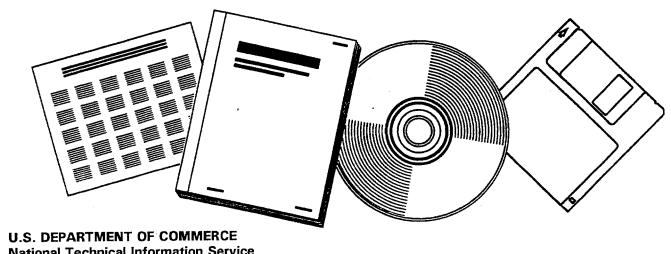# LIQUID PHASE METHANOL LAPORTE PDU: MODIFICATION, OPERATION, AND SUPPORT STUDIES. TASK 3.4, ADSORBENT EVALUATION FOR REMOVAL OF CATALYST POISONS FROM SYNTHESIS GAS

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ALLENTOWN, PA

28 SEP 1990

FOSSIL

LIQUID PHASE METHANOL LAPORTE PDU: MODIFICATION,
OPERATION, AND SUPPORT STUDIES

Topical Report

Task 3.4: Adsorbent Evaluation for Removal of Catalyst Poisons
From Synthesis Gas

September 28, 1990

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For
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

and

Chem Systems, Inc.
Tarrytown, New York

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MODIFICATION, OPERATION, AND SUPPORT STUDIES

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Task 3.4:   Adsorbent Evaluation for Removal of Catalyst Poisons
From Synthesis Gas

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DISCLAIMER

Abstract

Operation of a methanol synthesis reactor in the liquid phase requires an efficient catalyst poison removal system. A number of commercially available adsorbents were screened for their ability to remove the following methanol catalyst poisons: $Fe(CO)_5$, $Ni(CO)_4$, COS, H_2S, and HCl. Adsorption isotherms were measured at various carrier gas pressures and two temperatures on several adsorbents, including active carbons, zeolites, alumina, silica gel, metal oxide impregnated active carbons, metal oxide promoted zinc oxide, metal oxide promoted alumina, and spent methanol catalyst. By monitoring the approach to equilibrium as a function of time, mass transfer coefficients for the adsorption of these trace impurities were also determined. From this adsorbent screening, the preferred adsorbent for removal of each catalyst poison was identified. The equilibrium and kinetic adsorptive properties for each poison/adsorbent system were used to design a poison removal scheme. This design will be tested in a pilot unit using coal gas from a commercial gasifier.

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INTRODUCTION

Traditionally, catalytic conversion of synthesis gas (mixtures of CO and H_2) to chemicals or fuels is carried out in a fixed bed reactor. In 1975, Chem Systems Inc. began to investigate the possibility of producing methanol from synthesis gas in a liquid phase reactor (1). Air Products began research to further develop this technology in 1981. In this scheme, the catalyst is suspended in an inert liquid, typically a hydrocarbon oil. The reactor may be designed as an ebullated bed using a particulate catalyst, or may be designed as a slurry reactor with a catalyst powder. In either case, the synthesis gas bubbles up through the reactor and is converted to methanol. The methanol leaves the reactor as a vapor with the unreacted gas. Because of the large heat sink provided by the liquid phase process, heat removal is greatly facilitated and reactor temperature control is quite straightforward. The catalyst zone is essentially isothermal, and an operating temperature can be selected that is low enough to avoid the equilibrium constraints of gas phase reactors, yet high enough to produce a substantial rate of reaction. Since temperature rise is less of a constraint, it is possible to achieve a high conversion of synthesis gas to methanol on each pass through the reactor as well as reduce catalyst deactivation rates.

The copper-based, low-temperature catalyst used for methanol synthesis is, however, very susceptible to poisons. Sulfur, halogens, and trace metals, even in small quantities, quickly and permanently deactivate the catalyst. Therefore, it is essential that the feed synthesis gas, whether it be derived from coal or natural gas, is free from such trace components. This is

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necessary for either gas phase or liquid phase systems – these poisons impacting catalyst pellets or powder equally.

Due to the importance of catalyst poison removal, the current investigation was initiated. Table 1 shows typical impurities and their concentrations in synthesis gas generated from coal gasification (refer to Appendix C for more detailed information). This investigation involved measuring both the equilibrium and kinetic adsorptive characteristics of various commercial adsorbents for a variety of methanol catalyst poisons including $Fe(CO)_5$, $Ni(CO)_4$, H_2S, COS, and HCl. From these data, a catalyst removal system was designed. This design was tested at the pilot unit scale with actual coal gasifier off-gas.

