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Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers

November, 1980

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FORWARD

In order to determine if an alternative fuel could replace or extend the supply of petroleum, it is essential to achieve an extremely high degree of reliability. This requires solutions to many real and potential problems. The work reported here deals with the evaluation of a mixture of methyl aryl ethers derived from coal liquids as a gasoline extender and octane improver.

The Department of Energy is pleased to have this highly professional addition to alternative fuels application knowledge as reported by Dr. Gary M. Singerman.

Ralph D. Fleming
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and Western coals, the solvent refined coal process produces 1% phenol and 4% mixed cresols based on coal input (2).

A Battelle study shows that the H-coal liquefaction process gives 7.93 wt. % of phenols in the C₄ - 204°C (400°F) fraction. A coal hydrogenation plant with a daily production capacity of 30,000 bbl. liquid will produce 1,380 bbl/day of a mixture of phenol, cresols, and xylenols (2). Another study of the H-coal process showed that when the process is producing fuel oil, the product boiling below 203°C (397°F) contains 22.3 wt. % C₆ - C₉ phenols (7.94 wt. % total distillate). When producing Syncrude, the product boiling below 197°C (387°F) contains 14.5 wt. % C₆ - C₉ phenols (5.01 wt. % total distillate) (3).

In experimental coal liquefaction studies on a variety of Eastern bituminous coals performed at Gulf Research & Development Company using a one ton per day SRC II process demonstration unit, the phenols in raw liquid product have been studied. The phenols in a raw liquid product cut that boils in a range of about 55°C (150°F) to 260°C (500°F) were determined by gas chromatography. This cut represents about 18-20% of the coal fed to the demonstration unit and about 50% of the liquid product. For a series of eight runs, phenolic content varied in this cut from 10.2% to 51.7%. The phenols in a 55°C (131°F) to 249°C (480°F) cut from a typical run on the SRC II process demonstration unit are shown in Table 1. The amount of phenols in this cut was 24.7 wt. %.

Table 1

Phenolic Compounds Identified by Gas Chromatography
in a 55° - 249°C Raw SRC II Coal Liquid Fraction

<u>Phenolic Compound</u>	<u>Weight %</u>
Phenol	5.58
Ortho-Cresol	2.31
Meta-Cresol	3.65
Para-Cresol	2.30
2,4-Dimethylphenol	0.77
2,5-Dimethylphenol	0.38
2,6-Dimethylphenol	0.20
3,4-Dimethylphenol	0.12
3,5-Dimethylphenol	0.82
Ortho-Ethylphenol	0.32
Para-Ethylphenol	0.91
Propylphenol	1.86
Unidentified Phenols	<u>5.48</u>
Total	24.70

The raw coal liquid used in the present work came from a composite of fifty-one coal liquefaction runs on Eastern bituminous coals fed to Gulf Research & Development Company's one ton per day SRC II process demonstration unit. From this liquid composite, we used a cut having a boiling range of 55°C (131°F) to 260°C (500°F). This cut contained 28.8 wt. % of phenolics.

Almost certainly, if direct coal liquefaction becomes commercially significant, far more phenolics will be produced than can be absorbed by the combined demand of all chemical industries utilizing phenolics. Other, non-chemical industry uses must be found for coal phenolics. But they cannot be blended into gasoline to extend supplies and improve octane. This is unfortunate because phenols are excellent non-metallic octane improvers. Nevertheless, our studies have shown that phenols in gasoline are corrosive, may cause gum formation, and will cause some plastics and elastomers currently used in automotive gasoline systems to swell, harden, or crack (4). Just as important, phenols are poisonous by all routes of entry into the systemic circulation of mammals, absorption through the skin being the primary route of entry into the blood stream. Liquid phenol in contact with the skin may cause local irritation or chemical burns.

On the other hand, coal phenols could be left in the raw coal liquid and the mixture further processed by hydrotreatment as one step in producing high quality gasoline or distillate fuel. Hydrotreatment would reduce the phenolics to fuel-compatible materials. But hydrotreatment to reduce phenolics would require severe conditions and consume large amounts of hydrogen. From a processing standpoint, refining of raw coal liquids is hampered by the presence of phenolics because:

1. Excessive hydrogen consumption is required to reduce the phenols.
2. The combination of coal phenols (or some component therein) and chlorides is much more corrosive to processing equipment than either one alone. Many coals have high chloride content (5).
3. Water produced when phenols are hydroreduced sinters refinery catalyst supports.
4. Presence of phenols hampers ease of nitrogen removal from coal liquids by hydrorefining. Kinetic studies by Suntech show that the rate constants for removal of nitrogen from phenol-free SRC II coal liquid by hydrorefining are increased by over a factor of six at 375 and 400°C compared to rate constants for whole, unextracted SRC II liquid. The significance of the increased hydrodenitrogenation rate constants is that the reactor can be smaller for a given capacity or more throughput can be obtained at milder conditions, both of which can result in lower operating costs (6).

Taking all factors into account, extraction of phenolics from raw coal liquid and conversion of the phenolics into MAE's may have significant merit in terms of gasoline octane improvement and possible improvements in the overall efficiency and economics of coal processing.

