United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-87-001
August 1987

Air

EPA

Vapor Generation of Fuels

EPA 460/3-87-001

Vapor Generation of Fuels

by

Lawrence R. Smith

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

Contract No. 68-03-3353
Work Assignment B-7

EPA Project Officer: Craig A. Harvey

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

August 1987

This report was furnished to the Environmental Protection Agency by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, in fulfillment of Work Assignment No. B-7 of Contract 68-03-3353. The contents of this report are reproduced herein as received from Southwest Research Institute. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-460/3-87-001

FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The program, authorized by Work Assignment B-7 under Contract 68-03-3353, was initiated April 9, 1987 and completed in June 1987. It was identified within Southwest Research Institute as Project 08-1193-007. The EPA Project Officer for the program was Mr. Craig A. Harvey of the Emission Control Technology Division, Ann Arbor, Michigan. The SwRI Project Leader and principal researcher for the project was Dr. Lawrence R. Smith. Mr. Charles T. Hare was Project Manager and was involved in the initial technical and fiscal planning.

ABSTRACT

This report combines the data from two previous work assignments (Work Assignments 12 and 18 of Contract 68-03-3192) conducted at Southwest Research Institute for the Environmental Protection Agency, and analyzes the resulting data set. When possible, the combined results have been generalized in order to draw conclusions. In Work Assignment 12, vapors from twelve gasolines and gasoline/alcohol blends were analyzed for butanes, total hydrocarbons, methanol, and appropriate cosolvent alcohols. The analyses were conducted in duplicate for each fuel at FTP diurnal SHED temperatures (60-84°F) and at typical hot soak temperatures (160 ± 10°F). The fuels were prepared with different levels of aromatic content and Reid Vapor Pressure. The Work Assignment 18 study involved generating vapors from seven gasolines and gasoline/alcohol blends during simulated diurnal test conditions (15-40°F, 35-60°F, and 60-84°F). These vapors were analyzed for total hydrocarbons, alcohols, and individual hydrocarbons up to and including C_6. The Reid Vapor Pressure of the seven fuels varied from 9.2 to 15.0 psi.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

Fuel vapors generated from the SHED testing of a variety of gasolines and gasoline/alcohol blends, utilizing three diurnal temperature rise situations (15-40°, 35-60°, 60-84°F) as well as a high temperature (160° ± 10°F) situation, were characterized as to total SHED hydrocarbons, individual hydrocarbons (up to and including C_6), and alcohols. Twelve gasolines and gasoline/alcohol blends (Work Assignment 12) were evaluated as to alcohol content, Reid Vapor Pressure, and aromatic content using the 60-84°F diurnal temperature rise and the high temperature test, while seven other gasolines and gasoline/alcohol blends (Work Assignment 18) were evaluated as to fuel volatility using all three of the diurnal temperature rise situations. In the twelve-fuel study, gasoline and gasoline/methanol, gasoline/methanol-TBA, and gasoline/methanol-ethanol blends were evaluated in the following combinations of fuel properties: low RVP-low aromatic content, high RVP-low aromatic content, and low RVP-high aromatic content. In the seven-fuel study, three of the gasoline fuels were representative of ASTM (D-439) Class C, D, and E fuels, while a fourth gasoline was Indolene. Three gasoline/alcohol blends were also high-volatility Class C, D, and E fuels and contained 5.0% methanol and 2.5% ethanol as a cosolvent. The three diurnal temperature rise situations included: the standard summer diurnal temperature rise, 60-84°F, for the Class C gasoline and gasoline/alcohol blend and Indolene testing; a winter diurnal temperature rise, 15-40°F, for the Class E gasoline and gasoline/alcohol blend testing; and a spring diurnal temperature rise, 35-60°F, for the Class D gasoline and gasoline/alcohol blend testing.

A 10-gallon fuel tank filled to 40 percent capacity was used to generate the vapors in the diurnal SHED tests (no test vehicle was used), and a 250 ml flask filled with 125 ml of fuel and heated with a water bath to 160°F was used to generate vapors in the high-temperature tests. Duplicate tests were conducted at each test condition.

The most significant observations made from the data (not necessarily in order) are as follows:

- In the diurnal test, total SHED hydrocarbons appear to follow fuel RVP trends, with the higher RVP fuels giving higher total hydrocarbons. In the higher temperature tests this trend was also noted, but a closer relationship of the fuel distillation curve with the SHED total hydrocarbons was observed. Fuels with a larger fraction of the fuel boiling at temperatures lower than the 160°F test temperature gave correspondingly higher SHED hydrocarbon emissions.

- Variations in fuel aromatic content did not appear to alter total hydrocarbon emissions in the diurnal and high-temperature SHED tests as significantly as the RVP and distillation temperature variations. The aromatic content of the fuel, however, did influence the fuel RVP and distillation curve.

- In general, SHED total hydrocarbons were found to increase with increasing diurnal temperature rise (15-40°F < 35-60°F < 60-84°F) despite a corresponding decrease in test fuel volatility.

- Individual hydrocarbons in the diurnal SHED tests followed the same trends as the total hydrocarbons.

- Propylene, ethylene, ethane, and methane were found in fuel vapors in small but measurable quantities and were apparently present in the fuel itself at trace levels.

- Propane was detected in the fuel vapors for all the fuels tested, with average levels ranging from 0.13 to 0.33 g/test.

- Benzene was found to constitute one percent or less of the total vapor hydrocarbons for the seven fuels. Test fuels prepared from similar base stock fuels gave similar benzene levels in the hydrocarbon vapors.

- Isobutane, n-butane, isopentane, and pentane made up the majority of the total diurnal SHED hydrocarbons in the Work Assignment 18 study, with combined percentages ranging from 71.2% to 81.6%.

- Butane and isobutane SHED levels in the Work Assignment 12 study were found to be directly related to the butane and isobutane levels in the fuels.

- Generally, the alcohol blends had lower levels of isobutane and n-butane in the total SHED hydrocarbons than their corresponding base gasolines. This was likely due to both the removal of some of the light ends during the preparation of the blends and to the dilution of these compounds by the addition of the alcohols. Many of the higher boiling C_5 and C_6 compounds, however, were generally present in higher percentages in the alcohol blend vapors than in the base gasoline vapors. The formation of methanol/hydrocarbon azeotropes in the alcohol blends may have contributed to these higher percentages.

- Percentages of olefins in the SHED hydrocarbons (7-14%) were high in relation to levels typically found in gasoline (<10%). This higher percentage may be a result of higher concentrations of fuel olefins in the C_4 to C_6 fuel fraction as opposed to the whole fuel.

- As was the case for total hydrocarbons, SHED methanol levels increased with increasing diurnal test temperatures despite a decrease in fuel volatility.

- In general, higher-RVP fuels gave higher levels of alcohols in both the Work Assignment 12 diurnal and the high-temperature SHED tests. SHED methanol levels were 1.5 to 7 fold higher in diurnal SHED tests and 1.2 to 2 fold higher in the high-temperature tests for the higher-RVP fuels when compared to the lower-RVP fuels of equal alcohol content. Levels of methanol in the high-temperature SHED tests appeared to be roughly proportional to the levels of methanol in the fuel. Levels of ethanol and TBA found in the diurnal and in the high-temperature SHED tests were much lower than the corresponding levels of methanol. In the Work Assignment 18 study, ethanol was detected during the 60-84°F testing of the Class C gasoline/alcohol blends, but not in any of the lower temperature tests.

- Methanol content of the total diurnal hydrocarbons, with methanol/cosolvent blends, ranged from 4.3-9.3% in the Work Assignment 18 study and 5.4-15.6% in the Work Assignment 12 study. In the high temperature part of Work Assignment 12, the corresponding range was 13.7-18.3%.

I. INTRODUCTION

The objectives of this work assignment were to combine the data generated in two previous work assignments (Work Assignments 12 and 18 of Contract 68-03-3192) and to reanalyze the resulting data set to give a single final report. In the Work Assignment 12 evaluations, vapors from twelve gasolines and gasoline/alcohol blends were analyzed for butanes, total hydrocarbons, methanol, and appropriate cosolvent alcohols. The analyses were conducted in duplicate for each fuel at FTP diurnal SHED temperatures (60-84°F) and at typical hot-soak temperatures (160 ± 10°F). The fuels were prepared with different levels of aromatic content and Reid Vapor Pressure. The Work Assignment 18 study involved generating vapors from seven gasolines and gasoline/alcohol blends (representing fuel volatility Classes C, D, and E) during simulated diurnal test conditions (15-40°F, 35-60°F, and 60-84°F). These vapors were analyzed for total hydrocarbons, alcohols, and individual hydrocarbons up to and including C_6. In the two previous work assignments, total hydrocarbons were calculated for gasoline/alcohol blends from uncorrected FID total hydrocarbon levels. In this study, the FID response for the alcohols has been subtracted from the FID total hydrocarbon levels to give a total non-oxygenated hydrocarbon level. This non-oxygenated hydrocarbon SHED value is then combined with the alcohol SHED values to give a corrected total SHED hydrocarbon value.

A ten-gallon fuel tank (no test vehicle) filled to 40 percent capacity was used to generate the vapors for the diurnal tests in both work assignments, and a 250 ml vacuum flask filled with 125 ml of fuel and heated with a water bath to 160°F was used to generate vapors in the simulated hot soak tests in Work Assignment 12. SHED vapors were collected in Tedlar bags and analyzed for total uncorrected FID hydrocarbons, individual hydrocarbons, and the alcohols methanol, ethanol, and tertiary butyl alcohol (TBA).

