Option 1 included a grass-roots pilot plant design, construction, and operation of a pilot plant plus the associated control hardware/software. This option would allow flexibility in the design and give a “no compromises” pilot plant. While no firm price for this option was determined, it was estimated to be \$500,000 to \$750,000.

For option 2, SwRI estimated the cost for their work as \$338,343. The use of Concorde Technologies for computer modeling was thought to be redundant as this system was already modeled in concept development Phase I using commercially available computer simulation software. The proposed use of an outside consultant by SwRI implied there was no “in-house” expertise in gas treatment. The proposal did not provide any details of the stripper equipment with respect to packing heights, sampling points, or HETP calculation methods.

GTI would charge \$10,000 per month for rental of their pilot unit if Option 3 were chosen. GTI’s cost did not include the cost for transportation of the leased pilot plant to the site, or its installation and start-up. GTI would provide onsite personnel to operate the equipment during the testing phase. The GTI pilot unit required major modifications. Literature articles by Fractionation Research Inc. indicated that the desired column diameters should be larger than

305 mm (12 in.) with packing heights at least 1.5 meters (m) (5 feet (ft)) with 3 m (10 ft) preferred. Sampling should be done from multiple points along the vertical axis of the packing for HETP calculation purposes. A column to packing diameter ratio of at least 10 would be needed otherwise wall effects would need to be addressed. GTI's pilot unit consisted of an absorber with a 102 mm (4 in) diameter and 2012 mm (6.6 ft) of packing. The stripper has a 152 mm (6 in) diameter column with no packing. Both columns were rated for 8274 kPa (1200 psia) and are 316 stainless steel (SS). To utilize this unit, modifications would include a new larger diameter absorber with sampling points along the packing height or the installation of sampling points along the existing 102 mm (4 in.) column plus corrections for wall effects. Additionally, control valves, mass flow controllers, and other hardware would have to be evaluated. Due to the required changes mentioned above a cost estimate for this option was not developed.

For option 4, DBR made a proposal for determining the vapor-liquid equilibrium data for CO₂ and/or H₂S in a 45-wt% MDEA solution under nitrogen at 2,413 kPa (350 psia). The equilibrium data would be collected for each of the components separately as well as mixed loadings of both acid gases in the MDEA solution. The data would be collected at 2,414 kPa (350 psia) with MDEA temperatures ranging from 355 K (180 °F) to 378 K (220 °F). DBR's cost for this option was \$28,350. The equilibrium data obtained by DBR would be compared with computer simulation estimates at the same conditions to determine the validity of computer simulation to correctly predict CO₂/H₂S/N₂ equilibrium at 2,414 kPa (350 psia).

Table 1 summarizes these four options. Option 4 (DBR to develop equilibrium data for the CO₂/H₂S/MDEA/N₂ system) and in-house evaluation against computer simulation was selected as the most cost effective approach for this task of the EECF Phase II RD&T program.

Table 1

Summary of Options

Options	Pros	Cons
1. Grass Roots Pilot Unit	No compromises Pilot Unit Commercial "host" unit for rich amine source	Construction required Operation required Total cost estimate – \$ 500 - 750 K
2. Southwest Research Inst	Reputable research organization	No in-house expert Scope of work was redundant with prior work from Phase I Total cost estimate - \$ 340 K
3. Gas Technologies Institute	GTI pilot unit already constructed GTI would provide operating personnel	Major modifications required Unit shipping required Installation plus start-up

		required Rental charge - \$ 10K/month Total cost estimate – Expensive & not developed
4. DB Robinson & Associates	Fundamental data collection Results incorporated into commercial simulation packages Low cost	Packing effects not accounted for Estimated cost - \$28 K

A. Experimental

DBR utilized a static, conventional equilibrium cell equipped with a vapor recirculation pump for the Vapor-Liquid Equilibrium (VLE) work. The equilibrium cell was a Jerguson liquid level gauge (Model 17-T-30), strengthened by two steel bars spaced evenly between the ends of the cell. The cell was mounted in an insulated air bath of dimensions 0.61 x 0.91 x 1.22 m. The bath was equipped with a 3000-watt heater as well as a refrigeration unit. The range of operation of the air bath was 255 to 433 K (0 to 320°F). In order to increase the total cell volume, a 50 cm³ vapor reservoir was added on top of the cell. A magnetic pump was used to recirculate the gas phase and bubble it through the liquid phase. The total volume of the apparatus was about 250 cm³. A heated vapor sampling line joined the reservoir to a Valco sampling valve of the gas chromatograph located outside of the air bath. All sampling lines and tubing were Teflon-lined 316 stainless steel with 3.175 mm outside diameter (OD) and 1.78 mm inside diameter (ID). The temperature of the contents of the cell was measured by a calibrated iron-constantan thermocouple and the pressure in the cell was measured by digital Heise gauge (Stratford, CT; range 0-10,343 kPa (0-1500 psi)). The Heise gauge has an accuracy of 0.1% of full scale according to a calibration against a dead-weight gauge. The thermocouple has an accuracy of ±0.2°F by comparison with a platinum resistance thermometer. The schematic of the experimental apparatus is given in Schematic 1.

