

**THE LUBRICITY PROPERTIES OF JET FUEL  
AS MEASURED BY THE BALL-ON-CYLINDER LUBRICITY EVALUATOR**

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**ABSTRACT**

In recent years the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. Unfortunately these processes remove the compounds that are responsible for a fuel's inherent lubricity. As a result, fuel lubricated engine components are experiencing greater wear and mechanical failure. The Ball-on-Cylinder Lubricity Evaluator (BOCLE) was developed to predict a fuel's tendency to cause lubricity related problems. This paper discusses the influence of trace polar species on lubricity, the use of additives to increase lubricity, changes in a fuel's lubricity during storage, and inadequacies of the BOCLE. Finally, a suggested long term solution to lubricity problems by hardware modifications will be discussed.

**INTRODUCTION**

The incidence of lubricity related problems in commercial and military jet aircraft has increased over the past twenty years. This is a result of the need for more severe refinery processes to remove trace fuel species that adversely affect thermal stability and water removal by coalescence.<sup>1-4</sup> These processes also remove trace polar species that are responsible for a fuel's inherent lubricity properties.

Lubricity is a qualitative description of the relative abilities of two fluids, with the same viscosity, to limit wear and friction between moving metal surfaces.<sup>2,4</sup> It may be the most critical fuel property degraded by refinery processes.<sup>3,5</sup> The continued use of low lubricity fuel can lead to a decrease in the operational lifetime of fuel lubricated engine components. This leads to increased maintenance costs and down-time of aircraft. Furthermore, the use of low lubricity fuel has been implicated in the loss of certain military aircraft.

In the late 1960s, it was serendipitously found that a pipeline corrosion inhibitor had a significant effect on lubricity enhancement. The additive's original intended purpose was to decrease corrosion to fuel handling systems and transfer lines.<sup>4</sup> The additive is effective as a corrosion inhibitor due to its surface-active nature. The active

ingredient in most corrosion inhibitors is a dimeric organic acid, usually dilinoleic acid (DLA). It is the surface-active nature of the dimeric acid that causes the corrosion inhibitor to be an effective lubricity enhancer.

The use of a corrosion inhibitor as a lubricity enhancer is now required in all military JP-4 and JP-5 jet fuel.<sup>7</sup> Unfortunately the additive can hinder water removal by coalescence. In other cases a fuel may have adequate lubricity initially and would preclude the use of the additive. Currently there is no lubricity specification for either commercial or military jet fuel. This has been due primarily to the lack of a test method; hence, the mandatory addition of the additive to assure adequate lubricity.

During the past fifteen years considerable effort has been made to develop a mechanical method to measure fuel lubricity. The current and most widely accepted method is the Ball-on-Cylinder Lubricity Evaluator (BOCLE). The lubricity of a fuel is determined by the measurement of an oval wear scar on a ball that has been in contact with a rotating cylinder partially immersed in a fuel sample under controlled conditions.<sup>8</sup> The reported value is the average of the major and minor axes of the oval wear scar in millimeters. Two limitations to this method are: First, the BOCLE is run at 25°C, a temperature that is not characteristic in aircraft environments. Second, the test is limited to a measurement of boundary lubrication, a lubrication regime not characteristic of currently used aircraft fuel pumps.<sup>9,10</sup>

In the United Kingdom a second method is being used. This method, developed and used exclusively by Shell Research, Ltd., is known as the Thorton Aviation Fuel Lubricity Evaluator (TAFLE). This consists of a stationary cylinder loaded onto a rotating cylinder both of which are completely immersed in the fuel sample. Measurements can be obtained at both ambient and elevated temperatures. This test also measures scuffing load which is generally characteristic of fuel system failures.<sup>9,10</sup>

## EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. JP-5 and Jet A jet fuel samples were obtained from the Naval Air Propulsion Center (NAPC). JP-4 jet fuel samples were obtained from Wright-Patterson Air Force Base (WPafb). Carboxylic acid standards were obtained from a variety of sources including; Aldrich Chemical Company, Inc., LaChat Chemicals, Inc., and PolyScience, Inc. Trimethylsilyl ester derivatives of the carboxylic acids and jet fuel base extracts were prepared using Power Sil-Prep obtained from Alltech Associates, Inc.

Equipment and Materials- For HPLC analyses, samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30 cm x 8.0 mm i.d.). Uninhibited THF was used as a mobile phase. The THF was periodically purged with dry nitrogen to inhibit the formation of hazardous peroxides. The injector was a Rheodyne loop/valve Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer

for detection. A Varian Model 9176 strip chart was used to record peaks. A Fisher Accumet pH Meter Model 610A and a Fisher Standard Combination Electrode Catalog Number 13-639-90 were used for pH adjustments.

Gas Chromatography/Mass Spectrometry (GC/MS) analyses were performed using a Hewlett-Packard Model 5890 GC coupled to a Finnigan MAT ion trap detector. An all glass GC inlet was used in combination with a 0.2 mm x 50 m OV-101 fused silica capillary column. Data were collected using an IBM AT Personal Computer with ITDS software (version 3.0).

BOCLE analyses were performed using an InterAv Model BOC 100. The cylinders used were Timken Rings Part Number F25061 obtained from the Falex Corp., Aurora, IL. The test balls used were 12.7 mm diameter, Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

**Methods-** HPLC analyses of fuel extracts were performed using a previously developed method.<sup>11-13</sup> This involved the extraction of 100 mL of jet fuel with an equal volume of 0.2 M NaOH. The aqueous phase was drained and acidified with concentrated HCl. The acidified aqueous phase was subsequently back-extracted with 100 mL of HPLC methylene chloride which was then drained and allowed to evaporate. The residue was dissolved in 2.0 mL HPLC THF for analysis.

BOCLE measurements were performed according to the method described in appendix Y of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.<sup>8</sup>

## RESULTS

Figure 1 is an HPLC chromatogram of a base extract from a typical JP-5 jet fuel. The active ingredient of the lubricity enhancer additive, DLA, has an elution volume of 5.85 mL. The DLA component has a molecular weight of 562. This material is prepared by a 1,4- cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid moieties which are the points of attachment to the active surface sites.

The peak that elutes at approximately 5.4 mL corresponds to trilinoleic acid (TLA). The TLA component, which is also a product of the Diels-Alder reaction, has a molecular weight of approximately 840. It may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings.

The components with elution volumes of approximately 6.5 mL and 7.0 mL correspond to naturally occurring base extractable materials. These peaks are designated regions 3 and 4 respectively. These peaks can be clearly seen in Figure 2. The components that elute in what are designated regions 3 and 4 are believed to play a significant role in the inherent lubricity of jet fuel as measured by the BOCLE. Earlier work has shown a relation between the presence of these components and BOCLE measured lubricity.<sup>14-15</sup> In general, as the concentration of components that

elute in regions 3 and 4 increase, the lubricity of a fuel sample measured by the BOCLE increases.

While performing routine analyses of jet fuel samples, an interesting change in the fuel samples was noted. A series of JP-5 field samples were analyzed for base extractable material. After nine months of ambient storage, these same samples were analyzed a second time. It was found that the amount of base extractable material that elutes in regions 3 and 4 had increased. Table 1 lists the peak heights of regions 3 and 4 before and after nine months of ambient storage. o

BOCLE analyses were run to determine if there had been a concomitant change in lubricity. Since these were actual field samples of JP-5 jet fuels and, therefore, contained the mandatory lubricity enhancer additive, these fuel samples were all considered to be high lubricity fuels originally. It was found, however, that lubricity had increased. Previous work with an early version of the BOCLE yielded similar results. The lubricity of eight additive-free JP-5 and Jet A fuel samples were measured before and after 18 months of ambient storage. The change in wear scar diameter measurements for these fuels are listed in Table 2. It can be seen that the lubricity had increased in most cases. The wear scar diameters measured are smaller than those that would be measured on the current version of the BOCLE. This is a result of a metallurgical change in the cylinders to increase repeatability and reproducibility.

The increase in base extractable material with a concomitant increase in BOCLE measured lubricity is probably a result of oxidative changes in the fuel. Free radical autoxidation mechanisms are well known and readily occur in some fuels. These mechanisms can lead to the formation of trace levels of carboxylic acids that are known to enhance BOCLE measured lubricity.

The relation between lubricity and fuel composition is of great interest. Attempts have been made to correlate a number of fuel properties to lubricity measurements with little or no success. Early work performed by Grabel showed that straight chain carboxylic acids were among the most effective lubricity enhancers at very low concentrations.<sup>16</sup> The effect of straight chain carboxylic acids on boundary lubrication is well known and well documented. It's not surprising that an corrosion inhibitor based on carboxylic acids is also an effective lubricity enhancer. Grabel attempted to correlate the total acid number of a fuel to its lubricity as measured by the BOCLE. It was found that there was a relation, however, it would not serve as a adequate prediction of a fuel's lubricity. The conclusion is that there are acids that contribute substantially to the total acid number that are not involved in lubricity.

Combined gas chromatography/mass spectrometry (GC/MS) was used to identify components present in regions 3 and 4. With the knowledge of the effect of carboxylic acids on BOCLE measurements, comparison between fuel extracts and carboxylic acid standards were made. Both the fuel extracts and standards were derivatized to form their trimethylsilyl analogs to facilitate GC/MS analysis. After analysis of a standard mixture of derivatized carboxylic acids, a variety of fuel extracts were analyzed. Carboxylic acids were found to be present at low concentrations. These

were identified by both GC retention time and by their mass spectra. To aid in identification, multiple ion detection was also used for samples with overlapping peaks. The specific alkanolic acids found ranged from heptanoic acid (C<sub>7</sub>) to undecanoic acid (C<sub>11</sub>). The total concentration of the alkanolic acids varied with different samples. In most cases the total concentration was on the order of a few parts per million. Previous work has shown that as little as 2 ppm of added alkanolic acids can significantly improve BOCLE measured lubricity.

In addition to the acids, the majority of the species present in the fuel extracts were substituted alkyl phenols. Earlier work by Grabel has shown that these materials are not effective lubricity enhancers at low concentrations. At higher concentrations they may, however, contribute to BOCLE measured lubricity.

#### SUMMARY

The BOCLE is a useful tool in the laboratory for jet fuel lubricity measurements. Its limitations, however, must be recognized. The test is performed at 25°C, well below the operating temperature of aircraft fuel systems. Compounds that exhibit a beneficial influence on lubricity in the BOCLE test may fail at higher temperatures. The BOCLE analysis is performed in a different lubrication regime than is found in current aircraft fuel systems. This may lead to erroneous conclusions about a fuel's ability to impart lubricity in actual fuel systems. For instance, the BOCLE measured lubricity of a fuel is not influenced by the presence of sulfur compounds. Jet fuel lubricity as measured by the TAFLE, indicates that sulfur compounds increase the load limit of a fuel before scuffing occurs. This means that the BOCLE may fail a fuel that is capable of high loads in an actual fuel pump.

Lubricity related problems have been associated with only certain specific aircraft. The use of the lubricity enhancer additive has been found to adequately alleviate these problems. Other aircraft have not been found to exhibit any lubricity related problems. One may ask why there is a concern about lubricity. In the past the Navy has had problems with lubricity as a result of shipboard fuel handling practices. As JP-5 fuel is depleted from shipboard storage tanks, seawater is pumped in for ballasting. Seawater has been shown to effectively remove the lubricity enhancer additive by forming dicationic salts of the DLA.<sup>12,13</sup> This results in jet fuel with inadequate lubricity.

Another cause for recent lubricity problems is the lack of a lubricity specification. Additives used for lubricity enhancement are used, not for their ability to enhance lubricity, but their ability to inhibit corrosion. Of the additives qualified for use in jet fuel<sup>17</sup>, some are not effective surface active lubricity enhancers.

Two recommendations as an approach to short term and long term lubricity concerns are as follows: First, delete the additives from the Qualified Products List that are not found to enhance lubricity. Of the additives remaining, select those additives that are most effective for lubricity enhancement, are most cost effective, and are readily available.

Second, design aircraft components that are not affected by the continued use of low lubricity fuel. Long term problems with jet fuel lubricity should be approached by hardware modification not by the continued use of additives.

#### REFERENCES

(1) Vere, R.A.; Soc. Automot. Eng., SAE Reprint Number 690667, National Aeronautic and Space Engineering and Manufacturing Meeting, Los Angeles, CA, 1969; pp. 2237-2244.

(2) Moses, C.A., Callahan, T.J., Cuellar, Jr., J.P., Dodge, L.G., Likos, W.E., Naegeli, D.W., Valtierra, M.L.; "An Alternative Test Procedure to Qualify Fuels for Navy Aircraft," Final Report, Naval Air Propulsion Center Contract Number N00140-80-C-2269, Report Number NACP-PE-145C; Southwest Research Institute, San Antonio, TX, 1984.

(3) Petrarca, Jr., J.; "Lubricity of Jet A-1 and JP-4 Fuels," NTIS Number AD-784772; Report Number AFAPL-TR-74-15, Air Force Aero Propulsion Laboratory, Wright-Patterson AFB, OH, 1974.

(4) Goodger, E., Vere, R.A.; Aviation Fuels Technology; MacMillan Publishers Ltd.: Houndmills, Basingstoke, Hampshire, England, 1985; pp. 80-82.

(5) Biddle, T.B., Meehan, R.J., Warner, P.A.; "Standardization of Lubricity Test," Report Number AFWAL-TR-87-2041, Air Force Wright Aeronautical Laboratories, Aero Propulsion Laboratory (AFWAL/POSF), Wright-Patterson AFB, OH, 1987.

(6) Master, A.I., Weston, J.L., Biddle, T.B., Clark, J.A., Gratton, M., Graves, C.B., Rone, G.M., Stoner, C.D.; "Additional Development of the Alternative Test Procedure for Navy Aircraft Fuels," Naval Air Propulsion Center Contract Number N00140-84-C-5533, Report Number NACP-PE-160C; United Technologies Corporation, Pratt and Whitney, West Palm Beach, FL, 1987.

(7) Military Specification, MIL-T-5624M, Turbine Fuel, Aviation, Grades JP-4 and JP-5, 25 March 1988.

(8) Coordinating Research Council; "Aviation Fuel Lubricity Evaluation," CRC Report Number 560, CRC Inc., Atlanta, GA, 1988.