III. PREPARATION OF MAE

A composite of raw coal liquid from fifty-one coal liquefaction runs on Eastern bituminous coals fed to Gulf Research & Development Company's one ton per day SRC II process demonstration unit was used as the source of phenols. A cut (1019 gallons, 7574 lbs.) boiling in the range 55°C (131°F) to 260°C (500°F) was extracted with aqueous sodium hydroxide to give 2180 lbs. (28.8%) of mixed phenols. The phenols were allowed to react with dimethyl sulfate to yield the MAE product. Details for these operations are given in Appendix A. Ideally, one would produce MAE by direct reaction of phenols with methyl alcohol. This has been done in small scale experiments, but process improvements and scale-up studies are needed.

IV. ANALYTICAL INSPECTION OF MAE

Samples of the MAE product were analyzed for density, distillation curve, nuclear magnetic resonance spectrum, gas chromatography, infrared spectrum, and carbon, hydrogen, oxygen, and nitrogen content. The nuclear magnetic resonance and infrared spectra showed absorptions expected from a mixture of methyl aryl ethers corresponding to a mixture of phenols as shown in Table 1, but did not show any free, unreacted phenols. Gas chromatography also showed an absence of free phenol in the MAE product. Other inspection data are shown in Table 2.

Table 2 - MAE Inspection

Inspection:	
Density, 20°C, D941, g/ml	0.9807
Carbon, Wt. %	79.60
Hydrogen, Wt. %	8.61
Nitrogen, Wt. %	0.15
Oxygen, Wt. %	12.39
Distillation, D86, 760 mm	
Over: °C	140
End: °C	226
5% at: °C	168
10%	171
20%	173
30%	176
40%	177
50%	180
60%	183
70%	187
80%	193
90%	202
95%	213
Recovery: %	99.5
Residue: %	0.5
Loss: %	0.0

V. GASOLINE BLENDING AND COMPATIBILITY

The MAE product was blended at 5 volume % with a commercial unleaded gasoline. Typical inspections of the base gasoline and the blend are given in Table 3. Apparently, some of the light ends were lost from the base gasoline when it was blended with MAE in large lots. This is indicated by the loss of vapor pressure and higher initial distillation point for the blend compared to the base gasoline in Table 3. An earlier inspection of a 5% MAE/gasoline blend was done on a small sample that had been hand-blended in glassware (Table 4). In this case, the base gasoline is a commercial, unleaded gasoline very similar to that described in Table 3. The loss of vapor pressure for the blend in Table 4 is much less than for the blend in Table 3, and no loss in initial distillation point is shown for the blend in Table 4.

Table 3

Inspection of Base Gasoline A and a Blend
of Base Gasoline A and 5 Vol. % MAE

Inspection:	Base A: (Commercial Unleaded Gasoline)	Base A + 5 Vol. % MAE
Gravity, API, D 287	58.7	--
Lead in Gasoline, D 3237, G/Gal	<0.005	--
Carbon, Gulf 1500, Wt. %	86.82	--
Hydrogen, Gulf 1500, Wt. %	13.18	--
Gum, Existent, D 381, Mg/100 ml	2	--
Oxidation Stability, D 525, Min	>1440	--
Hydrocarbon Analysis, D 1319, V %		
Aromatics	26.5	--
Olefins	13.0	--
Saturates	60.5	--
Motor Octane Number, D 2700	84.1 ^a	84.5 ^a
Research Octane Number, D 2699	93.2 ^a	93.8 ^a
Vapor Pressure, Reid, D 323: psi	11.0	9.8
Distillation, D 86, 760 mm		
Over: °C	28	31
End: °C	212	216
5% at: °C	39	41
10	44	49
20	58	64
30	74	81
40	89	97
50	104	111
60	118	126
70	131	140
80	147	156
90	170	172
95	192	197
Recovery: %	97.5	98.0
Residue: %	1.4	1.2
Loss: %	1.1	0.8

a) Average of two ratings.

Table 4

Inspection of Base Gasoline B and a Blend
of Base Gasoline B and 5 Vol. % MAE

Inspection:	Base B: (Commercial Unleaded Gasoline)	Base B + 5 Vol. % MAE
Gravity, D 287: °API	56.8	53.7
Alkalinity, Gulf 832		
Procedure A: pH	5.0	5.0
Viscosity, D 445, 25°C: cs	0.56	0.57
Vapor Pressure, Reid, D 323: psi	10.6 (10.1) ^a	9.9
Vapor Pressure, D 2551: psi	10.60	10.10
Oxidation Stability, D 525: min	1440	1440
66°C (150°F) Gum Time: mg/100 ml		
1 day interval unwashed	2 (2)	2
1 day interval washed	2 (1)	1
3 day interval unwashed	3 (3)	2
3 day interval washed	2 (1)	1
6 day interval unwashed	6 (4)	3
6 day interval washed	6 (2)	2
Gum, D-381, as received unwashed	2 (2)	1
Gum, D-381, as received washed	1 (1)	1
Existent Gum, D-381: mg/100 ml	1 (1)	1
Copper Dish Gum, D-910: mg/100 ml	10 (4)	11
Copper Strip, 50°C (122°F), D 130: 3 hr	1	1
Potential Gum, D-873: mg/100 ml	9 (5)	4
Distillation, D 86: 760 mm		
Over: °C	26	25
End: °C	211	211
5% at: °C	40	41
10	50	51
20	66	70
30	83	88
40	100	105
50	116	120
60	129	134
70	141	145
80	152	155
90	171	174
95	192	191
Recovery: %	97.9	97.9
Residue: %	1.1	1.1
Loss: %	1.0	1.0

a) Numbers in parentheses are duplicate runs.

