

Section 10

THE TVA AMMONIA FROM COAL PROJECT: 1985 UPDATE

D. A. Waitzman
R. G. Lee
D. E. Nichols
P. C. Williamson

Tennessee Valley Authority
National Fertilizer Development Center
Muscle Shoals, Alabama 35660

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INTRODUCTION

The TVA Ammonia from Coal Project (ACP) was begun in 1976 to construct a facility and to carry out research, development, tests, and demonstration on substituting abundant coal for scarce natural gas to produce ammonia. The main objectives of the project will be accomplished at the end of fiscal year 1985. At that time we will have a facility and an organization which we can make available to others on a reimbursable basis as a test center for further development work. We believe it will be in the national interest to use the facility in a positive manner, and we are studying various alternatives as to what can be done.

BACKGROUND

In August 1975, the president of The Fertilizer Institute appealed to the TVA Board of Directors for funding to be authorized to find an alternate feedstock to natural gas to produce ammonia. The facts were and still are that at least one-third to one-half of the food and fiber produced in this country is attributed to fertilizer, and nitrogen is the most most widely used nutrient. Essentially all nitrogen fertilizer is made from ammonia, and 95 percent of the ammonia produced in this country is made from natural gas. Therefore, if we were to lose natural gas from high price or unavailability, we would lose one-third of the food and fiber produced in this country. We were able to quickly respond to the president's request and began the TVA Ammonia from Coal Project. We had at Muscle Shoals a small but modern natural gas-fed ammonia plant, and we saw that we could retrofit this plant to operate with gas produced from coal. We selected the Texaco coal gasification process because it appeared to best meet the following criteria:

- Accepts a variety of U.S. coals.
- Produces a gas compatible with ammonia processes.
- Operates at pressures compatible with ammonia processes.
- Avoids undesirable gas contaminants such as tars, oils, and phenols, and byproducts such as char.
- Uses U.S.-based technology, methods, and equipment.
- Is developed to the extent that it is essentially ready for commercial use.

- Is economically attractive in comparison with other coal gasification processes.

The plant was completed at a cost of about \$43 million and was operated for the first time in October 1980. It was the first coal gasification plant to be built in the United States, in modern times, with all environmental controls, and on a semiproduction-size basis. Being a first-time-out plant, we suffered some initial agonies. It was not until November 1982 that we actually made ammonia, but now the plant can be run on a routine basis and without major difficulties. Our original objective was to make sure the farmer had fertilizer, and we believe we have developed and demonstrated a good technology and viable alternative for the industry when the economics are right. In the course of doing this, we have also developed a medium-Btu synthesis gas plant that produces H₂ and CO from coal; this is a building block from which methanol, gasoline, medium-Btu fuel gas (and therefore electric power), synthetic natural gas, or a host of other materials can be produced. Since operation of the plant was started, we have had over 2,000 technical visitors and only 300 of these were fertilizer people. The others were synfuels and energy people.

PLANT DESCRIPTION AND CHANGES

The plant has undergone a number of changes since it was built and some of these changes are described as part of the following description of the plant. We have operated the plant with Illinois No. 6, Kentucky No. 9, and Utah coals and bottoms material from the Exxon Donor Solvent Process. Illinois No. 6 and Utah coal data will be given as part of this description. Table I presents a comparison of the ultimate analyses and heating values of the Utah and Illinois No. 6 coals.

A flow scheme for the TVA Ammonia from Coal Project is shown in Figure 1. Coal is received by rail and is either sent to open storage and later recovered by front-end loader or it is crushed in a primary crusher to minus 1/2-inch and conveyed directly to the coal slurry preparation area. A metal detector was added to the incoming conveyor to stop the conveyor when tramp metal was in the coal. The hammer mill crusher clearances were adjusted at times to obtain finer grind in the downstream disc mills.