II. TEST FUELS, PROCEDURES, INSTRUMENTATION, AND CALCULATIONS

This section describes the fuels, procedures, instrumentation, and calculations used in the two Work Assignments. A total of nineteen fuels, three simulated diurnal temperature rise scenarios, and a simulated hot-soak scenario were utilized in these programs. Evaporative emissions were collected in Tedlar bags from a sealed housing for evaporative determinations (SHED) and analyzed for total hydrocarbons, various individual hydrocarbons up to and including C_6 hydrocarbons, and the alcohols methanol, ethanol, and tertiary butyl alcohol.

A. Test Fuels

Nineteen fuels were used in this study, twelve in the Work Assignment 12 investigations and seven in the Work Assignment 18 investigations. The twelve fuels evaluated in Work Assignment 12 were tested in duplicate at diurnal SHED temperatures (60-84°F) and at high temperatures (160 ± 10°F). The seven fuels evaluated in Work Assignment 18 were tested in duplicate over three diurnal SHED temperature ranges (15-40°F, 35-60°F, and 60-84°F).

1. Work Assignment 12 Fuels

The twelve fuels tested in Work Assignment 12 were all prepared from a single batch of fuel having the SwRI Code EM-616-F (regular unleaded Gulf Crest). This fuel had a Reid Vapor Pressure (RVP) of 9.2 psi and aromatic content of 26.8 percent. Three groups of fuels were prepared from the base fuel: a low RVP (8.4 to 9.2 psi), low aromatic (~25 percent) group; a high RVP (11.5 to 12.0 psi), low aromatic (~25 percent group); and a low RVP (8.8 to 9.5 psi), high aromatic (~45 percent) group.

The low RVP - low aromatic fuels consisted of the starting base fuel, EM-616-F, and three alcohol blends. These blends were prepared by bubbling nitrogen through the base fuel until the RVP was reduced to 6.9 psi, followed by the addition of alcohols. Blend EM-642-F was prepared by adding 4.75 volume percent methanol and 4.75 volume percent TBA to the reduced-RVP fuel. Blend EM-643-F was prepared from the reduced-RVP base fuel by the addition of 5.0 volume percent methanol and 2.5 volume percent ethanol; and blend EM-644-F was prepared by the addition of 5 volume percent methanol. Selected fuel properties for these four test fuels are presented in Table 1. The RVP values for the alcohol blends, EM-642-F (8.45) and EM-643-F (8.40), were lower than anticipated (expected RVP of 9.0), because the addition of the alcohols produced only a 1.5 psi increase in RVP. Addition of the alcohols to the unaltered base fuel (RVP of 9.2) gave increases of 2.4 to 2.8 psi in RVP. These observations illustrate the complexity of preparing alcohol blends.

The second group of fuels, high RVP with low aromatics, consisted of three alcohol blends prepared by the direct addition of alcohols to the base fuel, EM-616-F (blend EM-638-F, 4.75 volume percent methanol, 4.75 volume percent TBA; blend EM-639-F, 5.0 volume percent methanol, 2.5 volume percent ethanol; and blend EM-640-F, 5.0 volume percent methanol); and a fourth fuel (EM-641-F) prepared by the addition of n-butane to fuel EM-616-F to give an RVP in the range of the three alcohol blends. These four fuels are described in Table 2.

TABLE 1. LOW RVP - LOW AROMATIC TEST FUELS (WORK ASSIGNMENT 12)

Fuel Code	EM-616-F	EM-642-F	EM-643-F	EM-644-F
Methanol, Vol. %	--	4.75	5.00	5.00
Cosolvent, Vol. %	--	4.75(TBA)	2.50(EtOH)	--
RVP, psi	9.20	8.45	8.40	9.15
Aromatics, %	26.8	26.8[a]	NR[b]	NR
Butane, g/gal	94	14	NR	NR
Isobutane, g/gal	32	2.1	NR	NR
Distillation-D86 °C (°F)				
IBP	31(88)	36(97)	36(97)	32(89)
5%	44(112)	47(117)	47(116)	47(116)
10%	51(124)	51(123)	51(123)	48(119)
15%	58(136)	55(131)	54(129)	51(123)
20%	64(148)	58(137)	57(134)	53(128)
30%	77(170)	69(157)	68(154)	80(176)
40%	90(194)	85(185)	89(193)	96(204)
50%	104(219)	101(214)	104(220)	107(225)
60%	118(245)	118(244)	118(244)	121(250)
70%	133(272)	133(272)	134(273)	134(274)
80%	151(303)	149(300)	151(303)	149(300)
90%	174(345)	171(340)	171(340)	170(338)
95%	195(383)	192(378)	187(368)	187(368)
EP	208(406)	208(407)	208(406)	208(407)
Recovery, %	97.5	98.0	98.0	99.0
Residue, %	1.5	1.0	1.0	1.0

[a]Calculated value based on 9.5% loss of light-end saturates and the addition of 9.5 volume percent alcohols. The ASTM FIA method gave an aromatic concentration of 33.3 percent, however this method was designed for gasoline fuels and its reliability for alcohol blends is unknown

[b]NR - not required

TABLE 2. HIGH RVP - LOW AROMATIC TEST FUELS (WORK ASSIGNMENT 12)

Fuel Code	EM-641-F	EM-638-F	EM-639-F	EM-640-F
Methanol, Vol. %	—	4.75	5.00	5.00
Cosolvent, Vol. %	—	4.75(TBA)	2.50(EtOH)	--
RVP, psi	11.55	11.60	11.85	12.00
Aromatics, %	21.5	24.3[a]	NR[b]	NR
Butane, g/gal	139	85[c]	NR	NR
Isobutane, g/gal	23	29[c]	NR	NR
Distillation-D86 °C(°F)				
IBP	26(79)	30(86)	31(87)	29(85)
5%	37(99)	39(103)	39(103)	38(101)
10%	44(111)	44(111)	44(111)	41(106)
15%	50(122)	48(119)	48(118)	45(113)
20%	57(135)	53(127)	52(125)	48(118)
30%	71(160)	61(141)	57(135)	60(140)
40%	86(187)	77(170)	73(163)	82(180)
50%	101(214)	92(198)	97(206)	98(208)
60%	116(240)	109(228)	112(234)	113(236)
70%	131(267)	128(262)	128(262)	128(263)
80%	149(300)	145(293)	145(293)	146(294)
90%	172(342)	168(334)	168(334)	167(332)
95%	197(386)	185(365)	186(366)	186(366)
EP	208(406)	206(402)	207(405)	208(406)
Recovery, %	98.0	98.0	98.0	98.0
Residue, %	1.0	1.0	1.0	1.0

[a]Calculated value based on the addition of 9.5% alcohols to the base fuel EM-616-F, which had an aromatic content of 26.8. The ASTM FIA method gave an aromatic concentration of 26.8 percent, however this method was designed for gasoline fuels and its reliability for alcohol blends is unknown

[b]NR - not required

[c]Calculated value, EM-638-F prepared by blending EM-616-F (90.5%) with methanol (4.75%) and TBA (4.75%). EM-638-F Butane and Isobutane values calculated by multiplying EM-616-F concentrations by a 0.905 factor.

The third group of fuels was prepared by initially adding mixed xylenes to base fuel EM-616-F to give a high aromatic fuel (~45 percent aromatics), followed by subsequent mixing with alcohols to give blends EM-646-F, EM-647-F, and EM-648-F, or with n-butane to give base fuel EM-645-F. Table 3 gives selected properties for these fuels.

2. Work Assignment 18 Fuels

The seven test fuels that were evaluated in the Work Assignment 18 segment of the study, along with their corresponding RVP and distillation data, are listed in Table 4. Fuel EM-697-F (Gasoline, Class E) is a commercial grade unleaded gasoline and was obtained in two 55-gallon drums from Mr. Pete Gabele of RTP-EPA. Fuel EM-690-F (Gasoline, Class D) is winter grade regular unleaded Gulf Crest and was obtained locally. Fuel EM-702-F (Gasoline, Class C) was prepared by blending EM-690-F and EM-616-F in a 3:2 ratio. EM-616-F was also used as the base fuel in the Work Assignment 12 investigations. EM-700-F was unleaded Amoco Indolene and was obtained in 55-gallon drum quantities. Alcohol blends EM-703-F, EM-701-F and EM-698-F were prepared from the corresponding volatility class base fuels, EM-702-F, EM-690-F, and EM-697-F, respectively. To prepare the blends, the base fuels were first bubbled with nitrogen to lower the RVP, followed by the addition of appropriate quantities of methanol and ethanol.

B. Diurnal Test Procedures

Three different diurnal temperature rise scenarios were used in the combined study: 60-84°F, 35-60°F, and 15-40°F. The 60-84°F scenario was used for all fuels in Work Assignment 12, for the Class C gasoline and gasoline/alcohol blend in Work Assignment 18, and for Indolene in Work Assignment 18. The 35-60°F scenario was used for the Class D gasoline and gasoline/alcohol blend in Work Assignment 18, and the 15-40°F scenario was used for the Class E gasoline and gasoline/alcohol blend in Work Assignment 18. The three scenarios were conducted in a manner similar to the diurnal test as specified in the Federal Test Procedure (FTP) for light-duty gasoline-fueled vehicles; with the exceptions that only a vehicle fuel tank (no test vehicle) was used in the tests, and evaporative vapors were collected from the SHED in Tedlar bags for subsequent analysis as opposed to vapor analysis with a continuous hydrocarbon analyzer.