Looking at Tables 3 and 4 together, we see that MAE is compatible with gasoline. It does not affect significantly the gasoline's specific gravity, distillation curve, alkalinity, viscosity, Reid vapor pressure, oxidation stability, existent gum value, copper dish gum value, copper strip test, or potential gum value. In addition, MAE does not separate from gasoline at low temperatures or because of water contamination.

VI. PLASTICS COMPATIBILITY

To test the effects of 5% MAE in gasoline on plastics and elastomers commonly found in automotive gasoline distribution systems, samples of plastics and elastomers were immersed in Table 4 base gasoline and in Table 4 base gasoline containing 5 volume % MAE for five weeks at room temperature. Materials tested were Neoprene, Urethane, Adiprene, Nylon, and Nitrile rubber. Nylon was unaffected by the presence of MAE in the gasoline. The other materials swelled somewhat more in the MAE/gasoline blend than in the base gasoline but probably little more than would be caused by addition of toluene to the base gasoline. None cracked, hardened, or otherwise deteriorated (4).

VII. MICROBISTATIC PROPERTIES

Microbial contamination of fuels can be a serious problem. To be sure that 5% MAE in gasoline does not increase the incidence of microbial contamination of the gasoline, we prepared cultures in sterile, cotton-stoppered dilution bottles. The aqueous phase consisted of Bushnell-Haas mineral salts medium inoculated with a known number of bacterial cells cultured from contaminated water bottoms from a commercial, unleaded gasoline storage tank. The medium was aseptically dispensed into the bottles in 40, 20, and 4 ml amounts to give (in total culture volumes of 80 ml) aqueous concentrations of 50%, 25%, and 5% respectively.

In addition to the 5% MAE/base gasoline (Table 4), we also tested the base gasoline itself and the base gasoline containing a commercially-available fuel-soluble microbicide at the recommended concentration of 270 ppm. The gasoline formulations were layered over the inoculated medium in the dilution bottles to give a final volume of 80 ml. Cultures were incubated at room temperature in a fume hood. To more closely approximate gasoline storage tank conditions, the samples were not shaken. At intervals of 4, 11, and 18 days, a representative aliquot of the aqueous phase of each culture was aseptically taken, serially diluted, and plated to nutrient agar to ascertain the number of viable bacteria. In each case the bacteria were able to grow in cultures containing 25% and 50% water. When water in the culture medium was reduced to 5%, growth was inhibited in the culture containing 5% MAE/gasoline blend and in the culture containing gasoline and the fuel-soluble, commercial microbicide. Bacterial growth was not inhibited in the 5% aqueous culture by base gasoline alone. The MAE inhibited growth of the inoculum in the 5% aqueous culture to approximately the same extent as the commercial microbicide. While microbistatic, neither was microbicidal under these test conditions. Since gasoline storage tanks normally contain less than 5% water, the presence of 5% MAE in gasoline should help control bacterial contamination (4).

VIII. MAMMALIAN TOXICITY

Samples of Table 4 base gasoline and the Table 4 base gasoline containing 5 volume % MAE were sent to an independent testing laboratory for mammalian toxicity studies by acute oral toxicity in albino rats (4,7), acute dermal toxicity in albino rabbits (4,7), and acute vapor inhalation toxicity in rats (4,8). Both test samples were found to be relatively harmless to the rat by acute oral exposure and to be practically nontoxic to the rabbit by acute dermal exposure. In the acute vapor inhalation study in rats, body weight gains were within normal limits and necropsy did not reveal any gross

pathological alterations. By these tests, the mammalian toxicity of the base gasoline and the base gasoline containing 5% MAE was essentially the same.

IX. OCTANE QUALITY

A comparison of the research octane and motor octane values for the Table 3 base gasoline and the Table 3 base gasoline containing 5%, 10%, and 15 volume % MAE is given in Table 5. Based on averaging of duplicate measurements, 5% MAE increases octane of 93 RON, 84 MON base gasoline by 0.6 RON and 0.4 MON. At 10%, MAE increases octane by 2.2 RON and 0.9 MON. At 15%, MAE increases octane of the base gasoline by 3.1 RON and 1.3 MON.

Table 5

Research Octane and Motor Octane Values for Base Gasoline A and Base Gasoline A Containing MAE

<u>Gasoline</u>	<u>RON^a</u> <u>(D 2699)</u>	<u>MON^a</u> <u>(D 2700)</u>
Base	93.2	84.1
Base + 5 Vol. % MAE	93.8	84.5
Base + 10 Vol. % MAE	95.4	85.0
Base + 15 Vol. % MAE	96.3	85.4

a) Average of two ratings.