Coal is pulverized in wet disc mills as required for the gasifier operation. Grinding of Utah coal in wet disc mills at full load resulted in a slurry with a much coarser grind size than slurries produced from Illinois No. 6 coal. The coarse grind reduced gasifier performance. The slurry produced from Utah coal presented no pumping problems and had about the same viscosity as slurries produced from other coal types with the same concentration. However, when transferring Utah coal slurry through a 6-mesh screen, it would adhere to the screen wires and effectively slow the transfer rate. At times the slurry had to be washed through the screen resulting in an undesirable dilution of the slurry concentration. The problem of screen pluggage has been attributed to two causes. First, the ground Utah coal particles have a tendency to stick to adjacent coal particles or other surfaces such as the screen wires. Second, the coarse grind of the Utah coal slurry appears to worsen the problem. In tests where Illinois No. 6 coal was intentionally ground as coarsely as the Utah coal, it also adhered to the screen. Probably the coarse particles tend to dewater as they impact the screen leaving a thick cake behind. The electronic weight feed system and the water control to the disc mills required modification and attention initially. From the disc mills, the slurry goes to one of two mix tanks where the solids content of the slurry is adjusted to the desired level. The slurry is pumped to a 10-hour capacity feed tank and then metered to the reactor (gasifier) at the process rate of about 8 tons of coal per hour. The mix and run tanks required lining with a glass-reinforced polyester resin because of severe corrosion and/or abrasion despite maintaining a neutral pH.

The gasification process takes place in the reactor at a pressure of about 510 psig and at a temperature of about 2500°F. The carbon in the coal is reacted with steam to produce carbon monoxide and hydrogen. Gaseous oxygen from the air separation plant is fed to the reactor at about 8 tons per hour to burn part of the coal to provide heat for the endothermic reaction. In addition to the gasification reaction and coal combustion to form carbon dioxide (CO₂), sulfur compounds in the coal are gasified in the reactor reducing atmosphere to produce primarily hydrogen sulfide (H₂S) and some carbonyl sulfide (COS). Small quantities of other compounds such as ammonia and methane are also formed. Essentially no long-chain or aromatic hydrocarbons are formed.

Each of the feedstocks was tested under a wide range of operating conditions in the gasifier. Operating parameters which have been tested most extensively

are slurry concentration, gasifier temperature, gasifier load, and slurry grind-size distribution. Much has been learned from this type of testing which often pushes the gasifier operation to practical limits. Typical gasifier performance with the Utah and Illinois No. 6 coals is given in Table II.

With both feedstocks, an increase in slurry concentration results in an increase in gasifier performance, i.e., an increase in cold gas efficiency and a decrease in specific oxygen consumption. It follows then, that in a comparison of feedstocks, the relative gasifier performance is highly dependent on the highest slurry concentration which can be delivered to the gasifier. In a direct comparison between Utah coal and Illinois No. 6 coal at the same slurry concentration and slurry grind-size distribution, the Utah coal was more reactive than Illinois No. 6 coal and therefore produced better gasifier performance. However, the Illinois No. 6 coal was equal or superior to the Utah coal for two reasons. First, a higher slurry concentration can be achieved with Illinois No. 6 coal because of the problem discussed earlier in which thick Utah coal slurries had to be diluted to pass through a 6-mesh screen. Second, a finer grind can be achieved with Illinois No. 6 coal in our grinding system of disc mills. In a direct comparison study of coarse and fine grind Illinois No. 6 coal, the fine grind showed a significant improvement in carbon conversion in the gasifier.

A process problem which was related to a difference in feedstock properties was solved during the last year. With Illinois No. 6 coal, solids accumulated gradually in the gas line exiting the gasifier. Weeks of operation were possible before the line required cleaning. With Utah coal, the buildup was rapid. In less than a day, the solids accumulated to the point that a shutdown was required for cleaning. Analysis of the deposits revealed a high calcium content. The calcium acted as a cement to bond fly ash to the pipe walls. After modifications were made to correct this problem, the plant was operated for 20 days with Utah coal with no solids accumulation on the pipe walls.

