

INTEGRATION AND TESTING OF HOT DESULFURIZATION
AND THE TEXACO COAL GASIFICATION PROCESS FOR POWER GENERATION

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Keywords: Texaco Gasifier, Coal Gasification, In-Situ and
External Desulfurization.

OBJECTIVE:

The overall objective of this project is to develop and demonstrate an improved, high efficiency, integrated coal gasification combined cycle (IGCC) electric power generation system on a process development unit (PDU) scale. The work includes investigations of in-situ desulfurization and hot gas cleanup as applied to the Texaco Coal Gasification Process. New specialized instrumentation, being developed by DOE/METC for coal gasification, also will be tested during this project.

BACKGROUND STATEMENT:

The Texaco Coal Gasification Process (TCGP) is a second generation, commercially proven coal gasification process that is capable of meeting all present and proposed environmental regulations. There are currently three commercial plants in operation (excluding the Cool Water plant which has been shut down after a five year successful demonstration) with two more under construction.

The TCGP is a continuous, entrained flow, pressurized gasification process for converting coal, coal derived materials, or other suitable solid carbonaceous feedstocks into syngas, which is composed primarily of hydrogen and carbon monoxide. The solid feedstock is ground and fed as a concentrated water slurry into a refractory-lined pressure vessel through a special burner where it is mixed with an oxidant such as pure oxygen, air or oxygen enriched air to produce syngas. Syngas cooling is accomplished either indirectly by a syngas cooler or directly by quenching with water, depending on the end use for the gas. The syngas cooler mode is typically selected for process sequences in which methanol or fuel gas is the desired end product. The direct water quench mode is particularly attractive for those applications where pure hydrogen is required for ammonia or petrochemical synthesis.

Currently, gas contaminant removal is accomplished by conventional methods that require the gas to be cooled to ambient temperature or below. As in the TCGP based Cool Water 120-megawatt IGCC electric power plant, sulfur emissions are reduced to 10% of the New Source Performance Standards (NSPS). Economic studies indicate that, compared to a conventional pulverized coal plant with stack gas cleanup, a TCGP based IGCC system would be 15% more efficient, and have comparable investment costs. An additional increase in process thermal efficiency and a major reduction in capital cost can be realized if the hot gas does not have to be cooled down to ambient

temperature for cleaning before being fed to a combustion turbine. However, the major hot gas contaminants which include sulfur compounds, particulates, volatile metals and nitrogen compounds, still have to be removed.

Desulfurization, specifically, can be accomplished either in-situ, by including a sulfur sorbent with the coal water slurry feed to the gasifier, or external, by contacting the gas with a sorbent downstream of the gasifier vessel. In-situ desulfurization could provide the lowest investment cost and simplicity of design. External desulfurization has a potential for very high sulfur removal and the production of a salable by-product. A significant amount of work has been done by other investigators in the areas of in-situ and external desulfurization using either a fluidized bed or a moving bed coal gasifier. However, little work, except for that reported here, has been done to study hot desulfurization in conjunction with an entrained bed gasifier such as that used in the TCGP.

PROJECT DESCRIPTION:

To help achieve the goal of clean, low cost power generation from coal, Texaco submitted an unsolicited proposal in July, 1986 to develop and demonstrate the integration of high temperature desulfurization with the TCGP. The proposal resulted in a Cooperative Agreement with the DOE/METC which was awarded on September 30, 1987. This project is expected to take five years to complete at a cost of \$17 MM which will be shared between Texaco and the DOE/METC.

The test program is divided into five phases defined as follows:

- o Phase I - Preliminary Desulfurization Research.
- o Phase II - Process Optimization.
- o Phase III - Prepare Integrated System.
- o Phase IV - Integrated System Commissioning.
- o Phase V - Integrated PDU Tests.

The first three years (Phases I and II) are devoted to proof of concept and selection of the optimum processes which will make up the integrated system. The following two years (Phases III - V) will be devoted to the design, construction and operation of the integrated system. The project is currently in its third year. This paper discusses the results achieved during the Phase I and part of the Phase II work.