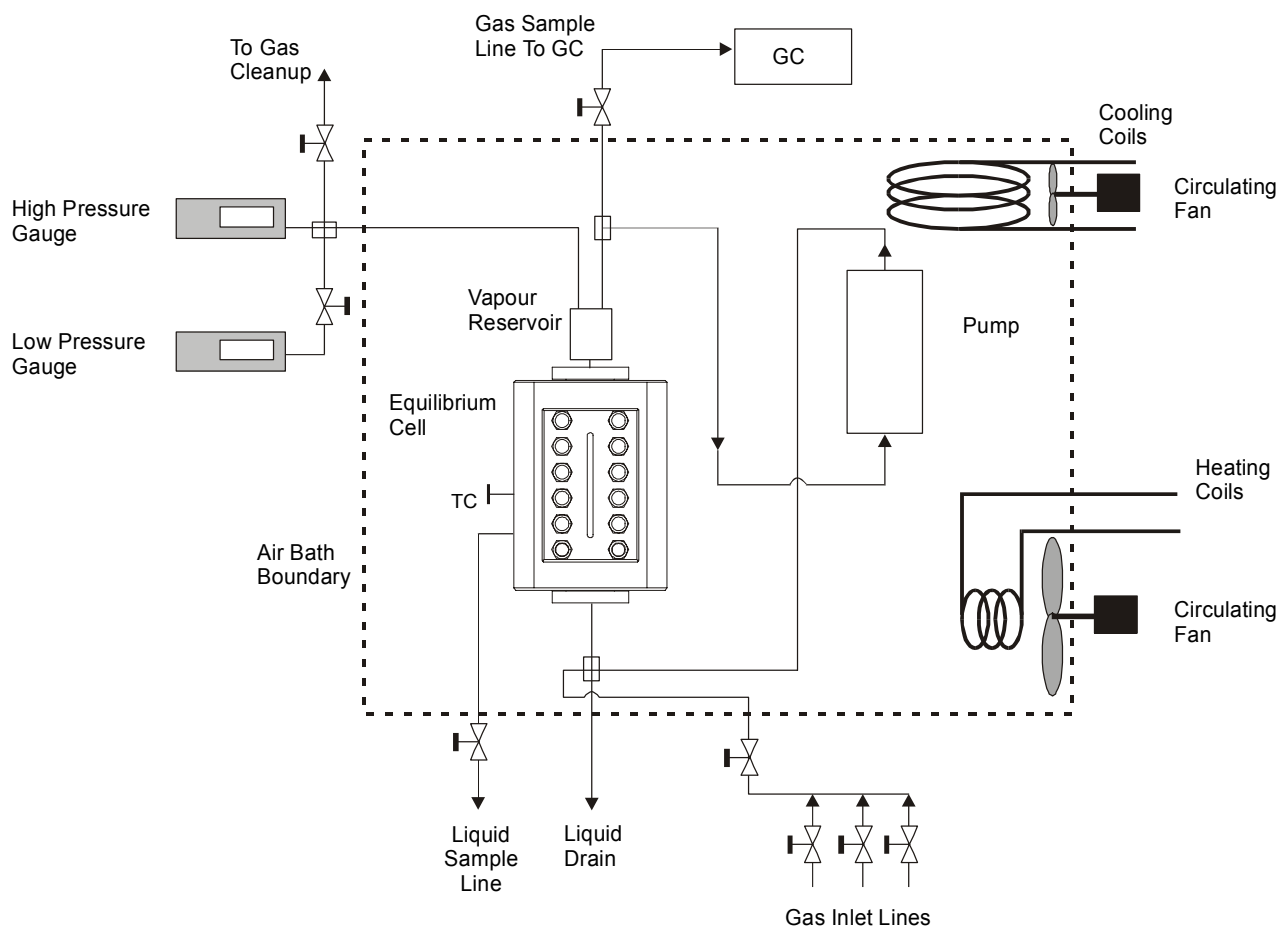
An HP 5890 Gas Chromatographic (GC) instrument was equipped with columns and a thermal conductivity detector (TCD) to suitably cover the wide ranges of chemical species and concentrations that were used for this study.

The experimental procedure for each data point was carried out according to the following steps:

1. An MDEA solution was prepared using a balance and then a sample was titrated with 0.1 N standard HCl (Certified, Fisher) to check the concentration of the amine.
2. The cell was cleaned and dried.
3. The cell was evacuated to 0.49 kPa (0.07 psia) for one minute; then the cell was purged with nitrogen. This step was repeated three times.
4. About 100 cm³ (6.1 in³) of the prepared amine solution was introduced into the cell at room temperature 21°C (70 °F).

5. Nitrogen was added into the cell to bring the pressure to 101.4 kPa (14.7 psia); then the nitrogen was circulated for 5 minutes using the magnetic pump to reduce the oxygen content in the charged MDEA solution.
6. The cell was evacuated to 4.8 kPa (0.7 psia) for a few seconds. This step was repeated twice.
7. Nitrogen was added into the cell again to 101.4 kPa (14.7 psia) and then a 0.5 g liquid sample was withdrawn for titration with 0.1 N HCl. The resulting amine solution was verified to within 0.1 wt% of the required value.
8. After establishing the correct amine solution in the cell, CO₂ and/or H₂S gases were charged into the cell, and the gas was circulated for 10 minutes; then the cell was heated to the desired temperature and the pressure was adjusted with nitrogen to about 2,413 kPa (350 psia).
9. The system was equilibrated at 2,413 kPa (350 psia) and the specified temperature by vapor circulation for at least 10 hours (overnight).

After equilibration, samples of vapor were taken and injected directly into the GC for N₂, H₂S and/or CO₂ concentration determination. The GC detector was calibrated at concentrations close to the experimental value for each system. Samples of 2-3 g of liquid phase were displaced into a sample bomb that had been loaded with a known amount of monoethanolamine (MEA) solution. The MEA solution was to fix the acid gases in the withdrawn liquid sample at ambient conditions. The acid gas concentrations in the amine solution were determined by GC as well as by the titration method.



Schematic 2 Experimental Apparatus

B. Results and Discussion

In order to determine the accuracy of the computer simulator in predicting H₂S/CO₂ equilibrium at medium pressures (i.e. 2,413 kPa (350 psia)) in the presence of nitrogen, computer simulations were performed. These results were then compared to experimental results from the study conducted by DBR.