Road octane quality of the base fuel (Table 3) and a blend of 5% MAE in the base fuel was examined by testing in a selection of four different late-model cars. The experimental fuel and the base fuel were tested for direct comparison. All ratings were made in duplicate by trained raters using the Modified Unifontown rating procedure on a chassis dynamometer.

The cars tested were a 1979 Chevrolet Malibu 267 CID V-8, a 49-state 1979 Ford Thunderbird 302 CID V-8, a 1979 Pontiac Catalina 301 CID V-8, and a 49-state model, 1980 Plymouth Volare equipped with a 225 CID, 6-cylinder engine. Results are shown in Table 6. For these particular cars, the four-car average gain in road octane for the MAE-containing fuel over the base fuel was 0.4 units.

Table 6
Road Octane Performance for Base Gasoline A and Base Gasoline A Containing 5 Vol. % MAE

Test Car	Road Ratings ^a	
	Base Fuel	Base Fuel + 5% MAE
1979 Chevrolet Malibu	89.9	89.9
1979 Ford Thunderbird	89.4	89.9
1979 Pontiac Catalina	90.0	91.3
1980 Plymouth Volare	<u>87.7</u>	<u>87.8</u>
4-Car Average	89.3	89.7

a) Average of ratings from two different raters.

X. CARBURETOR CLEANLINESS

To evaluate the tendency of MAE in gasoline to form gum and varnish deposits in engine carburetors, a carburetor cleanliness test on Table 3 base gasoline and Table 3 base gasoline containing 5% MAE was performed. The test equipment consisted of a laboratory engine-dynamometer set-up using a 1978 Ford six-cylinder, 300 CID engine. The test is a modified version of the currently proposed CRC carburetor cleanliness test. In our test cycle, the

engine is idled for three minutes at 700 RPM, accelerated to 2000 RPM, held at 2000 RPM for seven minutes, then decelerated to idle. Increased crankcase blow-by return to the carburetor is continuous through the test cycle, whereas exhaust gas recirculation is employed only during the 2000 RPM portion of the cycle. The air/fuel ratio at idle is 11/1 to 13.7/1 while dynamometer loading is 45-50 ft. lbs. at an engine speed of 2000 RPM. With controlled operating temperatures and a test duration of 22 continuous hours, selected reference gasolines cause repeatable deposit formation on a removable sleeve in the throttle body. In this case, the base gasoline gave a deposit weight of 12.4 mg and the base gasoline containing 5% MAE gave a deposit weight of 13.0 mg. For this particular test set-up, the conclusion is that there is no difference in deposit forming characteristics between the two fuels.

XI. DRIVEABILITY PERFORMANCE

The driveability performance of Table 3 base fuel and Table 3 base fuel containing 5% MAE was tested on an all-weather chassis dynamometer to evaluate the experimental fuel's cold starting and warm-up characteristics. Both fuels were tested in turn in each of two test cars. Each was tested at 5°F, 25°F, and 45°F (-15°, -4°, +7°C). Duplicate runs of each test were made to improve accuracy.

The chassis dynamometer used for this test program has single four foot diameter rolls, an eddy current dynamometer, an inertia weight system and an independent fan control for the cooling air. A detailed description of this precisely temperature controlled, all-weather dynamometer is given elsewhere (9). The first test car was a 1978 Ford Pinto equipped with a California 3-way exhaust catalyst and a 2.3 liter, 4-cylinder engine. The second test car was a 1979 Pontiac LeMans equipped with a California 3-way exhaust catalyst and a 231 cubic inch, V-6 engine.

Testing was done under a specially developed driving procedure patterned after the CRC driveability procedure. Details of the driving procedure are given in Appendix B. Driveability demerit ratings by this procedure come out the same as in the CRC driveability procedure. The CRC demerit rating system was used, taking into account driving stall, idle stall, backfire, idle roughness, hesitation, stumbling, and surge.

Test data analysis indicates that the base fuel and the base fuel containing 5 volume % MAE are not significantly different in driveability at the 90% confidence level in the Student t test. On the other hand, the same base fuel containing 10 volume % ethanol (i.e. Gasohol) was found to be significantly poorer in driveability at the 90% confidence level (Table 7).

Table 7

Driveability Performance of Base Gasoline A,
Base Gasoline A + 5 Vol. % MAE, and Base
Gasoline A + 10 Vol. % Ethanol

Test Car	Fuel	Demerits ^a		
		+7°C	-4°C	-15°C
1978 Ford Pinto	Base Gasoline	42 (54)	58 (114)	69 (94)
	Base + 5% MAE	28 (66)	122 (171)	100 (146)
1979 Pontiac LeMans	Base Gasoline	40 (65)	83 (35)	55 (48)
	Base + 5% MAE	65 (90)	48 (80)	58 (33)
	Base + 10% Ethanol	165 (245)	190 (168)	163 (183)

a) Numbers in parentheses are duplicate runs.

XII. FUEL ECONOMY AND DURABILITY TESTS

Fuel economy and durability tests were made by driving each of four late-model cars (two matched pairs) for 20,000 miles on a road simulator using a typical city-suburban driving cycle. These tests evaluated fuel economy, oil economy, intake system deposits, engine sludge and varnish deposits, engine wear, spark plug fouling, and the effects of the fuel on octane requirement increase and on exhaust gas catalyst efficiency. One car of each pair was operated on Table 3 base fuel while the other car used Table 3 base fuel containing 5% MAE. The engines were prepared with clean, measured parts and new exhaust catalysts. The engines in all four vehicles were in newly overhauled condition; each received a 500 mile break-in before the 20,000 mile test was started.