(9) Report of the Ministry of Defence (PE), Aviation Fuel Committee Lubricity Steering Group, March 1985 to October 1987.

(10) Report of the Ministry of Defence (PE), Aviation Fuel Lubricity Steering Group, Summary of Activities: November 1987 to October 1988.

(11) Black, B.H., Wechter, M.A., Hardy, D.R.; J. Chromatogr., 1988, 437, 203-210.

(12) Hardy, D.R., Black, B.H., Wechter, M.A.; J. Chromatogr., 1986, 366, 351-361

(13) Wechter, M.A.; "Quantitative Determination of Corrosion Inhibitor Levels in Jet Fuels by HPLC," Final Report, Naval Research Laboratory Contract Number N00014-85-M-0248; Southeastern Massachusetts University, North Dartmouth, MA, 1986.

(14) Black, B.H., Hardy, D.R.; Preprints of the Division of Fuel Chemistry, American Chemical Society, Vol. 34, No. 2, 1989, pp. 573-580.

(15) Black, B.H., Hardy, D.R.; Preprints of the Division of Fuel Chemistry, American Chemical Society, Vol. 34, No. 2, 1989, pp. 581-588.

(16) Grabel, L.; "Lubricity Properties of High Temperature Jet Fuel," Report Number NAPTC-PE-112, Naval Air Propulsion Test Center, Trenton, NJ, August 1977.

(17) QPL-25017-14, Qualified Products List of Products Qualified Under Military Specification MIL-I-25017, Inhibitor, Corrosion/Lubricity Improver, Fuel Soluble (Metric), 1984; U.S. Air Force, ASD/ENES, Wright-Patterson AFB, OH.

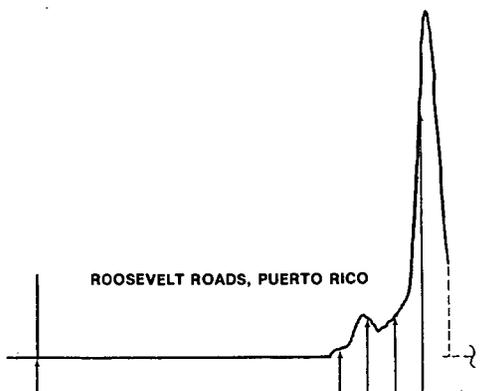


FIGURE 1

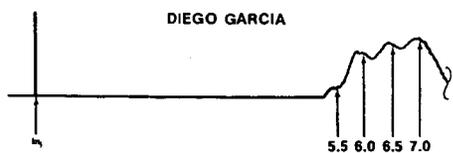


FIGURE 2

HPLC CHROMATOGRAMS OF JP-5 FIELD SAMPLES

TABLE 1

SAMPLE	Reg. 3 Pk Hgt		Reg. 4 Pk Hgt	
	Before	After	Before	After
Roosevelt Roads	14.5	28.0	128.0	65.0
Guantanamo Bay	11.0	28.0	25.0	200
Diego Garcia	20.0	22.0	22.0	65.0
Iorlaki, Japan	4.0	4.0	3.5	11.0
Gatun, Panama	12.0	15.0	24.0	250
Cartagena, Spain	5.0	12.0	8.5	29.0
Azorea	7.5	7.0	6.5	13.0

CHANGE IN CONCENTRATION OF BASE EXTRACTABLE MATERIAL AFTER NINE MONTHS OF STORAGE

TABLE 2

SAMPLE	ORIGINAL WSD	REMEASURED WSD
1	0.28 mm	0.23 mm
2	0.32 mm	0.28 mm
3	0.28 mm	0.27 mm
4	0.43 mm	0.28 mm
5	0.31 mm	0.34 mm
6	0.62 mm	0.36 mm
7	0.53 mm	0.36 mm
8	0.52 mm	0.41 mm

CHANGE IN WEAR SCAR DIAMETER MEASUREMENT FOR ADDITIVE-FREE JET FUELS AFTER 18 MONTHS OF STORAGE

## THE INTERACTION OF A METAL DEACTIVATOR WITH METAL SURFACES

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### INTRODUCTION

In modern aircraft fuel systems, the fuel is used as a heat transfer medium to dissipate heat from the avionics and hydraulic systems. Under these conditions, the fuel can undergo autoxidation. Autoxidation of jet fuel can result in the formation of insoluble gum and sediment which can impair operation of the jet engine. In addition, hydroperoxides which form during autoxidation have been known to attack certain elastomeric fuel system components. Thus, the thermal oxidation stability of the fuel becomes an important consideration. Trace quantities of certain transition metals will catalyze fuel autoxidation. Dissolved copper has been shown to be the most reactive (Pederson, 1949; Smith, 1967). Copper contamination of fuels can and does occur, particularly in shipboard fuel handling systems from contact with copper lines, brass fittings, admiralty metal, and other copper-bearing alloys.

Metal deactivator additives (MDA) were developed to counteract the catalytic activity of dissolved metals. These additives (N,N'-disalicylidene-1,2-propanediamine and N,N'-disalicylidene-1,2-cyclohexanediamine) can act as polydentate ligands for copper (Pederson, 1949). Chelate complexes derived from similar hydroxyaromatic Schiff bases are known to be thermally stable (Marvel, et al., 1956). The military specification, MIL-T-5624, allows for the addition of up to 5.8 mg MDA per liter in JP-4 and JP-5, while the ASTM specification for aviation turbine fuels, D1655-85a, (Annual Book of ASTM Standards, 1987) allows up to 5.7 mg per liter.

Laboratory scale tests, such as the Jet Fuel Thermal Oxidation Tester (JFTOT), have been relied upon to evaluate the thermal oxidation stability of aviation fuels. In the ASTM Method for assessing thermal oxidation stability of aviation fuels (Annual Book of ASTM Standards, 1988), the fuel is passed once over the outside of a resistively heated aluminum tube (the heater tube) at a flow rate of approximately three ml/min. In previous work (Morris, et al., 1988; Morris and Turner, in press), we have observed that the addition of a metal deactivator resulted in significant reductions in deposits on 304 stainless steel JFTOT heater tubes from 280 to 310°C.

In tests conducted with an injector feed-arm simulator, metal deactivator reduced deposit formation in two fuels by two and fourteen fold respectively onto clean steel surfaces (Kendall and Earls, 1985). However, after an induction period,

rapid deposition ensued at a rate similar to that observed in the absence of MDA. From this it was concluded that MDA passivated the clean steel surface towards thermal deposits, but was ineffective once the surface became coated with an organic deposit (Kendall, et al., 1987). The effectiveness of MDA in JFTOT testing of metal-free hydrotreated fuels was also attributed to passivation of the clean metal surface of the JFTOT heater tube (Clark, 1988).

The strong influence exerted by MDA in JFTOT testing has raised questions about the applicability of the method for ranking fuels with respect to thermal oxidation stability in the presence of metal deactivators. If MDA produces a disproportionately strong inhibition of deposition in the JFTOT, then fuels ranked stable may form insolubles during use. We have thus directed our efforts at ascertaining the various mechanisms by which MDA can act, particularly in accelerated stability testing. One objective of this study was to determine to what extent interactions with metal surfaces of the test apparatus govern the effectiveness of metal deactivators. This paper describes an examination of metal surfaces exposed to MDA solutions to determine under what, if any, conditions metal passivation can occur.

#### EXPERIMENTAL

X-ray photoelectron spectroscopy (XPS) was used to determine the presence of a continuous layer of MDA on metal surfaces. Analyses were performed using a Surface Science Instruments SSX-100-03 X-ray Photoelectron Spectrometer. Quantitative estimates of the surface composition were obtained using the analysis program supplied with the spectrometer. The base pressure was at least  $2 \times 10^{-8}$  torr for all samples analyzed. Fourier transform infrared spectroscopy (FTIR) was performed with a Digilab FTS-15/90 Fourier transform infrared spectrometer. Secondary ion mass spectroscopy (SIMS) was performed in a static mode with a time of flight instrument constructed at the Naval Research Laboratory (Hues, et al., 1988). A pulsed alkali ion gun with a thermionic emitting source was used which produced 2-5 ns pulses of 13.0 keV cesium ions, resulting in an impact energy of 8.0 keV for positive ions.

In order to minimize the risk of surface contamination from trace impurities in a fuel, a model fuel consisting of n-dodecane (Philips 66, Pure grade, 99 mol% min.) was used. XPS analyses were conducted on flat metal coupons exposed to the model fuel and the model fuel containing MDA. N,N'-Disalicylidene-1,2-propylene-diamine (MDA) was obtained from Pfalz and Bauer and dissolved into the dodecane to obtain a final concentration of 5.8 mg/l. MDA-copper complex was prepared by combining equimolar quantities of MDA and copper(II) ethylacetoacetate in dodecane.

Coupons measuring 2.5cm x 1.2cm consisting of copper, 6061 aluminum and 304 stainless steel were used as substrates. All surfaces were ground to 4000 grit using silicon carbide paper with triply distilled water as the lubricant. Coupon samples used for (FTIR) were further polished with 0.05 micron alumina. The stainless steel samples examined by SIMS were 1cm x 1cm and were prepared as described above. After polishing, the coupons were rinsed with triply distilled water and allowed to air dry in acid cleaned glassware. Samples were immersed in either pure dodecane or dodecane containing MDA at room temperature for two and one half hours. Afterwards the samples were withdrawn from this solution and rinsed with HPLC grade n-heptane, covered with aluminum foil and analyzed

within an hour. Samples that were analyzed by SIMS and FTIR were also rinsed with low residue toluene (Baker).

Stainless steel and aluminum JFTOT heater tubes were also examined by XPS. JFTOT stressing was carried out with dodecane and solutions of MDA at 5.8 mg/l in dodecane at 260°C and 310°C for one hour. The tubes were washed with hexane immediately after a JFTOT experiment.

#### RESULTS AND DISCUSSION

XPS signal intensity ratios for carbon, nitrogen and oxygen cannot be utilized as a quantitative measure of the amounts of MDA on the surface and can only be used as a qualitative indication of the presence of MDA. Almost any surface that has been exposed to air will have adsorbed oxygen and carbon. It was thus necessary to rely on the intensity of the nitrogen signal alone as the most reliable indication of the presence of MDA on the surface since it is unique to that compound and is not present in the pure dodecane.

An XPS survey scan of the copper-MDA complex demonstrated that the surface binding energies were similar to those reported for a copper-Schiff base analog of MDA (Dillard, et al., 1974). It is clear from analysis of the observed peaks that all the expected elements are present. The nitrogen peak was quite intense relative to both the carbon and oxygen peaks. Although nothing definitive can be said from the spectrum about the relative atomic concentrations, the relative intensities of the carbon, nitrogen and oxygen peaks should give a reasonable indication of the expected intensity ratios for this chelate if it were present as a very thick film. Analysis of signal intensities from high resolution scans of these peaks allowed an estimation of the atomic concentration of the elements present. The calculated copper concentration was a factor of two higher than expected, while the atomic ratios of the other elements were what were expected. Although the exact reason for this discrepancy is not understood, the relative intensities of the peaks should provide a reasonable indication of the amount of MDA present on an uncontaminated surface.

Copper coupons: While it is not practical to attempt to remove all copper-bearing components from shipboard fuel delivery systems, MDA may play a role in inhibiting the dissolution of copper into the fuel. For this reason it was felt that MDA adsorption onto copper surfaces should be studied to provide an insight into the role it may play, if any, in passivating the exposed copper parts. Prepared copper coupons were exposed to dodecane and dodecane containing MDA at room temperature for 2.5 hours. The strips were then removed and rinsed with heptane (HPLC grade), mounted onto the XPS carousel and introduced into the vacuum system within two hours using a quick insertion system that is part of the apparatus. The XPS survey scan from the freshly cleaned copper surface, which was mounted as soon as it was air dried, had weak carbon and oxygen peaks and strong copper peaks, indicating that the sample preparation procedure used produced an acceptably clean surface. Exposure to the MDA solution had clearly increased the amount of carbon on the surface but no nitrogen was observed in the broad scan. This indicated that at most there could only be a very thin film of the MDA on this surface. Otherwise, the nitrogen intensity would be comparable with that found in the complex above. High resolution scans of the peaks for each element were obtained and the composition of the surface was estimated. The results of this are shown in Table I for the freshly polished

surface and after exposure to MDA. The carbon and oxygen levels, although still quite high, are small compared with those found from any other cleaning procedures that were tried. As expected, the calculated carbon contents on surfaces that were exposed to the organic solutions were higher than on the freshly cleaned surfaces. In addition, the quantities of carbon were about the same for the surfaces of both the sample exposed to pure dodecane and to MDA. Nitrogen levels were at or below the detection limit of 1-2 atomic percent. The lack of any nitrogen signal suggests that the formation of an MDA coating on the copper surface was not occurring, since XPS can easily resolve monolayer thicknesses.

Examination of the copper surface by FTIR revealed the presence of an organic acid on all samples exposed to the dodecane. The magnitudes of the C-H and C=O stretches that characterized the surface adsorbed acids were influenced by the MDA concentration. This may indicate some interactive effects between acids adsorbed on metal surfaces and the MDA.

**Stainless steel coupons:** The results from the XPS examination of 304 stainless steel coupons exposed to dodecane and dodecane containing 5.8 mg MDA/l for 2.5 hours at room temperature are shown in Table I. Higher levels of oxygen were found on the freshly cleaned stainless steel surface than on the copper surface, presumably because of the presence of metal oxides. Nitrogen content was at or below the limit of detection. FTIR analysis of stainless steel strips exposed to dodecane again revealed the presence of a carboxylic acid on the surface, from strong C-H and C=O absorptions. No changes in surface acid concentration were evident, nor was MDA detected on surfaces exposed to dodecane containing 5.8 mg MDA/l. Treatment of the dodecane with silica gel before use was sufficient to eliminate the presence of adsorbed carboxylic acids on the metal surfaces. The presence of a few parts per million of dodecanoic acid was confirmed by HPLC analysis of the base-extractable component of the dodecane. Thus, the acid adsorbed on the metal surface was most likely dodecanoic acid, derived from autoxidation of the dodecane.