The first step in modeling the experiment was to create the feed stream to the equilibrium flash. This was done by blending, within the computer simulation model, the experimental equilibrium liquid with the vapor streams. An equilibrium flash unit operation was then performed on the blended stream in order to determine the “new” equilibrium liquid and vapor streams established by the computer simulation model. The “new” equilibrium data were then compared to the experimental equilibrium data. The “feed loadings” were calculated by adding the total moles of acid gases (CO₂ and H₂S) from the DBR equilibrium vapor and liquid streams and dividing by the total moles of pure MDEA found in these same streams. These loadings represent liquid loadings of the rich MDEA feeding the equilibrium flash in the computer simulator. In a commercial operating unit these loadings are the rich MDEA loadings from the H₂S absorber. These loadings are important in determining how well the computer simulation package predicts equilibrium at certain “feed loadings” (i.e., how well does the computer simulator predict the equilibrium in the N₂ stripper at a targeted rich MDEA loading?)

Figures 1 and 2 show the vapor phase trend for the CO₂ only and H₂S only systems, respectively, as function of different feed loadings. Figures 3, 4, 5, 6 and 7 show the trend comparison of the combined H₂S/CO₂ system. Figures 3, 4, and 5 shows the H₂S partial pressure trend and Figures 6 and 7 shows the CO₂ partial pressure trend as a function of feed loadings.

Table 2 shows the EECF Phase I design point loadings and comparison of DBR experimental values for H₂S partial pressure and CO₂ partial pressure at design amine loadings with computer simulation results. The computer simulation satisfactorily estimates the H₂S and CO₂ partial pressures for the expected EECF loadings.

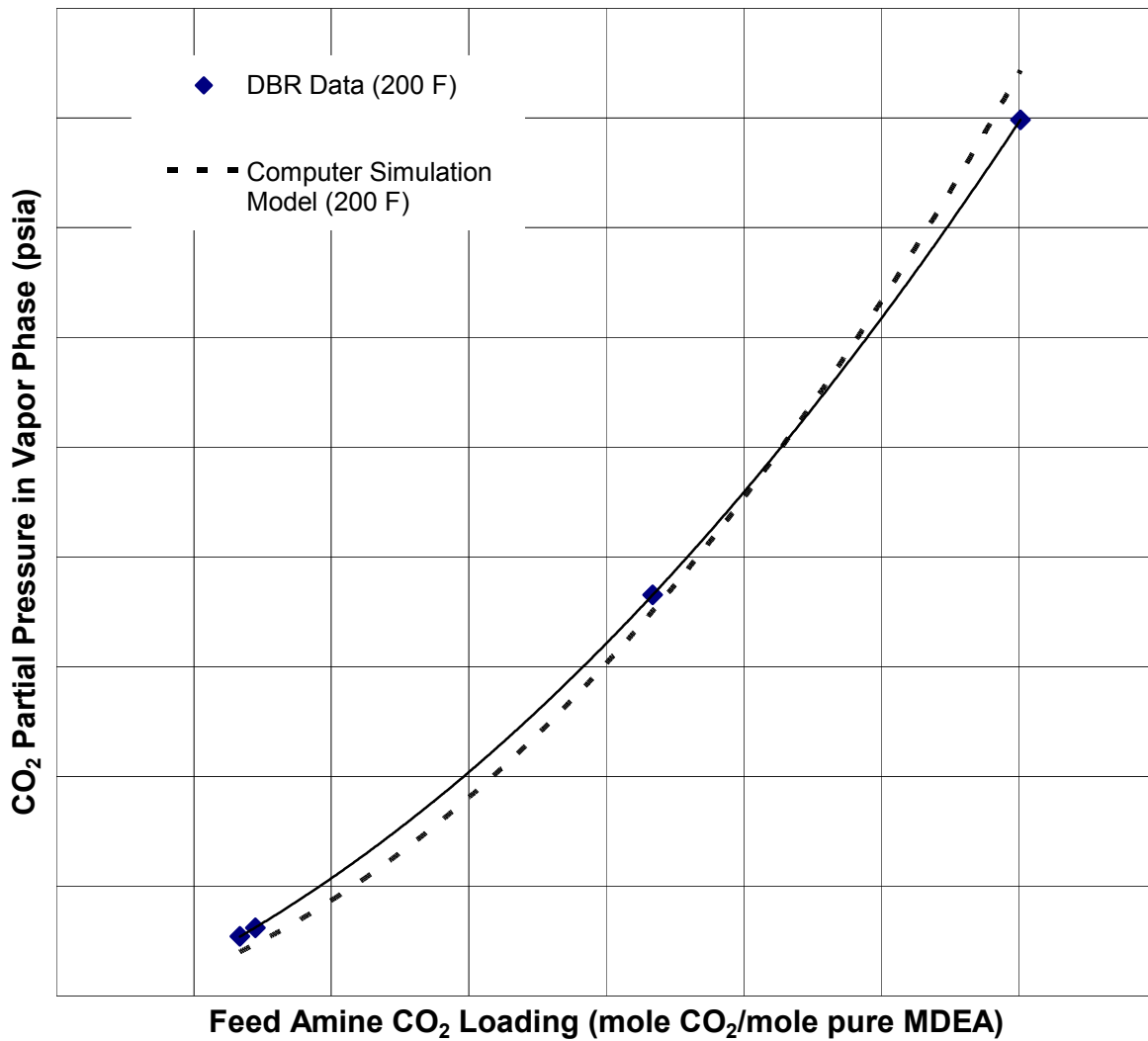


Figure 1. CO₂ Vapor Phase Concentration- CO₂ Only System @ 366 K (200 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