Slag produced from the ash in the coal is removed from the reactor through a lockhopper system. The slag is glassy in appearance and is very similar to the bottom ash produced in a coal-fired power plant boiler. Trucks are used to transport the solids to a disposal area. The gasification area required extensive modifications initially to get the slag out of the quench section

and also to remove the slag from the gasification area. The internals in the gasifier were revised including thermocouple and liquid level sensing element changes, a forced water circulation system with cooling was installed, a drag conveyor replaced a sluicing system which had replaced a screw conveyor, a screening system was eliminated, and lockhopper valves were replaced. Also, refractory test panels in the gasifier have indicated that high-chrome refractory bricks will give acceptable refractory life.

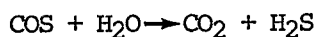
The gas leaving the reactor is water-quenched and particulate matter (fly ash) is removed in a scrubber. The on-stream gas analyzer system depends on continuous sampling to gas chromatographs, infrared analyzers, H₂S and total sulfur analyzers, and workplace safety monitoring systems. Sample lines were changed from carbon steel to stainless steel and adequate filtering and condensation systems were installed. The electronic instrumentation system required quite a bit of initial revision. All these systems were finally corrected to the point that now we are able to obtain on-stream heat and material balances to within 1 percent closures.

A blowdown is taken from the water recirculating loop and pumped to a wastewater treatment facility, which uses both chemical and biological treatment processes. The wastewater is first treated in a clarifier by addition of ferrous sulfate and caustic. The clarifier underflow is sent to a sludge conditioner unit and then to a filter press for solids removal. The liquid fraction from the clarifier is steam-stripped to remove ammonia. The stripped aqueous material containing some organic matter, primarily as formates and cyanates, along with water from washdown operations, is sent to an equalization-cooling basin for pH control, mixing, and cooling. After aeration, the combined waste then flows to the sludge conditioner unit where it is treated with ferric chloride. The material then flows to the filter press where the solids are removed for disposal. The water from the unit is metered and sampled on its way to discharge. The wastewater system was and still is partly hydraulically overloaded. To correct this, the effluent from the drag conveyor is clarified and recycled instead of going to wastewater treatment. Flow measurement and control were installed on seal water to pumps and blowers, and ammonia is now vented to the atmosphere with EPA approval.

The process gas from the quench scrubber flows to two carbon monoxide (CO) shift converters as shown in Table III. The converters were charged with sulfur-activated catalyst developed by Haldor Topsoe. Since the original

installation, other manufacturers have developed sulfur-tolerant shift catalysts. Currently, Shell Chemical's catalyst is being used. The CO content of the gas entering the converter is about 11 percent (wet basis). After full shift, the CO content is about 2 percent which matches the CO content of the gas entering the low-temperature shift converter in the existing ammonia plant. After about 2800 hours of operation, the first-stage shift catalyst lost its activity and it is believed that an upstream liquid level system had allowed water to get to the catalyst. The level system has been changed to correct this.

The COS produced during the gasification process is hydrolyzed to H₂S because the Stretford sulfur recovery process has no effect on COS and thus the COS would pass through that unit to the atmosphere. To decrease the quantity of COS, a hydrolysis unit containing a catalyst also developed by Haldor Topsoe is provided between the CO converter and the acid-gas removal (AGR) system to promote the reaction:



The process gas from the COS hydrolysis unit flows to the AGR system as shown in Table IV which reflects the loss of shift catalyst activity by the high level of CO during the Utah coal run. The AGR system uses Norton's Selexol process (a physical absorbent system) to remove the CO₂, H₂S, and the remaining COS from the process gas. This system decreases the total sulfur in the synthesis gas stream to about 1 ppm as shown in Table V. The AGR system performed satisfactorily process-wise but there were difficulties with mechanical equipment such as a vacuum compressor, refrigeration equipment, and mist eliminators. The ability of the acid gas removal unit to operate satisfactorily with each feedstock was demonstrated. The total sulfur composition of the outlet gas was below 1 ppmv for each feedstock. The major difference in operations was that when using the low-sulfur Utah coal the unit could be operated with a lower solvent flow rate and still maintain the 1 ppmv sulfur content in the outlet gas. Two reject acid gas streams are produced during regeneration of the Selexol solvent as shown in Table VI. One stream containing up to 4 percent H₂S is sent to the Stretford sulfur-recovery system. The Stretford system uses a proprietary solution containing an oxidized form of vanadium salts. The H₂S is oxidized in the solution to produce elemental sulfur according to the following reaction:



The reduced metal salt is regenerated by blowing air through the solution. This operation also floats the elemental sulfur to the surface. The sulfur is skimmed off and filtered to produce a wet cake. The tail gas from the Stretford system contains less than 190 ppmv total sulfur.