In an effort to gain a more sensitive measure of the presence of MDA on the surface, SIMS analysis was performed on a stainless steel surface which had been exposed to neat dodecane and a dodecane solution of 5.8 mg MDA/l for 2 hours at room temperature. The positive secondary ions thus formed showed that indeed some MDA was present on the surface, while none was detected on the neat dodecane exposed blank. Since the surface had been rinsed with toluene, it is assumed that the MDA present was tightly bound to the surface. However, a more intense signal was obtained at 52 Daltons higher than the MDA peaks, suggesting that most of the MDA was bound to chromium. These findings demonstrate that after exposure of 304 stainless steel to a solution of MDA at room temperature, some MDA will be bound to the surface, predominantly at chromium sites. However, the coating is far from complete and would not significantly alter the surface reactivity towards deposition.

**Stainless steel JFTOT heater tubes:** While 6061 aluminum is the material most commonly used in the construction of JFTOT heater tubes, 304 stainless steel is often employed in research efforts involving the JFTOT apparatus. Furthermore, many fuel system components are constructed from stainless steel. XPS analyses were performed on selected areas of stainless steel JFTOT heater tubes used to stress samples of dodecane with and without 5.8 mg MDA/l in the JFTOT apparatus for one hour. Nitrogen on heater tubes heated at 260°C was near the detection

limit. The metal contents (i.e., Fe, Cr, Mn, etc.) on the tube surfaces were very low (Table II). Chromium levels were at or below the detection limit of 1 atomic percent, compared to a nominal level of 18% in the base metal. This indicates multilayer deposit formation was taking place regardless of whether MDA was present or not. At 310°C in the presence of MDA, similar results were obtained except that the carbon levels were higher. These findings demonstrate that within one hour of JFTOT testing, it is possible to produce multilayer coatings of carbonaceous thermal oxidation products on the stainless steel JFTOT heater tube surface from a relatively unreactive "fuel", i.e., dodecane.

Aluminum JFTOT heater tubes: XPS examinations of 6061 aluminum JFTOT heater tubes tested at 260°C for one hour in dodecane and dodecane with 5.8 mg MDA/l revealed that, in both cases, carbon levels were lower than on the stainless steel tube surfaces (Table III). There was no evidence of multilayer structure of thermally degraded dodecane over the full length of the tube. This substantiates earlier reports that while the liquid-phase chemistry is identical for both tube materials (Hazlett, et al., 1977), heavier deposits tend to form on stainless steel heater tubes (Faith, et al., 1971; Kendall, et al., 1987). Nitrogen was at or below the detection limit in both cases, however, slightly more nitrogen was evident on tubes heated in the MDA solution.

#### CONCLUSIONS

Surface analyses of copper, aluminum and stainless steel exposed to MDA in static solutions and in JFTOT testing, point towards a different mechanism than what would be expected if the surface were deactivated towards deposition by a contiguous layer of MDA. While these findings suggest that the surface contains some MDA, it is sparsely distributed. In addition, there may be some interactive effects between MDA and surface bound carboxylic acids. On stainless steel, it appears that the MDA is predominantly bound to chromium sites on the surface but this coating is also a fraction of a monolayer and thus would not significantly change the surface activity. There was no evidence that MDA was coating a pure copper surface.

In the JFTOT, there was more deposition onto the 304 stainless steel tubes than on the 6061 aluminum. If surface passivation was responsible for the strong response of the JFTOT to the presence of MDA, then one would expect to observe at least a monolayer of MDA on the tube surface over the entire test duration of two and one half hours. However, in this study, multilayer thermal oxidation deposits were produced on 304 stainless steel JFTOT tubes after only one hour of JFTOT testing at the specification test temperature, 260°C. Therefore, the time required for monolayer deposition of thermal oxidation products onto stainless steel heater tubes during JFTOT testing was well within the limits of the test.

While it does not seem likely that surface passivation is occurring in the JFTOT, there is still no doubt that MDA exerts a powerful inhibiting influence on thermal deposition and the question of validity of the JFTOT results in the presence of MDA remains to be answered. Measurements of oxidation of JFTOT effluent have shown inhibition by MDA in some cases and none in others. This suggests the possibility that the effects exerted by MDA in the JFTOT may be a consequence of interactions in the liquid-phase.

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#### REFERENCES

ASTM "Specification for Aviation Turbine Fuels". In Annual Book of ASTM Standards; ASTM: Philadelphia, 1987; part 23, ASTM D1655-f2a.

ASTM "Standard Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)" In Annual Book of ASTM Standards; ASTM: Philadelphia, 1988; vol. 05.02, ASTM D 3241-85.

Clark, R. H.; "The Role of Metal Deactivator in Improving the Thermal Stability of Aviation Kerosines". In Proceedings of 3rd International Conference on Stability and Handling of Liquid Fuels; R.W. Hiley, R.E. Penfold and J.F. Pedley, Ed., The Institute of Petroleum: London, UK, 1989, p. 283.

Dillard, J. G. and Taylor, L. T.; "X-Ray Photoelectron Spectroscopic Study of Schiff Base Metal Complexes". J. Elect. Spect. & Rel. Phenom., 1974, 3, 455.

Faith, L. E.; Ackerman, G. H.; Henderson, H. T.; Richie, A. W. and Ryland, L. B.; "Hydrocarbon Fuels for Advanced Systems". Shell Development Company, Air Force Report AFAPL-TR-70-71, Part III, 1972.

Hazlett, R. N., Hall; J. M. and Matson, M.; "Reactions of Aerated n-Dodecane Liquid Flowing over Heated Metal Tubes", Ind. Eng. Chem., Prod. Res. Dev., 1977, 16(2), 171.

Hues, S. M.; Colton, R. J.; Mowery, R. L.; McGrath, K. J.; and Wyatt, J. R.; "Determination of Hydrogen in Perfluorinated Polyalkylethers Using Time-of Flight Secondary Ion Mass Spectrometry, Infrared Spectroscopy, and Nuclear Magnetic Resonance Spectrometry". Appl. Surf. Sci. 1988, 35, 507.

Kendall, D. R. and Earls, J. W.; "The Assessment of Aviation Fuel Thermal Stability". Presented at the 25th IATA Aviation Fuel Subcommittee, September 17-18, 1985, Geneva.

Kendall, D. R.; Houlbrook, G.; Clark, R. H.; Bullock, S. P.; Lewis, C.; "The Thermal Degradation of Aviation Fuels in Jet Engine Injector Feed-Arms, Part I - Results from a Full-Scale Rig". Presented at the 1987 Tokyo International Gas Turbine Congress, October 26-31, 1987, Tokyo, Japan.

Marvel, C. S.; Aspey, S. A. and Dudley, E. A.; "Quadridentate and Sexadente Chelates. Some Preliminary Studies in their Preparation and Thermal Stability". J. Amer. Chem. Soc. 1956, 78, 4905.

Morris, R. E.; Hazlett, R. N.; McIlvaine, C. L. III; "The Effects of Stabilizer Additives on the Thermal Stability of Jet Fuel". Ind. Eng. Chem. R&D 1988, 27(8), 1524.

Morris, R. E. and Turner, N. H.; "Influences Exerted by Metal Deactivator on the Thermal Stability of Aviation Fuel in the Presence of Copper". Fuel Sci. & Tech. Int. (in press).

Pederson, C. J.; "Inhibition of Deterioration of Cracked Gasoline During Storage". Ind. Eng. Chem. 1949, 41, 924.

Smith, J. D.; "The Effect of Metals and Alloys on the Thermal Stability of Avtur 50". J. Aero. Eng. 1967, 33(4), 19.

Table I. Composition of Films Formed on Polished Flat Coupons Exposed to Dodecane and 5.8mg MDA/l Dodecane in Atomic Percent

Copper

Condition	C	O	Cu
Freshly Polished	39	27	35
Dodecane, 2.5 hrs	63	23	12
MDA/dodedane, 2.5 hrs	54	28	18

304 Stainless Steel

Condition	C	O	Fe
Freshly Polished	21	58	14
Dodecane, 2.5 hrs	46	37	8
MDA/Dodedane, 2.5 hrs	35	49	11

Table II. Composition of Films Formed on Stainless Steel JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Dodecane, 260°C			
Temp. (°C)	C	O	Fe
174-208	57	38	3
208-238	41	49	7
238-257	52	40	5
257-260	78	20	1

5.8 mg MDA/l in Dodecane, 260°C			
Temp. (°C)	C	O	Fe
174-208	56	38	2
208-238	43	46	4
238-257	48	42	4
257-260	82	18	0

5.8 mg MDA/l in Dodecane, 310°C			
Temp. (°C)	C	O	Fe
212-253	40	45	11
253-287	56	38	4
287-305	82	14	0
305-310	93	6	0

Table III. Composition of Films Formed on Aluminum JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Dodecane, 260°C			
Temp. (°C)	C	O	Al
141-193	31	47	20
193-232	29	47	21
232-256	32	46	18
256-260	28	48	19

5.8 mg MDA/l in Dodecane, 260°C			
Temp. (°C)	C	O	Al
141-193	31	45	19
193-232	33	43	18
232-256	34	43	19
256-260	44	36	17

HYDROCRACKING WITH NEW SOLID ACID CATALYSTS:  
LOW SEVERITY LIQUEFACTION PRODUCTS FROM LOW RANK COAL:

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Solid acid catalysts, prepared by supporting zinc chloride on silica gel and on acid-exchanged montmorillonite, were tested for catalytic hydrocracking of first stage liquefaction products from Wyodak subbituminous coal. Unsupported acid-exchanged montmorillonite was also tested. The reactions were carried out by heating the high molecular weight, THF-soluble, low-severity product with the supported zinc chloride catalyst in a microreactor at 400°C for three hrs with 1000 psig of hydrogen (repressurized at 1-hr intervals). These reactions gave good yields of distillates (53-68%), which exceeded those obtained with conventional hydrotreating catalysts under similar conditions. Coking or retrograde condensation reactions were minimal. The distillate compositions, determined by GC/FTIR/MS/AED, consisted of phenolics, one and two ring aromatics and hydroaromatics, and alkanes. The nonvolatiles were examined by elemental analysis, FTIR, NMR, and m.w. determinations by GPC and LALLS. The hydrotreated liquefaction products, both volatiles and nonvolatiles, showed a complete absence of organo sulfur compounds, as determined by the very sensitive helium afterglow discharge emission and elemental analysis.

Key words: Liquefaction, hydrocracking, solid acid catalyst

#### INTRODUCTION

The preparation of new catalysts for the production of a distillate with a low content of heteroatoms such as sulfur, oxygen, and nitrogen is a major goal in coal liquefaction. More than 50 years ago Eugene Houdry (1) reported that acid modified smectites can produce gasoline in high yields when used as petroleum cracking catalysts. In contrast to thermal cracking, catalytic cracking produces gasoline of higher octane rating (2). Many cracking catalysts are combinations of alumina and silica oxides, known to exhibit acidic properties (3). The mechanism of the acid-catalyzed cracking reactions is understood to involve carbonium ion intermediates (4). The catalytic cracking of cumene has been extensively used to characterize the acidity of various catalysts (5). Synthetic silica alumina catalysts or zeolites were more stable both structurally and catalytically, gave superior product distributions compared to naturally occurring clays, and, thus revolutionized the catalytic cracking (6-10).

Petroleum hydrocracking catalysts are not necessarily effective for coal liquefaction, however. Highly acidic catalysts may result in coking on the catalyst as well as in the equipment. Although molten zinc chloride effectively depolymerizes coals (11,12), significant hydrodesulfurization of aryl sulfur compounds is not affected by this reagent (13). Other disadvantages of zinc chloride are its difficulty of recovery and corrosive nature.

In a recent paper we reported a solid acid catalyst prepared by supporting zinc chloride on silica gel to be effective in hydrodesulfurization of diphenyl sulfide and dibenzothiophene (14). The preparation and characterization of three solid acid catalysts: 1) supporting zinc chloride on silica gel, 2) supporting zinc chloride on acid-exchanged montmorillonite, and 3) unsupported acid-exchanged montmorillonite have already been reported (14,15). In this paper, we report the catalytic

hydrotreatment of the first stage products from the low-severity liquefaction of Wyodak subbituminous coal with zinc chloride supported on silica gel and on acid-exchanged montmorillonite, unsupported acid-exchanged montmorillonite, and commercial Trilobe 60 HDN catalyst.

## EXPERIMENTAL

Zinc chloride on silica gel, zinc chloride on acid-exchanged montmorillonite, and unsupported acid-exchanged montmorillonite catalysts were prepared as described earlier (14,15). Total acidity and pKa's of the solid acid catalysts were determined by n-butyl amine titrations using Hammett indicators (16).

Analytical procedures; instrumentation:

Carbon, hydrogen, and nitrogen analyses were performed on Control Equipment Corporation Model 240XA Elemental Analyzer. Total sulfur was determined with a LECO Model 532 Sulfur Analyzer using ASTM D1551 method. Oxygen was determined by difference. The method of Vogel (17) was used for chlorine analysis.

<sup>13</sup>C NMR, CP/MAS solid state spectra were recorded on a Varian XL200 NMR spectrometer with Doty Scientific solids probe operating at 50.3 MHz. Infrared spectra were obtained in KBr on either a Perkin-Elmer Model 283 spectrophotometer or a Nicolet 205XB FTIR spectrometer equipped with a mercury cadmium telluride (MCTA) detector and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Quantitative GC/FID analyses were performed with a Hewlett-Packard 5880A gas chromatograph equipped with J&W 60 m x 0.25 mm (i.d.), 1.0 micron DB-1701 capillary column. n-Octadecane was used as the internal standard. Isotope dilution GC/MS were performed on a Finnigan 800 ITD ion trap detector with an HP-5890A gas chromatograph and a J&W 30 m x 0.32 mm (i.d.), 1.0 micron film of DB-5. Phenol, tetralin, and naphthalene were determined with the per-deuterated analogs as the respective internal standards. A 15 m x 0.25 mm (i.d.) 0.25 micron DB-5 column was used for the analysis of high boiling components. Quantitative analysis of organo sulfur compounds in the distillate was done by GC/AED.