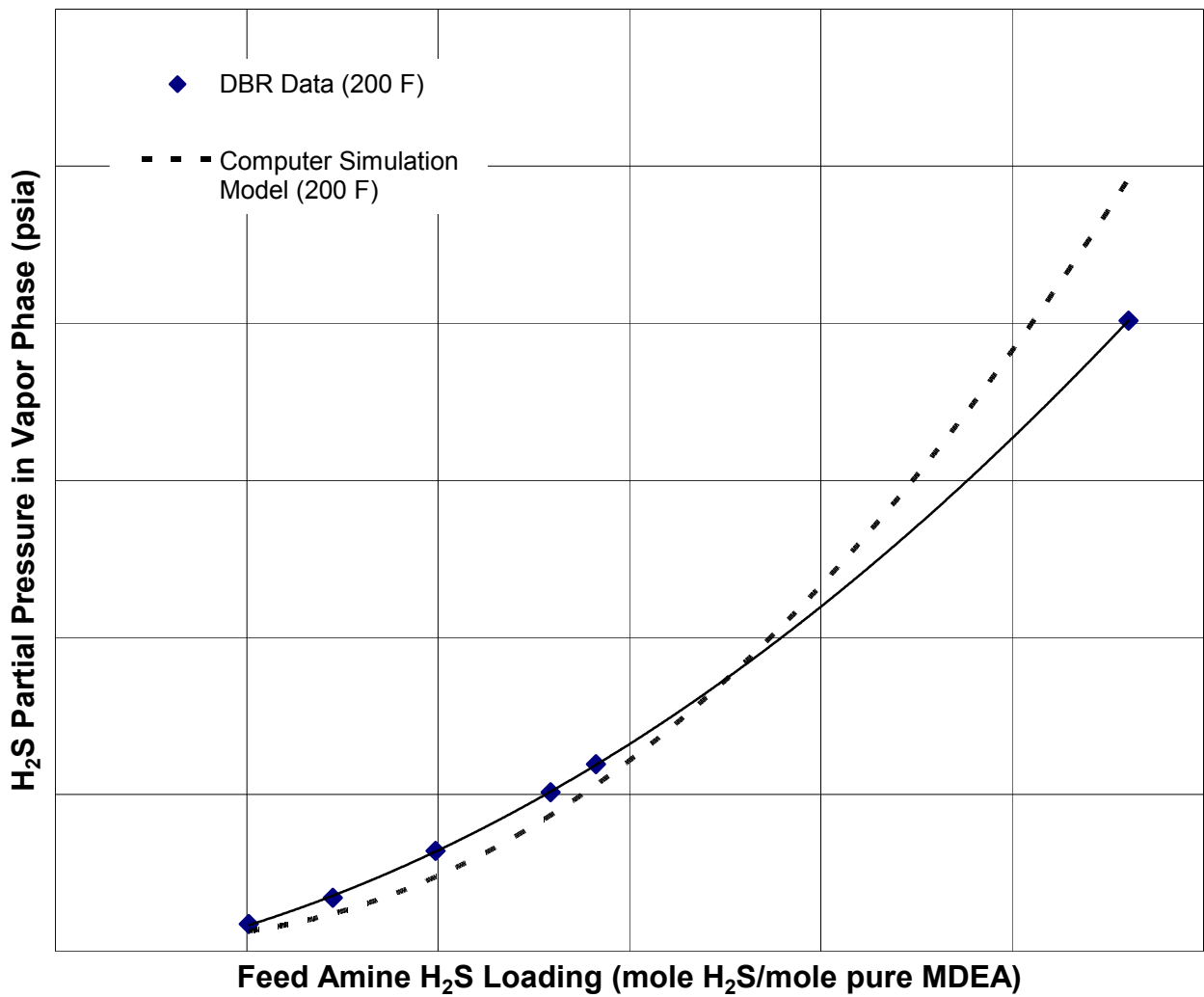


Figure 2. H₂S Vapor Phase Concentration - H₂S Only System @ 366 K (200 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

