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B. L. Bhatt[a]; T. C. Golden[a]; T. H. Hsiung[a]
[a] Air Products and Chemicals, Inc., Allentown, Pennsylvania

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Adsorptive Removal of Catalyst Poisons from Coal Gas for Methanol Synthesis

B. L. BHATT, T. C. GOLDEN, and T. H. HSIUNG
AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PENNSYLVANIA 18195-1501

Abstract

As an integral part of the liquid-phase methanol (LPMEOH) process development program, the present study evaluated adsorptive schemes to remove traces of catalyst poisons such as iron carbonyl, carbonyl sulfide, and hydrogen sulfide from coal gas on a pilot scale. Tests were conducted with coal gas from the Cool Water gasification plant at Daggett, California. Iron carbonyl, carbonyl sulfide, and hydrogen sulfide were effectively removed from the coal gas. The adsorption capacities of Linde H-Y zeolite and Calgon BPL carbon for $Fe(CO)_5$ compared well with previous bench-scale results at similar CO_2 partial pressure. Adsorption of COS by Calgon FCA carbon appeared to be chemical and nonregenerable by thermal treatment in nitrogen. A Cu/Zn catalyst removed H_2S very effectively. With the adsorption system on-line, a methanol catalyst showed stable activity during 120 h of operation, demonstrating the feasibility of adsorptive removal of trace catalyst poisons from the synthesis gas. Mass transfer coefficients were estimated for $Fe(CO)_5$ and COS removal which can be directly used for design and scale up.

INTRODUCTION

Since 1982, Air Products has been developing a liquid-phase process to produce methanol from synthesis gas under the sponsorship of the U.S. Department of Energy and the Electric Power Research Institute (*1*). Conventionally, the commercial catalytic conversion of synthesis gas to methanol is carried out in a gas-phase fixed-bed reactor. In the liquid-phase process, the catalyst is suspended in an inert liquid and synthesis gas is bubbled through it. The liquid phase provides an effective medium for heat removal and enables excellent temperature control, allowing isothermal operation of the highly exothermic methanol synthesis. High conversions per pass are achieved even with coal gas which contains a high amount of CO. However, the coal gas typically contains trace catalyst poisons like carbonyls and sulfides, which have to be removed from the feed prior to introduction in the reactor.

A study was conducted to screen adsorbents as temperature swing guard bed materials for removal of poisons from coal gas (2). Both equilibrium and kinetic adsorptive characteristics of various commercial adsorbents were measured for catalyst poisons including iron carbonyl, nickel carbonyl, hydrogen sulfide, carbonyl sulfide, and hydrochloric acid. A coal gas clean-up system was designed and built based on these data. The current study involved testing of the clean-up system at pilot scale with actual coal gasifier off-gas.

EXPERIMENTAL TECHNIQUES

Coal gas was filled in a tube trailer on 23 August 1988 after several volume purges at the Cool Water gasification plant in Daggett, California. Radian Corp. was subcontracted to conduct on-site measurements of impurities in the coal gas during the fill up. The coal feed at the time was low-sulfur Utah coal. The tube trailer was transported to Air Products in Allentown, Pennsylvania, where a laboratory pilot-scale unit consisting of a temperature swing adsorption system and an autoclave reactor was set up. A simplified schematic of the unit is given in Fig. 1.

Adsorption System

Four 0.75 in. o.d. stainless steel columns were used in series to remove the poisons from the coal gas. Column length varied from 1 to 4 ft, and each column was filled with a different adsorbent, specific for a particular catalyst poison. The coal gas from the tube trailer was compressed, and its flow of up to 10 L/min was controlled by using a mass flow controller. The flow direction was downward through the columns at ambient temperature (22–32°C). Each column had a number of sample ports along its length. Breakthrough curves for the various catalyst poisons were measured by monitoring the effluent impurity concentration as a function of time. A backpressure regulator maintained the system pressure up to 1000 psig. The regeneration was conducted by using a nitrogen flow of about 1 L/min, flowing upwards (countercurrent) through each column at 260°C.

Autoclave System

A stirred 300-cm^3 stainless steel (316 SS) autoclave was used as a reactor to conduct methanol synthesis. The clean coal gas from the adsorption system was compressed and fed to the heated autoclave which contained a slurry of catalyst and oil. Flow through the autoclave was controlled by using a mass flow controller. A backpressure regulator maintained up to