The cars used in these tests were two 1979 Chevrolet Malibus having 305 cubic inch, V-8 engines and two 1979 Ford Granadas having 302 cubic inch, V-8 engines. All cars were equipped with California 3-way exhaust catalysts. Following completion of the 20,000-mile runs, the engines were disassembled for inspection and measurement of intake system deposits, engine sludge and varnish deposits, engine wear, and spark plug fouling. Exhaust catalysts were opened for inspection at conclusion of the test.

The road simulator used in the 20,000-mile test is a chassis dynamometer system for mileage accumulation. It is equipped with automatic magnetic tape control. Tight speed control is utilized, with the corresponding torque signal controlling the throttle position. This acknowledges engine degradation as it occurs throughout an extended mileage accumulation driving schedule.

The driving cycle used on the road simulator was the "EPA Durability Driving Schedule for Light Duty Vehicles and Light Trucks" (10). Each test cycle is 11 laps of a 3.7 mile closed test course. The only variation from the EPA schedule is that in our test, speed on the eleventh lap was changed from 70 MPH to 55 MPH.

A. FUEL ECONOMY

Fuel economy measurements were made at the start, at the end, and at 5,000-mile intervals throughout the 20,000 mile road simulator test. Measurements were made on a chassis dynamometer using the 1975 Federal Test Procedure and the EPA highway economy procedure. Detailed data are given in Appendix C. One cannot draw conclusions about fuel economy changes in this test because the base fuel and experimental fuel were not used in the same car and a total of only four cars was used. However, a comparison of fuel economy at start of test and end of test can be made for each car to see if MAE influences fuel economy trends over the 20,000-mile test. This comparison is shown in Table 8 where data was abstracted from Appendix C. Duplicate runs in Appendix C were averaged for use in Table 8.

Table 8

Fuel Economy Performance (mpg) of Base Gasoline A
and Base Gasoline A Containing 5 Vol. % MAE^a
(Data taken from Appendix C)

1979 Chevrolets						
Test Miles	Base Gasoline (Car 1)			Base Gasoline + 5% MAE (Car 2)		
	City ^b	City ^c	Highway ^c	City ^b	City ^c	Highway ^c
Nil	13.95	13.50	21.70	13.95	13.80	20.05
20,000	<u>15.25</u>	<u>14.60</u>	<u>22.10</u>	<u>15.25</u>	<u>15.25</u>	<u>20.85</u>
Change	+1.30	+1.10	+0.40	+1.30	+1.45	+0.80
1979 Fords						
Test Miles	Base Gasoline (Car 1)			Base Gasoline + 5% MAE (Car 2)		
	City ^b	City ^c	Highway ^c	City ^b	City ^c	Highway ^c
Nil	15.10	14.90	22.15	15.00	15.10	21.20
20,000	<u>14.60</u>	<u>13.90</u>	<u>21.40</u>	<u>14.75</u>	<u>14.40</u>	<u>21.05</u>
Change	-0.50	-1.00	-0.75	-0.25	-0.70	-0.15

-
- a) City portion determined by 1975 city-suburban FTP; highway portion determined by EPA highway fuel economy procedure.
 - b) Determined by the carbon balance method.
 - c) Determined gravimetrically.

Table 8 shows that both Chevrolets gained in fuel economy during the 20,000-mile test, the one using fuel containing 5% MAE apparently gaining most. Both Fords lost in fuel economy during the test, the Ford using fuel containing 5% MAE losing least. This test is too small to say if these differences are real. Basically, the fuel economy trends over 20,000 miles appear the same whether MAE is present in the fuel or not.

B. SPARK PLUG FOULING

No instance of spark plug fouling occurred in any car over the 20,000-mile test.

C. OIL CONSUMPTION

Oil consumption, measured in miles per quart over the 20,000-mile test was normal (Appendix D). Both the Ford and the Chevrolet using base fuel containing 5% MAE consumed less oil than their counterparts using base fuel, but the difference is not significant.

D. OCTANE REQUIREMENTS

The octane requirements of all four vehicles were measured on a chassis dynamometer at the start, the end, and at 5000-mile intervals throughout the 20,000-mile test (Appendix E). Analysis indicates that the presence of MAE in the fuel has no significant effect on octane requirement.

E. ENGINE WEAR

Engine wear overall was very low in all four vehicles. Presence of MAE in the fuel did not cause a significant difference in engine wear (Appendix F).

F. ENGINE DEPOSITS

All four vehicles had fairly clean engines after the 20,000-mile test, showing only light sludge and varnish. Generally, the presence of MAE in the fuel caused no significant difference in engine deposits except that in the Ford using fuel containing 5% MAE, varnish appeared somewhat heavier on the rocker arm covers, pistons, and valve lifters (Appendix G).