Low severity liquefaction:

A slurry consisting of 904.5 g Wyodak coal (as received) and 1254.9 g of solvent (tetralin) was placed in a two-gallon reactor, and the reactor was sealed. The reactor was evacuated and charged with a mixture of 900 psig carbon monoxide and 100 psig hydrogen sulfide. The reactor was slowly heated to 384°C, and left at this temperature for one hour. At the end of the reaction, the reactor was cooled to room temperature, and the gases collected in a gas bag. The product slurry was separated into THF-soluble and insoluble fractions by extracting with THF. The THF-insoluble fraction was dried in vacuo at 110°C overnight, and weighed.

Preparation of solvent free low-severity product (LS-W) for second stage catalytic hydrotreatment :

A large batch of THF-soluble fraction was distilled under reduced pressure (2 torr) to remove solvents. The residue, a viscous oil, solidified upon cooling to room temperature (LS-W) was used for catalytic hydrotreatment. This product was analyzed by elemental analysis and the results are given in Table 1.

Catalytic hydrotreatment of LS-W:

In a typical run 1.0 g of LS-W and 0.50 g of the desired catalyst were placed in a tubing bomb (12-ml microreactor). The microreactor was evacuated and pressurized

with 1000 psig of hydrogen, and placed in a rocking autoclave heated to 400°C. The heating continued for three hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened.

The tubing bomb was attached to a set of three pre-weighed traps cooled in air, dry ice-acetone, and liquid nitrogen. The tubing bomb was slowly heated (3°C/min.) to 250°C, and heating was continued until distillation stopped. The distillate was weighed and dissolved in 10 ml of methylene chloride. The distillate was mixed with appropriate internal standards and analyzed by GC/FID and GC/FTIR/MS/AED. The undistilled residue was separated into THF-soluble and insoluble fractions by extracting with THF. These fractions were dried in vacuo and weighed. The mass balance data are given in Table 2.

In a separate reaction, the tubing bomb was depressurized and repressurized with 1000 psig of hydrogen at one hour intervals. The total heating time was three hours.

## RESULTS AND DISCUSSION

### Catalytic hydrotreating; Liquefaction:

#### Catalytic hydrotreating of LS-W with silica gel zinc chloride (SZC):

Hydrotreating of solvent free low severity liquefaction product from Wyodak coal (LS-W) was carried out to determine the catalytic activities of supported zinc chloride catalysts. The three-hour tests were performed with an initial (cold) hydrogen pressure of 1000 psig, which increased to 3000 psig at the final reactor temperature of 400°C. In one test, the microreactor was cooled and repressurized with hydrogen (1000 psig) after each hour, while in another test, no additional hydrogen was added over the three-hour experiment. In calculating the conversions for the reaction, it is necessary to consider that the low-severity starting material for the test consisted mostly of high molecular weight material, but did contain a small amount of tetralin and naphthalene derived from solvent used in the low severity liquefaction and a small amount of volatile coal-derived material. The yields in the hydrotreating tests were determined by measuring the amount of vacuum distillate and corrected by subtraction of the distillable material present in LS-W (20%) to obtain the actual yield.

The hydrotreatment of LS-W with silica gel-zinc chloride catalyst (SZC) in the three hour test without depressurizing and repressurizing with hydrogen gave a distillate yield of 35%. Subtraction of the LS-W volatiles resulted in an actual yield for the hydrotreating step of 15%. The most striking aspect of the composition of the distillate is the complete absence of sulfur containing compounds, as determined by the very sensitive helium afterglow discharge atomic emission detection. The GC/FTIR/MS data indicated that benzene, alkylbenzenes, cyclohexane, phenolics, tetralin, naphthalene, and a series of alkanes were the major components of the distillate.

The residue from the distillation was separated into THF-soluble and insoluble fractions. The THF-soluble fraction amounted to 54% of the weight of the starting material. This material had a hydrogen-to-carbon ratio of 1.01, identical to the starting LS-W product. <sup>13</sup>C NMR, CP/MAS spectrum shows a large increase in the hydroaromatic bond at 30 ppm. This data also indicates removal of phenolics, carboxylic acids and carboxylate groups during hydrotreating. Infrared spectrum shows a larger aromatic ring absorption at 1600 cm<sup>-1</sup>, which may have resulted from a change in the type of aromatic groups present. An increased aromatic content could have resulted from either cleavage and loss of alkyl groups to the distillate fraction or from condensation, dehydration, and dehydrogenation reactions to give

TABLE 1  
ELEMENTAL ANALYSES OF COAL LIQUEFACTION PRODUCTS

Catalyst	Produce	C	H	N	S	O	H/C
None	Wyodak (maf)	70.9	5.2	0.9	0.6	22.3	0.88
None	LS-W	82.9	6.9	1.1	0.71	8.3	1.00
*SZC	THF-S THF-I Dist.	87.3	7.35	0.68	0.14 0.84 0.0	4.53	1.01
SZC	THF-S THF-I Dist.	88.0	6.02	1.07	0.0 0.74 0.0	4.91	0.82
AM	THF-S THF-I Dist.	83.7	5.58	1.24	0.42 0.0	9.48**	0.80
AMSZC-B	THF-S THF-I Dist.	85.4	6.38	0.94	0.0 1.47 0.0	7.28	0.90

• Single H<sub>2</sub> pressurization  
\*\* Includes sulfur

TABLE 2  
CATALYTIC HYDROTREATING OF LS-W

CATALYST	LS-W (g)	PRODUCTS (%)		
		THF-I	THF-S	Distillate
*SZC	1.02	11.8	54.0	35.0
SZC	1.00	1.9	28.6	67.7
AM	1.00	20.0	46.0	28.0
AMZC-A	1.00	--	49.0	53.0
AMZC-B	1.00	--	41.0	62.0
HDN	1.00	14.3	49.61	35.0

• Single H<sub>2</sub> Pressurization

more aromatic structures. Experience with model compound hydrotreating with this catalyst (14) suggests that single rings are not hydrogenated, but naphthalenes, and polynuclear aromatics are readily hydrogenated (19). Thus the hydrotreating at 400°C appears to consist mainly of hydrocracking alkylaromatics and hydrogenation of multi-ring aromatics. Hydrotreating may predominate over hydrogenation, because of the higher concentration of single ring aromatics in the low-rank coals.

The THF-insoluble fraction from the experiment without repressurization consisted mainly of catalyst, but did contain organic material amounting to 12% of the starting LS-W. This material was also more aromatic than the original LS-W.

The hydrotreating of LS-W with silica gel-zinc chloride catalyst with repressurization of hydrogen at one-hour intervals gave a distillate yield of 68% (actual 48%). The composition of the distillate was similar to that of the product from the single pressurization with hydrogen. The THF-soluble fraction amounted to 24% of the starting material. As in the experiment discussed above, the infrared spectrum indicated this fraction to be more aromatic than the original LS-W. The THF-soluble fraction was essentially the recovered catalyst with only a small amount (<3%) of carbonaceous material.

#### Catalytic hydrotreating with montmorillonite-zinc chloride (AMZC):

Catalytic hydrotreating of LS-W with acid-exchanged montmorillonite (AM) and hydrogen depressurizing and repressurizing at one-hour intervals gave 28% distillate. Since, 20% distillate was already present in the LS-W, only 8% of the distillate was actually produced during the second stage of the reaction. The GC/MS data indicated the major components of the distillate to be tetralin, naphthalene, and phenols. Tetralin is more likely to be solvent-derived and naphthalene could either be solvent-derived, coal-derived or both. Other products in the distillate were cresols, benzene, alkylbenzenes, and alkylnaphthalenes. A significant portion of the starting material (20%) became insoluble in THF after the second stage reaction, which may be due to condensation reactions catalyzed by the acidity of the clay.

Catalytic hydrotreating with zinc chloride supported on acid-exchanged montmorillonite prepared from clay dried at 110°C in vacuo (AMZC-A) gave 53% distillate (actual 33%). The stability and catalytic activity of the catalyst was found to depend on the drying temperature of the clay. The zinc chloride supported catalyst that was prepared from clay dried at 250°C (AMZC-B), was not only more stable on long standing but also gave higher distillate yield, 62% (42% actual). The distillate yield with this catalyst was comparable to that obtained from silica gel-zinc chloride catalyst. Furthermore, no coking or enhanced aromatic residue was formed during catalytic upgrading.

#### Catalytic hydrotreatment with commercial Ni-Mo catalyst (HDN):

In order to evaluate the catalytic activity of the zinc chloride supported silica gel and acid-exchanged montmorillonite, reaction of low severity Wyodak (LS-W) product with commercially available HDN catalyst was carried out under the same conditions as described above, and the results compared. The distillate yield was only 35% (actual 15%), which is significantly lower than those obtained with zinc chloride supported on silica gel and acid-exchanged montmorillonite. The product distribution of the distillate was much the same as with supported zinc chloride catalysts. The THF-soluble fraction was 50% of the starting material. A significant amount of organic material became insoluble in THF, which may have been formed due to dealkylation or condensation reactions (15).

Catalytic hydrotreating: Desulfurization:

Table 3 shows the sulfur removal for four different catalysts. The distillates obtained from these reactions did not contain any sulfur as indicated by very sensitive helium afterglow atomic emission spectroscopy. Therefore, sulfur amounts in the recovered catalyst (THF-insolubles) and THF-soluble fraction were used to determine desulfurization during catalytic hydrotreating of LS-W. Elemental analysis of the THF-insoluble fraction gave 0.74% sulfur (0.0075 g S). This amount of sulfur is essentially the same as that present in the starting LS-W (0.0071 g). These data demonstrate that the catalyst is highly effective in removing sulfur from the bottoms as well as the distillate. The occurrence of zinc sulfide in the catalyst is expected (14) but has not yet been confirmed. However, only 73.6% sulfur was removed from LS-W in the test without hydrogen repressurization. These results suggest that hydrogen repressurization is needed for the efficient removal of organic sulfur from coal products. Acid-exchanged montmorillonite removed only 42.3% sulfur from LS-W. However, on supporting zinc chloride on acid-exchanged montmorillonite, the desulfurization activity of the clay was considerably increased.

TABLE 3  
SULFUR BALANCE

Catalyst	S(g)				% S Removed
	Reactant	Products			
	LS-W	Distillate	THF-S	Recovered Catalyst	
*SZC	0.0072	0.0	--	0.0053	73.6
SZC	0.0071	0.0	0.0	0.0074	100
AM	0.0071	0.0	--	0.0030	42.3
AMZC-B	0.0071	0.0	0.0007	0.0060	84.5

\* Single H<sub>2</sub> Pressurization

CONCLUSIONS

Comparing the results of hydrocracking of low-severity liquefaction Wyodak products with supported zinc chloride catalysts to the results with HDN catalyst shows that these supported catalysts give higher distillate yields and effectively remove organic sulfur under mild conditions. The strong acid hydrotreating catalyst (acid-exchanged montmorillonite) was not very effective in hydrotreating. The experiments showed that repressurizing the hydrogen is needed to sustain hydrogenation and prevent condensations at this temperature. These acid catalysts are effective in removing organic sulfur from coal-derived products.

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name or manufacturer does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The assistance of Jonathan Kautz is greatly appreciated.

#### REFERENCES

1. E. Houdry, and A. Joseph, Bull. Assoc. Fr. Tech. Pet., 117 1956 177.
2. V. Haensel, Adv. Catal., 3 1951 194.
3. F.M. Gayer, Ind. Eng. Chem., 29 1933 1122.
4. F.C. Whitmore, Ind. Eng. Chem., 26 1934 94.
5. A. Corma, B.W. Wojciechowski, Catal. Rev. Sci. Eng., 24(1) 1982 165.
6. C. Walling, J. Am. Chem. Soc., 72 1950 1169.
7. E.J. Demmel, A.V. Perella, W.A. Stover and J.P. Shambaugh, Proc. A.P.I. Div. Refining, 46 (1966) 165.
8. A.G. Oblad, Oil Gas J., 70 (13) 1972 84.
9. C.J. Plank and E.J. Rosinski, Chem. Eng. Prog. Symp. Ser., 73 (63) 1967 26.
10. C.J. Plank, E.J. Rosinski, and W.P. Hawthorne, Ind. Eng. Chem., Prod. Res. Dev., 3 1972 165.
11. D.P. Mobley and A.T. Bell, Fuel, 59 1980 507-510.
12. C.W. Zielke, R.T. Struck, J.M. Evans, C.P. Costanza, E. Gorin, Ind. Eng. Chem. Proc. Des. Dev., 5 1966 158-164.
13. R.T. Struck and C.W. Zielke, Fuel, 60 1981 795-800
14. R.K. Sharma, J.W. Diehl, and E. S. Olson, 3rd Int. Conf. on Proc. and Utilz. of High Sulfur Coals, Ames, Iowa, Nov. 14-16, 1989.
15. R.K. Sharma, J.W. Diehl, and E.S. Olson, ACS Div. of Fuel Chem., Boston, MA, April, 1990 (communicated).
16. K. Tanabe, Solid Acids and Bases, their catalytic properties, Academic Press, New York/London, (1970) 528.
17. A. Vogel, Textbook of Quantitative Inorganic Analysis, 4th edn., Longman Sci. and Tech. Group, Essex, Eng., (1978) 434.
18. E.S. Olson, and J.W. Diehl, Anal. Chem., 59 1987 443-448.
19. R.K. Sharma, E.S. Olson, and J.W. Diehl (Unpublished results).

## DISPERSED PHASE MOLYBDENUM CATALYST RECOVERY IN COPROCESSING

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### INTRODUCTION

Dispersed-phase molybdenum catalysts are being used at PETC to enhance the simultaneous conversion of petroleum bottoms material and coal to distillate products. A series of tests were performed in micro-autoclaves, 1-liter semi-batch stirred autoclaves, and a 1-liter continuous unit aimed at maximizing the production of distillates while minimizing the catalyst requirements [1]. Similar product yield structures and conversions have been demonstrated using molybdenum concentrations from 200 ppm (based on coal weight) to 1000 ppm in the 1-liter continuous unit. Dispersed-phase catalysis using molybdenum may require catalyst recovery. This paper examines the potential for the recovery of a dispersed-phase molybdenum catalyst.