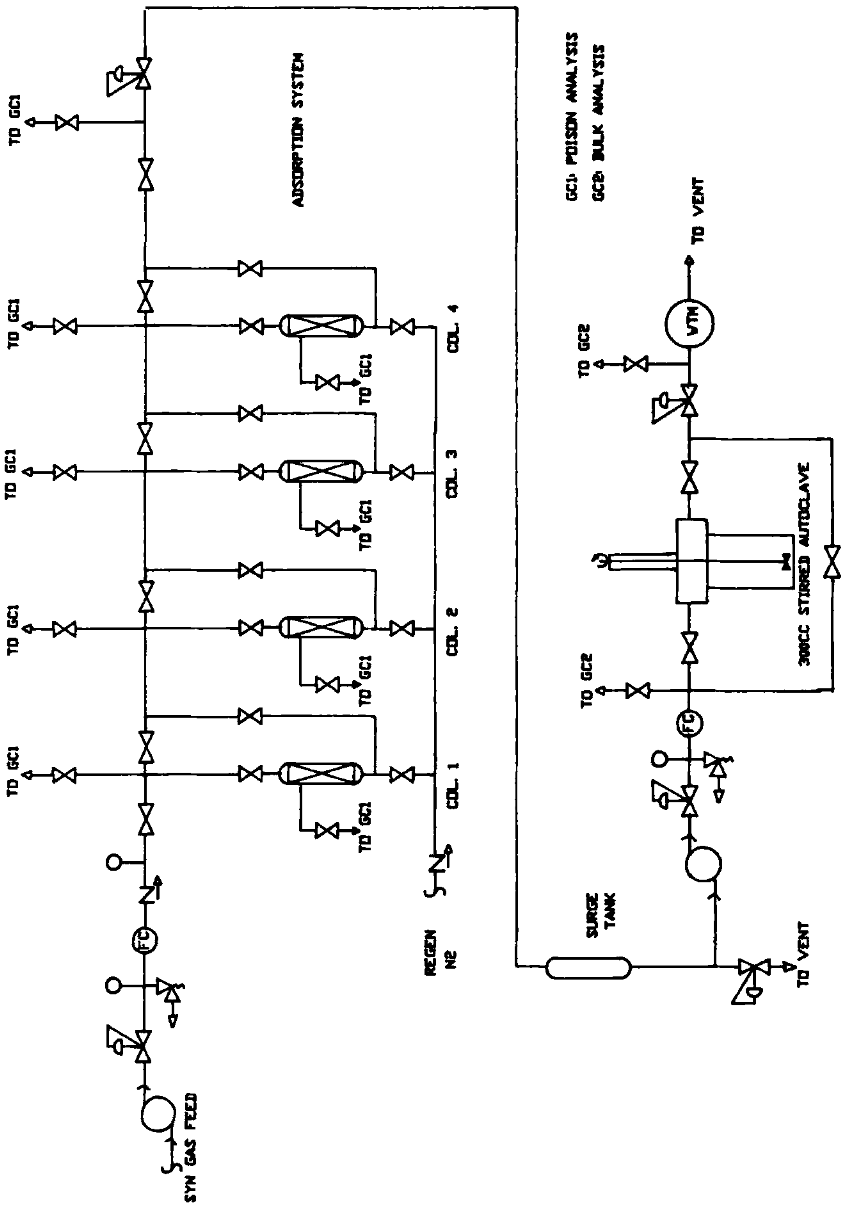

FIG. 1. Coal gas clean-up unit schematic.

1000 psig in the autoclave. The product was vented after sampling. A 1-gal surge tank was used between the adsorption unit and the autoclave system. The adsorption system was operated at a slightly higher flow rate (about 5%) than the autoclave system. The excess flow was vented through a backpressure regulator.

Analytical System

Gas analysis was conducted by using two on-line gas chromatographs (GCs). One was dedicated to poison analysis; the other was used for bulk components. The poison GC consisted of an electron capture detector (ECD) for iron and nickel carbonyl analysis with a detection limit of 0.005 ppmv and a photoionization detector (PID) for hydrogen sulfide and carbonyl sulfide analysis with a detection limit of 0.25 ppmv. The bulk components were analyzed by two thermal conductivity detectors (TCDs); one for CO, CO_2, CH_4, N_2, CH_3OH, C_2H_5OH, and CH_3OCH_3, and the other for H_2.

RESULTS AND DISCUSSION

Lab Test 1

The first test involved a study on the removal of $Fe(CO)_5$, $Ni(CO)_4$, COS, and H_2S from the Cool Water coal gas. The gas analysis (wet chemical/GC) during the fill up indicated on average about 11 ppmv COS, 30 ppmv H_2S, 0.14 ppmv $Fe(CO)_5$, and no $Ni(CO)_4$ (see Table 1). Wet chemical analysis before the coal gas clean-up study (February 1989) found no H_2S, about 8 ppmv $Fe(CO)_5$, and no $Ni(CO)_4$. GC analysis of the coal gas during the study (March 1989) indicated about 55 ppmv COS in addition to confirming results from the wet chemical analysis. While generation of $Fe(CO)_5$

TABLE 1
Trace Component Analysis for Cool Water Coal Gas[a]

Component (ppmv)	Wet chemical/GC analysis during filling (8/88)	Wet chemical analysis before poison study (2/89)	GC analysis during poison study (3/89)
COS	7–13	NA	55
H_2S	18–53	<0.2	ND
HCl	<0.022	<0.06	NA
$Fe(CO)_5$	0.14	8	7
$Ni(CO)_4$	0.01	<0.023	ND

[a] NA = not available, ND = not detected.