THEORETICAL STUDIES AND BENCH SCALE TESTS

Theoretical studies and bench scale tests were done to select suitable in-situ and external high temperature desulfurization sorbents for later evaluation on a process development unit (PDU) scale. These studies and tests were done at three different locations: Texaco Research Center, Beacon (TRCB), Texaco's Montebello Research Laboratory (MRL), and the Massachusetts Institute of Technology (MIT).

The work done at TRCB⁽³⁾ and MRL was to identify and characterize in-situ desulfurization sorbents suitable for use with the TCGP. The

results indicated that for in-situ desulfurization, only two throw-away systems; iron oxide and iron oxide/sodium oxide, had potential for success during oxygen and air gasification in the slagging mode. The results also indicated that the most effective use of calcium oxide would be to inject it into hot syngas at a location after the slag has solidified.

The work done at MIT was to identify external desulfurization sorbents suitable for use with the TCGP. Four different mixed metal oxide sorbents (Zn-Fe-O, Zn-Ti-O, Cu-Al-O, Cu-Fe-Al-O) were synthesized and tested. Also, a commercial iron oxide and a zinc ferrite (L-3201/UCI) sorbent were evaluated in cyclic sulfidation-regeneration tests. The MIT results indicated that the ZnO-based sorbents were limited to operating temperatures below 1100 deg. F in the highly reducing TCGP syngas streams. The Zn-Ti-O sorbent showed a higher temperature capability up to 1300 deg. F. The Cu-Fe-Al-O sorbent showed merit for regenerative desulfurization of TCGP syngas at all temperatures up to 1400 deg. F.

PDU TESTING - IN-SITU DESULFURIZATION

The PDU testing was conducted at MRL using an existing pilot plant gasification unit modified to test in-situ and external desulfurization. The gasifier in the PDU is equipped with a syngas cooler in addition to a water quench. The gasifier is normally operated at a pressure of 350 psig and, at a temperature between 2000 and 3000 deg. F. The capacity of the PDU is 15-20 tons/day of moisture free coal. A PFD of the modified MRL pilot plant is shown in Figure 1. Sulfur removal was accomplished primarily in-situ by including sorbent(s) with the coal water slurry feed to the gasifier. External high temperature desulfurization was examined in a downstream fixed bed system using a slip stream of syngas generated during PDU operations.

During the Phase I PDU testing, a 1-day shakedown run and three 3-day screening runs were completed. All of the runs were made at a gasifier pressure of 350 psig using high purity oxygen (99.75 vol%) as the oxidant. A medium sulfur Pittsburgh No.8 coal (2.1 wt% S) was used for all runs except the last run; in the last run, a high sulfur Powhatan coal (5.1 wt%) was gasified. Table 1 lists the key properties of the two coals. Two different in-situ sulfur sorbents, Fine OX (high purity iron oxide, Fe₂O₃) and soda ash (high purity sodium carbonate, Na₂CO₃), were selected for testing based on the results of thermodynamic calculations and bench scale tests. Soda ash was tested only as a co-sorbent with Fine OX.

Limestone or dolomite initially selected for use as an in-situ sulfur sorbent, was rejected when the bench scale testing indicated that the calcium would preferentially react with the silicate phase in the coal slag instead of with the H₂S in the syngas.

A summary of the operating conditions and %H₂S reduction in the syngas for each test period/run is shown in Table 2. The data indicate that a nominal 50% reduction of H₂S in the syngas was achieved at a normal gasifier operating temperature, using iron oxide as the in-situ sulfur sorbent. The slag generated during the tests was stable. This level of H₂S reduction in the syngas was achieved

Table 1 Charge Stock Test Results

Coal	Pitts. No.8	Powhatan
Moisture	2.80	4.36
Proximate Analysis (dry basis)		
Volatile Matter, wt%	37.37	41.13
Fixed Carbon	56.08	48.07
Ash	6.55	10.80
Ultimate Analysis (dry basis)		
Carbon	78.41	71.16
Hydrogen	5.13	5.09
Nitrogen	1.45	1.04
Sulfur	2.14	5.07
Ash	6.55	10.80
Oxygen (by diff.)	6.32	6.84
Gross Heating Value, btu/lb	14092	13037
Ash Fusion Temp., deg. F		
Initial	1995	1960
Softening	2195	2005
Hemispherical	2280	2095
Fluid	2350	2355