For each test, a 10-gallon capacity fuel tank was filled with 4 gallons of precooled test fuel. With the exceptions of the tubing that had been previously connected to the evaporative charcoal canister, all openings to the fuel tank were then plugged. For the 60-84°F and the 35-60°F tests, heating blankets were attached to the bottom of the tank; the tank was placed in the SHED, and appropriate electrical and thermocouple connections were made (Figure 1). No external heating was required for the fuel tank in the 15-40°F tests, so the heating blankets were not attached to the bottom of the tank before placing it in the SHED. In fact, some additional tank insulation was required to keep the tank from warming up too rapidly in the SHED. This additional insulation was accomplished by placing the tank on sealed Tedlar bags containing polystyrene foam peanuts (Figure 2).

When the fuel temperature was within 4 to 5 minutes of reaching the initial temperature point, the SHED purge system was closed and the SHED sealed. At this point a background Tedlar bag sample (~5 cubic feet of sample) was collected from

TABLE 3. LOW RVP - HIGH AROMATIC TEST FUELS (WORK ASSIGNMENT 12)

Fuel Code	EM-645-F	EM-646-F	EM-647-F	EM-648-F
Methanol, Vol. %	—	4.75	5.00	5.00
Cosolvent, Vol. %	—	4.75(TBA)	2.50(EtOH)	--
RVP, psi	9.36	8.80	9.10	9.55
Aromatics, %	49.1	44.3[a]	NR[b]	NR
Butane, g/gal	157	57	NR	NR
Isobutane, g/gal	20	17	NR	NR
Distillation-D86 °C(°F)				
IBP	28(85)	24(75)	36(97)	32(89)
5%	41(105)	49(121)	48(119)	47(117)
10%	50(122)	54(129)	53(128)	51(123)
15%	61(141)	58(137)	57(135)	53(127)
20%	72(161)	63(145)	59(139)	57(135)
30%	94(201)	82(179)	77(171)	94(201)
40%	113(235)	104(219)	109(229)	113(236)
50%	125(257)	123(253)	125(257)	127(260)
60%	133(272)	133(271)	134(274)	134(274)
70%	139(282)	138(281)	141(286)	139(282)
80%	144(292)	144(291)	146(295)	146(294)
90%	156(312)	154(309)	157(315)	157(314)
95%	177(350)	171(340)	176(348)	186(366)
EP	204(400)	203(398)	203(397)	204(400)
Recovery, %	98.0	98.0	98.0	98.0
Residue, %	1.0	1.0	1.0	1.0

[a]Calculated value based on the addition of mixed xylenes to raise the aromatics to 48.9% followed by the addition of 9.5% volume percent alcohols. The ASTM FIA method gave an aromatic concentration of 48.6 percent, however this method was designed for gasoline fuels and its reliability for alcohol blends is unknown

[b]NR - not required

TABLE 4. TEST FUELS (WORK ASSIGNMENT 18)

Fuel	Gasoline	Gasoline	Gasoline	Indolene	Blend	Blend	Blend
Volatility Class	E	D	C	--	C	D	E
Fuel Code	EM-697-F	EM-690-F	EM-702-F	EM-700-F	EM-703-F	EM-701-F	EM-698-F
Methanol, Vol%	--	--	--	--	5.0	5.0	5.0
Ethanol, Vol %	--	--	--	--	2.5	2.5	2.5
RVP, psi	14.0	12.0	10.9	9.2	11.5	13.2	15.0
Distillation - D86 °C(°F)							
IBP	23 (74)	24 (76)	26 (79)	26 (79)	33 (91)	31 (87)	24 (75)
5%	33 (92)	38 (101)	40 (104)	43 (110)	43 (109)	40 (104)	36 (96)
10%	39 (103)	44 (112)	46 (114)	54 (130)	46 (115)	44 (111)	40 (104)
15%	46 (114)	50 (122)	52 (126)	64 (148)	49 (120)	47 (116)	44 (111)
20%	53 (127)	56 (132)	58 (137)	74 (165)	52 (125)	50 (122)	48 (119)
30%	69 (157)	67 (152)	70 (158)	91 (195)	57 (135)	55 (131)	56 (133)
40%	88 (190)	78 (172)	82 (180)	102 (215)	73 (163)	65 (149)	69 (157)
50%	103 (217)	89 (193)	95 (203)	109 (228)	93 (200)	76 (168)	99 (211)
60%	113 (236)	104 (220)	109 (229)	115 (239)	109 (228)	102 (215)	112 (233)
70%	123 (254)	118 (245)	124 (256)	123 (253)	123 (254)	117 (242)	122 (252)
80%	139 (283)	134 (274)	141 (286)	138 (280)	140 (284)	134 (274)	136 (276)
90%	167 (332)	156 (312)	164 (328)	170 (338)	162 (323)	157 (314)	164 (327)
95%	185 (365)	173 (344)	184 (363)	194 (382)	178 (352)	178 (352)	181 (358)
EP	202 (395)	197 (386)	206 (402)	218 (424)	199 (391)	190 (374)	192 (377)
Recovery, %	98.0	98.0	98.0	98.0	98.0	98.0	98.0
Residue, %	1.0	1.0	1.0	1.0	1.0	1.0	1.0

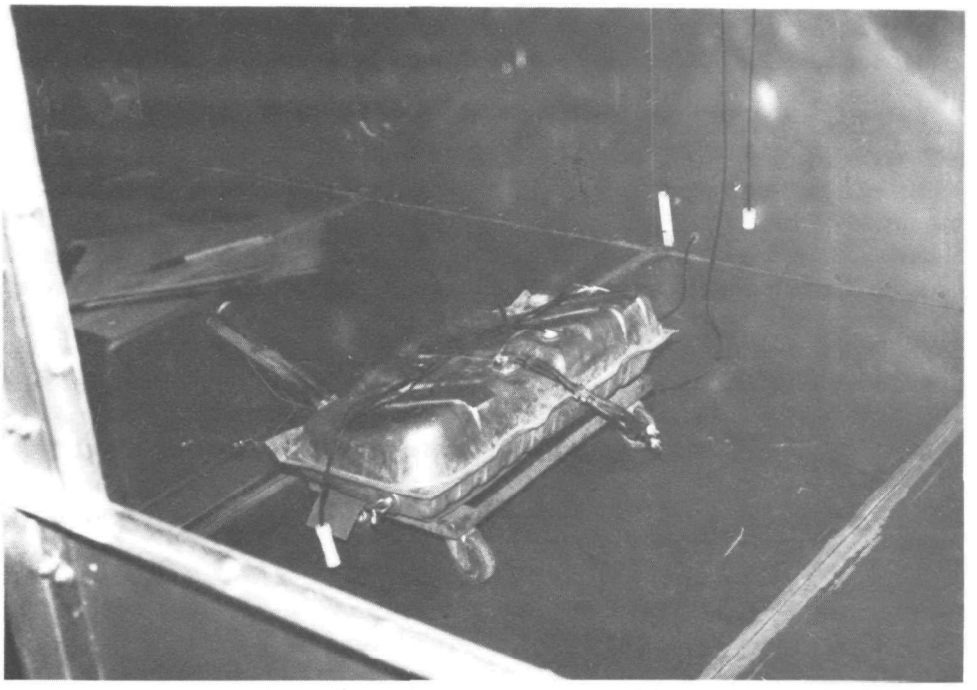

FIGURE 1. FUEL TANK AS USED IN THE 60-84°F AND 35-60°F TESTS

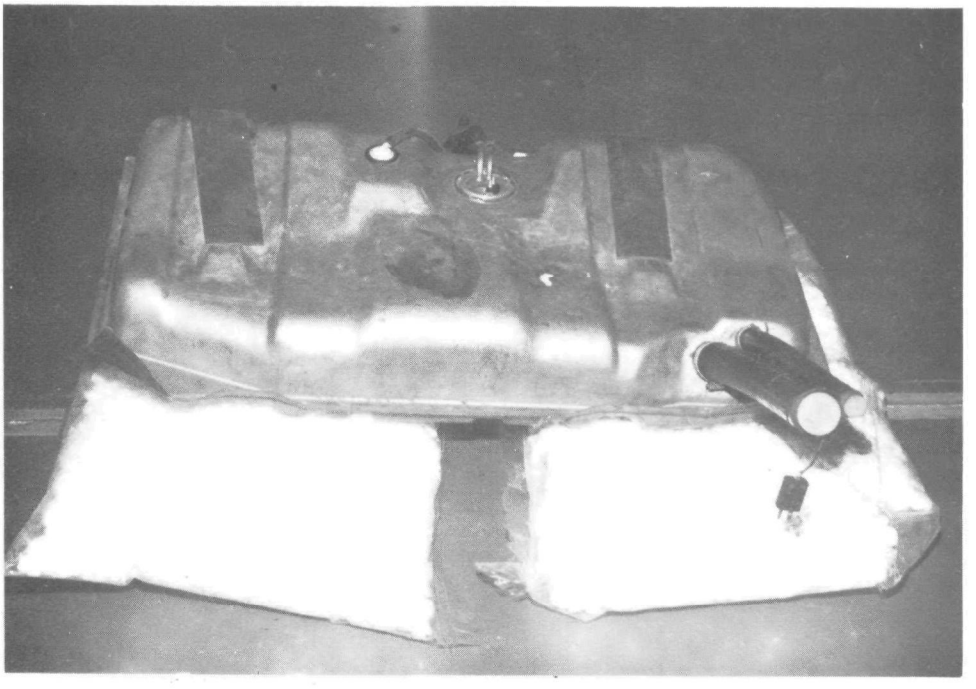

FIGURE 2. FUEL TANK AS USED IN THE 15-40°F TESTS

the SHED over a six- to eight-minute time period. This collection period is necessary in order to obtain a sufficient volume of sample for the alcohol analysis, as well as sample for the total and individual hydrocarbon analyses. The midpoint of this background sample period was targeted for the initial test temperature (15, 35, or 60°F). For the 60-84°F test, the fuel tank was then heated, over a 60 minute period, from 60 to 84°F. For the 35-60°F test, intermittent heating was used to raise the temperature from 35 to 60°F over a 60 ± 6 minute time period. Because of the lack of external heating control, the temperature rise for the 15-40°F was not as linear as for the 60-84°F and the 35-60°F tests. A Tedlar bag sample was collected for each test starting at 3 to 4 minutes before the fuel reached the final test temperature (40, 60, or 84°F), and for an equal time period after the fuel reached the final temperature. Once again, the midpoint of the sample collection period was targeted for the appropriate final test fuel temperature. After sample collection, the SHED was opened, the fuel tank removed, and the SHED purged for the next test. The fuel was drained from the fuel tank, and the fuel tank rinsed with the next test fuel before the test sequence was repeated.