TABLE 2
Cool Water Coal Gas Clean Up Lab Test 1: Adsorption Beds[a]

Column	Adsorbent	Poison	Length (ft)	Weight (g)	Particle size
1	Cu/Zn catalyst	HCl, H_2S	1	79	1–3.35 mm crushed
2	Linde H-Y zeolite	$Fe(CO)_5$	1	38.6	1.6 mm diameter pellet
3	Calgon BPL carbon	$Ni(CO)_4$	1	29.6	1–3.35 mm powder
4	FCA carbon (with Cu/Cr oxide)	COS	4	141.5	0.55–1.4 mm powder

[a] The columns have 3/4″ o.d. × 0.049″ wall and are made of 316 SS.

could be expected, the apparent conversion of H_2S into COS by reaction with either CO or CO_2 beyond equilibrium can not be explained. About 7 ppmv of H_2S was hence added to the coal gas stream to evaluate the adsorbents for its removal. Bulk analysis of the coal gas indicated about 42.6% CO, 39.2% H_2, 17.3% CO_2, 0.4% N_2, 0.25% CH_4, and 0.17% Ar.

The columns were loaded up with fresh adsorbents as given in Table 2. The Cu/Zn catalyst in Column 1 was activated by using 2% H_2 in N_2 at 100 psig with temperature ramping (10°C/h) and held for 8 h at 200°C. The zeolite in Column 2 was dried by using N_2 at 260°C for about 12 h.

The operating parameters for each adsorption and regeneration are summarized in Table 3. All adsorption measurements were conducted at 450 psig inlet pressure (430 psig outlet) and ambient temperature (22–28°C). All regenerations were conducted by using 1 L/min nitrogen countercurrent (up) flow for each column. The regeneration temperature was about

TABLE 3
Cool Water Coal Gas Clean Up Lab Test 1

Run[a]	Columns on-line	Breakthrough information	Conditions	Comments
1	1, 2, 3, 4	1, 2, 3, 4	5 L/min for 140 h; 10 L/min for 15 h	
1R	1, 2, 3, 4		2–3 h at 260°C	
2	1, 2, 3, 4	1, 2, 4	5 L/min for 63 h	
2R	4		7 h at 260°C	
3	3, 4	3, 4	5 L/min for 16 h; 10 L/min for 11 h	
3R	1, 2, 3, 4		4 h at 260°C	
4	1, 3	1, 3	10 L/min for 14 h	+ H_2S
5	1, 2	2	10 L/min for 16 h	+ H_2S

[a] R = regeneration.

TABLE 4
Cool Water Coal Gas Clean Up, Lab Test 1

	Poison				
	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	COS	COS
Column	1	2	3	1	4
Total length (in.)	12	12	12	12	48
Adsorbent	Cu/Zn catalyst	H-Y zeolite	BPL carbon	Cu/Zn catalyst	FCA carbon
Cycle 1:					
Capacity (mmol/g)	0.02	0.19	0.64	0.19	0.56
Mass transfer zone (in.)	2	3.3	1.8	2.7	34
Sample port at (in.)	12	12	3	12	48
Syngas flow (L/min)	5	5	10	5	5
Cycle 2:					
Capacity (mmol/g)	0.005	0.19	0.41	0	0.13
Mass transfer zone (in.)	10.7	2.2	1.9	—	68
Sample port at (in.)	12	9	3	12	48
Syngas flow (L/min)	5	5	10	5	5
Cycle 3:					
Capacity (mmol/g)	0.006	0.19	0.29	0	0.019
Mass transfer zone (in.)	14.4	4	3.2	—	14
Sample port at (in.)	12	6	3	12	48
Syngas flow (L/min)	10	10	10	10	5

260°C. Capacity and mass transfer zone results for various adsorbents are given in Table 4.

Removal of Iron Carbonyl

The Cu/Zn catalyst (Column 1), which was designed for H_2S and HCl removal, showed significant capacity for $Fe(CO)_5$ (0.02 mmol/g at the process conditions) in the initial cycle. The breakthrough curves (given in Fig. 2) plot the concentration of $Fe(CO)_5$ as a function of on-stream time at inlet, outlet, and various ports in the column. From the breakthrough curve the mass transfer zone (MTZ) was calculated to be about 2 in. The capacity, however, was reduced to insignificant levels in the second and third cycle (see Table 4). This indicates that the removal of $Fe(CO)_5$ by the catalyst is chemical and nonregenerable thermally.