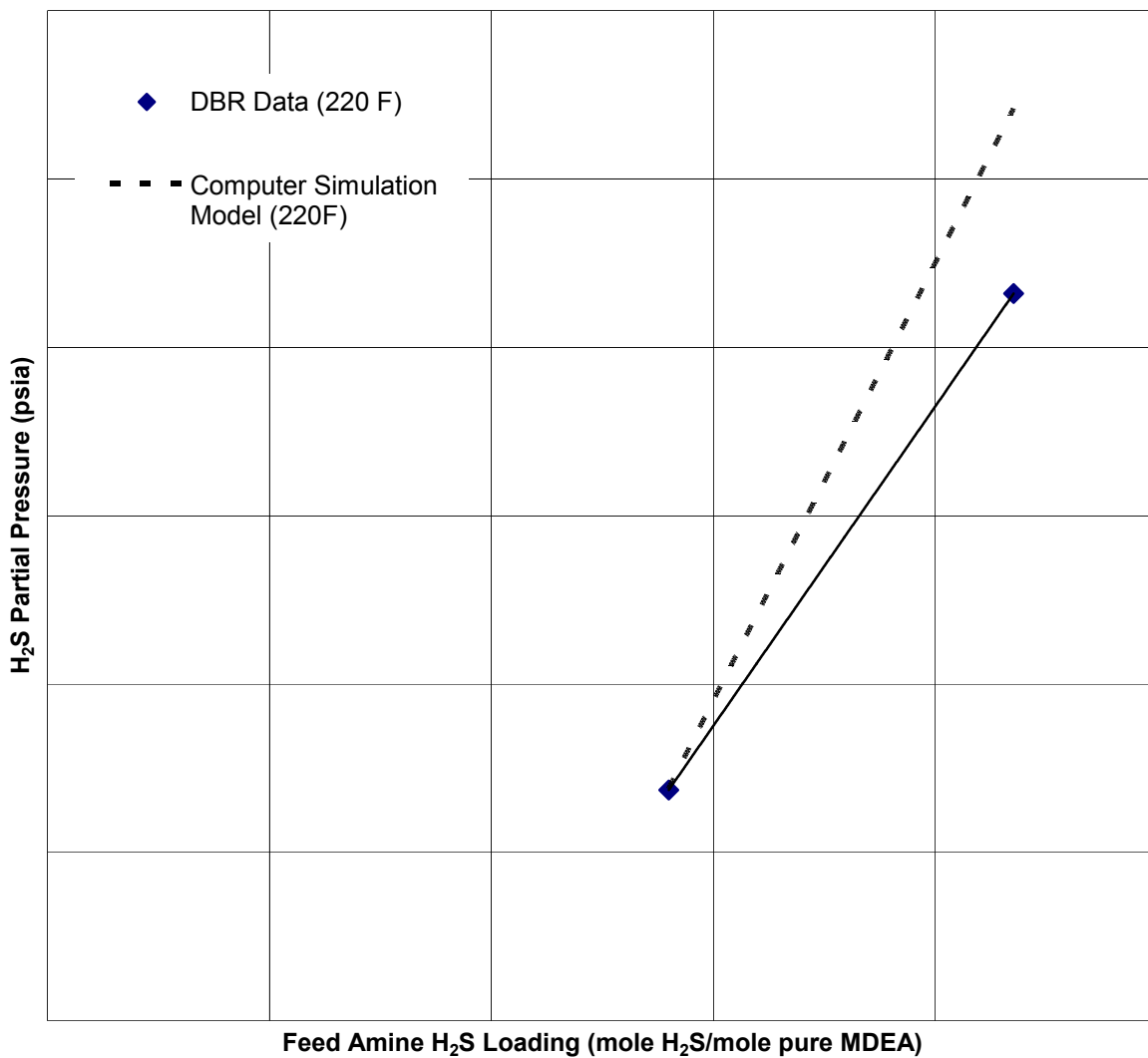


Figure 3. H₂S Vapor Phase Concentration - H₂S/CO₂ system @ 378 K (220 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

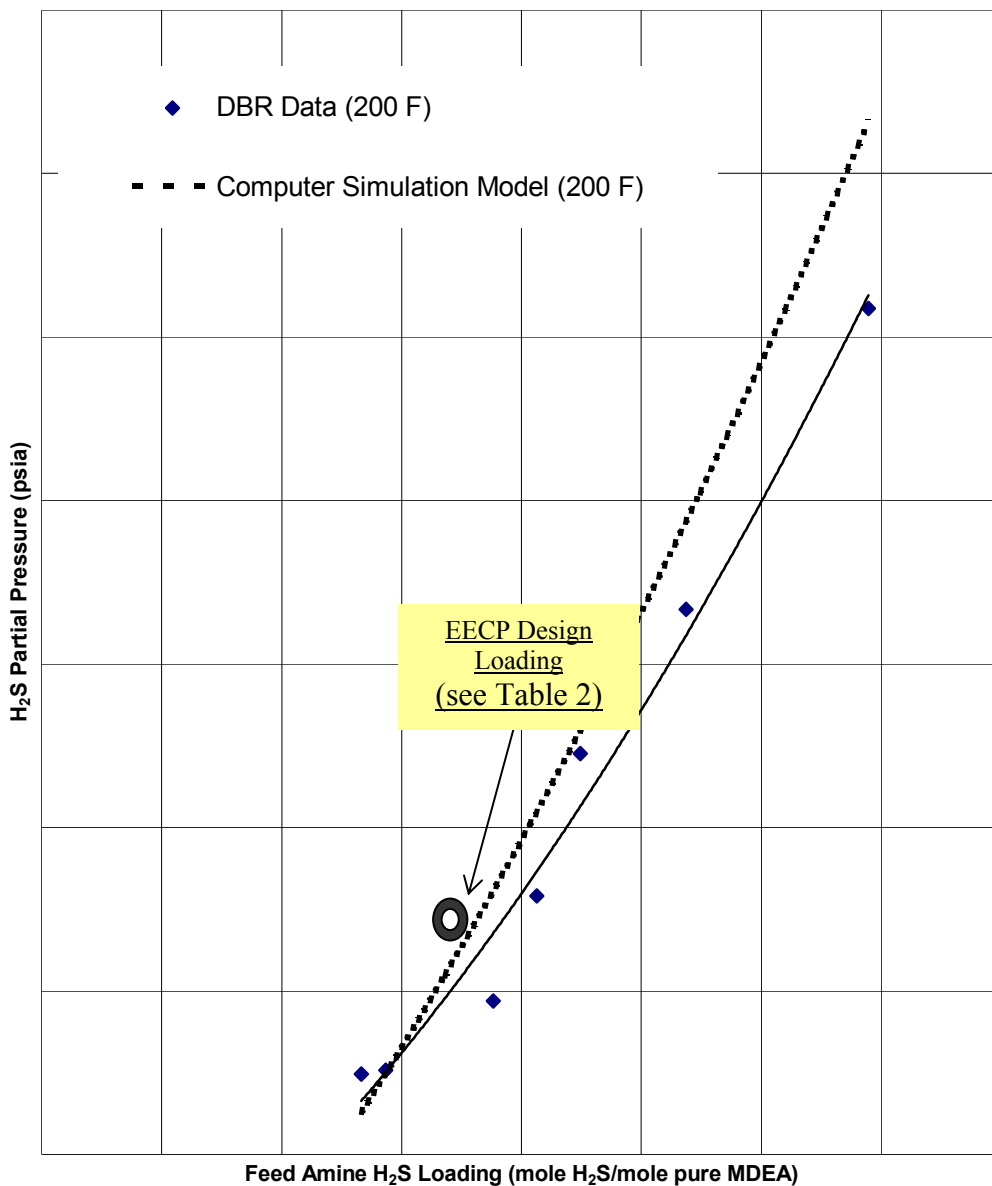


Figure 4. H₂S Vapor Phase Concentration - H₂S/CO₂ system at 366 K (200 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