G. EXHAUST EMISSIONS

Exhaust emissions of HC, CO, and NO_x were made at the start, at the end, and at 5000-mile intervals throughout the 20,000-mile test. Measurements were made on a chassis dynamometer (Appendix H). Emissions for the two Chevrolets at the start and at the conclusion of the test are given in Table 9. The data in Table 9 are abstracted from Appendix H. Duplicate runs in Appendix H are averaged for use in Table 9.

Table 9

Exhaust Emissions (grams/mile) From Two 1979
Chevrolet Malibu Test Cars Using 1975 FTP
(Data taken from Appendix H)

<u>Test Miles</u>	<u>Base Gasoline (Car 1)</u>			<u>Base Gasoline + 5% MAE (Car 2)</u>		
	<u>HC</u>	<u>CO</u>	<u>NOx</u>	<u>HC</u>	<u>CO</u>	<u>NOx</u>
Nil	0.40	6.12	0.79	0.42	5.58	0.62
20,000	0.69	8.05	0.77	0.45	5.55	0.68
Change	+0.29	+1.93	-0.02	+0.03	-0.03	+0.06

We see in Table 9 that emissions at the end of the test are somewhat lower from the Chevrolet using base fuel containing 5% MAE than from the Chevrolet using base fuel alone. But since both fuels were not tested in the same car, no conclusion can be drawn, except to say that MAE does not appear to increase exhaust emissions.

Exhaust emissions from the Ford using the 5% MAE/base fuel blend are all slightly lower at start of test compared to emissions from the Ford using base fuel alone. However, emissions from the Ford using the MAE-containing fuel increased significantly during the 20,000-mile test (Appendix H). Examination of the monolith catalyst after test conclusion on the Ford using MAE-containing fuel showed it to have a deformed area of about two square inches in the center of the catalyst (Appendix I). Catalyst deformation is probably unrelated to the particular fuel used. Being a monolithic catalyst, this channel may have allowed the increase in exhaust emissions. Exhaust emissions results on this car are probably invalid.

XIII. CONCLUSIONS

The research discussed in this paper indicates that the mixture of methyl aryl ethers (MAE) derived from phenols present in raw coal liquids is an excellent non-metallic gasoline blending agent and octane improver. Use of MAE in gasoline should help alleviate the current need for increased petroleum refining severity to make metal-free, high octane gasoline. Additionally, removing phenols from raw coal liquids for conversion to MAE may reduce some coal liquid refining problems and should allow a significant reduction in hydrogen consumption needed to upgrade coal liquids.

APPENDIX A

PREPARATION OF METHYL ARYL ETHERS (MAE) - A composite of raw coal liquid from 51 runs on a variety of Eastern bituminous coals fed to Gulf Research & Development Company's one ton/day SRC II process demonstration unit was used as the source of phenols. The fraction of the composite used was that boiling in the range 55°C (131°F) to 260°C (500°F). This composite fraction (1019 gallons, 7574 lbs) was shipped to Chemsampco (now known as Albany International, Chemical Division) in Columbus, Ohio, where phenols were extracted from the coal liquid and converted to MAE.

Two runs of about 510 gallons of coal liquid were extracted with 175 gallons of 20% aqueous sodium hydroxide per run. The extractions were run at 35°C with stirring for 6 hours. The lower aqueous layer (pH 10) containing the sodium salts of the phenols was separated from the top neutral layer. The lower, basic aqueous layers from the two extractions were combined and washed by stirring with 200 gallons of ether for 6 hours at 20°C to remove non-phenolic organic compounds. The top ether layer was separated and discarded. The lower aqueous layer was checked for non-phenolic, neutral hydrocarbons by a small scale extraction of an aliquot with ether and found to contain insignificant amounts. The basic, aqueous layer was then stripped of residual ether to a pot temperature of 55°C with stirring.

The basic, aqueous layer (still containing the sodium salts of the phenols) was then acidified with aqueous 20% hydrochloric acid to a pH of 2 with stirring and cooling to maintain a temperature of 20°C in the reactor. This acidification converted the sodium salts of the phenols to free phenols. Sodium chloride (500 lbs) was added to decrease the solubility of the free phenols in the water. After 2 hours to allow complete phase separation into a lower aqueous phase and an upper phenols phase, the lower aqueous layer was checked by gas chromatography for phenols; none were found. The lower aqueous layer was then discarded. The remaining phenolic layer was washed twice with a mixture of 50 gallons of water, 100 lbs of sodium carbonate, and 50 lbs. of sodium chloride. The lower wash water layer was checked by gas chromatography for phenols (none found) and was discarded.