The H-Y zeolite (Column 2) had a capacity of about 0.19 mmol/g for $Fe(CO)_5$ at an inlet concentration of 8 ppmv with a 3.3 in. MTZ (see Fig. 3 for breakthrough curves) in the first cycle. As anticipated, the capacity of H-Y zeolite for $Fe(CO)_5$ remained the same in the second and third cycle, indicating the regenerability of the adsorbent. The zeolite capacity

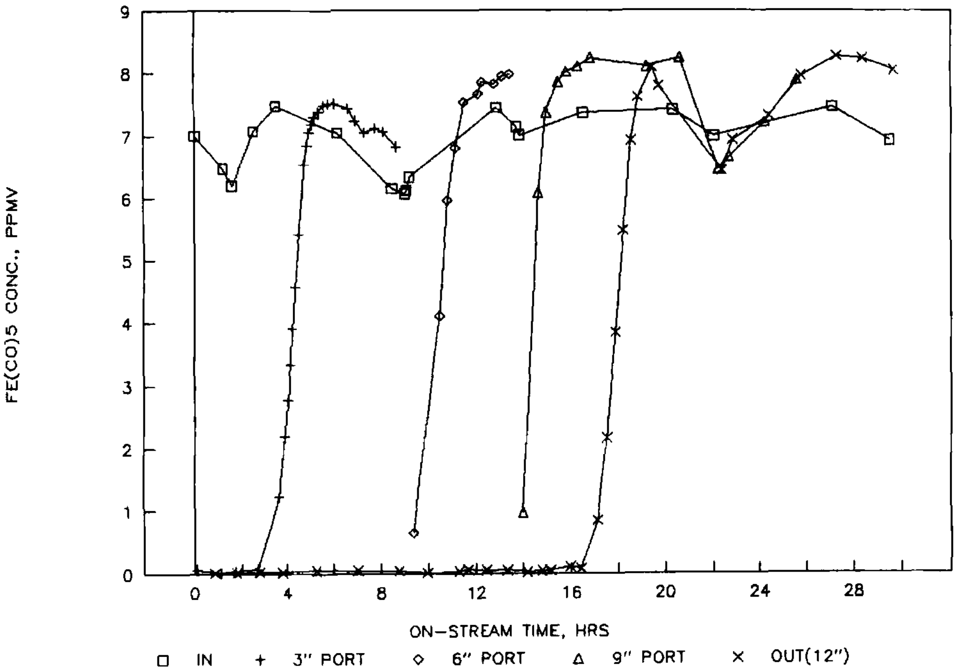

FIG. 2. Cool Water coal gas study—Lab Test 1. Cycle 1 for Cu/Zn catalyst (Column 1).

matches well with the capacity observed earlier at a similar CO_2 partial pressure (*2*).

The initial capacity of BPL carbon (Column 3) for iron carbonyl was calculated to be 0.64 mmol/g (see Fig. 4 for breakthrough curves). It dropped to 0.41 mmol/g in the second cycle and 0.29 mmol/g in the third cycle. The decline in BPL carbon's capacity was expected from previous experiments (*2*). The capacity also matches well with the capacity observed earlier at a similar CO_2 partial pressure.

Removal of Carbonyl Sulfide

The Cu/Zn catalyst (Column 1) showed significant capacity for COS (0.19 mmol/g) initially. The mass transfer zone (MTZ) was estimated to be 2.7 in. (see Fig. 5 for the breakthrough curves). However, the capacity was practically zero in subsequent cycles, indicating chemical reaction. Capacities of the zeolite (Column 2) and BPL carbon (Column 3) were insignificant for COS.

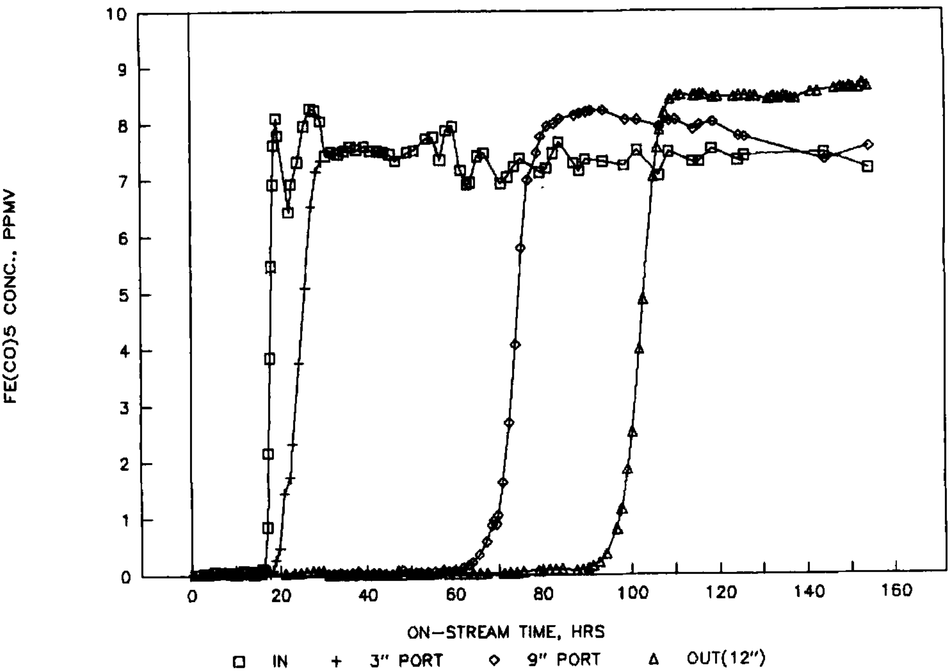

FIG. 3. Cool Water coal gas study—Lab Test 1. Cycle 1 for H-Y zeolite (Column 2).