OBJECTIVE:

The objective of this investigation was to gather adsorption data on the trace removal of methanol catalyst poisons $Fe(CO)_5$, $Ni(CO)_4$, H_2S, COS, and HCl using various commercial adsorbents. These data were then used to design a catalyst poison removal system which was tested with actual coal gasifier off-gas. The pertinent data needed to design such a system include 1) the equilibrium capacity of the chosen adsorbent for the given trace impurity and the shape of the adsorption isotherm, 2) the length of the mass transfer zone (MTZ) required for the removal of the trace compound, 3) the interactions that exist between individual trace compounds and the carrier gas which effect adsorption equilibrium and MTZ lengths, and 4) the ease and effect of regeneration on the spent adsorbents.

TABLE 1
MAJOR TRACE CONTAMINANTS IN LPMEOH SYNGAS FEED

Trace Component	Design Concentration, ppmv Adsorber Feed Limit	Catalyst Design Limit	Turbine Fuel Gas Specs., ppmv
Sulfur Compounds*			
H_2S	5		
COS	10		
Total Sulfur	15	0.06	
Halides			
Chloride	20		<10
Fluoride	5		
Total Halides		0.01	
Hydrocarbons			
Ethylene, Benzene and Other Unsaturates	2	300	
Acetylene	1	5.0	
Nitrogen Compounds			
NH_3	5	10.0	
NO_x	0.001	0.1	
HCN	6	0.01	
Oxygen		1500	
Water	0-1500		
Selexol (polyethylene glycol dimethyl ether)	0.02**		
Formate	49		
Iron, as $Fe(CO)_5$	5	0.01	0.1
Nickel, as $Ni(CO)_4$	1	0.01	0.1

*Much higher levels have been reported. Limit set based on apparent economic operating range of guard bed materials.

**Based on a vapor pressure of 0.0007 mm Hg at 77°F, and assuming no entrainment of liquid.

SUMMARY AND CONCLUSIONS:

1. Seven adsorbents including active carbons, silica gel, alumina, H-Y zeolite, and spent methanol catalyst were screened for $Fe(CO)_5$ adsorption. Table 2 lists these adsorbents along with some pertinent properties. The $Fe(CO)_5$ adsorption capacity of the adsorbents decreased in the order: active carbon > H-Y zeolite > silica gel > alumina > spent methanol catalyst.

2. The effect of temperature on $Fe(CO)_5$ adsorption was investigated on adsorbents H-Y zeolite and BPL carbon. It was determined that the effect of temperature on $Fe(CO)_5$ adsorption is quite marked. The apparent heat of $Fe(CO)_5$ adsorption from 40 psig carrier (73% CO_2/70% N_2/1% CO) on H-Y at low surface coverage is about 13 kcal/mole, while that value for BPL is about 20 kcal/mole. These high heats of adsorption indicate that $Fe(CO)_5$ capacity can be significantly enhanced by reducing the adsorption temperature. In addition, the apparent heat of $Fe(CO)_5$ adsorption on both H-Y and BPL carbon decreased as surface coverage increased, indicative of adsorbent heterogeneity.

3. The effect of carrier gas composition on $Fe(CO)_5$ adsorption was also investigated. It was determined that the presence of CO_2 in the carrier gas stream produced reductions in $Fe(CO)_5$ capacity. At 100°F and 40 psig total pressure, the equilibrium capacities of BPL and H-Y at 5 ppm $Fe(CO)_5$ were reduced 30% and 50% respectively as the carrier gas composition was changed from 95% N_2/5% CO to 73% CO_2/26% N_2/1% CO.

TABLE 2

Physical Properties of Adsorbents for $Fe(CO)_5$ Adsorption

Adsorbent	Manufacturer	(m^2/g) Surface Area	(lbs/ft^3) Bulk Density	(A) Average Pore Diameters
BPL Carbon	Calgon	1100	30.0	20
PCB Carbon	Calgon	1200	27.4	15
CAL Carbon	Calgon	1000	25.0	25
Silica Gel, Grade 40	Davison	750	46.0	22
Activated Alumina, S-100	Alcoa	340	45.0	60
Methanol Catalyst, EPJ-19	United Catalysts	100	80.0	–
H-Y Zeolite	Linde	900	42.0	10

4. The effect of thermal regeneration on $Fe(CO)_5$ adsorption was studied because the $Fe(CO)_5$ adsorption capacities of BPL and H-Y are too low for throw-away application. Thermal regeneration of BPL in N_2 at 250°F after $Fe(CO)_5$ adsorption showed that 25% of the adsorption capacity was lost after regeneration. On the other hand, H-Y zeolite showed the same percentage of $Fe(CO)_5$ after three adsorption/regeneration cycles.