At this point there remained 2180 lbs (28.8 wt. %) of phenolics. Of the 2180 lbs. of phenolics, 1850 lbs. was used for conversion to MAE. To 1850 lbs. phenolics was added 2 drums of 50% aqueous sodium hydroxide and 1200 lbs. water (to give a 25 wt. % aqueous sodium hydroxide solution). The reaction mixture was stirred with cooling (18°C) for 8 hours. Dimethyl sulfate (2200 lbs.) was then added with stirring over 10 hours, keeping the temperature of the reaction mixture below 34°C. The reaction mixture was then stirred at 20°C for 36 hours. Aqueous 50% sodium hydroxide (20 gallons) was then added to destroy excess dimethyl sulfate and remove any unetherified phenol from the crude MAE product. The mixture was stirred one hour, allowed to separate into layers, and the lower aqueous, basic phase was discarded. The remaining MAE product layer was washed with a mixture of 50 gallons water, 25 gallons of 50% aqueous sodium hydroxide, and 25 lbs. of sodium chloride. The lower, aqueous wash layer was discarded to give 1801 lbs. of MAE. The crude MAE was distilled to give 65 lbs. of non-MAE-containing first cut (boiling 44° - 69°C at 58-100 mm Hg), 1440 lbs. (176 gallons) of MAE (boiling 73 - 117°C at 30-50 mm Hg), and 99 lbs. of a heavy, dark residue. Material loss was due to light material being pulled through traps and pumps. Also some material caked to the walls of the distillation unit.

APPENDIX B

DRIVEABILITY PROCEDURE - The driveability test is performed by operating the car at specific throttle openings over the driving cycle which is pre-recorded on a visual drivers aid. This cycle includes the following: (1) set choke and start engine, (2) fast idle in neutral for 15 seconds, (3) transmission in drive for 5 seconds, (4) part throttle acceleration 0-25 mph, (5) 25 mph cruise for 0.1 miles, (6) detent acceleration 25 to 40 mph, (7) 40 mph cruise for 0.2 miles then decelerate to 20 mph, (8) part throttle acceleration from 20 to 40 mph, (9) brake to a stop and idle for 30 seconds.

The above cycle is repeated 3 times for a total of 2.2 miles. Then the following cycle is performed 4 times for a total test of 5.1 miles: (1) part throttle acceleration 0-45 mph, (2) cruise for 0.2 miles then decelerate to 25 mph, (3) detent acceleration to 40 mph and cruise for 0.1 miles, (4) decelerate to 20 mph and cruise for 0.1 miles, (5) part throttle acceleration to 40 mph, (6) brake to a stop and idle for 30 seconds.

APPENDIX C

FUEL ECONOMY TESTS, MPH, 1975 CITY-SUBURBAN FTP AND EPA HIGHWAY FUEL ECONOMY PROCEDURES

1979 Chevrolets

Test Miles	Base Fuel			Base + 5% MAE		
	City Carb. Bal.	City Gravim.	Highway Gravim.	City Carb. Bal.	City Gravim.	Highway Gravim.
0	13.7	13.5	21.6	14.1	13.8	19.9
0.	14.2	-	21.8	13.8	-	20.2
5,000	15.3	15.4	-	14.8	14.3	-
10,000	14.5	14.0	-	14.9	14.6	-
15,000	15.6	15.0	-	14.6	14.3	-
20,000	15.3	14.7	22.3	15.2	15.2	20.7
20,000	15.2	14.5	21.9	15.3	15.3	21.0

1979 Fords

Test Miles	Base Fuel			Base + 5% MAE		
	City Carb. Bal.	City Gravim.	Highway Gravim.	City Carb. Bal.	City Gravim.	Highway Gravim.
0	14.9	14.9	22.2	15.1	15.1	21.0
0	15.3	-	22.1	14.9	-	21.4
5,000	16.1	15.1	-	15.8	15.3	-
10,000	16.2	15.4	-	15.3	14.9	-
15,000	16.1	15.0	-	14.8	14.2	-
20,000	13.8	13.0	21.1	14.6	14.4	20.8
20,000	15.4	14.8	21.7	14.9	14.4	21.3

APPENDIX D

OIL CONSUMPTION DURING 20,000-MILE ROAD SIMULATOR TEST

Test Miles	1979 Chevrolets (Miles/Qt)		1979 Fords (Miles/Qt)	
	Base Fuel	Base + 5% MAE	Base Fuel	Base + 5% MAE
0-7,500	2335	2475	2135	2799
7,500-15,000	3393	3277	3225	2755
15,000-20,000	<u>3915</u>	<u>4213</u>	<u>2822</u>	<u>3897</u>
Average	3214	3321	2727	3150

APPENDIX E

OCTANE REQUIREMENTS

Test Miles	Reference Fuels ^a	1979 Fords				1979 Chevrolets			
		Base		Base + 5% MAE		Base		Base + 5% MAE	
		Full Throttle	Part Throttle	Full Throttle	Part Throttle	Full Throttle	Part Throttle	Full Throttle	Part Throttle
0	FBRU	94	92	90	80	82	80	88	80
	FBRSU	96	-	91	-	82	-	88	-
	PRF	90	-	88	-	80	-	86	-
5,000	FBRU	>102	>102	98	98	88	<78	88	80
	FBRSU	-	>101	100	101	88	-	88	-
	PRF	94	-	92	-	86	-	87	-
10,000	FBRU	>102	>102	-	100	88	<80	90	80
	FBRSU	>101	>101	101	101	88	-	90	-
	PRF	98	-	95	93	86	-	87	-
15,000	FBRU	102	102	100	100	88	-	89	80
	FBRSU	101	101	101	101	89	-	90	-
	PRF	98	-	96	-	86	-	86	-
20,000	FBRU	102	101	100	100	91	<78	91	82
	FBRSU	101	101	101	101	92	-	92	-
	PRF	96	-	96	-	88	-	87	-

-
- a) FBRU are 1979 CRC Full Boiling Range Unleaded fuels.
 FBRSU are 1979 CRC Full Boiling Range Sensitive Unleaded fuels.
 PRF are Primary Reference Fuels.