The initial capacity of the FCA carbon (Column 4) for COS was higher than expected (0.56 mmol/g). However, its MTZ was quite long (see Fig. 6). Also, we observed significant fluctuations in the COS concentration during breakthrough. The COS concentration was lower in the morning following nightly shutdown, and it came back up during the day. Presumably, COS was being consumed by a slow chemical reaction during the shutdown which involved leaving the adsorbents under coal gas pressure. The capacity decreased substantially to 0.13 mmol/g in the second cycle. This was in contrast to the regenerability of FCA carbon observed in the bench-scale recirculating apparatus (*2*). Part of the adsorption probably occurs through a slow chemical reaction as indicated by the long MTZ and fluctuation in COS concentrations. Hence, much higher on-stream time in the pilot unit caused the loss of capacity. Even after a longer regeneration, the capacity reduced further to 0.019 mmol/g in the third cycle. We recommend investigation of different regeneration methods (e.g., use of steam) for FCA carbon as well as use of hot ZnO for COS removal.

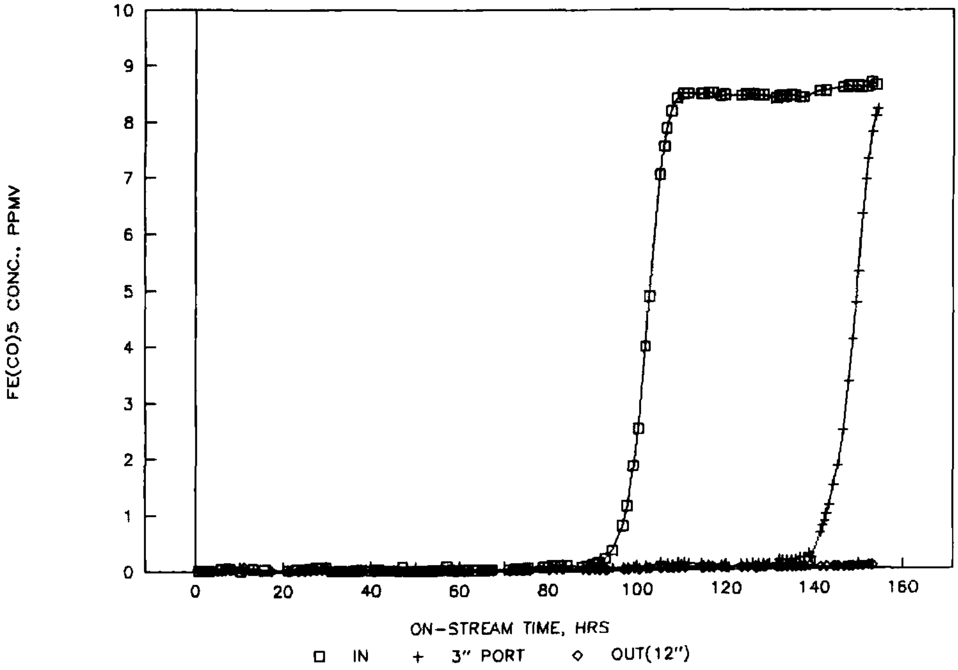

FIG. 4. Cool Water coal gas study—Lab Test 1. Cycle 1 for BPL carbon (Column 3).

Removal of Hydrogen Sulfide

Since the Cool Water gas lost almost all of its original H_2S before the study, about 7 ppmv of H_2S was added to the coal gas stream to evaluate the adsorbents for its removal. The Cu/Zn catalyst appeared to be removing H_2S adequately. In 30 h on-stream with 7 ppmv H_2S added, we did not see any H_2S breakthrough at the sample port closest (3 in.) to the inlet. The minimum H_2S capacity of the Cu/Zn catalyst calculated from the 3-in. port is 0.13 mmol/g.