C. High-Temperature (160 ± 10°F) Test Procedure

For the twelve Work Assignment 12 fuels, high-temperature tests were performed to simulate vapor generated from a carbureted vehicle under hot soak conditions. In these tests, a 125 ml volume of test fuel was placed in a 250 ml flask with a side arm opening. The top of the flask was sealed, and a vent tube of approximately two feet in length (tubing obtained from an actual evaporative control system) was attached to the side arm and closed with a pinch clamp. The flask of fuel, containing a thermocouple to monitor fuel temperature, was then placed in the SHED along with a preheated water bath (Figure 3). For a background

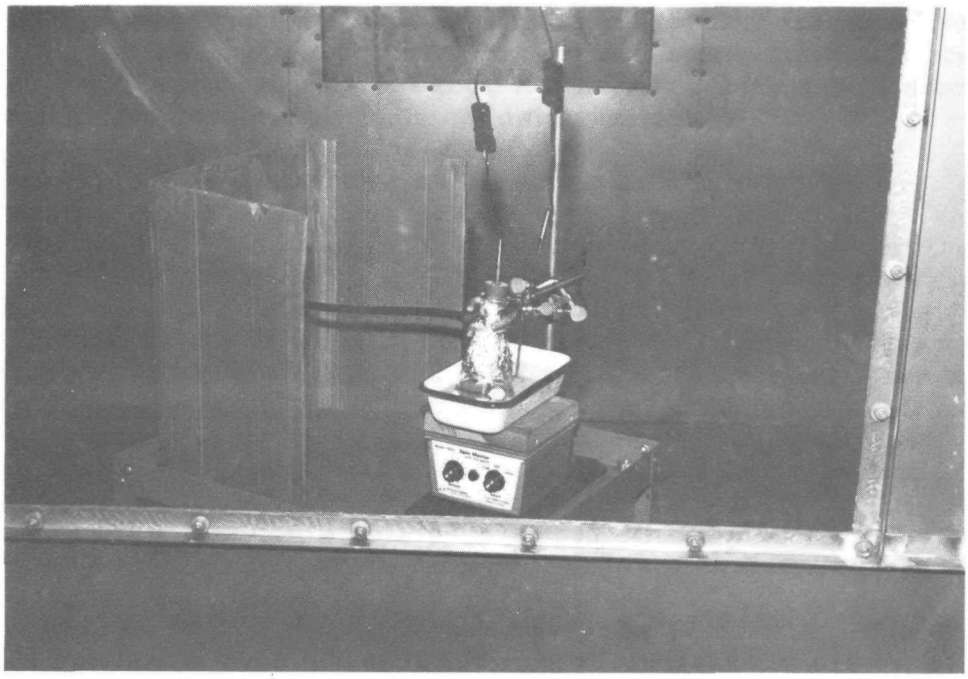

FIGURE 3. FLASK AND WATER BATH FOR HIGH TEMPERATURE TESTS

sample, the SHED purge system was closed, the SHED sealed, and a six-to-eight-minute bag sample was collected in a Tedlar bag. The SHED was then briefly opened to allow someone to enter the SHED, open the pinch clamp on the tubing and lower the flask of fuel into the water bath. The SHED was then quickly sealed and the test initiated. Within approximately 10 minutes the fuel temperature reached the 150 to 160°F temperature range. For an additional 50 minutes the fuel temperature in the flask was maintained at 160 ± 10°F. At 56 to 57 minutes into the test, the collection of a Tedlar bag sample was initiated and continued for 6 to 8 minutes, with the midpoint of the sampling time at 60 minutes into the test. After sample collection the SHED was opened, the flask of fuel removed, and the SHED purged for the next test. During the initial part of the test (0-10 minutes) the fuel simply distilled from the flask until the lower-boiling materials were removed by distillation. This distillation period accounts for the fuel temperature remaining below 160 ± 10°F during the first 10 minutes of the test. In some cases, the fuel condensed in the two feet of vent tubing, and as a result, liquid dripped from the tubing to the SHED floor. While this volume of liquid was small, at the conclusion of each test it was necessary to wipe this fuel from the SHED floor before proceeding to the next test.

D. Analytical Procedures and Calculations

Evaporative emissions were collected in Tedlar bags from the SHED at the beginning (background) and end (sample) of each diurnal and high-temperature test. Analyses for total hydrocarbons, various individual hydrocarbons, and alcohols (methanol, ethanol, or tertiary butyl alcohol) were conducted on each background and sample bag. Total hydrocarbon and individual hydrocarbon analyses were conducted directly on the vapors in the bags; however, for the alcohol analyses, 4 to 5 cubic feet of vapor from each background or sample bag were concentrated in water by pulling the bagged vapors through two impingers, each containing 25 ml of water. The water samples from these impingers were then analyzed for the alcohols with the aid of a gas chromatograph. The instrumentation, procedures, and calculations used to quantify the total hydrocarbons, individual hydrocarbons, and alcohols are discussed briefly in the following sections.

1. Alcohols (methanol, ethanol, and tertiary butyl alcohol)

The analyses for the alcohols methanol, ethanol, and tertiary butyl alcohol were conducted using the GC-FID procedure described in the report "In-Use Evaporative Canister Evaluation," EPA Report No. 460/3-85-003, Work Assignment 27 of EPA Contract 68-03-3162. In this study, the evaporative vapors were first collected from the SHED in Tedlar bags (4 to 5 ft^3 of vapors) and then bubbled through two glass impingers each containing 25 ml of deionized water maintained at ice bath temperatures. This two-step process allowed the evaporative vapors to be pulled through the impingers at a more optimum flow rate than would be practical for direct SHED sampling. For analysis, a portion of the aqueous solution was injected into a gas chromatograph equipped with a flame ionization detector. Appropriate external alcohol standards were used to quantify the results.

Calculations for the mass of alcohols in the SHED were performed using the results from the analytical procedure in $\mu g/m^3$ (dry volume) and the net dry SHED volume in cubic meters. Relative humidity measurements were taken in the SHED during each test to permit the dry SHED volume calculations to be made.

2. Total Hydrocarbons (THC)

The bagged evaporative emission samples were analyzed for total hydrocarbons using the FID analyzer in SwRI Bag Cart Number 1. This bag cart was designed, calibrated, and operated in accordance with the appropriate sections of the Code of Federal Regulations for light-duty vehicle emissions certification. To calculate the amount of total hydrocarbons (grams) in the SHED for each test with a non-alcohol-containing fuel, the following equation from the Code of Federal Regulations (Title 40, Part 86, Section 143-78) for calculating evaporative emissions was used:

$$M_{HC} = kV_n \times 10^{-4} \left[\frac{C_{HC_f} P_{B_f}}{T_f} - \frac{C_{HC_i} P_{B_i}}{T_i} \right]$$

where:

M_{HC} = hydrocarbon mass, grams
C_{HC} = hydrocarbon concentration as ppm carbon
V_n = net enclosure volume, ft^3. Determined for this study by subtracting 2 ft^3 for the fuel tank volume (diurnal test) or 1 ft^3 for flask and water bath (hot soak tests) from the enclosure volume
P_B = barometric pressure, in. Hg
T = enclosure ambient temperature, R
k = 0.208 (12 + H/C)
H/C = 2.33 for the diurnal test
H/C = 2.20 for the hot-soak test (and used in this study for the high temperature tests)
i = indicates background bag for this study
f = indicates sample bag for this study

Because alcohols have a FID hydrocarbon response that differs significantly from the non-oxygenated gasoline-derived hydrocarbons, and the equation in the Code of Federal Regulations for calculating evaporative emissions does not include a term for oxygen mass in the calculations, an alternate method must be used to determine the total hydrocarbons in the tests with alcohol-containing fuels. The method used in this study consists of first subtracting appropriate ppmC values for the alcohols from the bag cart FID total ppmC values. The ppmC for the remaining non-oxygenated hydrocarbons is then used in the Code of Federal Regulation equation to determine a mass value. This non-oxygenated hydrocarbon mass can then be added to the mass of each of the individual alcohols to give a total hydrocarbon value.