Molybdenum catalyst recovery schemes typically involve ashing the non-distillate process residue and converting the metals to their oxide form. Certain metal oxides are selectively solubilized by dissolution in ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), including molybdenum, which forms water-soluble ammonium heptamolybdate. A recovery process patented by AMAX [2] involves mixing a gasifier residue with an alkali metal hydroxide, heating the mixture between 600°C and 800°C in the presence of air, adding water to the mixture, and then acidifying and ammoniating the aqueous solution to extract and selectively crystallize as ammonium heptamolybdate. Universal Oil Product Incorporated [3,4] (UOP) has recovered a dispersed vanadium catalyst by first performing a particle size classification of the reactor product with hydroclones, followed by calcination (ashing) of the solids at 500°C, and extraction with an ammonium hydroxide solution.

Earlier experiments at PETC [5] indicated that the nickel and vanadium, present as contaminants in the petroleum bottoms, appear to be incorporated into the carbonaceous material. Thus, these metals are also present in the bottoms material produced in dispersed-phase catalytic coprocessing along with the catalyst and coal mineral matter. The catalyst recovery procedure consisted of extracting the reactor product with tetrahydrofuran (THF), ashing the extract at elevated temperature, and extracting the ash with an ammonium hydroxide solution. Initial recovery experiments used the ASTM procedure for ashing coal [6]. The effects of ashing temperature, coal mineral matter, and the choice of hydroxides (strength of the base) on molybdenum recovery were examined.

### EXPERIMENTAL

Reagents were ACS grade and obtained from Alfa Chemicals. Coals used included an Illinois No. 6 (Burning Star Mine) hvBb coal that was ground to less than 75 microns, and a deep-cleaned Kentucky (Blue Gem Mine) hvAb coal that was ground to less than 7.5 microns and physically cleaned by the Otisca T-Process [7]. Analyses of the feed coals and the coal ash are presented in Table 1. Maya atmospheric tower bottoms (Maya ATB) was used as the vehicle. An analysis of the Maya ATB is

presented in Table 2.

The semi-batch 1-liter autoclave was charged with 150 grams of coal, 350 grams of oil, and 35 grams of 0.045 M ammonium molybdate solution. The unit was operated with a continuous gas stream ( $3\text{H}_2\text{S}:97\text{H}_2$ ) at a rate of 4 SCFH (113 standard liters/hr). Water and volatile products (light oils) from the reactor were condensed in a trap maintained at room temperature. The reactor was maintained at run temperature for 2 hours, cooled, depressurized, drained, and washed with methylene chloride to quantitatively recover the product. Typical heatup and cool-down times of the autoclave tests were two hours. All semi-batch experiments were performed using reactor conditions of 435°C, 2500 psig, and 2 hours residence time.

The catalyst recovery scheme is depicted in Figure 1. Reactor product was slurried with a 5:1 wt ratio of n-heptane and then decanted. The heptane insoluble residue was then washed/extracted with THF and pressure-filtered through a 0.45 micron Durapore® membrane filter, using a 142-mm Millipore Hazardous Waste Filtration System and 40 psig nitrogen. The THF-insoluble residue was vacuum dried and weighed. A portion of the insoluble residue was ashed in a Fisher Model 495 Programmable Ashing Furnace. The residue was heated at a rate of 5°C/min to 250°C, held for an hour at 250°C, heated to the final temperature (700°C, 675°C, 510°C), and held at temperature for 600 minutes.

Solubilizations of the ash were performed at 65°C for one hour. Five grams of ash were used for experiments conducted with residues produced from Illinois No. 6 coal. One or three grams of ash were used for experiments that were conducted with residues produced from Kentucky (Blue Gem) coal or coal-free experiments. The ash was first mixed with approximately 100 ml of deionized water. Ammonium hydroxide was then added to give a weight ratio of ammonia-to-molybdenum of 10:1 and the mixture diluted to 300 ml with additional deionized water. A magnetic stirrer provided agitation during the solubilization. A water-cooled condenser prevented some vapors from escaping. The suspension was then filtered hot in a 47-mm Millipore vacuum filtration apparatus using a water aspirator. The ammonium hydroxide-soluble filtrate was evaporated to dryness using a rotoevaporator. Both the soluble and insoluble filter cakes were dried in a vacuum oven.

Selected samples were examined by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) energy dispersive analysis, X-ray diffraction, and inductively couple plasma emission spectroscopy (ICP). TGA was performed in a Perkin-Elmer TGS-2 Thermogravimetric system using a temperature profile of 5°C per minute in an air atmosphere. Samples were examined with an SEM equipped with an energy-dispersive spectrometer. ICP analysis was carried out at the University of Pittsburgh Applied Research Center (UPARC) using a Bausch and Lomb ARL Model S34000 system.

## RESULTS AND DISCUSSION

By ashing at 700°C and extraction with ammonium hydroxide, over 95 % of the molybdenum could be recovered from physical mixtures of coal ash, molybdenum trioxide, vanadium pentoxide, and nickel oxide. When experiments were performed using residues generated from continuous unit operations, only 50 percent of the molybdenum could be recovered in the ammonium hydroxide soluble extract. Since the melting point of  $\text{V}_2\text{O}_5$  is 695°C, the ashing temperature was reduced to 675°C. Recoveries

of molybdenum were still unsatisfactory. Consequently, a series of semi-batch experiments were performed using different feedstocks and dispersed molybdenum catalyst to produce samples that could determine the effects of ashing temperature, other metals present, and of coal ash constituents on catalyst recovery.

The first set of experiments, experiment A in Table 3, were performed with a THF-insoluble reactor product from liquefaction reactions conducted with Maya ATB and catalyst. The THF-insoluble residue was ashed at a temperature of 675°C producing a glassy solid. The glassy solid was difficult to remove from the crucible and extract with  $\text{NH}_4\text{OH}$ . SEM analysis indicated that the glassy solid was chemically homogeneous to a resolution of 1 cubic micron. X-ray diffraction analysis of the ash was unable to identify the major constituent of the ash.  $\text{MoO}_3$ ,  $\text{NaVMoO}_6$ , and  $\text{Fe}_4\text{V}_2\text{Mo}_3\text{O}_{20}$  were identified as minor constituents. The literature suggested [8] that vanadium-molybdenum complexes form at temperatures of 635°C and that lowering the ashing temperature to below 635°C would eliminate the formation of this complex and possibly the glassy solid.

The effect of ashing temperature on carbon removal from a THF-extracted reactor product was studied by TGA. The weight profile versus temperature indicated that carbon loss was occurring at temperatures as low as 510°C. By lowering the ashing temperature to 510°C, the ash obtained was the expected consistency and weight. Experiments were repeated at the lower ashing temperature of 510°C, (experiment B in Table 3), and the ash produced was a granular material rather than a glassy solid. X-ray diffraction analysis of the ash identified alpha- $\text{MoO}_3$  and  $\text{NaVMoO}_6$  as the major constituents of the ash. The unidentified major constituent observed at the higher ashing temperature (675°C) was not present. In an attempt to identify the compound present in the 675°C ash, a sample was ashed at 600°C. The 600°C ash sample contained the unidentified compound,  $\text{NaVMoO}_6$ ,  $\text{Na}_2\text{V}_2\text{Mo}_3\text{O}_{15}$ , and beta- $\text{MoO}_3$  as major constituents. Thus the molybdenum bound with the vanadium at 510°C is transformed to more complex structures at 600°C and possibly even more complex structures at 675°C which are inhibiting the recovery of molybdenum. Extraction of the 510°C ash residue with  $\text{NH}_4\text{OH}$  resulted in solubilization of the molybdenum and recoveries were greater than 90 percent. In these experiments, and all subsequent experiments, recoveries are defined as the percentage of molybdenum that is recovered in the basic solution. The range of values in Table 3 for molybdenum purity and ammonium molybdate recovery were from multiple experiments. Solubilized fractions were not selectively crystallized to recover the pure heptamolybdate salt.

The second set of experiments, experiments C and D in Table 3, were done to determine the effect that coal ash has on molybdenum recovery. Semi-batch liquefaction experiments were performed with Illinois No. 6 coal, Maya ATB, and catalyst. The THF-insolubles were ashed at a temperature of 510°C and extracted with  $\text{NH}_4\text{OH}$  but the recovery of molybdenum as a soluble species was only approximately 50 percent. X-ray diffraction analysis of the ammonium hydroxide-insoluble material indicated the presence of calcium molybdate. ICP analysis indicated a 1:1 molar ratio of calcium to molybdenum, consistent with the identification of calcium molybdate by X-ray diffraction.

Experiments were performed to determine if the formation of  $\text{CaMoO}_4$  was interfering with molybdenum recovery. Semi-batch experiments, experiment E in Table 3, were performed using a deep cleaned coal, Kentucky Blue Gem, containing 0.8 wt% ash, rather than the Illinois No.

6 coal containing 11.1 wt% ash. The purpose of using a deep-cleaned bituminous coal was to reduce the effect of the calcium (present in the coal mineral matter) on molybdenum recovery. The THF-insoluble residue was ashed and extracted with  $\text{NH}_4\text{OH}$  and the observed molybdenum recovery as a soluble species was now greater than 95 percent. The results of these experiments demonstrate that the calcium present in the mineral matter reacts with  $\text{MoO}_3$  in the ashing step to form  $\text{CaMoO}_4$ .  $\text{NH}_3$  does not appear to be a strong enough base to react with  $\text{CaMoO}_4$  to solubilize molybdenum.

Pure calcium molybdate was treated with  $\text{NH}_4\text{OH}$  at temperatures as high as  $90^\circ\text{C}$  but it was unreactive and not solubilized. Since ammonium hydroxide was ineffective, the stronger base, sodium hydroxide, was tested. Calcium molybdate was decomposed to form insoluble calcium hydroxide and soluble sodium heptamolybdate when treated with sodium hydroxide. These results demonstrate that stronger bases, such as sodium hydroxide, are capable of decomposing calcium molybdate and removing calcium as an insoluble salt. It also suggests that sodium hydroxide might be used as a substitute for ammonium hydroxide. Treatment of a solution containing sodium heptamolybdate with  $\text{NH}_4\text{OH}$  should result in the selective crystallization of ammonium heptamolybdate, the catalyst precursor.

A typical material balance for metals in a run made with cleaned Kentucky Blue Gem coal is indicated in Figure 2. Molybdenum present as ammonium heptamolybdate comprises 78 percent of the  $\text{NH}_4\text{OH}$ -soluble material. Analyses were not performed for the remaining constituents of the soluble fraction. Experiments with Illinois No. 6 coal typically did not yield as high an ammonium heptamolybdate concentration in the  $\text{NH}_4\text{OH}$ -soluble material. It is thought that some of the coal ash components are being solubilized with the ammonium hydroxide. Typically, for these experiments, molybdenum accounts for 50 percent of the  $\text{NH}_4\text{OH}$ -soluble material.

#### CONCLUSIONS

It has been demonstrated that molybdenum can be recovered from coal liquefaction coprocessing experiments. High recoveries of molybdenum required an ashing temperature of  $510^\circ\text{C}$  to avoid the formation of a refractory molybdenum-vanadium complex, which appeared to form at higher ashing temperatures ( $675^\circ\text{C}$ ) and inhibited molybdenum recovery. X-ray diffraction and elemental analyses of the ash produced from experiments that used coal indicate the presence of calcium molybdate in the ammonium hydroxide-insoluble material. Calcium molybdate that is formed from calcium in the coal mineral matter and the molybdenum catalyst is unreactive with ammonium hydroxide and inhibits the recovery of molybdenum. This was supported by conducting experiments with deep-cleaned coal wherein most mineral matter, to include calcium, had been removed. More than 90% of the molybdenum was recovered from deep-cleaned coal. Preliminary experiments have shown that stronger hydroxides, such as sodium hydroxide, react with calcium molybdate to form a soluble molybdate salt and would result in improved molybdenum recovery. As a result of optimizing the conditions, a recovery scheme has been developed that can recover the molybdenum when calcium has been removed from the feed coal. This scheme most likely will apply to raw coals using sodium hydroxide as a substitute for ammonium hydroxide.

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#### DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

#### REFERENCES

- [1] Lett, R.G.; Cugini, A.V.; Utz, B.R.; Krastman, D.; Cillo, D.L.; Jin, G.T. U.S./Korea 6th Joint Workshop on Coal Utilization, Seoul, Korea, 1989.
- [2] Sebenik, R.F.; Hallada, C.J.; Barry H.F.; Tsigdinos, G.A. U.S. Patent 4,374,100, Feb. 15, 1983.
- [3] Gatsis, J.G.; Nelson, B.J.; Lea, C.L.; Nafis, D.A.; Humbach, M.J. Coal Liquefaction Co-processing, Topical Report Number 2 ,DE-AC22-84PC70002, Aug. 19, 1988.
- [4] Nafis, D.A.; Fullerton, H.E.; Gatsis, J.G., Miller, M.A. Sixth Annual International Pittsburgh Coal Conference, September, 1989.
- [5] Cugini, A.V.; Ruether, J.A.; Cillo, D.L.; Krastman, D.; Smith, D.N.; Balsone, V. Preprints, Div. Fuel Chem., Am. Chem. Soc. 33(1), 6 (1988).
- [6] ASTM D3174-82 "Standard test method for Ash in the Analysis sample of coal and coke from coal," 1988 Annual book of ASTM standards, 5.05, 1988.
- [7] Simmons, F.J.; Keller Jr., D.V. 10th International Coal Preparation Congress, Sept. 1986.
- [8] Strupler, N.; Morette, A.; in Phase diagrams for Ceramists 1975 Supplement, (Ed. K.R. Reser) The American Ceramic Society, 1975.

Table 1. Analysis of Feed coals.

	Illinois No. 6 Burning star	Cleaned Kentucky Blue Gem Mine
Ultimate Analysis, wt% (Moisture Free)		
Carbon	70.2	80.3
Hydrogen	4.8	5.1
Nitrogen	0.9	1.9
Sulfur	3.1	0.8
Oxygen(difference)	9.9	11.1
Ash	11.1	0.8
Major Elements in Ash		
SiO <sub>2</sub>	44.6	29.1
Al <sub>2</sub> O <sub>3</sub>	18.3	25.9
Fe <sub>2</sub> O <sub>3</sub>	21.9	25.1
TiO <sub>2</sub>	0.9	3.2
P <sub>2</sub> O <sub>5</sub>	0.1	0.4
CaO	5.1	4.9
MgO	0.6	1.4
Na <sub>2</sub> O	1.6	1.4
K <sub>2</sub> O	1.1	1.7

Table 2. Analysis of Vehicle oil.