Lab Test 2

In addition to studying the poisons removal, we also monitored the performance of a methanol catalyst downstream of the adsorbents during the second test. This would confirm the effectiveness of the adsorption system. The columns were loaded with fresh adsorbents similar to the first lab test except that the H-Y zeolite and BPL carbon columns were short loaded (0.5 ft) to get quicker cycles (see Table 5). The activation of Cu/Zn catalyst in Column 1 and drying of the zeolite in Column 2 were also

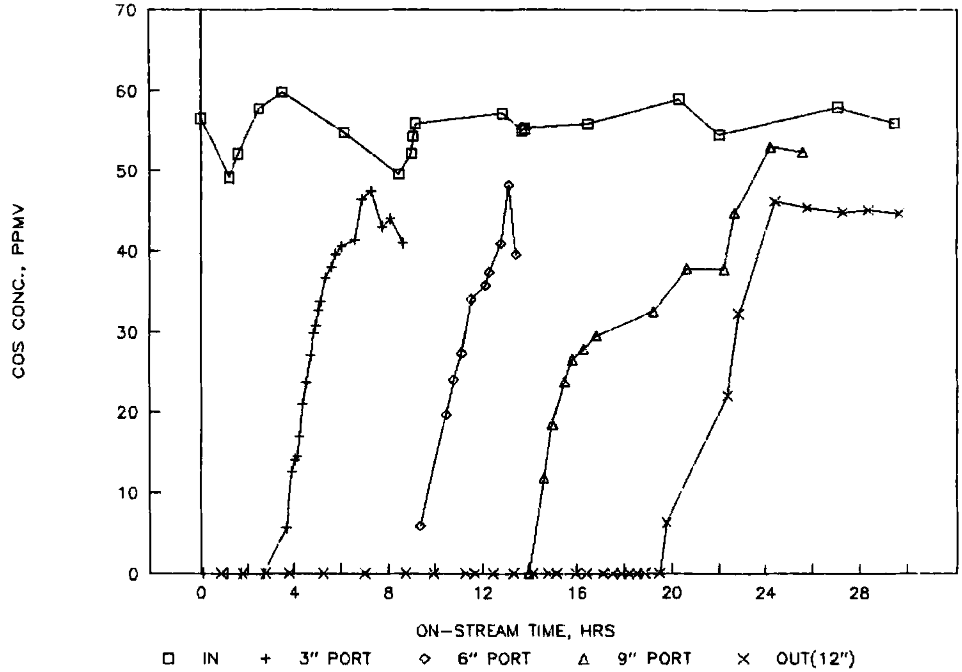

FIG. 5. Cool Water coal gas study—Lab Test 1. Cycle 1 for Cu/Zn catalyst (Column 1).

carried out similar to the first test. The autoclave was loaded with about 50 g of a methanol catalyst powder and 115 g of a paraffinic oil. The catalyst slurry was activated in the autoclave by using 2% H_2 in N_2 at 100 psig with temperature ramping.

Removal of Iron Carbonyl

In the first cycle the capacity of H-Y zeolite for iron carbonyl was found to be significantly lower than the first test (0.09 vs 0.19 mmol/g). Perhaps the drying wasn't complete. The capacity increased after regeneration (0.14 mmol/g). However, it was still lower than the first test. Higher ambient temperature may be partly responsible.

Removal of Carbonyl Sulfide

This test confirmed nonregenerability of FCA carbon (for COS) using N_2 at 260°C. The capacity dropped from 0.7 mmol/g in the first cycle to 0.09 mmol/g in the second cycle.

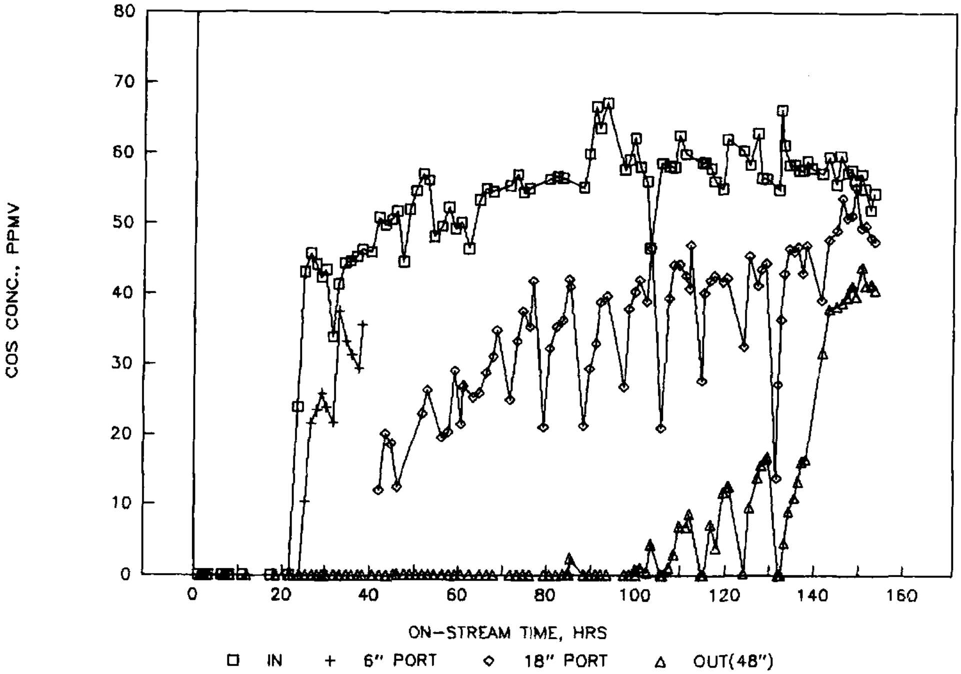

FIG. 6. Cool Water coal gas study—Lab Test 1. Cycle 1 for FCA carbon (Column 4).