The ppmC subtracted for each of the alcohols is determined by first converting the alcohol mass in $\mu g/m^3$ to ppm alcohol. This can be accomplished by dividing the $\mu g/m^3$ alcohol value by 1333 μg/ppm for methanol, 1916 μg/ppm for ethanol, and 3083 μg/ppm for TBA. For ethanol and TBA, the ppm alcohol values must be multiplied by the number of carbons in each alcohol, 2 and 4, respectively, to give the ppmC values. Before the ppmC alcohol values can be subtracted from the bag cart FID ppmC values, they must be corrected for humidity removal and for their non-unity response in the FID. Methanol and ethanol were found to have 0.79

FID response factors, while TBA was found to have an FID response factor of 0.94 (i.e., an FID "sees" 10 ppmC methanol as 7.9 ppmC, therefore 10 ppmC methanol must be multiplied by 0.79 before the methanol value can be subtracted from the bag cart FID value).

2. Individual Hydrocarbons

The individual hydrocarbon analyses (C_1 to C_6 plus toluene and 2,4-dimethylpentane) were conducted using two separate gas chromatograph systems. The first system provides concentrations for selected individual hydrocarbons including methane, ethane, ethylene, acetylene, propane, propylene, benzene, and toluene. This system is described in detail in EPA Report 600/2-79-017, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles," and is illustrated in Figure 4. It utilizes a gas chromatograph system containing four separate columns and a flame ionization detector. Sample peak areas are compared to an external calibration blend containing each of the eight hydrocarbons analyzed. Reported hydrocarbon concentrations include FID response corrections for each of these eight hydrocarbons. A standard and sample chromatogram are illustrated in Figures 5 and 6. This system was modified in the Work Assignment 12 investigations to provide concentrations for n-butane and isobutane.

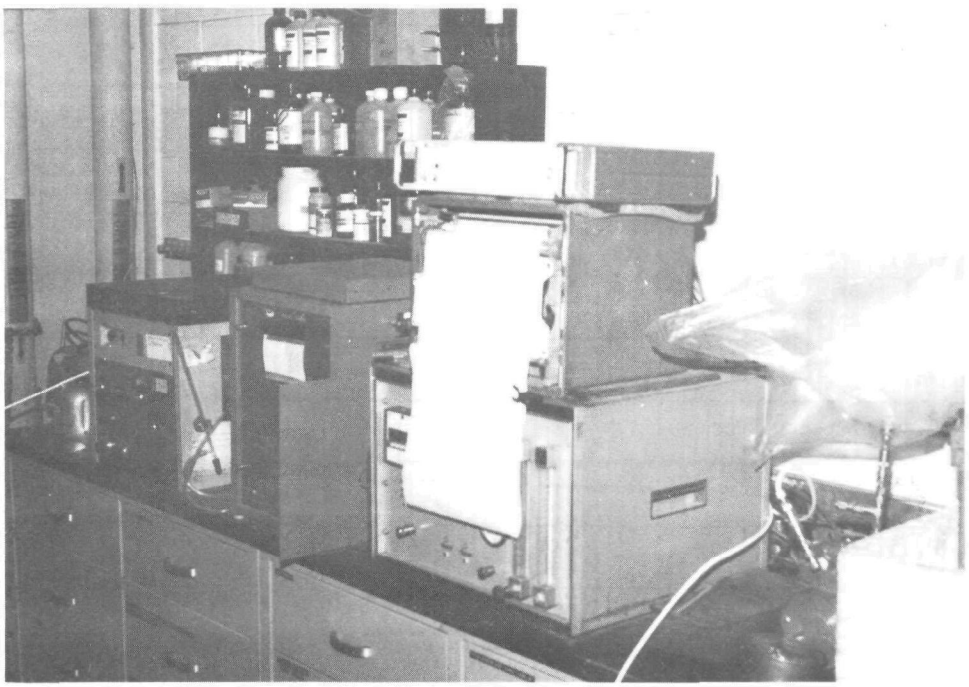

FIGURE 4. INDIVIDUAL HYDROCARBON ANALYSIS SYSTEM FOR METHANE, ETHANE, ETHYLENE, ACETYLENE, PROPANE, PROPYLENE, BENZENE, TOLUENE, BUTANE, AND ISOBUTANE