The second stream from the AGR system is relatively pure CO₂. This gas is also sent to a Stretford unit and then to a sulfur guard containing zinc oxide to decrease the sulfur content to less than 0.5 ppm to meet requirements for urea manufacture. A condenser was installed in the AGR stripper overhead to prevent vaporized AGR solvent from going to the Stretford unit. Also a number of physical and chemical system changes were made to the sulfur recovery unit to prevent excessive foaming and to improve sulfur removal efficiency. The streams from sulfur recovery are shown in Table VII.

Nitrogen from the air separation plant is added to the process gas from the AGR system to produce an H₂:N₂ ratio of 3:1. The gas then flows through a zinc oxide sulfur guard to decrease the sulfur content to less than 0.1 ppm. Demineralized water is added to bring the steam to dry gas ratio to 0.44:1. The gas is then heated to about 600°F prior to its entry into the existing ammonia plant at a point immediately upstream of the low-temperature CO shift converter. The pressure of the gas at the battery limits is about 385 psig.

Composition of process gas manufactured from coal is very nearly the same as the composition of gas leaving the high-temperature CO shift converter in the ammonia plant and is shown in Table VIII. We had some difficulty in meeting the sulfur content level however because there were leaks across a raw gas-to-product heat exchanger that allowed H₂S-rich gas to get into the 0.1 ppm sulfur product gas and the exchanger required back-welding of the tubes. Also under earlier operating procedures, the sulfur guard was bypassed and the carbon steel walls of the downstream lines, vessels, and exchangers became sulfided. A considerable amount of purging with product gas was required to remove sulfur contamination. In addition, the boiler feedwater (initially added to the product gas to obtain the necessary steam-to-gas ratio for low temperature shift in the existing ammonia plant) was found to contain about 25 ppm sulfates and was replaced with demineralized water.