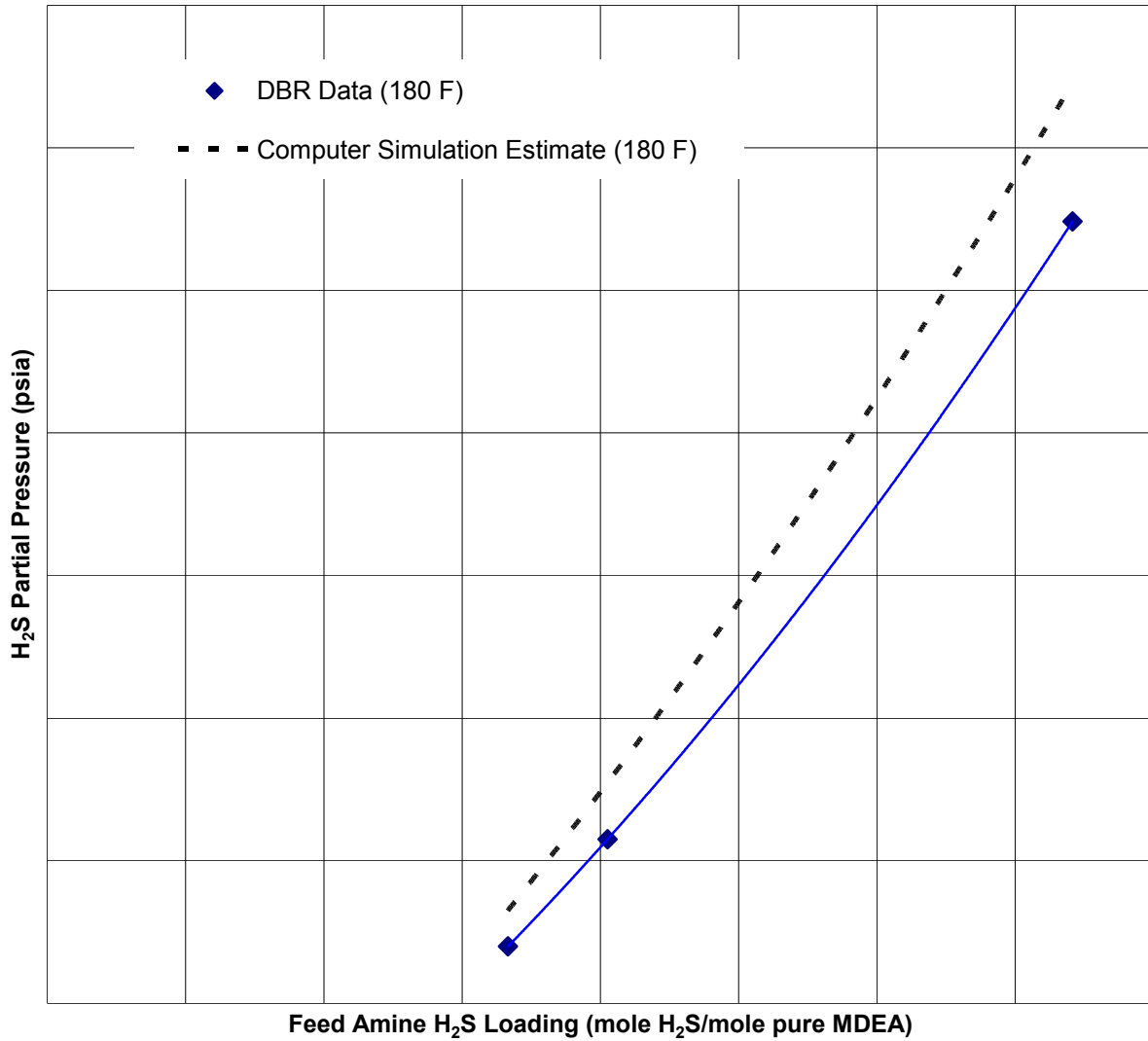


Figure 5. H₂S Vapor Phase Concentration - H₂S/CO₂ system @ 355 K (180 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