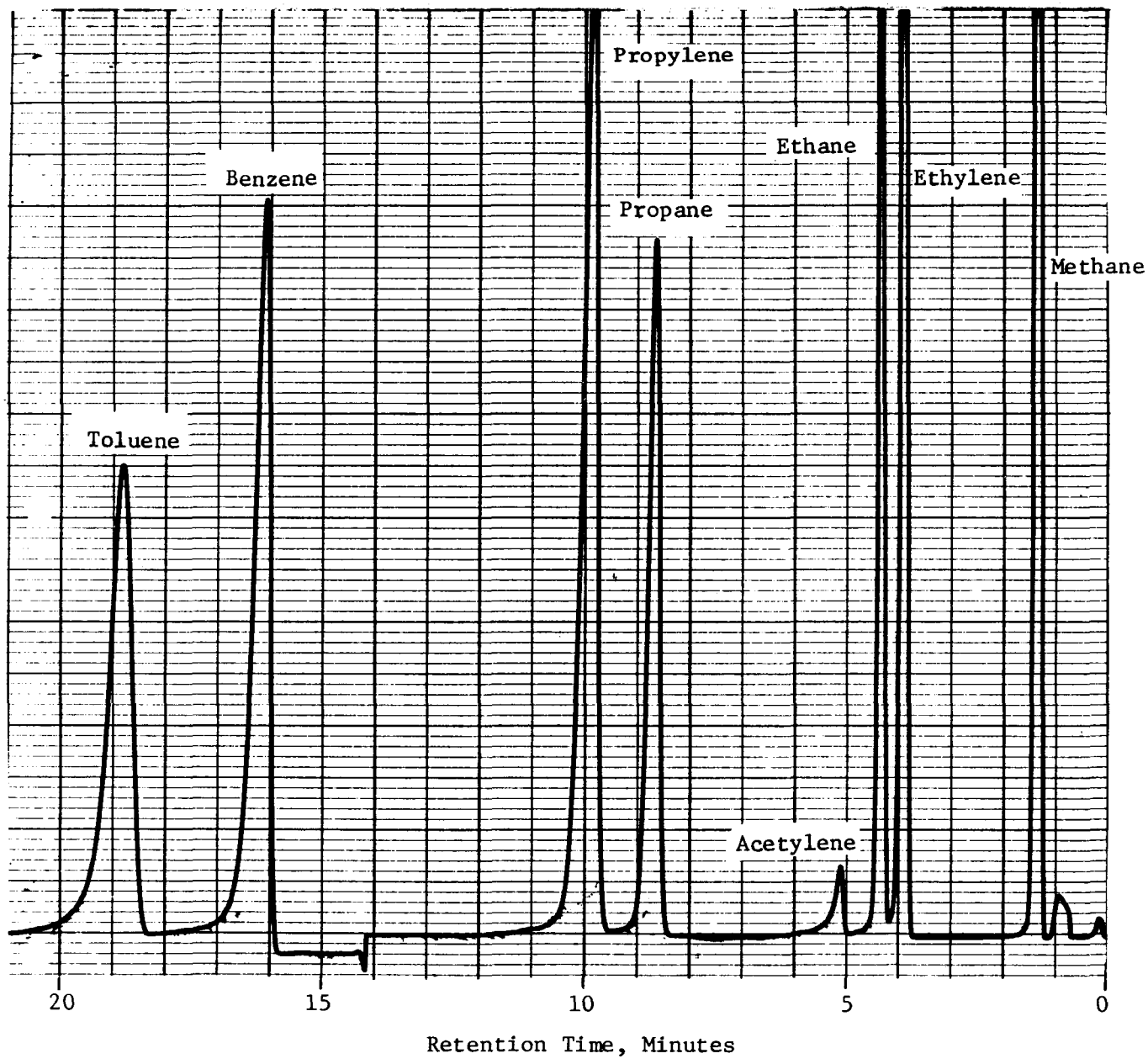

FIGURE 5. STANDARD CHROMATOGRAM FOR C_1 - C_3 HYDROCARBONS, BENZENE, AND TOLUENE

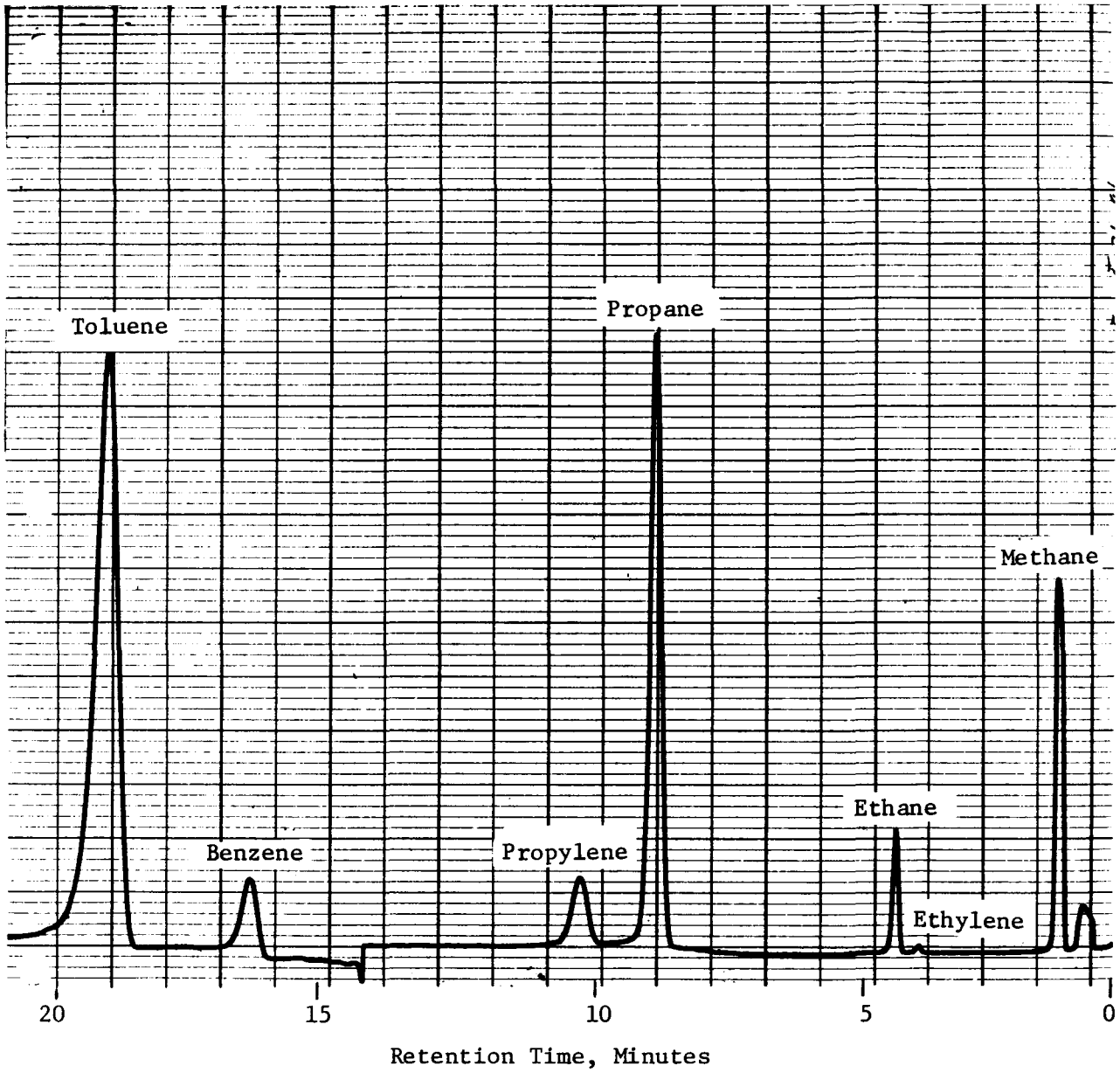

FIGURE 6. SAMPLE CHROMATOGRAM (TEST 2, FUEL EM-700-F) FOR C_1 - C_3 HYDROCARBONS, BENZENE, AND TOLUENE

In the Work Assignment 12 investigations, the analysis time for the procedure was extended to permit C_4 peak elution and quantification. Butane standards (n-butane) were prepared by adding n-butane gas to zero air in Tedlar bags. The butane standard bags were named with a FID hydrocarbon analyzer against propane standards traceable to NBS standards. Relative response factors for propane and n-butane from "Basic Gas Chromatography" by H. M. McNair and E. J. Bonelli, Varian Aerograph, 1968, were used to give actual n-butane concentrations in ppmC (n-butane has a relative response factor of 1.11 per carbon in relation to 1.00 for propane). For this study, the FID response factor for isobutane was assumed to be equivalent to that for n-butane.

In the Assignment 18 investigations, butane, isobutane and the remainder of the hydrocarbons, C_4 - C_6 plus 2,4-dimethylpentane, were analyzed using a second gas chromatograph system. It was equipped with subambient capabilities, a capillary column and a FID detector; and the individual hydrocarbons were quantified using a standard containing n-butane, isobutane, isopentane, pentane, 2,2-dimethylbutane, cyclopentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, hexane, methylcyclopentane, 2,4-dimethylpentane, and benzene. Because individual FID response factors were not available for all of the compounds, the standard was named using propane as a reference gas. As a result, the values for these compounds do not include the individual FID response factor corrections (all assumed to be 1.00). The capillary column used in the system is a Perkin-Elmer F-50 Versilube, 150 ft x 0.020 inch WCOT stainless steel column. The column is initially cooled to -139°F (-95°C) for sample injection. Upon injection, the temperature is programmed at a 7°F (4°C) increase per minute for approximately 31 minutes (until benzene elutes). A chromatogram of a 995 ppmC individual hydrocarbon standard is illustrated in Figure 7, and a chromatogram of a sample (Test 2, Fuel EM-700-F) is illustrated in Figure 8.

Calculations for determining the mass of each individual hydrocarbon in the SHED were performed using the equation for the total hydrocarbons. The ppmC value of the individual hydrocarbon concentrations was used in place of the total hydrocarbon ppmC concentrations, and an actual H/C ratio for each individual hydrocarbon was used in both the diurnal and high temperature calculations in place of the 2.33 diurnal THC value and the 2.20 high temperature THC value.

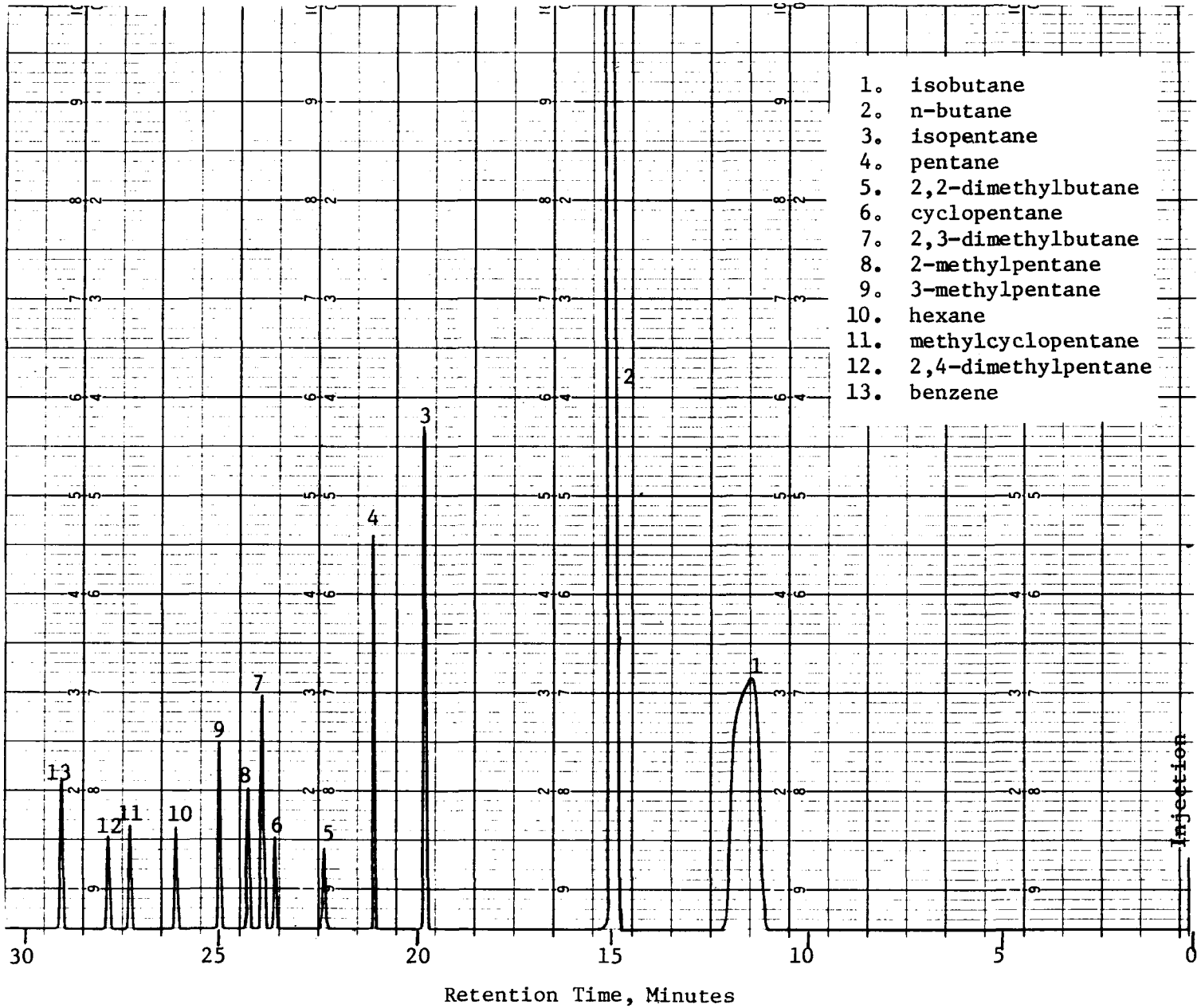

FIGURE 7. CHROMATOGRAM OF 995 PPMC INDIVIDUAL HYDROCARBON STANDARD (C_4 - C_6)