PLANT OBJECTIVES AND ACCOMPLISHMENTS AS OF 1985

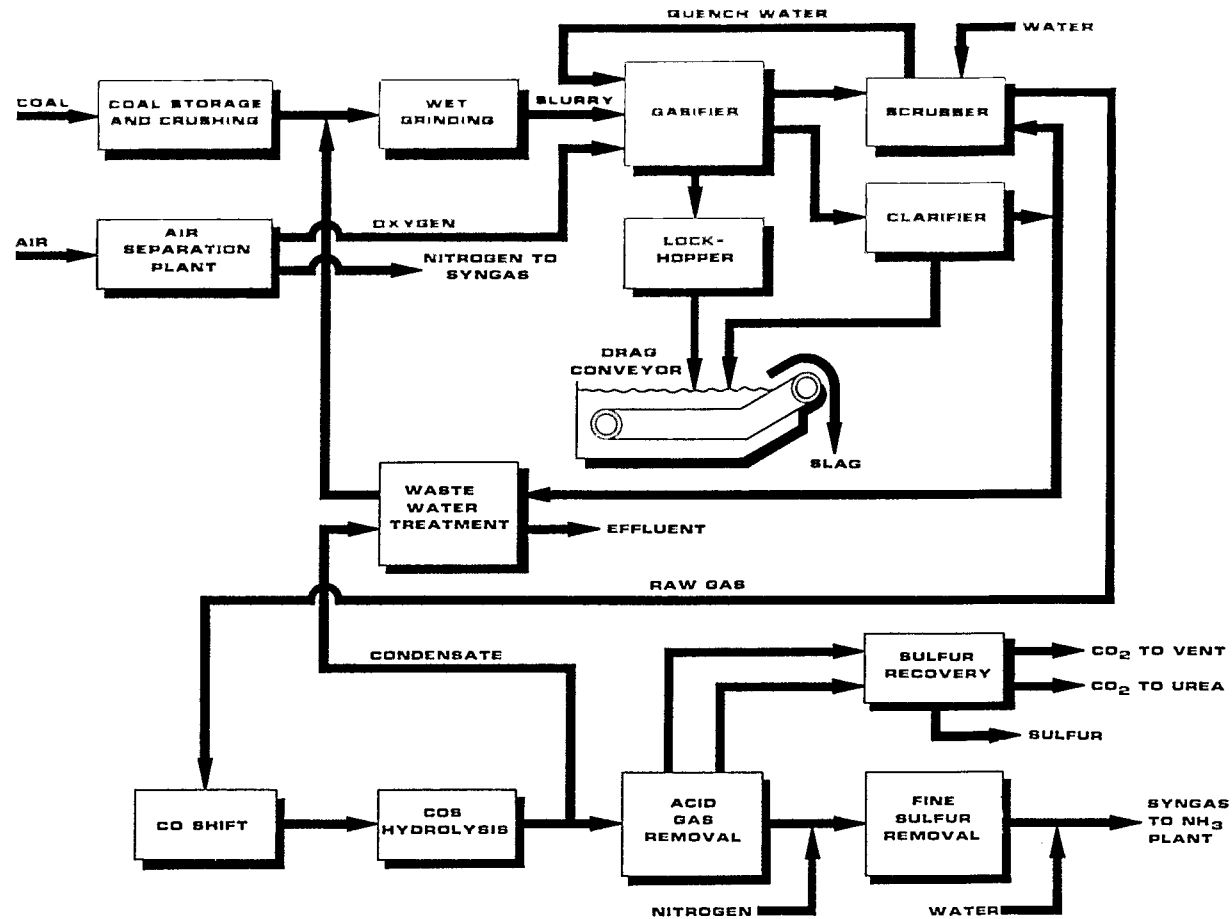
The objectives of the TVA Ammonia from Coal Project have been to obtain technical, economic, and environmental information and pass it on to the industry. The project solved numerous first-time-out plant problems in gasification and gas purification portions of the plant. Problems ranged from basic process chemistry, mechanical equipment, corrosion and erosion, instrumentation and controls, to environmental and occupational health and safety matters. Some specific problems solved were: slag removal from gasifier, slag removal from plant, liquid level sensing element problems in quench section of gasifier, metallurgy problems to avoid excessive abrasion in valving, pump seal water problems, problems in coal slurry charge pumps, solids buildup problems in both liquid and gas lines exiting gasifier, solid pluggage problems in gas line due to ammonium carbamate formation from reaction of ammonia and CO₂ in the gas stream, wastewater treatment problems involving (1) controlling and monitoring waste flow to wastewater treatment unit, (2) installing clarifier in gasifier blowdown to wastewater unit, (3) venting ammonia from stripper to atmosphere, and (4) substituting caustic for limestone in feed to ammonia stripper, sulfur in product gas caused by sulfur leak across exchanger requiring backwelding tubes and installing sulfur guard using spent CO shift catalyst as absorbent.

The facility capability now provides excellent and comprehensive test data on process performance with different coals and under varying conditions of operation. We have complied with State of Alabama gas and stream environmental emission permits. We have provided design and operational information and personnel training services to commercial installations at Tennessee Eastman plant at Kingsport, Tennessee, Cool Water plant, Daggett, California, and Ube Industries, Ltd., Ube City, Japan. All plants had good and speedy startups. We are currently assisting NASA on a project at Kennedy Space Center. We recently had ten fertilizer companies in for a 2-day meeting and we continue to have many individual company contacts. We have proven that producing ammonia from coal is technically viable when economics are right and have established that environmental and occupational health and safety aspects of producing ammonia from coal are manageable. We have established Muscle Shoals as a widely recognized major center for technical and economic information in coal gasification and gas purification technology.