Removal of Hydrogen Sulfide

With about 7 ppmv H_2S added to the coal gas, no H_2S breakthrough was observed in Column 1 (Cu/Zn catalyst) during 100 h of H_2S injection. The minimum H_2S capacity of the Cu/Zn catalyst calculated from the 3-in. port is 0.37 mmol/g.

TABLE 5
Cool Water Coal Gas Clean Up Lab Test 2: Adsorption Beds[a]

Column	Adsorbent	Poison	Length (ft)	Weight (g)	Particle size
1	Cu/Zn catalyst	HCl, H_2S	1	81	1–3.35 mm crushed
2	Linde H-Y zeolite	$Fe(CO)_5$	0.5	19.7	1.6 mm diameter pellet
3	Calgon BPL carbon	$Ni(CO)_4$	0.5	15.5	1–3.35 mm powder
4	FCA carbon (with Cu/Cr oxide)	COS	4	141	0.55–1.4 mm powder

[a] The columns have 3/4" o.d. × 0.049" wall and are made up of 316 SS.

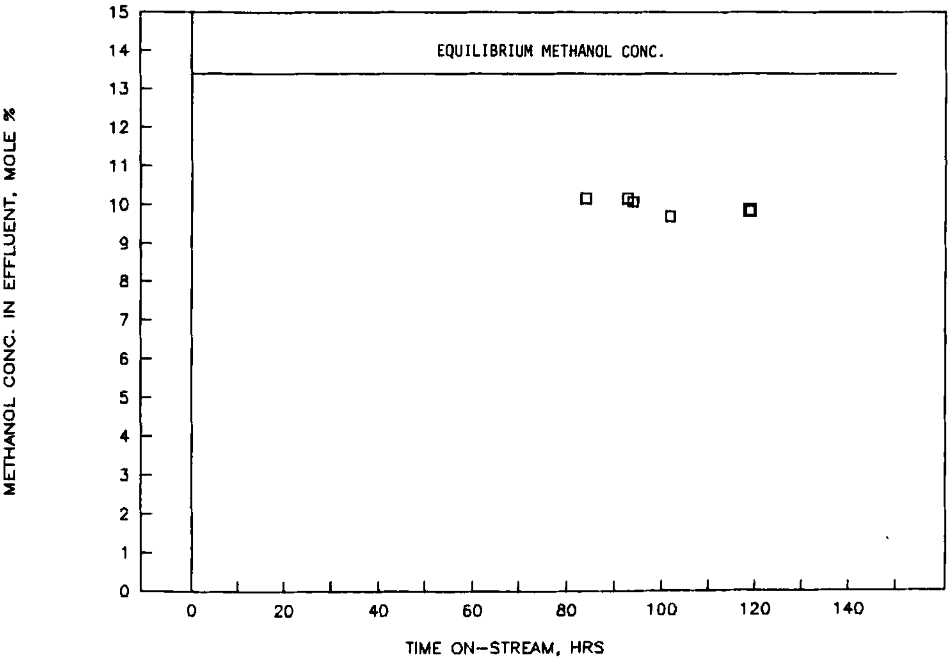

FIG. 7. Lab Test 2 (Cool Water coal gas): 250°C, 750 psig at 5000 ghsv.

Methanol Catalyst Performance

The autoclave was operated at 5000 sL/kg·h (where sL = standard liter), 750 psig, and 250°C for about 120 h. Initially, a scatter in the product analysis data was observed, probably due to condensation of product methanol in a backpressure regulator (BPR). Additional heat tape was installed on the BPR with individual temperature control. Raising the BPR temperature from 60 to 140°C eliminated the problem. The expected methanol concentration of about 10% was observed in the effluent after about 96 h on-stream (see Fig. 7). This is below the thermodynamic equilibrium concentration of 13.4%. The methanol production appeared to be stable.