	Maya ATB 650°F*
Ultimate Analysis, wt%	
Carbon	84.5
Hydrogen	10.6
Nitrogen	0.5
Sulfur	4.0
Oxygen(direct)	0.3
Ash	0.1
850°F (Vol%)	30
Heptane insols, wt%	20
Nickel (ppm)	70
Vanadium (ppm)	370

Table 3. Effect of extraction conditions on Molybdenum recovery.

Exp	Coal	Solvent	Ni+V gm	Mo gm	Ash temp °C	Ash gm	Recovery Mo in sols wt%	(NH <sub>4</sub> ) <sub>2</sub> Mo <sub>7</sub> O <sub>24</sub> Purity wt% sols
A	None	Maya	0.23	1.6	675	4.0	ND	ND
B	None	Maya	0.23	1.6	510	4.2	88	73
C	Ill. # 6	Maya	0.15	2.4	675	20.0	35	44
D	Ill. # 6	Maya	0.15	1.0	510	18.5	49 - 57	34 - 38
E	Blue Gem	Maya	0.15	1.0	510	3.4	90 - 98	66 - 78

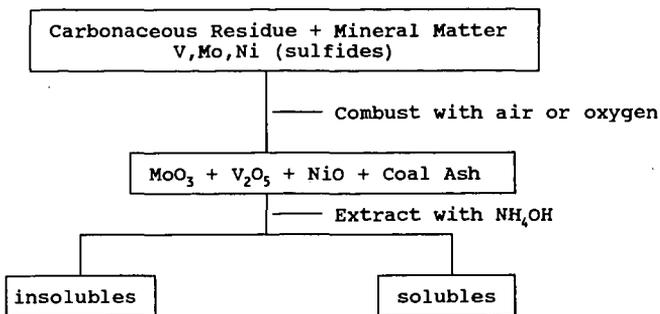


Figure 1. Catalyst Recovery in Coprocessing.

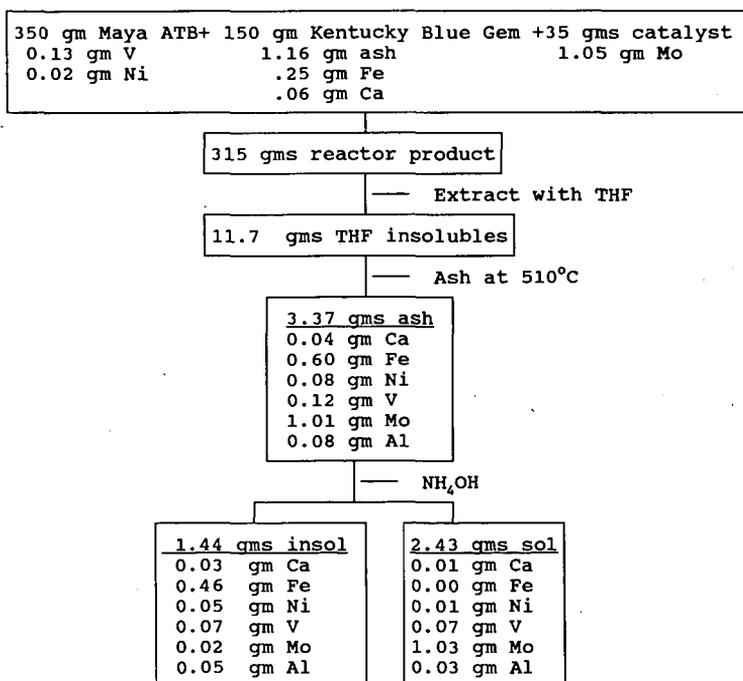


Figure 2. Catalyst Material Balance for Batch Run

CYCLIC OLEFINS AS NEW HYDROGEN DONOR COMPOUNDS  
FOR COAL LIQUEFACTION

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ABSTRACT

A new set of hydrogen donor compounds, cyclic olefins (CLO), has been evaluated to determine their effectiveness as hydrogen donors to coal. These cyclic olefins are hydroaromatic species which do not contain aromatic rings. The efficacy of these donors has been compared to conventional hydroaromatics. The CLO's under study are 1,4,5,8-tetrahydronaphthalene, also known as isotetralin, and 1,4,5,8,9,10-hexahydroanthracene. CLO's are much more reactive than their conventional hydroaromatic analogues, both in model reactivity studies and in reactions with Western Kentucky No. 9 coal. In this paper, the thermal and catalytic reactivity of the CLO's under nitrogen and hydrogen at coal liquefaction temperature is discussed. Results for the reactions of the CLO's and their conventional hydroaromatic analogues, e.g. tetralin, 9,10-dihydroanthracene, and octahydroanthracene, with Western Kentucky No. 9 coal are discussed.

INTRODUCTION

In both thermal and catalytic coal liquefaction reactions, hydrogen transfer reactions are important avenues by which hydrogen is transferred to coal and substantially increases the amount of coal conversion and upgrading. Hydrogen donors typically used are hydroaromatic and phenolic compounds (1-6). A new set of hydrogen donor compounds has been discovered that are much more effective than conventional hydroaromatics in transferring hydrogen to coal. These donors are cyclic olefins (i.e. hydroaromatic species which do not contain aromatic rings). An example is isotetralin, 1,4,5,8-tetrahydronaphthalene.

The efficiency of isotetralin for converting coal to THF solubles has been shown to be much higher than its conventional hydroaromatic analogue, tetralin (1). In reactions with Western Kentucky No. 9/14 coal, isotetralin converted 80.6% of the coal to THF solubles compared to only 58% for tetralin. This dramatic increase in coal conversion with isotetralin leads to the current investigation of cyclic olefins as hydrogen donors for coal liquefaction.

The objective of this research is to test cyclic olefins as donors for coal liquefaction. The cyclic olefins under study are 1,4,5,8,9,10-hexahydroanthracene (HHA) and 1,4,5,8-tetrahydronaphthalene, isotetralin (ISO). The first step in fulfilling this objective was to investigate the chemistry of these compounds. Both the thermal and catalytic reactivity under hydrogen and nitrogen atmospheres has been determined. The catalysts used were presulfided, pulverized NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub>. Secondly, these compounds were thermally reacted with Western Kentucky No. 9 coal under a nitrogen atmosphere to evaluate their hydrogen donability.

## EXPERIMENTAL

The reactivity and stability of the cyclic olefins were tested in a stainless steel tubing bomb reactor with a volume of 20 cc under the following conditions: 380°C, horizontal agitation at 425 cpm, 1250 psig nitrogen or hydrogen pressure at ambient temperature, reaction times ranging from 15 minutes to 1 hour, 2.0 g hexadecane as the diluent solvent, 3 weight percent CLO, and for catalytic reactions a total active metal loading of 3000 ppm. Two catalysts were used, Shell 324, NiMo/Al<sub>2</sub>O<sub>3</sub>, and Amocat 1B, Mo/Al<sub>2</sub>O<sub>3</sub>, to evaluate the catalytic reactivity of ISO at liquefaction conditions. Each catalyst was presulfided, pulverized, and sized between 100 and 200 mesh before being used.

The reactions of both CLO's and three conventional hydroaromatic donor compounds with Western Kentucky No. 9 were also performed. For this study the following reaction conditions were employed: 30 minute reaction time, 1250 psig nitrogen atmosphere at ambient temperature, 380°C reaction temperature, 2.0 g coal, 4.0 g total solvent mixture including 0.1-0.5 weight percent donable hydrogen of the model compound with the balance being fluorene as a diluent solvent, 700 cpm vertical agitation rate, stainless steel tubing bomb reactor of approximately 50 cm<sup>3</sup> volume.

The chemicals used were obtained from the following manufacturers and used as received: tetralin, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, and 9,10-dihydroanthracene from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene from Wiley Organics Inc.; Western Kentucky No. 9 coal from PSU/DOE sample bank.

For this work coal conversion is defined as

$$\text{conversion} = 1 - [ \text{IOM (maf)} / \text{coal charge (maf)} ] \times 100$$

In order to use this definition of coal conversion, both the moisture and ash contents were needed. The moisture content was 4.5 ± 0.6% and the ash 10.16 ± 0.14%.

## RESULTS AND DISCUSSION

### ISOTETRALIN SYSTEM

In the model reactivity studies, ISO was very reactive at the catalytic conditions studied; none was observed in the reaction products even at reaction times as short as 15 minutes. Two different presulfided hydrogenation catalysts were used: Shell 324, NiMo/Al<sub>2</sub>O<sub>3</sub>, and Amocat 1B, Mo/Al<sub>2</sub>O<sub>3</sub>. These catalysts were chosen because of their different hydrogenation activities with NiMo/Al<sub>2</sub>O<sub>3</sub> usually being more active. With ISO in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and a hydrogen atmosphere, tetralin (TET) was produced as a major product, while no measurable amount of naphthalene (NAP) was formed. With increasing reaction times, less TET was produced, while more decalin (DEC) was formed. With the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, the trans to cis isomer ratio was approximately 3 to 1. The DEC isomer ratio was independent of reaction time, within experimental error. With Mo/Al<sub>2</sub>O<sub>3</sub>, the predominant product formed was TET; cis and trans DEC as well as NAP was also formed, yielding approximately 20 weight percent DEC and one weight percent NAP. The trans to cis DEC isomer ratio was approximately 2.5 to 1 and was constant for reaction times ranging from 15 minutes to 1 hour. For ISO, NiMo/Al<sub>2</sub>O<sub>3</sub> was a more active hydrogenation catalyst than Mo/Al<sub>2</sub>O<sub>3</sub>, as evidenced by the greater amounts of DEC produced. The product slate was independent of time, within experimental error, for the reactions performed with the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst under equivalent

conditions but varying reaction times; i.e. all the products were formed within the first 15 minutes yielding the same product slate regardless of reaction time.

The thermal reactivity study of ISO showed that all ISO was converted at reaction times of 15, 30, and 60 minutes. The product slate for the thermal reactions differed from that of the catalytic reactions. 1,2-dihydronaphthalene (1,2-DHN) and 1,4-dihydronaphthalene (1,4-DHN) were formed thermally, whereas catalytically they were not. In a nitrogen atmosphere, the predominant product was NAP, with other major products being 1,2-DHN 1,4-DHN, and a minor amount of TET. Approximately 55 weight percent NAP and 40 weight percent DHN's were produced. In a hydrogen atmosphere, the observed products were TET, 1,2-DHN, 1,4-DHN, and NAP. The product slate for the thermal reactions was time dependent. Although the same products were observed, different amounts of each were formed at different reaction times. With increasing reaction time, the amount of NAP produced increased while the amount of 1,2-DHN and 1,4-DHN decreased. The 1,2-DHN to 1,4-DHN isomer ratio varied widely with varying reaction times. At a reaction time of one hour, the 1,4-DHN produced was unexpectedly small; it is believed that 1,4-DHN was rehydrogenated to TET, which would account for the increased TET produced at this reaction time.

#### HEXAHYDROANTHRACENE SYSTEM

The thermal and catalytic reactivity of 1,4,5,8,9,10-hexahydroanthracene, (HHA) was also examined. As in the ISO reactions, NiMo/Al<sub>2</sub>O<sub>3</sub> was a more active hydrogenation catalyst than Mo/Al<sub>2</sub>O<sub>3</sub> in the HHA reaction system. With NiMo/Al<sub>2</sub>O<sub>3</sub>, the predominant products from HHA hydrogenation were isomers of fully hydrogenated anthracene, perhydroanthracene (PHA); the other major products were isomers of octahydroanthracene (OHA) with a minor amount of tetrahydroanthracene isomers (THA) observed. Increasing reaction times favored the formation of the more hydrogenated product PHA, while decreasing the amount of OHA produced. For all reaction times, HHA was totally converted, with either NiMo/Al<sub>2</sub>O<sub>3</sub> or Mo/Al<sub>2</sub>O<sub>3</sub>. With the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, the predominant product was OHA; other products in lesser amounts were PHA and THA. Increasing reaction times increased the amount of hydrogenated product formation. Both OHA and PHA production increased, while that of THA decreased.

In the thermal reaction system for HHA, under both nitrogen and hydrogen atmospheres, the predominant products were isomers of dihydroanthracene (DHA) with 9,10-dihydroanthracene being the major isomer observed. Lesser products included THA and anthracene (ANT). In a nitrogen atmosphere, a trace amount of HHA was observed at the end of the 30 minute reaction time. In a hydrogen atmosphere, with increasing reaction times, HHA recovery decreased. DHA formation decreased, while ANT and THA formation increased. After 60 minutes of reaction in a hydrogen atmospheres, a minor amount of OHA was formed.

#### COMPARISON OF CYCLIC OLEFINS AND CONVENTIONAL DONORS

The reactivity of the conventional hydrogen donor analogues, DHA, OHA, and TET were compared to that of HHA and ISO under equivalent reaction conditions.

With NiMo/Al<sub>2</sub>O<sub>3</sub> in a hydrogen atmosphere, ISO completely reacted, whereas, approximately 25% of TET remained unconverted. The products formed from ISO were TET and DEC, while those from TET were primarily DEC. However, it should be noted that the trans to cis DEC isomer ratio was the same for both compounds, (3 to 1), within experimental error, and that neither ISO nor TET formed NAP as product.

This suggests that ISO was converted to TET by some pathway before forming the more hydrogenated products. With Mo/Al<sub>2</sub>O<sub>3</sub> in a hydrogen atmosphere, ISO was also completely reacted, whereas, TET remained almost 95% unconverted. However, as was the case with NiMo/Al<sub>2</sub>O<sub>3</sub>, the trans to cis DEC isomer ratio was the same for both ISO and TET (2.5 to 1), within experimental error. This result also suggests that ISO was converted to TET prior to forming DEC.

In thermal reactions, ISO completely reacted under both nitrogen and hydrogen atmospheres. By contrast, TET reacted only slightly in nitrogen producing NAP and was less than 4% converted in a hydrogen atmosphere, forming 1,2-DHN and 1,4-DHN.