5. The effect of carrier gas pressure on $Fe(CO)_5$ adsorption was also studied. As the carrier gas pressure increased from 40 to 90 psig, the $Fe(CO)_5$ capacities of both BPL and H-Y were reduced. For BPL, as the carrier gas pressure increased from 40 to 90 psig, the $Fe(CO)_5$ capacity at 75°F and 5 ppm was reduced by 55%. The corresponding reduction in H-Y capacity was 65%.

6. A mixed Langmuir approach was used to estimate the $Fe(CO)_5$ capacity on H-Y. This approach underpredicted the $Fe(CO)_5$ capacity on H-Y by approximately 40%, indicating that using the mixed Langmuir theory to estimate adsorption capacities at higher carrier gas pressure will give conservative estimates of capacity.

7. Adsorption of trace $Ni(CO)_4$ was measured on BPL and H-Y. The capacity for $Ni(CO)_4$ on both adsorbents is significantly less than that for $Fe(CO)_5$. From 40 psig carrier (95% N_2/5% CO) at 75°F and 1 ppm equilibrium concentration, the $Ni(CO)_4$ capacities are 2.7 and 3.4 times lower than those for $Fe(CO)_5$ for BPL and H-Y, respectively.

8. The effect of temperature on $Ni(CO)_4$ adsorption on BPL and H-Y was investigated. As in the case of $Fe(CO)_5$ adsorption, the apparent $Ni(CO)_4$ heat of adsorption is quite large, about 17 and 12 kcal/mole at low surface coverage for BPL and H-Y, respectively. This indicates that $Ni(CO)_4$ capacity can be enhanced significantly by reduction in adsorption temperature. Also, each adsorbent demonstrates energetic heterogeneity with respect to $Ni(CO)_4$ adsorption as noted by the decrease in apparent heat of adsorption with increasing surface coverage.

9. The effect of carrier gas pressure on $Ni(CO)_4$ adsorption was investigated. Increasing the carrier gas pressure from 40 to 90 psig at 75°F caused a decrease in $Ni(CO)_4$ capacity. The $Ni(CO)_4$ capacity of BPL at 1 ppm decreased by a factor of 4 as the carrier gas pressure increased from 40 to 90 psig. This decrease is larger than that noted with $Fe(CO)_5$ adsorption which is expected since $Fe(CO)_5$ is more strongly adsorbed than $Ni(CO)_4$.

10. Thermal regeneration studies on $Ni(CO)_4$ adsorption on BPL carbon showed that regeneration in N_2 at 250°F was sufficient to completely restore the $Ni(CO)_4$ capacity.

11. The adsorption of trace COS was measured on eight different adsorbents at 75°F from 90 psig carrier. These adsorbents included BPL, H-Y, various metal oxide loaded carbons, a metal oxide promoted alumina, a metal oxide promoted zinc oxide, and spent methanol catalyst. The adsorption capacities for those adsorbents decrease in the order: FCA carbon (copper oxide/chromium oxide loaded carbon) > spent methanol

catalyst > BPL > H-Y. Both adsorbents with high COS capacity contain copper.

12. It was determined that FCA carbon could be regenerated in N_2 at 500°F to restore its COS capacity.

13. The apparent heat of COS adsorption is -13 kcal/mole at low surface coverage, indicating that adsorption temperature will have a large effect on COS capacity. The reduction in heat of adsorption with increasing surface coverage denotes adsorbent heterogeneity.

14. Nine adsorbents were screened for trace H_2S adsorption at 75°F and 90 psig. The adsorbents screened include two zeolites, active carbon, three impregnated carbons, two spent methanol catalysts, and a promoted zinc oxide. All adsorbents that contain copper demonstrate high H_2S capacity. The capacity of these materials decrease in the order: BASF S3-85 > EPJ-19 > FCA > desulf 12. The impregnated carbons, FCA and desulf 12, are steam regenerable, while the spent methanol catalysts, BASF S3-85 and EPJ-19, would be throw-away adsorbents.