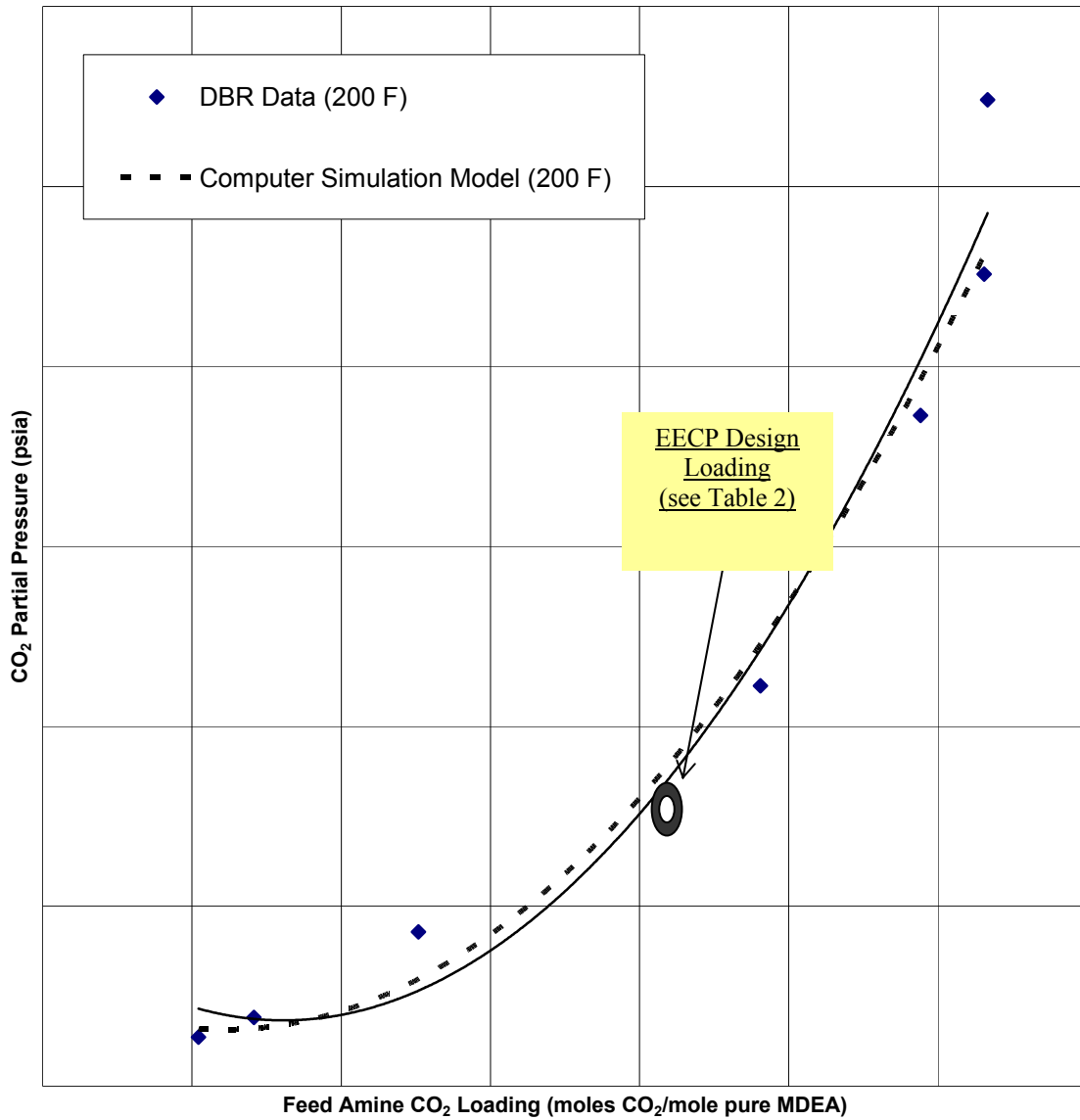


Figure 6. CO₂ Vapor Phase Concentration - H₂S/CO₂ system @ 366 K (200 °F)
 (Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

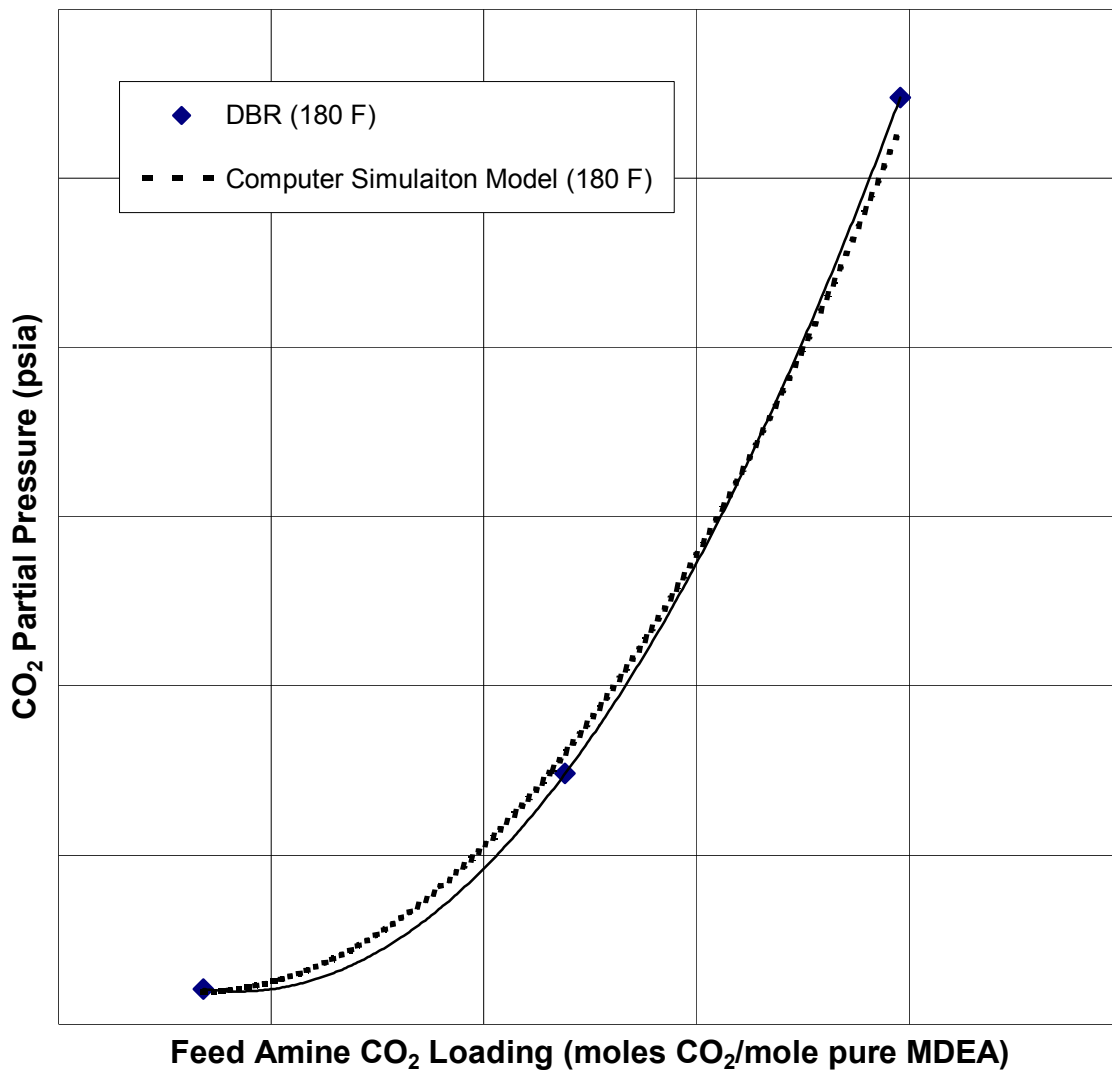


Figure 7. CO₂ Vapor Phase Concentration - H₂S/CO₂ system @ 355 K (180 °F)

(Note: The scale on X and Y axis is removed for protection of confidential information licensed to ChevronTexaco.)