The reactions of DHA, OHA, and HHA with NiMo/Al<sub>2</sub>O<sub>3</sub> in a hydrogen atmosphere produced hydrogenated anthracenes as the predominant products. All three reactants formed PHA, OHA, and THA. DHA and HHA were completely converted to hydrogenated products, whereas OHA remained approximately 32% unconverted. With the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, HHA was completely converted, approximately 8% of the DHA remained unreacted, and 98% of the OHA remained unreacted. These comparisons show that catalytically, HHA was much more reactive than either of the conventional hydrogen donor compounds, DHA or OHA.

A comparison of the thermal reactions of HHA, OHA, and DHA showed that in a nitrogen atmosphere HHA completely reacted, the predominant product from HHA hydrogenation being DHA, with lesser amounts of THA and ANT being formed. By contrast, OHA did not react and DHA remained 95% unconverted, with ANT being the only product. In a hydrogen atmosphere more than 98% of HHA was converted, with the predominant product again being DHA. By comparison OHA did not react and only 8% of DHA was converted to dehydrogenated products. The results from the thermal reactions show that HHA was much more reactive than either OHA or DHA at 380°C under both hydrogen and nitrogen atmospheres.

To summarize, when ISO is compared to TET, it is important to note that both thermally, under nitrogen and hydrogen, as well as catalytically, ISO completely converted. By comparison TET did not react thermally, only converted 5% with Mo/Al<sub>2</sub>O<sub>3</sub> and converted 75% with NiMo/Al<sub>2</sub>O<sub>3</sub>. The comparison of the conventional analogues to HHA showed that DHA was only converted 10% in a thermal reaction system, converted 100% with NiMo/Al<sub>2</sub>O<sub>3</sub>, and converted 90% with Mo/Al<sub>2</sub>O<sub>3</sub>. In a thermal system, under both nitrogen and hydrogen, OHA did not react; with the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, OHA was 68% reacted, while with the Mo/Al<sub>2</sub>O<sub>3</sub> only 2% converted. HHA was completely converted by both NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub>. In a thermal system under nitrogen, HHA was completely reacted and was more than 90% converted under hydrogen. Thus, ISO was more reactive than TET, and HHA was more reactive than either DHA or OHA.

#### REACTIONS WITH WESTERN KENTUCKY NO. 9 COAL

A series of thermal reactions using ISO, HHA, TET, OHA, and DHA with Western Kentucky No. 9 coal in a nitrogen atmosphere was performed. The results for coal conversion to tetrahydrofuran solubles (THFS) is presented in Table I. Each datapoint represented in Table I is the result of at least a duplicate analysis. These are two important aspects to this table. The first is the ranking of the five donor species at the equivalent loading of 0.5 weight percent donable hydrogen. The second is the comparison of HHA and OHA at three different levels of donable hydrogen, 0.5, 0.2, 0.1 weight percent. Important to note in the rankings of the donor species at 0.5 weight percent, is that the two cyclic olefins, HHA and ISO, yielded greater coal conversions than did their conventional

hydroaromatic analogues, TET, OHA or DHA. HHA produced an increase in coal conversion of approximately 12% over its nearest analogue DHA. HHA also showed more than 13% greater conversion than did OHA. ISO yielded approximately 14% greater conversion than did its conventional analogue, TET. All of these comparisons were made on an equivalent amount of donable hydrogen.

When the level of donable hydrogen was varied, HHA consistently converted more than did OHA, albeit, in decreasing differential amounts as the level of donable hydrogen decreased. This result implies that a deficiency of donable hydrogen occurred at these lower levels of donable hydrogen.

For each of the reactions, the THFS fraction was then further analyzed to determine the effect of the coal reaction on the amount of the model hydrogen donor compound that was present in the reaction products. Important to note from this analysis is that for a given hydrogen donor compound, as the level of donable hydrogen was decreased, the products shifted to less hydrogenated species.

A plot of coal conversion versus net grams of H donated from the hydrogen donor is represented in Figure 1. These values were obtained in the following manner. Net grams of hydrogen released (grams of H donated from model compound) - (grams of H going to form other hydrogen donor species). For these calculations, the only other H donor formed was OHA. The solid line shown is the linear best fit to all the data points. The general trend is that as coal conversion increased, the amount of hydrogen donated also increased.

#### SUMMARY

As seen in both the model compound reactions as well as reactions with Western Kentucky No. 9 coal, the new hydrogen donor compound, cyclic olefins, HHA and ISO, are much more reactive at model liquefaction conditions than either DHA, OHA, or TET. In the model compound reactivity studies, ISO was more reactive, both thermally and catalytically, than TET; HHA was more reactive, both thermally and catalytically, than either DHA or OHA. In reactions with Western Kentucky No. 9 coal in a nitrogen atmosphere, HHA produced an increase in coal conversion to THF solubles of greater than 12% compared to that obtained with OHA, and 12% greater conversion than that obtained with DHA. ISO produced an increase in coal conversion of approximately 14% more than obtained with TET.

#### REFERENCE

- (1) Curtis, C.W.; Guin, J.; Kwon, K.; "Coal Solvolysis in a Series of Model Compound Systems."; Fuel; 63, 1984.
- (2) Neavel, R.C.; "Liquefaction of Coal in Hydrogen Donor and Non-donor Vehicles"; Fuel; 55, 1976.
- (3) Utz, B.R.; Appell, H.R.; Blaustein, B.D.; "The Roles of Vehicles and Gaseous Hydrogen During Short Contact Time Coal Liquefaction"; Fuel; 65, 1986.
- (4) Kitaoka, Y.; Mikio, U.; Murata, K.; Ito, H.; Mikami, K.; "Effect of Catalyst and Vehicle in Coal Liquefaction"; Fuel; 61, 1982.
- (5) Bockrath, B.C.; "Chemistry of Hydrogen Donor Solvents"; Coal Science; Vol. 2, Academic Press, New York, NY; 1982

- (6) Franz, J.A.; Camaioni, D.M.; "Radical Pathways of Coal Dissolution in Donor Media During Reactions of Coal and Specifically Deuterated Tetralin"; Prep. Paper., ACS Div. Fuel Chem.; 1981, 26(1).

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Table I. Coal Conversion Summary for Western Kentucky No. 9

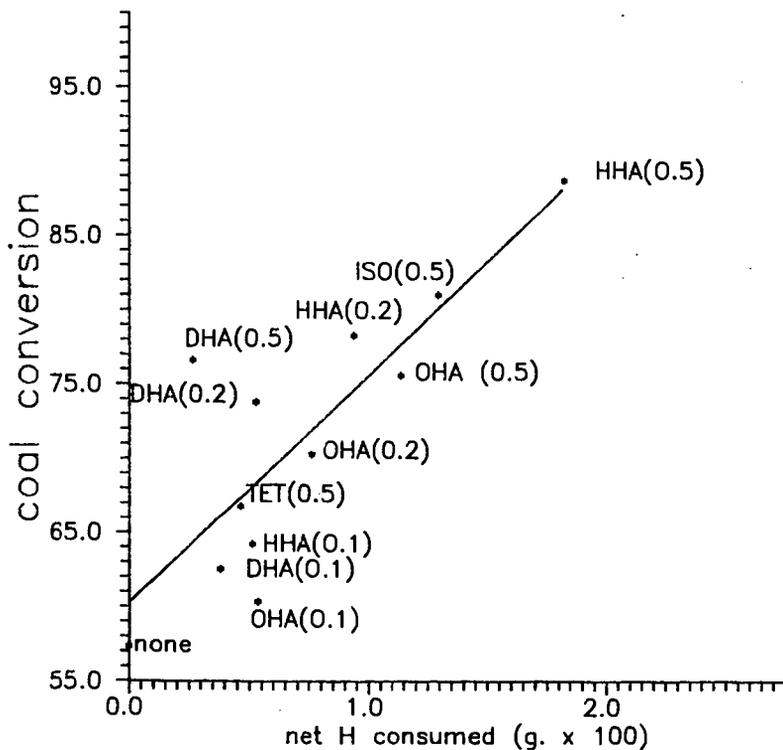
Donor Compound	Conversion* at		
	<u>.5wt% DH</u>	<u>.2wt% DH</u>	<u>.1wt% DH</u>
HHA	88.6(0.04)	78.2(0.5)	64.2(2.5)
ISO	81.0(0.9)		
DHA	76.6(0.8)	73.8(1.1)	62.5(1.2)
OHA	75.5(0.7)	70.2(2.7)	60.3(0.7)
TET	66.8(0.9)		
none	57.4(2.3)	57.4(2.3)	57.4(2.3)

\* conversion defined as  $1 - \frac{IOM(maf)}{\text{coal}(maf)}$   
and DH refers to donable hydrogen

\*\*All reactions at 380°C, 1250 psig (cold) N<sub>2</sub> atmospheres, 700 cpm, and 30 minute reaction time.

In the pairs of numbers above, the first is the conversion obtained. The second, in parenthesis, is the standard deviation for that data point.

Figure 1. COAL CONVERSION VERSUS HYDROGEN DONATED.  
 THREE LEVELS OF DONABLE HYDROGEN,  
 (0.5, 0.2, and 0.1 weight percent)



ACTIVATION OF METHANE BY TRANSITION METAL-SUBSTITUTED  
ALUMINOPHOSPHATE MOLECULAR SIEVES

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Keywords: methane activation, molecular sieve, catalysis

ABSTRACT

Recent experiments in our laboratory have demonstrated that aluminophosphate molecular sieves substituted with cobalt and cobalt/silicon combinations and having the  $AlPO_4-34$  or  $AlPO_4-5$  structure activate methane starting at  $\sim 350^\circ C$ . Between 400 and  $500^\circ C$  the rate of methane conversion increases steadily with typical conversion efficiencies at  $500^\circ C$  ranging from 15 to 60%. The cobalt and silicon substituted  $AlPO_4-34$  structure (CoAPSO-34) produces ethylene, ethane, propylene, and propane in varying proportions, depending on reaction conditions. The cobalt-substituted  $AlPO_4-5$  (CoAPSO-5) produces propylene in very high yield, with ethane, ethylene, and propane also seen. Analogous aluminophosphate molecular sieves substituted with magnesium or silicon, but containing no transition metal (e.g., SAPO-34, MAPO-5), do not activate methane under the conditions described above. The activation mechanism is based on reduction of the cobalt(III) form of the molecular sieve to the cobalt(II) form with accompanying oxidative dehydrogenation of the methane. Reoxidation of the cobalt(II) form to the cobalt(III) form can be done either chemically (e.g., using  $O_2$ ) or electrochemically.

INTRODUCTION

In a recently published paper (1) we reported the finding that when Co(II) is substituted for Al(III) in the framework of certain aluminophosphate ( $AlPO_4$ ) molecular sieves and the resulting Co(II)-containing  $AlPO_4$  (CoAPO) is calcined in oxygen, the Co(II) is oxidized to Co(III). Further work with these Co(III)APOs showed that they possess strong oxidizing capability, and, for example, can convert methanol to formaldehyde (at  $25^\circ C$ ), NO to  $NO^+$  (at  $25^\circ C$ ), and  $H_2$  to  $2H^+$  (at  $>300^\circ C$ ). These results inspired the thought that Co(III)APOs might actually oxidize methane and in the process convert the activated species directly to light hydrocarbons by virtue of their known Bronsted acid catalyzed homologation capacity (2,3) and the product selectivity constraints imposed by their pore dimensions. Recent experiments in our laboratory (summarized below) have demonstrated that this is in fact the case.

EXPERIMENTAL

The synthesis methods used to prepare the aluminophosphate molecular sieve materials employed in this work have been discussed elsewhere (1). Reactions of methane on these molecular sieve materials and on several other metal oxides known to activate methane (e.g.,  $Sm_2O_3$ ) were carried out in a quartz tube reactor having an 8 mm inside diameter. The catalyst sample ( $\sim 1$  gram) was supported on a quartz fritted disk fused into the midsection of the quartz tube. The tube was mounted in an electrically heated furnace (with the sample in the middle of the heated zone) and attached to the gas handling system. The gases used in the experiments [99.999% He, 10%  $CH_4$  in Ar ( $C_{2+}$  hydrocarbons/ $CH_4 \approx 0.002$ ), and "zero" air, all supplied by Matheson Gas Products] were introduced at the bottom of the

reaction tube. A quartz-sheathed thermocouple was positioned inside the reaction tube just above the bed of catalyst material. Electrochemical activation was accomplished by inserting two coiled sections of platinum wire that were flattened to conform to the side wall of the reaction tube and then mounted in the tube so that they faced each other with a spacing of  $\sim 3$  mm.

In a typical experiment with a molecular sieve material, the sieve sample was calcined in "zero" air at  $550^\circ\text{C}$  in the reaction tube to burn off any remaining template ions (for a fresh sample) or carbonaceous residues (for a used sample). This calcining restored the cobalt-containing molecular sieves to the Co(III) form as described previously (1). After calcining, the reaction tube was brought to the desired temperature and purged of residual oxygen with flowing helium, then  $\sim 10$  cc (STP) of the 10%  $\text{CH}_4$  in Ar mixture was introduced at a rate of  $\sim 0.5$  cc/min. The reaction products, unreacted  $\text{CH}_4$ , and Ar coming out the top of the reaction tube were collected in a liquid nitrogen cooled loop. The loop was then isolated from the reaction tube and warmed up to room temperature; after which a gas sample was withdrawn through a septum port on the side of the loop (using a gas syringe) and injected into a gas chromatograph (GC) equipped with a flame ionization detector (FID). In some experiments injections were also made into a GC equipped with a thermal conductivity detector (TCD) to determine the amounts of  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$  that were produced relative to the amount of  $\text{CH}_4$  reacted.

Electrochemical activation studies were performed using a constant voltage power supply. Potentials in the range from 3 to 10 V dc were applied across the two platinum wire electrodes (described above). Gas handling procedures employed in the presence of an applied potential were the same as those used on air calcined molecular sieve samples, except that the sieve sample was fully reduced (deactivated) with  $\text{CH}_4$  between the calcining and helium purging steps. The voltage was applied during purging and maintained throughout the  $\text{CH}_4$  introduction step.