15. Removal of COS and H_2S with zinc oxide at elevated temperature was investigated. Using HTZ-4, an activated zinc oxide from Haldor Topsoe, at 400°F and 90 psig, the H_2S capacity was determined to be -3.0 mmole/g. In addition, hydrolysis of COS occurred readily at these conditions. The appeal of this system for H_2S and COS removal is that it is a throw-away system, and the COS capacity is significantly higher than that noted for ambient temperature systems.

16. Seven adsorbents were screened for trace HCl adsorption at 75°F and 90 psig. The adsorbents screened include H-Y, BPL, metal oxide loaded carbons, spent methanol catalysts, and a metal oxide promoted alumina. The capacity of the spent methanol catalyst, S3-85, is highest followed by FCA carbon. The adsorption capacity of S3-85 at 5 ppm is 7.4 mmole/g which is sufficient for a throw-away adsorbent.

17. The results of adsorbent screening have led to a conceptual low temperature adsorption poison removal design. The first adsorbent bed would contain spent methanol catalyst to adsorb H_2S and HCl in a throw-away system. The next bed would contain H-Y for $Fe(CO)_5$ removal, followed by BPL for $Ni(CO)_4$ removal, and finally FCA carbon for COS removal. The H-Y, BPL, and FCA sections are thermally regenerable at 500°F. This design will be tested at the pilot unit scale with actual coal gasifier off-gas.

PATENT SITUATION:

To our best knowledge, there are no patentable concepts forthcoming from this work. All adsorbent materials investigated are commercially available and the process cycle is either conventional temperature swing adsorption (TSA) or throw-away. Nonetheless, the poison removal designs may contain patentable ideas, particularly with respect to the preferred sequence of adsorbents for efficient poisons removal.

SAFETY:

The primary hazard associated with this project is the toxic nature of the catalyst poisons. $Fe(CO)_5$, $Ni(CO)_4$, H_2S, COS, and HCl have TLV's of 0.1, 0.05, 10, 10, and 5 ppm, respectively. In addition, $Ni(CO)_4$ is a suspected carcinogen. In order to avoid exposure to these compounds, a number of precautions were taken: 1) placing the recirculating adsorption apparatus in a walk-in hood, 2) equipping the system with a low pressure pump shut-off in case of a system leak, 3) the poison concentration and total gas volume were kept low, 4) all vent lines in the system containing the poisons were scrubbed before venting in the hood, and 5) in all $Ni(CO)_4$ experiments, an air-line respirator was employed.

FUTURE PROGRAMS:

The results of this work will be used to design a poisons removal pilot unit, which will test the design concept for removal of catalyst poisons from coal gasifier off-gas. The pilot unit test will investigate interactions, if any, between catalyst poisons and adsorbent deactivation rates.

ACKNOWLEDGMENTS:

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EXPERIMENTAL APPARATUS AND PROCEDURES:

Equilibrium and kinetic adsorption measurements were measured volumetrically in a recirculating adsorption apparatus (Figure 1). The unit had previously been used to screen adsorbents for landfill gas pretreatment, and was modified considerably for these experiments (2). The recirculating adsorption apparatus was used because it offers a number of advantages over measuring adsorption capacities and kinetics by breakthrough experiments. Since the MTZ for removal of trace impurities is long, breakthrough experiments require a large volume of gas and a long time for complete breakthrough to occur. In addition, equilibrium capacity for only one concentration can be obtained at the conclusion of the experiment. The recirculating apparatus, on the other hand, requires a minimal amount of gas which is highly desirable due to the toxicity and carcinogenicity of the impurities studied. A complete isotherm can be measured in the span of a few days and by monitoring the approach to equilibrium as a function of time, mass transfer coefficients can be obtained. From these mass transfer coefficients, MTZs can be calculated. Hence, the recirculating adsorption apparatus is very economical with respect to time required for data generation and gas consumption.

The recirculating adsorption apparatus is primarily constructed of stainless steel 1/4 inch tubing and a Teflon diaphragm pump. The Teflon pump was chosen because it exhibits little adsorption affinity for the impurities studied. Due to the toxicity of the impurities studied, the recirculating apparatus and all gas supplies were located in a walk-in hood. Poison gas blends are equipped with a nitrogen purge captured vent flammable gas regulator. An ASCO solenoid valve (normally closed) is located on the feed line. It is configured to close in the event of a hood or electrical failure.

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