A wide spectrum of information from our plant has been obtained and passed on to others as follows: On-line heat and material balance performance data using a state-of-the-art Texaco burner, specific gas purification data including transient studies on the COS hydrolysis and Selexol acid gas removal units, environmental data for wastewater and slag characterization, data on trace contaminants in the synthesis gas, gasifier refractory performance evaluations, water chemistry data on scale deposition in water circulation systems, erosion data on vessels, pipe, valves and fittings, and data on solids deposition problems in gas lines. Ammonia production has been achieved for extended periods at full rates. Successful contractual tests have been completed. These include the 20-day test in 1983 for Exxon on the bottoms material, the 20-day Utah coal run and the 10-day Illinois No. 6 coal run, both in 1984.

CONCLUSION

The ammonia from coal project will come to an end in 1985. The project has been successful in that good technology has been developed and demonstrated for producing ammonia from U.S. coals. Decisions about future construction of coal-based ammonia plants will be primarily based on comparative economics. The potential future uses of the facility relate more to synthetic fuels than to fertilizer. Some of these are: methanol coproduction in an integrated gasification combined cycle power plant; fuel cell testing, development and demonstration; and specific tests with different coals, catalyst systems, special processes, and equipment components. The plant stands ready as a backup test facility for commercial plants and we hope to be of assistance to industry in this manner.



TVA AMMONIA FROM COAL PROJECT

FIGURE 1

TABLE I
FEEDSTOCKS TESTED AT ACP

<u>Feedstock</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Ultimate Analysis, Weight %		
Carbon	69.4	70.2
Hydrogen	4.6	4.3
Nitrogen	1.6	1.3
Sulfur	2.8	0.4
Oxygen	8.2	14.9
Ash	13.3	5.4
Chloride	0.09	<0.1
HHV, BTU/lb	12,706	11,930
Ash softening point		
Reducing atmosphere		
Initial deformation	1,980	2,070
Softening point	2,100	2,120
Fluid point	2,220	2,150

TABLE II
TYPICAL GASIFIER PERFORMANCE

<u>Type of Feedstock</u>	<u>Utah Coal</u>	<u>Illinois #6 Coal</u>
Coal feed rate, tons/hr, dry	7.4	7.7
Oxygen feed rate, tons/hr, 98% O ₂	7.1	7.2
Coal slurry concentration, %	61.7	62.2
Gasifier temperature, °F	2500	2500
Gasifier pressure, psig	496	484
Gas production, MSCFH H ₂ + CO	382	424
Gas composition, vol %, dry		
H ₂	33.6	34.7
CO	44.2	45.4
CO ₂	20.5	17.8
H ₂ S	0.1	0.8
CH ₄	0.056	0.056
N ₂ + Ar	1.5	1.2
Carbon content of slag, %	20	21
Carbon conversion, %	97	95
Cold gas efficiency ^a , %	70	70
SOC ^b , SCF O ₂ /MSCF CO + H ₂	431	394

^a[BTU (68°F) gas/BTU feedstock] x 100 %.

^bSpecific Oxygen Consumption.

TABLE III
RAW GAS TO SHIFT CONVERSION

<u>Feedstock</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Flow rate, SCFM*	18,607	16,367
Temperature, °F	450	450
Pressure, psig	475	470
Major components, vol %		
Hydrogen	17.4	16.9
Carbon monoxide	22.7	22.1
Carbon dioxide	8.9	10.2
Argon	0.4	0.5
Nitrogen	0.2	0.3
Water vapor	50.0	50.0
Sulfur species, vol %		
Hydrogen sulfide	0.4	0.1
Carbonyl sulfide	150 ppmv	20 ppmv
Hydrocarbons, vol %		
Methane	<0.1	<0.1

*SCFM at 60°F and 29.92 in hg.

TABLE IV
SHIFTED GAS TO ACID GAS REMOVAL

<u>Feedstock</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Flow rate, SCFM*	12,472	10,593
Temperature, °F	60	58
Pressure, psig	435	425
Major components, vol %		
Hydrogen	56.8	52.5
Carbon monoxide	2.9	7.5
Carbon dioxide	38.4	38.3
Argon	0.7	0.9
Nitrogen	0.5	0.6
Water vapor	0.1	0.1
Sulfur species, vol %		
Hydrogen sulfide	0.6	0.1
Carbonyl sulfide	7 ppmv	10 ppmv
Hydrocarbons, vol %		
Methane	<0.1	<0.1

*SCFM at 60°F and 29.92 in hg.