DESIGN CONSIDERATIONS

Estimation of Henry's Law Constant

The Henry's law constants for adsorption were calculated based on data from Lab Test 1 by using the following relationship, assuming a linear isotherm:

$$\text{Henry's law constant } (K_H) = \frac{\text{adsorbent capacity}}{\text{inlet impurity concentration } (y_0)}$$

The y_0 value was 7 ppmv for $Fe(CO)_5$ and 55 ppmv for COS. The K_H estimates are given in Table 6. Based on these constants, the adsorption columns can be scaled up by using the following mass balance equation:

$$t_m = \frac{(L)(BD)(K_H)}{G}$$

where t_m = time to midpoint of breakthrough (h)
L = length of bed (ft)
BD = bulk density of adsorbent (lb/ft^3)
K_H = Henry's law constant (lb·mol/lb)
G = gas flow rate (lb·mol/ft^2·h)

Estimation of Mass Transfer Coefficients

The mass transfer coefficients were calculated for data from Lab Test 1 by using Rosen's solution (*3*):

$$t_i = t_m - (2)(X)(t_m/K)^{1/2}$$

where t_i = time to initial breakthrough (h)
t_m = time to midpoint of breakthrough (h)
K = mass transfer coefficient (h^{-1})
X is a factor that takes into account the initial and final impurity concentration as given by

$$X = \text{erfc}^{-1}(2y/y_0)$$

where y = initial impurity concentration in outlet
y_0 = final impurity concentration in outlet (same as inlet impurity concentration)

The y value was 0.1 ppmv for $Fe(CO)_5$ and 1 ppmv for COS. The corresponding Xs were calculated to be 1.86 for $Fe(CO)_5$ and 1.49 for COS. The estimated mass transfer coefficients are given in Table 6. Rosen's solution given above can be used to scale up the adsorption columns.

TABLE 6
Design Estimations, Lab Test 1

	Poison				
	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	COS	COS
Adsorbent	Cu/Zn catalyst	H-Y zeolite	BPL carbon	Cu/Zn catalyst	FCA carbon
Cycle 1:					
Henry's law constant K_H (lb·mol/lb)	2.9	27.1	91.4	3.5	10.2
Mass transfer coefficient K (h^{-1})	110.7	7.6	5.9	31.3	0.6
Cycle 2:					
Henry's law constant K_H (lb·mol/lb)	0.7	27.1	58.6	0	2.4
Mass transfer coefficient K (h^{-1})	—	16.2	8.0	—	—
Cycle 3:					
Henry's law constant K_H (lb·mol/lb)	0.9	27.1	41.4	0	0.4
Mass transfer coefficient K (h^{-1})	—	7.6	4.6	—	—

Applications

The results shown in Table 6 indicate that the H-Y zeolite is the preferred adsorbent for $Fe(CO)_5$ with a stable capacity and a reasonable mass transfer coefficient of about 7.6/h. In comparison, BPL carbon has unstable capacity and lower mass transfer coefficient. The Cu/Zn catalyst, in addition of being useful for H_2S removal, may have some practical use for both $Fe(CO)_5$ and COS removal with small one-time capacity. FCA carbon may not be useful for COS removal because of regeneration difficulties and an extremely low mass transfer coefficient (0.6 /h).

SUMMARY AND CONCLUSIONS

An adsorption system designed to clean up coal gas for the LPMEOH process was successfully tested for Cool Water coal gas. Iron carbonyl, carbonyl sulfide, and hydrogen sulfide were removed from the coal gas. The effectiveness of the adsorption system was confirmed by measuring the methanol catalyst performance downstream.

The H-Y zeolite showed stable capacity for $Fe(CO)_5$ through three adsorption/regeneration cycles (0.19 mmol/g). All adsorption measurements were made at ambient temperature (20–25°C) with 7 ppmv $Fe(CO)_5$ and 450 psig pressure from a gas stream containing 43% CO, 39% H_2, 17% CO_2, and small amounts of N_2, CH_4, and Ar. In contrast, BPL carbon had a higher but unstable capacity for $Fe(CO)_5$ (reduced from 0.64 mmol/g in Cycle 1 to 0.29 mmol/g in Cycle 3). The capacities for both adsorbents agreed well with those observed in a recirculating apparatus at a similar CO_2 partial pressure.

COS appeared to be chemisorbed on FCA carbon. The capacity was nonregenerable by hot nitrogen purge at 260°C. This is in contrast with the earlier results from the recirculating apparatus where the on-stream times were much lower. We recommend investigation of different regeneration methods (e.g., use of steam) for FCA carbon as well as use of hot promoted ZnO for COS hydrolysis and removal.

The Cu/Zn methanol catalyst appeared to remove H_2S adequately. With about 7 ppmv of H_2S added to the coal gas stream, no breakthrough was observed during 100 h of H_2S injection.

The performance of a methanol catalyst for methanol synthesis was monitored downstream of the adsorption system. At 5000 sL/kg·h, 750 psig, and 250°C, the expected concentration of about 10% methanol was observed in the effluent with the cleaned-up Cool Water gas. No significant deactivation was evident during the 120 h on-stream.

Mass transfer coefficients were estimated for $Fe(CO)_5$ and COS removal using different adsorbents. The results are directly applicable for design and scale up of the adsorption columns.

FUTURE WORK

The clean-up system needs to be tested for other coal gases. Testing the system with live coal gas at gasifier sites would further demonstrate the usefulness of the adsorption system.

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