Table 2 Phase I In-Situ Desulfurization Test Matrix

Run/Test Period	Length * Run/Test Period (Hr)	In-Situ Sulfur Sorbent Dosage (Lb/Lb S in Coal)		Gasifier Temp. (deg.F)	Vol% H2S In Gas	%Reduct. In H2S
		Fine OX	Soda Ash			
1/	26.4/	0	0	To	0.47	-
2/	69.4/					
A	14.4	3.5	0	To	0.26	44.7
B	16.7	3.5	0	To-200	0.23	51.1
C	9.3	3.5	0	To-300	0.17	63.8
D	15.5	3.5	0	To-100	0.26	44.7
E	11.0	4.5	0	To-100	0.26	44.7
3/	59.3					
A	11.6	3.5	1.5	To	**	-
B	13.0	3.5	1.5	To-200	**	-
C	23.0	3.5	2.0	To	0.20	57.4
D	9.0	3.5	2.0	To-100	0.20	57.4
4/	84.0					
A	15.3	0	0	To	1.50	-
B	12.0	1.7	0	To	0.90	40.0
C	12.0	1.7	0	To-150	0.83	44.7
D	12.0	2.6	0	To	0.76	49.3
E	12.0	2.6	0	To-150	0.71	52.7
F	12.0	2.6	0.25	To-125	0.69	54.0
G	6.2	2.6	0.25	To-175	0.71	52.7

* Run Length = Total on-stream time including the time between steady state operating periods.
 ** No stable readings from on-line mass spectrometer were available.

for both the medium sulfur Pittsburgh No.8 coal and the high sulfur Powhatan coal. Higher levels of desulfurization were achieved by lowering the gasifier temperature. However, this resulted in lower carbon conversions which produced too much char to be effectively handled in the PDU.

A higher H₂S reduction of about 60% in the syngas was achieved at a normal gasifier operating temperature using iron oxide plus a high dosage of sodium carbonate added to the Pittsburgh No.8 coal slurry. However, the slag generated was unstable (i.e. sulfide in the slag would oxidize on exposure to ambient air) and there were solids handling and plugging problems experienced during the tests because of the extremely small solid particles produced which were cemented together with condensed sodium compounds. A low dosage of sodium carbonate, tested during the Powhatan coal run, resulted in no improvement in H₂S reduction. Because of these results we decided to abandon further testing of sodium carbonate.

Most of work in the current Phase II program involves air gasification in the PDU. Three runs have been completed, using Pittsburgh No. 8 coal, in the same gasifier used for the Phase I PDU testing. A 4-day baseline run, a 3-day Fine OX in-situ desulfurization run and a 3-day dolomite desulfurization run have been made. The results indicate that a nominal 24% reduction of H₂S in the syngas was achieved at a normal gasifier operating temperature, using Fine OX as the in-situ sulfur sorbent. Higher levels of desulfurization were achieved by lowering the gasifier temperature or increasing the dosage of Fine OX. The highest level of H₂S reduction in the syngas achieved was 38%. Again, this resulted in lower carbon conversions which produced too much char to be effectively handled in the PDU.

Preliminary data indicate that a 65-70% reduction of H₂S in the syngas was achieved during the dolomite desulfurization run. The dolomite was injected as a water slurry into the syngas in the radiant syngas cooler. Most of the slag had been removed or solidified at the point of injection to prevent undesirable reactions between calcium and silica. Typical wet syngas compositions from the oxygen and air gasification runs with in-situ sulfur sorbent(s) can be seen in Table 3.