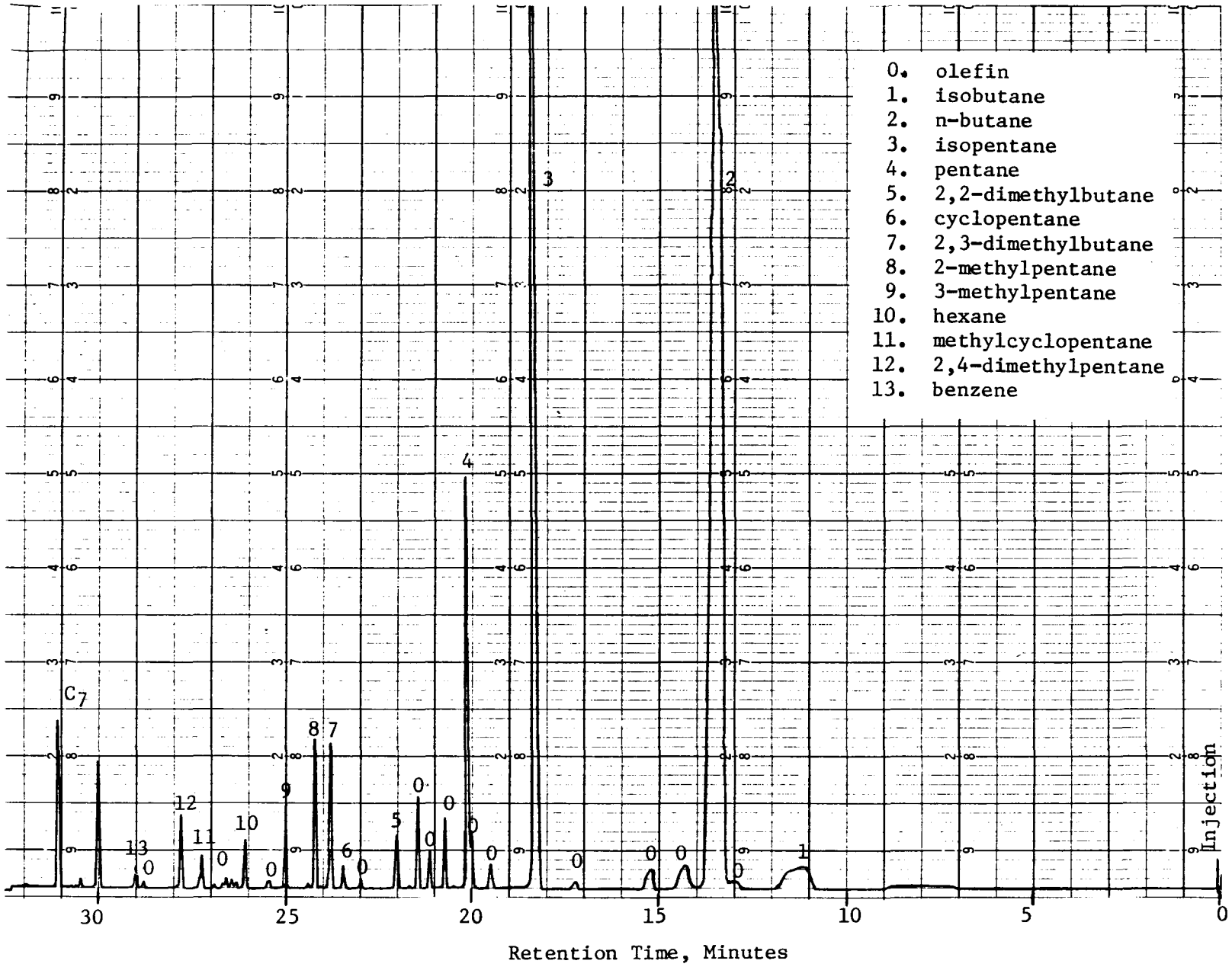

FIGURE 8. CHROMATOGRAM OF SAMPLE FOR C_4 - C_6 HYDROCARBONS (TEST 2, FUEL EM-700-F)

III. RESULTS

SHED tests were conducted in duplicate utilizing three diurnal temperature rise scenarios (15-40°, 35-60°, and 60-84°F) and nineteen gasolines and gasoline/alcohol blends. The 60-84°F diurnal test was used to evaluate twelve of the test fuels, while all three of the diurnal rise scenarios were used in evaluating the remaining seven fuels. The 60-84°F diurnal test was used for a Class C volatility gasoline and gasoline/alcohol blend and Indolene; the 35-60°F diurnal test was used for a Class D volatility gasoline and gasoline/alcohol blend; and the 15-40°F diurnal test was used for a Class E volatility gasoline and gasoline/alcohol blend. Twelve of the test fuels were also evaluated at high temperatures (160 ± 10°) to simulate vehicle hot soak losses.

A ten-gallon fuel tank (no test vehicle) filled to 40 percent capacity was used to generate the vapors for the diurnal tests, and a 250 ml vacuum flask filled with 125 ml of fuel and heated with a water bath to 160°F was used to generate vapors in the simulated hot soak tests. SHED vapors were collected in Tedlar bags and analyzed for total uncorrected FID hydrocarbons, individual hydrocarbons, and the alcohols methanol, ethanol, and tertiary butyl alcohol. The following sections discuss the results for the simulated diurnal and high-temperature tests.

A. Diurnal Tests

Two sets of experiments were conducted utilizing simulated diurnal tests. One set, conducted in Work Assignment 12, utilized the 60-84°F temperature rise with twelve test fuels, while the second, a Work Assignment 18 study, involved the use of three diurnal rise scenarios and seven test fuels. The average SHED results for these two sets of experiments are presented in Tables 5 and 6, and the individual SHED test results are presented as Appendix Tables A-1 through A-19. The following sections discuss diurnal SHED test results for total hydrocarbons, individual hydrocarbons, and alcohols.

1. Total Hydrocarbons

The total hydrocarbons, as reported in this study, include both the non-oxygenated hydrocarbon emissions (equivalent to the total hydrocarbons for the gasoline fuels) and the alcohol emissions. With the exception of Fuel EM-690-F, the repeatability of the total hydrocarbon test results for each fuel tested was good; individual test results were within 10% of the reported averages in Tables 5 and 6. The repeatability of the two tests on Fuel EM-690-F was not as good; the individual tests were 23% higher and lower than the average value in Table 5.

For the diurnal tests conducted at 60-84°F (in both Work Assignment 12 and 18 investigations), the total SHED hydrocarbons appear to follow fuel RVP trends, with the higher RVP fuels giving higher total hydrocarbons. A linear regression plot of the total SHED hydrocarbons versus the fuel RVP for all 15 fuels tested at 60-84°F gave an r^2 of 0.88. A plot of the total SHED hydrocarbons versus fuel RVP is displayed in Figure 9. Linear regression plots of total SHED hydrocarbons versus the fuel RVP for the gasoline fuels only and the gasoline/alcohol blends only were slightly better, with $r^2 = 0.90$ in both cases.

TABLE 5. AVERAGE DIURNAL EVAPORATIVE EMISSIONS, WORK ASSIGNMENT 12 STUDY

Fuel	Low RVP-Low Aromatic			
Fuel Code	EM-616-F	EM-642-F	EM-643-F	EM-644-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	9.2	8.5	8.4	9.2
	Evaporative Results, g/test			
Butane	5.3	1.6	1.9	2.2
Isobutane	2.7	0.6	0.7	0.7
Methanol	ND[a]	0.5	0.7	2.2
Ethanol	NR[b]	NR	<0.1	NR
TBA	NR	0.2	NR	NR
Total Non-oxygenated HC[c]	18.2	8.5	10.4	11.3
Total Hydrocarbons[d]	18.2	9.2	11.1	13.5

Fuel	High RVP-Low Aromatic			
Fuel Code	EM-641-F	EM-638-F	EM-639-F	EM-640-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	11.6	11.6	11.9	12.0
	Evaporative Results, g/test			
Butane	10.3	8.3	10.3	6.8
Isobutane	3.1	4.1	3.3	3.2
Methanol	0.4	3.4	3.2	4.5
Ethanol	NR	NR	0.1	NR
TBA	NR	0.3	NR	NR
Total Non-oxygenated HC	23.9	27.2	21.1	22.5
Total Hydrocarbons	24.3	30.9	24.4	27.0

Fuel	Low RVP-High Aromatic			
Fuel Code	EM-645-F	EM-646-F	EM-647-F	EM-648-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	9.4	8.8	9.1	9.6
	Evaporative Results, g/test			
Butane	7.2	2.5	3.0	3.4
Isobutane	1.5	1.2	1.5	1.6
Methanol	0.1	1.1	2.0	2.1
Ethanol	NR	NR	0.1	NR
TBA	NR	0.2	NR	NR
Total Non-oxygenated HC	15.5	8.9	10.7	12.8
Total Hydrocarbons	15.5	10.2	12.8	14.8

[a]ND - none detected, less than 0.02 g/test
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE 6. AVERAGE DIURNAL EVAPORATIVE EMISSIONS, WORK ASSIGNMENT 18 STUDY