## RESULTS

Methane activation experiments were performed on the following aluminophosphate molecular sieve materials: CoAPSO-34 (P:Co:Si = 12:1:1.8), CoAPO-5 (P:Co = 24:1), MAPO-5 (P:Mg = 12:1), and SAPO-34 (P:Si = 6.7:1). The onset temperature for activation of  $\text{CH}_4$  by the cobalt-containing  $\text{AlPO}_4$  (i.e., where a few percent of  $\text{C}_{2+}$  products are observed relative to the  $\text{CH}_4$ ) occurs in the  $350$  to  $400^\circ\text{C}$  range. At  $500^\circ\text{C}$  the reaction proceeds more rapidly, and single pass conversions of  $\text{CH}_4$  to  $\text{C}_{2+}$  hydrocarbons ranging from 15 to 30% have been observed. In single pass experiments without electrochemical stimulation,  $\sim 1$  cc (STP) of methane deactivates almost all of the active sites in  $\sim 1$  gram of the CoAPSO-34 or CoAPO-5, and recalcination with  $\text{O}_2$  is required to reactivate the sieve material. Many air calcinings have been run on some samples of CoAPSO-34 without evidence of significant permanent loss of activity, but in most other cases we have observed steady decreases in activity with extended use. In the presence of applied dc potentials in the 3 to 10 V range, it is possible to activate the reduced form of the cobalt-containing molecular sieves [(HCo(II)APSO-34 and HCo(II)APO-5)] and achieve significant ( $\geq 15\%$ ) methane conversion to  $\text{C}_{2+}$  hydrocarbons in a single pass at  $500^\circ\text{C}$ . However, even electrochemically activated samples tend to exhibit reduced activity with extended use.

Identical experiments were performed on the silicon-substituted  $\text{AlPO}_4$ -34 (SAPO-34) and magnesium-substituted  $\text{AlPO}_4$ -5 (MAPO-5), wherein air calcination and electrochemical stimulation were employed in the same manner as was used with the CoAPSO-34 and CoAPO-5. None of these experiments gave any evidence of methane activation to  $\text{C}_{2+}$  hydrocarbons. A test of air-calcined  $\text{Sm}_2\text{O}_3$ , a known methane

activation catalyst at  $\geq 700^\circ\text{C}$  (4), failed to produce any  $\text{C}_{2+}$  products in our apparatus for temperatures up to  $580^\circ\text{C}$ , using methane only as a reactant (no oxygen co-feed).

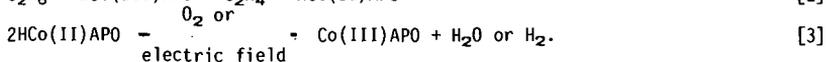
A summary of typical results from the experiments described above is given in Table I. Reproductions of FID gas chromatograms for the products of methane activation over an air calcined sample of CoAPSO-34, an electrochemically stimulated sample of CoAPSO-34, and an electrochemically stimulated sample of CoAPO-5 are shown in Figs. 1, 2a, and 2b, respectively. TCD gas chromatograms run on products from experiments where high yields of  $\text{C}_{2+}$  hydrocarbon were obtained typically showed relatively low levels of  $\text{CO}_2$  (a few percent at most) and hardly any  $\text{CO}$ . If care was not taken to remove oxygen (as  $\text{O}_2$ ) from the reaction environment prior to introduction of the methane, higher levels of  $\text{CO}_2$  and lower levels of  $\text{C}_{2+}$  hydrocarbons were normally observed, i.e., the yields of  $\text{C}_{2+}$  hydrocarbons and  $\text{CO}_x$  have tended to be inversely related to one another in the types of experiments described above.

Finally, we wish to note that electrochemical stimulation experiments done on samples of Co(II)-exchanged SAPO-34 (P:Co  $\leq 12$ ) and Co(II)-exchanged Y zeolite (Si:Co  $\sim 5$ ) at  $500^\circ\text{C}$  (using the same conditions as for the CoAPSO-34 and CoAPO-5 experiments) produced smaller (but nonetheless measurable) yields of the same products observed for CoAPSO-34 (see Table I). In the case of single pass experiments with Co(II)-exchanged Y zeolite, evidence of a few percent conversion of methane to  $\text{C}_{2+}$  hydrocarbons at  $500^\circ\text{C}$  was also seen for a sieve sample that was air calcined at  $550^\circ\text{C}$  prior to methane exposure.

#### DISCUSSION

The results presented in the preceding section give clear evidence that cobalt-substituted aluminophosphate molecular sieves have the capability to catalyze the coupling of methane to  $\text{C}_{2+}$  hydrocarbons at temperatures  $< 500^\circ\text{C}$ . The single pass yields which have exceeded 30% at  $500^\circ\text{C}$ , the high selectivity to  $\text{C}_{2+}$  hydrocarbons, the encouraging observation that molecular oxygen is not essential to the activation process, and the absence of large quantities of  $\text{CO}_x$  in the product stream represent a significant advance in the state-of-the-art for methane coupling using inorganic catalyst materials. The further finding that the cobalt-substituted molecular sieve can be maintained in the active state by an electric field allows for the development of continuous methane homologation processes using, e.g., packed or fluidized electrochemical bed reactors.

Data from comparative experiments -- CoAPSO-34 vs SAPO-34 and CoAPO-5 vs MAPO-5 -- show that cobalt is essential to the activation process. Prior work (1) indicates that the active state of the cobalt is tetrahedrally-coordinated Co(III) bound in framework metal atom positions of the molecular sieve. The overall reaction mechanism is believed to include the following steps:



The formation of  $\text{C}_3$  hydrocarbons could occur from reaction of methyl radicals ( $\text{CH}_3^\bullet$ ) with ethylene or from Bronsted acid catalyzed reactions involving

ethylene. All of the above reactions are believed to take place within the molecular sieve framework which selectively constrains the size and shape of the transition state species and the products.

Although we assume that the framework-bound cobalt is the active agent in this catalysis, there was evidence that air calcined and electrochemically stimulated beds of Co(II)-exchanged SAPO-34 and Co(II)-exchanged Y zeolite also produced detectable quantities of C<sub>2+</sub> hydrocarbons when exposed to methane at 500°C. This apparent catalytic activity of Co(II)-exchanged molecular sieves, which was actually predicted recently in the modeling work of Aparicio and Dumesic (5), is believed to occur by a mechanism that is separate from, but possibly related to, the one given above for framework-bound Co(II)/Co(III) in AlPO<sub>4</sub> molecular sieve structures.

The effectiveness of electrochemical stimulation as a redox activator was not unexpected in this work. There is increasing evidence (6) that molecular sieve materials are good ionic conductors at elevated temperature and have great potential for use in gas phase electrocatalysis applications. Also, Creasy and Shaw (7) recently demonstrated the electrocatalytic activity of CoAPSO-34 micro-electrodes in the presence of methane using cyclic voltammetry.

There are a number of aspects of the research findings described above that call for further, more detailed study. Other transition metals, such as manganese and iron, can be substituted into the framework of AlPO<sub>4</sub> molecular sieves (2,3) and these might also exhibit methane coupling activity. The fact that a variety of pore sizes and framework architectures are possible with AlPO<sub>4</sub> molecular sieves (2,3) should be exploited to determine the relationship between sieving properties and activity/selectivity. The optimum amount of transition metal substitution, the role (beneficial or otherwise) of non-redox type acid site creators (e.g., Si, Mg, Zn) in the framework, and the optimum balance between redox and non-redox framework metal atoms requires exploration. Factors such as framework demetalization, over-dehydrogenation (leading to soot formation), the need for oxygen potential control (to avoid destabilization of the framework structure), and the role of impurities (e.g., H<sub>2</sub>O) in the activation and ionic conduction processes all need to be elucidated. Foremost among the concerns stemming from our research to date are the causes of the gradual loss of catalytic activity observed for the CoAPSO-34 and CoAPO-5 sieve materials, and the implicit need for a methodology to identify/produce more stable, resilient transition metal-substituted AlPO<sub>4</sub> structures.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- (1) L. E. Iton, I. Choi, J. A. Desjardins, and V. A. Maroni, *Zeolites* **9**, 535 (1989).
- (2) R. J. Pellet, P. K. Coughlin, E. S. Shamsoum, and J. A. Rabo, in *Perspectives in Molecular Sieve Science*, W. H. Flank and T. E. Whyte, Jr., Eds., American Chemical Society Symposium Series No. 368 (1988) p.85.
- (3) E. M. Flanigen, R. L. Patton, and S. T. Wilson, in *Studies in Surface Science and Catalysis*, Vol. 37, P. J. Gobet, W. J. Mortier, E. F. Vansant, and G. Schulz-Ekloff, Eds. (Elsevier Publishers, Amsterdam, 1988) p. 189.

- (4) K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.* 100, 353 (1986).
- (5) L. M. Aparicio and J. A. Dumesic, *J. Molec. Catal.* 49, 205 (1989).
- (6) K. E. Creasy, *Electrochemical Society Extended Abstracts Vol. 89-2*, 972 (1989).
- (7) K. E. Creasy and B. R. Shaw, Department of Chemistry, University of Connecticut (work in progress).

Table I. Examples of Product Distributions from Typical<sup>a</sup> Methane Activation Experiments at 500°C

Molecular Sieve	Activation Method	Number of Passes	Product Distribution (Mole %)				
			CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
CoAPSO-34	Air calcine	Single	65	15	12	1	7
	Electrochem.	Single	91	5	1	2	1
	Electrochem.	Multiple <sup>b</sup>	85	4	3	4	4
SAPO-34	Air Calcine	Single	99	— nil —			
	Electrochem.	Single	99	— nil —			
CoAPO-5	Air Calcine	Single	54	1	5	1	39
	Air Calcine	Multiple <sup>b</sup>	21	1	10	1	67
	Electrochem.	Single	58	2	4	4	32
MAPO-5	Air Calcine	Single	99	— nil —			
	Electrochem.	Single	99	— nil —			
Co(II)-EX <sup>c</sup> SAPO-34	Electrochem.	Single	98 <sup>d</sup>	0.5	0.4	0.3	0.3
Co(II)-EX <sup>c</sup> Y Zeolite	Electrochem.	Single	98	1	1	-	-
	Electrochem.	Multiple <sup>b</sup>	94	1	1	1	3

- (a) The data presented in this table were derived from averages of several of the better results obtained with each material.
- (b) In multiple pass experiments the unreacted methane and products from the first pass are recycled through the bed four or five additional times.
- (c) Indicates Co(II) exchanged molecular sieve material.
- (d) A fifth undetermined low molecular weight product was observed with Co(II)-exchanged SAPO-34. It was not acetylene, cyclopropane, or CO.

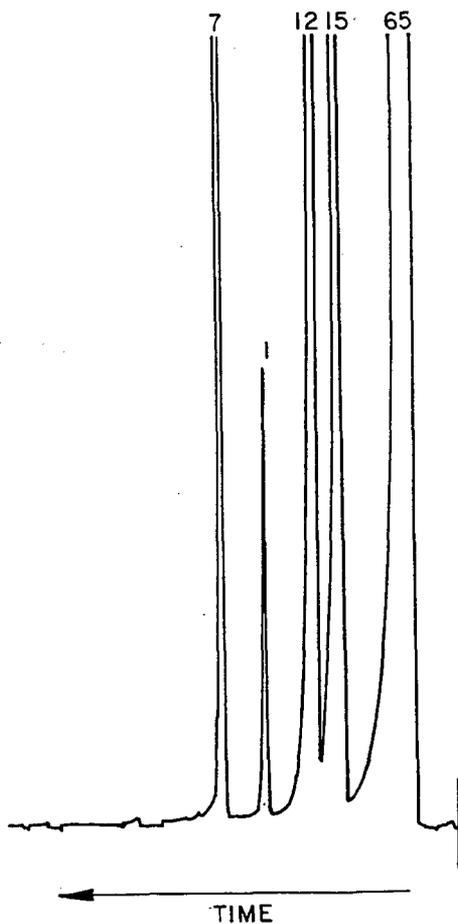


Figure 1. Gas chromatogram of the products from a typical single pass reaction of methane over air calcined CoAPSO-34 at 5000C. The numbers above each peak give the approximate mole percentages of each gas; i.e., 65% = CH<sub>4</sub>, 15% = C<sub>2</sub>H<sub>6</sub>, 12% = C<sub>2</sub>H<sub>4</sub>, 1% = C<sub>3</sub>H<sub>8</sub>, and 7% = C<sub>3</sub>H<sub>6</sub>.

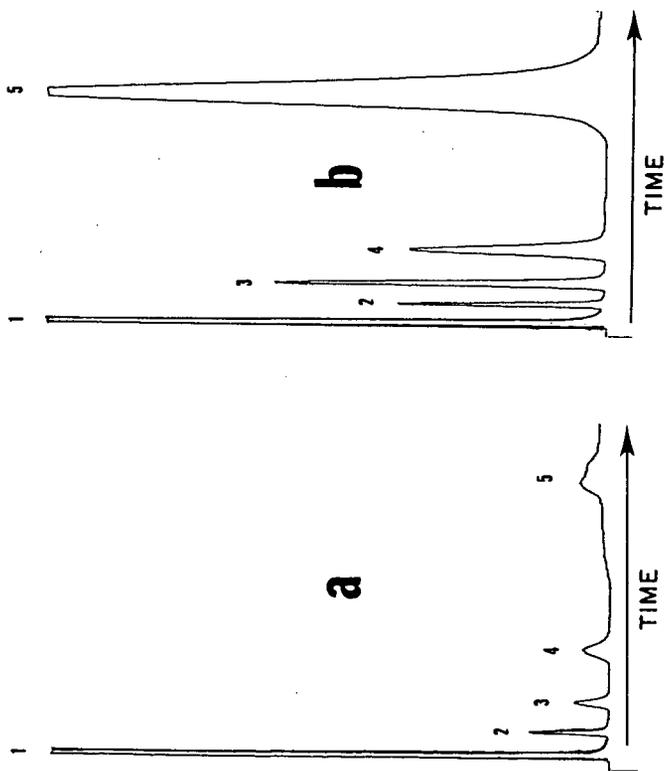


Figure 2. Results of single pass reactions of methane over electrochemically stimulated (10 V) CoAPSO-34 (insert a) and CoAPO-5 (insert b) at 5000C. Peaks 1 through 5 are  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ , and  $\text{C}_3\text{H}_6$ , respectively.