Table 2

EECP Design Point

mole H ₂ S / mole pure MDEA	0.17
mole CO ₂ / mole pure MDEA	0.43
H ₂ S partial pressure – DBR Experimental, psia	9.4
H ₂ S partial pressure – Computer Simulation, psia	11.3
CO ₂ partial pressure – DBR Experimental, psia	179
CO ₂ partial pressure – Computer Simulation, psia	186

IV. Conclusions

- 1) The current loadings for the design points for EECF Phase I of 0.17 mole H₂S / mole pure MDEA and 0.43 mole CO₂ / mole pure MDEA are shown in Figures 4 and 6 respectively. The design point for the EECF concept studied for Phase I for nitrogen stripping equipment is located in regions where the DBR equilibrium data and computer simulator differences are relatively small. As per Table 2:
 - a) The EECF design point for H₂S in Figure 4 has H₂S partial pressure error of -21 % when comparing DBR data to the computer simulator estimates. If equipment design is based on computer simulations, additional H₂S is predicted to evolve from the rich MDEA in the Nitrogen Stripper which leads to the need for additional re-absorption of H₂S in the down stream re-absorption column. Thus, the down stream equipment will be slightly oversized to handle this additional acid gas. This is a conservative and generally accepted approach.
 - b) The EECF design point for CO₂ in Figure 6 has a CO₂ partial pressure error of -4 % when comparing DBR data to the computer simulator estimates. This means that there will be slightly less CO₂ in the overhead stream from the nitrogen stripper and subsequently less going to the combustion turbines. This difference is judged as relatively insignificant and may be easily handled by normal process design margins.

The difference between the DBR data and the computer simulation estimate is judged acceptable, and the current AGR design is considered reasonable.

- 2) For CO₂ only systems as shown in Figure 1, there appear to be close matches between DBR data and the computer simulation package results. For the CO₂ only system, computer simulation over-predicts vapor phase CO₂ partial pressures at relatively high CO₂ loading in MDEA, and under-predicts at low loadings of CO₂ in MDEA.
- 3) Similarly for the H₂S only system shown in Figure 2, the computer simulation package over-predicts vapor phase H₂S partial pressure at relatively high H₂S loading in MDEA but under-predicts at low H₂S loadings in MDEA.
- 4) Figures 3 through 7 show the vapor phase H₂S and CO₂ partial pressures for different feed MDEA loadings in a combined system where both H₂S and CO₂ are present. Again, the general trends are over-prediction of H₂S vapor phase concentration by computer simulation at the relatively high acid gas loadings in MDEA versus under-prediction of H₂S vapor phase concentration at low acid gas loadings in MDEA. The trend for CO₂ vapor phase concentration shows a closer match of experimental values with computer simulations.
- 5) H₂S partial pressure deviations are mostly positive for combined H₂S and CO₂ systems which imply that use of computer simulator predictions would lead to higher quantities of H₂S in the gas phase than actually expected. Similarly, CO₂ partial pressure deviations are mostly negative which would lead to lower CO₂ in the gas phase than actually expected.

In summary, computer simulations for nitrogen stripping of MDEA aqueous solutions for a combined H₂S and CO₂ system predicts higher H₂S and lower CO₂ vapor phase compositions at relatively high acid gas MDEA loadings but low H₂S and CO₂ vapor phase compositions at lower acid gas MDEA loadings when compared to DBR data.

For the Nitrogen Stripper design proposed for the conceptual EECP MDEA Acid Gas Removal (AGR) Unit, H₂S vapor phase composition error between DBR data and computer simulation is less than 21% in magnitude. The computer simulation package predicts higher H₂S removal in the Nitrogen Stripper than actually occurs. This makes downstream re-absorption equipment oversized to handle the increased amine circulation required to meet the H₂S content in the re-absorber overhead stream that goes to the combustion turbine. This is generally conservative from an equipment design standpoint and an accepted design practice.

The magnitude of CO₂ vapor phase composition error is less than 5% and judged within normal design margins. The flow rates for the stripping nitrogen should remain relatively unchanged from what is predicted by the simulation model.

Recommendations

1. Because of acceptable error differences between DBR experimental data and computer simulation, the current EECP conceptual design for the AGR should be considered a reasonable engineering design. Final design that would be developed in the next phase of EECP should include the consideration of additional design margin to handle the possibility of increased rich MDEA acid gas loads in specific areas that may be exposed to mass loads above what has been simulated in conceptual Phase.
2. While additional engineering judgment is necessary to refine the AGR design, further MDEA equilibrium testing is considered unnecessary at this point within the proposed scope of work. It should be recognized that the above testing has concentrated on equilibrium testing. H₂S absorption in MDEA is normally equilibrium controlled but actual CO₂ absorption is primarily a kinetically limited reaction. For the Nitrogen Stripper, the rich MDEA feed already has CO₂ absorbed so kinetic limitations are assumed to be non-critical. Additional nitrogen stripper simulations should evaluate the impact of this assumption.
3. Temperature control of the Nitrogen Stripper feed is recommended to provide an additional degree of freedom in controlling CO₂ release from the rich MDEA feed.

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VI. List of Acronyms and Abbreviations

AGR – acid gas removal unit

cm - centimeters

CO₂ – carbon dioxide

DBR – DB Robinson and Associates Ltd.

DCRP – Delaware City Repowering Project

EECP – Early Entry Coproduction Plant

ft – feet

g – gram

GC – gas chromatograph

GTI – Gas Technologies Institute

HCl – hydrochloric acid

HETP – height equivalent to a theoretical plate

H₂S – hydrogen sulfide

ID – inside diameter

IGCC – Integrated Gasification Combined Cycle

in – inch

kPa – kilo Pascals

mm - millimeter

MDEA – methyldiethanolamine

MEA - monoethanolamine

N - normality

N₂ – Nitrogen

OD – outside diameter

Psia – pounds force per square inch absolute

ppm – part per million

SRU – Sulfur recovery unit

SwRI – Southwest Research Institute

TCD – thermal conductivity detector

TGTU – Tail gas recovery unit

VLE – Vapor-liquid equilibrium

WTC – Westhollow Technology Center

wt% - weight percent