Table 3 Typical Wet Syngas Composition

Coal Oxidant Syngas Composition	Pitts. No.8 Oxygen	Powhatan Oxygen	Pitts. No.8 Air
A, mole%	0.06	0.10	0.64
H ₂	29.96	28.39	11.36
CO	38.91	37.17	14.70
CO ₂	9.88	11.89	8.82
N ₂	1.57	2.28	53.78
CH ₄	0.09	0.00	0.04
H ₂ S	0.35	1.18	0.20
COS	0.03	0.05	0.00
H ₂ O	19.15	18.94	10.46
Total	100.00	100.00	100.00

PDU TESTING - EXTERNAL DESULFURIZATION

Four different external sulfur sorbents (zinc ferrite/T-2465, zinc ferrite/E-13A, zinc copper ferrite/L-2952, and zinc titanate/L-3014) were selected for the Phase I PDU testing based on the results of theoretical studies and the recommendations of METC. The external sorbent testing system, as shown in Figure 1, consists of three parallel, fixed sorbent beds mounted in the top of the convection syngas cooler vessel. The four external sorbents were evaluated in single pass sulfidation using a slip stream of 1000-1300 deg. F syngas fed to each of the three beds, with an H₂S concentration between 1,600 and 14,500 ppm.

The H₂S concentration was constant throughout each sorbent bed run; the variation in H₂S levels is a result of the different gasifier operating temperatures, in-situ sulfur sorbents and dosages, and the different coals used. The following conclusions and recommendations were made based on the Phase I performance of the external sorbents:

- o All four sorbents evaluated achieved H₂S removals greater than 99.9% before breakthrough.
- o The ferrite based sorbents evaluated are not suitable for use with the TCGP oxygen blown syngas because of a severe loss in crush strength that occurs after only a single sulfidation, and the catalyzing of the methanation reaction.
- o Zinc titanate retained more of its crush strength and had a higher sorbent utilization in sulfidation only testing.
- o Formulations of zinc titanate with more zinc should be tested to see if the maximum sulfur loading can be increased.

In the Phase II program, three external sulfur sorbents (zinc ferrite/T-2465, zinc titanate/L-3014/0.8 ZnT, and zinc titanate/1.5 ZnT) have been evaluated in single pass sulfidation using a slip stream of syngas during the air gasification baseline run at an inlet H₂S level of 2900 vppm. All three sorbents achieved H₂S removal of greater than 99.9% before breakthrough. Examinations of the spent sorbents after the baseline run indicated that all three were in good condition. The zinc titanates were expected to retain their crush strengths. However, we were pleasantly surprised to find that the zinc ferrite, which disintegrated during the previous oxygen gasification runs, had also retained much of its crush strength during the air gasification runs.

ADVANCED INSTRUMENTATION AND WESTINGHOUSE CERAMIC CROSS FLOW FILTER EVALUATION

Several advanced instruments being developed by METC, which could be used for process control and on-line measurements in entrained bed gasification systems with integral hot desulfurization, were identified for testing in the PDU. On-line testing of the instruments started in Phase II.

A Westinghouse ceramic cross flow filter, which was installed in the PDU, has been tested with over 100 hours of on-stream time. This

project is sponsored by the DOE with Texaco acting as a subcontractor to Westinghouse. The objective is to demonstrate the use of the filter to remove solids from the hot syngas.

FUTURE WORK:

We are currently making PDU equipment modifications to improve the reliability of the limestone/dolomite injection system for the air gasification runs.

External desulfurization testing will continue with emphasis on optimized formulations of zinc titanate. An iron oxide sorbent which we obtained from METC will also be tested.

We are continuing the testing of the advanced instrumentation and the Westinghouse ceramic cross flow filter.

REFERENCES:

- (1) Power Magazine, April 1985, p. 24-25
- (2) Robin, A.M., Becker, W.M., Leininger, T.F., "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems", Paper presented at Seventh Annual Gasification and Gas Cleanup Systems Contractors Review Meeting, June, 1987.
- (3) Robin, A.M., Wu, C.M., Najjar, M.S., "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems", Paper presented at Eighth Annual Gasification and Gas Cleanup Systems Contractors Review Meeting, May, 1988.
- (4) Robin, A.M., Wu, C.M., Kassman, J.S., "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems", Paper presented at Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, June, 1988.
- (5) Robin, A.M., Wu, C.M., Kassman, J.S., "Integration and Testing of In-Situ Desulfurization and the Texaco Coal Gasification Process for Power Generation", Paper presented at Sixth Annual International Pittsburgh Coal Conference, September, 1988.