TABLE V
PRODUCT GAS FROM ACID GAS REMOVAL

<u>Feedstock</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Flow rate, SCFM*	8,960	7,942
Temperature, °F	100	95
Pressure, psig	390	385
Major components, vol %		
Hydrogen	79.1	69.4
Carbon monoxide	3.2	9.4
Carbon dioxide	16.6	19.8
Argon	0.6	0.9
Nitrogen	0.5	0.5
Water vapor	-	-
Sulfur species, ppmv		
Hydrogen sulfide	<1	<1
Carbonyl sulfide		
Hydrocarbons, vol %		
Methane	<0.1	<0.1

*SCFM at 60°F and 29.92 in hg.

TABLE VI
OFF-GAS FROM ACID GAS REMOVAL

<u>Stream</u>	<u>Waste CO₂ To Sulfur Recovery</u>		<u>Product CO₂ To Sulfur Recovery</u>	
	<u>Illinois No. 6</u>	<u>Utah</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Flow rate, SCFM*	3,020	2,360	793	366
Temperature, °F	105	90	170	93
Pressure, psig	10	23	9	44
Major components, vol %				
Hydrogen	0.8	1.4	0.7	1.4
Carbon monoxide	1.9	1.7	1.5	1.5
Carbon dioxide	84.0	88.9	97.2	96.8
Nitrogen	10.8	7.4	-	-
Water vapor	0.2	0.2	-	-
Sulfur species, vol %				
Hydrogen sulfide	2.3	0.4	0.6	0.3
Carbonyl sulfide	33 ppm		13 ppm	
Hydrocarbons, vol %				
Methane	<0.1	<0.1	<0.1	<0.1

*SCFM at 60°F and 29.92 in hg.

TABLE VII

STREAMS FROM SULFUR RECOVERY

<u>Stream</u>	<u>CO₂ Vent To Atmosphere</u>		<u>CO₂ To Urea²Plant</u>		<u>Product Sulfur Cake</u>	
	<u>Illinois No. 6</u>	<u>Utah</u>	<u>Illinois No. 6</u>	<u>Utah</u>	<u>Illinois No.6</u>	<u>Utah</u>
Flow rate, SCFM*	4,401	4,612	798		520**	47.6**
Temperature, °F	100	90	90			
Pressure, psig	6	5	21			
Major components, vol %						
Hydrogen	1.0	0.8	0.9			
Carbon monoxide	<0.1	0.5	0.3			
Carbon dioxide	53.5	43.8	96.4			
Nitrogen	41.0	51.4	0.5			
Water vapor	4.5	3.5	1.9			
Sulfur species, ppmv						
Hydrogen sulfide		16.9 ppmv				
Carbonyl sulfide		2.2 ppmv				
Hydrocarbons, vol %						
Methane	<0.1		<0.1			
Moisture content of cake, %					73	66.4

*SCFM at 60°F and 29.92 in hg.

**Lb/hr, dry sulfur.

TABLE VIII
PRODUCT GAS TO AMMONIA PLANT

<u>Feedstock</u>	<u>Illinois No. 6</u>	<u>Utah</u>
Flow rate, SCFM*	11,472	10,079
Temperature, °F	580	580
Pressure, psig	380	385
Major components, vol %		
Hydrogen	46.3	41.0
Carbon monoxide	1.9	5.6
Carbon dioxide	9.7	11.8
Argon	0.4	0.5
Nitrogen	16.0	15.7
Water vapor	25.7	25.4
Sulfur species, ppmv		
Hydrogen sulfide	<.1	<.1
Carbonyl sulfide		
Hydrocarbons, vol %		
Methane	<0.1	<0.1

*SCFM at 60°F and 29.92 in hg.