APPENDIX F

ENGINE WEAR MEASUREMENTS

	1979 Chevrolets		1979 Fords	
	<u>Base Fuel</u>	<u>Base + 5% MAE</u>	<u>Base Fuel</u>	<u>Base, + 5% MAE</u>
PISTON RINGS:				
Top Compression:				
Avg, gms	0.022	0.037	0.068	0.079
Max, gms	0.030	0.071	0.081	0.114
Second Compression:				
Avg, gms	0.005	0.015	0.044	0.045
Max, gms	0.016	0.018	0.053	0.058
CONNECTING ROD BEARINGS				
Avg, gms	0.055	0.055	0.030	0.052
Max, gms	0.074	0.074	0.049	0.109
CAM AND LIFTERS, wear, in.				
Avg lobe	0.0002	0.0001	0.0011	0.0002
Max lobe	0.0004	0.0002	0.0022	0.0006
Avg lifter	0.0002	0.0002	0.0004	0.0006
Max lifter	0.0004	0.0005	0.0008	0.0013
Avg combined	0.0004	0.0003	0.0015	0.0009
Max combined	0.0005	0.0007	0.0026	0.0018
Lifter spalling, scuffing	nil	nil	trace to light	trace to light
Lobe spalling, scuffing	nil	nil	trace to light	trace to light
VALVE CLEAR WEAR:				
Valve tips	light	very light	very light	light to moderate
Rocker arm pads	light	trace to light	trace to light	trace to light

APPENDIX G

ENGINE DEPOSITS

(Numerical ratings from 0 to 10, 10 being clean according to CRC Rating Scale)

	1979 Chevrolets		1979 Fords	
	<u>Base Fuel</u>	<u>Base + 5% MAE</u>	<u>Base Fuel</u>	<u>Base + 5% MAE</u>
SLUDGE:				
Timing gear cover	9.5	9.5	9.4	9.0
Intake manifold	9.3	9.5	9.1	9.2
Left rocker cover	8.7	8.7	8.1	8.4
Right rocker cover	9.0	9.0	8.9	9.2
Oil pan	9.0	8.8	8.8	8.8
Oil screen	10.0	10.0	9.9	9.9
VARNISH:				
Timing gear cover	10.0	10.0	9.5	9.0
Intake manifold	7.8	8.5	6.8	7.0
Left rocker cover	6.2	6.5	7.7	4.0
Right rocker cover	8.3	8.0	9.0	8.0
Oil pan	9.2	9.5	9.5	9.0
Pistons, average	6.6	6.2	6.4	5.8
Valve lifters, average	8.9	9.1	6.6	5.9
OTHER:				
Intake valve stems	4.9	5.3	5.9	4.7
Intake valve fillets	7.7	6.8	5.9	5.3
Intake valve dep. wt, gms	2.4	2.4	3.4	5.0
Exhaust valve dep. wt, gms	0.24	0.23	0.01	0.02
Ring sticking	nil	nil	nil	three sluggish
Valve lifter sticking	nil	nil	nil	nil

APPENDIX H

EXHAUST EMISSIONS, GMS/MILE
1975 FEDERAL TEST PROCEDURE

1979 Chevrolets

Test Miles	Base Fuel			Base + 5% MAE		
	HC	CO	NOx	HC	CO	NOx
0	0.32	5.73	0.75	0.41	5.68	0.61
0	0.48	6.51	0.83	0.42	5.47	0.62
5,000	0.52	6.19	0.74	0.50	7.65	0.72
10,000	0.69	7.86	0.80	0.66	7.10	0.76
15,000	0.75	8.20	0.83	0.66	12.39	0.90
20,000	0.68	7.39	0.80	0.44	5.47	0.67
20,000	0.69	8.71	0.74	0.45	5.63	0.68

1979 Fords

Test Miles	Base Fuel			Base + 5% MAE		
	HC	CO	NOx	HC	CO	NOx
0	0.47	2.31	0.93	0.28	1.12	0.85
0	0.46	3.01	0.86	0.31	1.23	0.88
5,000	0.67	4.15	1.05	1.18	2.94	1.38
10,000	0.86	4.45	1.05	1.57	5.11	1.29
15,000	0.98	4.31	0.95	1.95	7.77	1.35
20,000	1.25	13.15	1.10	3.31	6.48	2.65
20,000	1.41	5.96	0.80	4.35	5.93	2.47

APPENDIX I

EXHAUST GAS CATALYST INSPECTION
AFTER 20,000 MILES OF OPERATION

Car:	Chevrolet	Chevrolet	Ford	Ford
Fuel:	Base	Base + 5% MAE	Base	Base + 5% MAE
Type Catalyst:	Pellet	Pellet	Monolith	Monolith
Plugging:	None	None	None	None
Condition:	Severe damage to lower shelf; melted areas, pellets spilled and several fused masses about 1/2 in x 1-1/2 in	Good	Good	Deformed area about 2 sq. in. in center of catalyst

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