Fuel Code	EM-697-F	EM-690-F	EM-702-F	EM-700-F	EM-703-F	EM-701-F	EM-698-F
Volatility Class	E	D	C	(Indolene)	C	D	E
Methanol, Vol%	--	--	--	--	5.0	5.0	5.0
Ethanol, Vol%	--	--	--	--	2.5	2.5	2.5
RVP, psi	14.0	12.0	10.9	9.2	11.5	13.2	15.0
	Average Evaporative Results, g/test						
Individual Hydrocarbons							
Methane	<0.01[a]	0.02	<0.01	<0.01	<0.01	ND	<0.01
Ethylene	<0.01	<0.01	ND	<0.01	ND	ND	ND
Ethane	<0.01	0.03	0.01	0.02	<0.01	<0.01	<0.01
Acetylene	ND[b]	ND	ND	ND	ND	ND	ND
Propane	0.19	0.31	0.33	0.15	0.15	0.15	0.13
Propylene	0.01	0.03	0.01	0.03	0.01	0.01	0.01
Benzene	0.02	0.09	0.18	0.02	0.24	0.10	0.03
Toluene	0.18	0.11	0.18	0.25	0.24	0.10	0.09
Isobutane	1.84	2.01	3.08	0.48	2.87	1.26	1.71
n-Butane	3.27	5.04	7.52	8.11	8.39	3.33	3.20
Isopentane	1.47	2.64	4.87	3.40	6.65	1.94	1.49
Pentane	0.21	1.16	2.11	0.78	3.18	0.87	0.29
2,2-Dimethylbutane	0.01	0.09	0.15	0.12	0.23	0.07	0.01
Cyclopentane	0.03	0.09	0.15	0.05	0.19	0.06	0.08
2,3-Dimethylbutane	0.04	0.11	0.22	0.28	0.32	0.08	0.03
2-Methylpentane	0.09	0.43	0.81	0.26	1.26	0.33	0.09
3-Methylpentane	0.04	0.23	0.27	0.15	0.73	0.21	0.06
Hexane	0.02	0.18	0.39	0.08	0.63	0.15	0.03
Methylcyclopentane	0.06	0.13	0.22	0.08	0.35	0.10	0.04
2,4-Dimethylpentane	0.01	0.03	0.05	0.14	0.09	0.03	0.02
C_4 Olefins	0.39	0.39	0.74	0.35	0.67	0.37	0.35
C_5-C_6 Olefins	0.85	1.26	2.08	0.75	3.25	0.96	0.83
Alcohols							
Methanol	ND[c]	ND	ND	ND	2.89	0.58	0.37
Ethanol	NR[d]	NR	NR	NR	0.31	ND	ND
Total Non-oxygenated HC[e]	9.0	13.9	22.8	15.8	28.0	10.4	8.2
Total Hydrocarbons[f]	9.0	13.9	22.8	15.8	31.2	11.0	8.6

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, < 0.001 g/test
[c] none detected, for methanol and ethanol, <0.01 g/test
[d] not required
[e] Total FID hydrocarbons corrected for alcohol content
[f] Sum of alcohols and non-oxygenated hydrocarbons

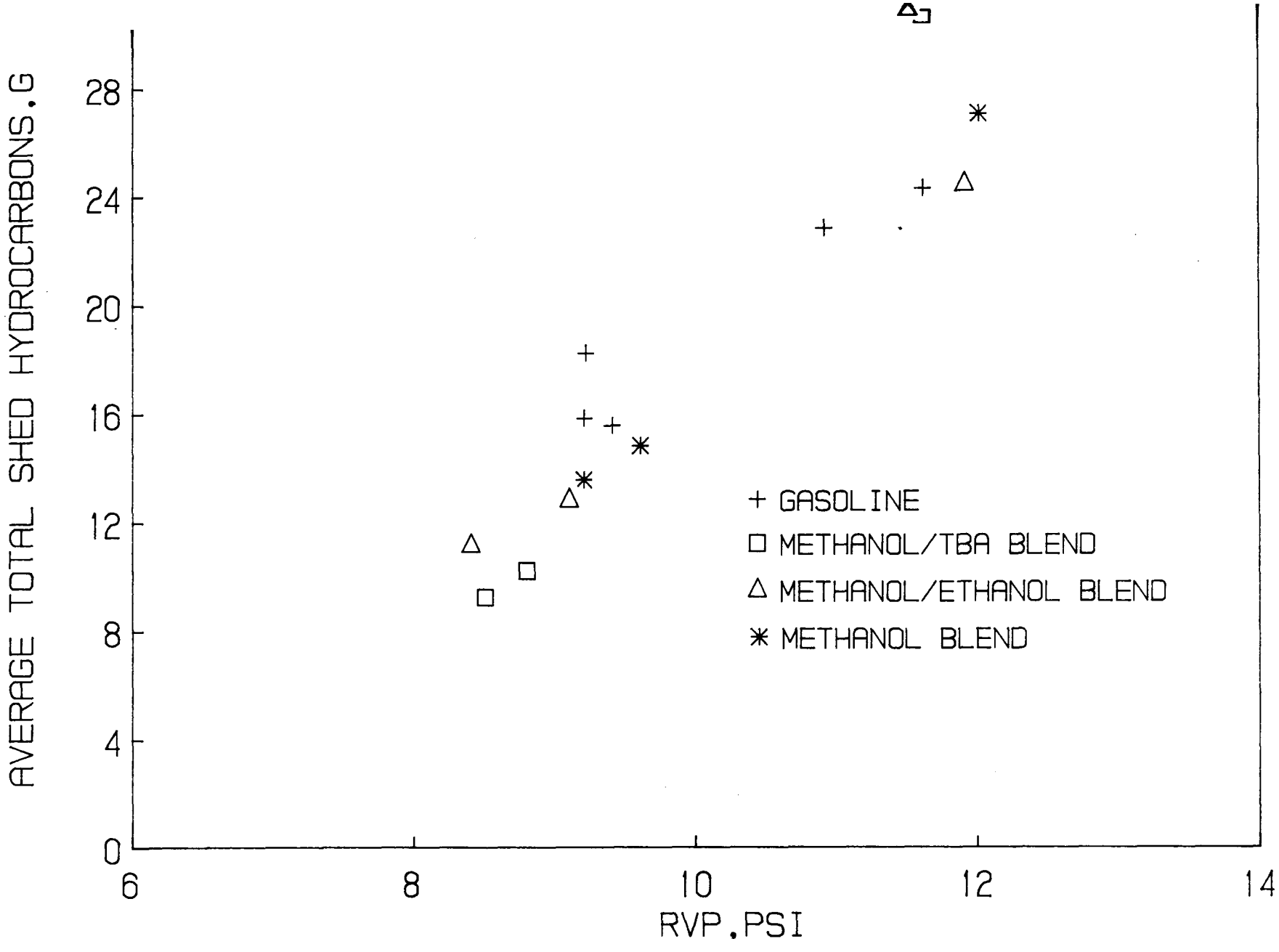

FIGURE 9. PLOT OF TOTAL SHED HYDROCARBONS VERSUS FUEL RVP FOR THE 60-84°F DIURNAL TESTS

In the Work Assignment 18 investigations, which utilized three diurnal temperature rise scenarios and three volatility classes of fuel, total SHED hydrocarbons were found to increase with increasing diurnal temperatures despite a decrease in corresponding fuel volatility. This trend is illustrated in Figure 10, which groups the fuels as to diurnal test temperatures. The alcohol blend EM-703-F gave higher SHED hydrocarbons than its corresponding lower RVP base fuel, EM-702-F. The remaining two blends, EM-701-F and EM-698-F, however, gave lower SHED hydrocarbons than their corresponding base fuels, EM-690-F and EM-697-F.

Total hydrocarbon emissions appeared to follow RVP trends in the Work Assignment 12 investigations, with higher RVP fuels giving higher total hydrocarbons. For the higher RVP fuels, the gasoline and gasoline/alcohol blends gave similar total hydrocarbon levels; however, at the lower RVP, total hydrocarbon levels were generally lower for the gasoline/alcohol blends than for the gasoline blends. Variations in fuel aromatic content did not appear to alter total hydrocarbon levels as significantly as RVP variations. These observations are illustrated in Figure 11.

2. Individual Hydrocarbons

Individual hydrocarbons, with one to six carbons plus the seven-carbon compounds toluene and 2,4-dimethylpentane, were characterized in the Work Assignment 18 program. Saturated hydrocarbons and C_2 and C_3 olefins were quantified individually in this program, whereas the C_4 to C_6 unsaturated olefins were grouped as a total for C_4 and a total for C_{5-6}. In the Work Assignment 12 program, only butane and isobutane were characterized.

In general, the individual hydrocarbons followed the same trends as the total hydrocarbons in the Work Assignment 18 study. Methane, ethane, ethylene, and propylene were found in small but measurable quantities in a number of the SHED tests. Acetylene was not detected in any of the samples analyzed. Propane was detected in all of the SHED tests, with higher levels found in the tests with the base gasoline fuels than in the tests with the corresponding alcohol blend fuels. This result was likely due to the partial removal of some of the base fuel light ends during the preparation of the alcohol blends. In order to further evaluate the effects of alcohol content and diurnal temperature on the composition of the SHED hydrocarbons, the percentages of the total non-oxygenated hydrocarbons for selected individual hydrocarbons were calculated and are presented in Table 7. Benzene was found to be one percent or less of the total hydrocarbons for all seven test fuels. The highest benzene percentage occurred with alcohol blend EM-701-F (1.0%) and the lowest with Indolene (0.13%).

Indolene, however, gave the highest percentage of toluene in the SHED hydrocarbons for the seven fuels. Fuels EM-690-F, EM-702-F, EM-703-F, and EM-701-F, which were prepared from similar base stock fuels, all had similar benzene and toluene percentages. Isobutane, n-butane, isopentane, and pentane made up the majority of the total SHED non-oxygenated hydrocarbons, with combined percentages ranging from 71.2% for fuel EM-701-F to 81.6% for fuel EM-698-F. Indolene, EM-700-F, had relatively low levels of isobutane, 3.0% compared to a range of 10.3% to 20.9% for the remaining fuels; but high levels of n-butane, 51.3% compared to a range of 30.0% to 39.0% for the remaining fuels. Generally the alcohol blends had lower levels of isobutane and n-butane in the total non-

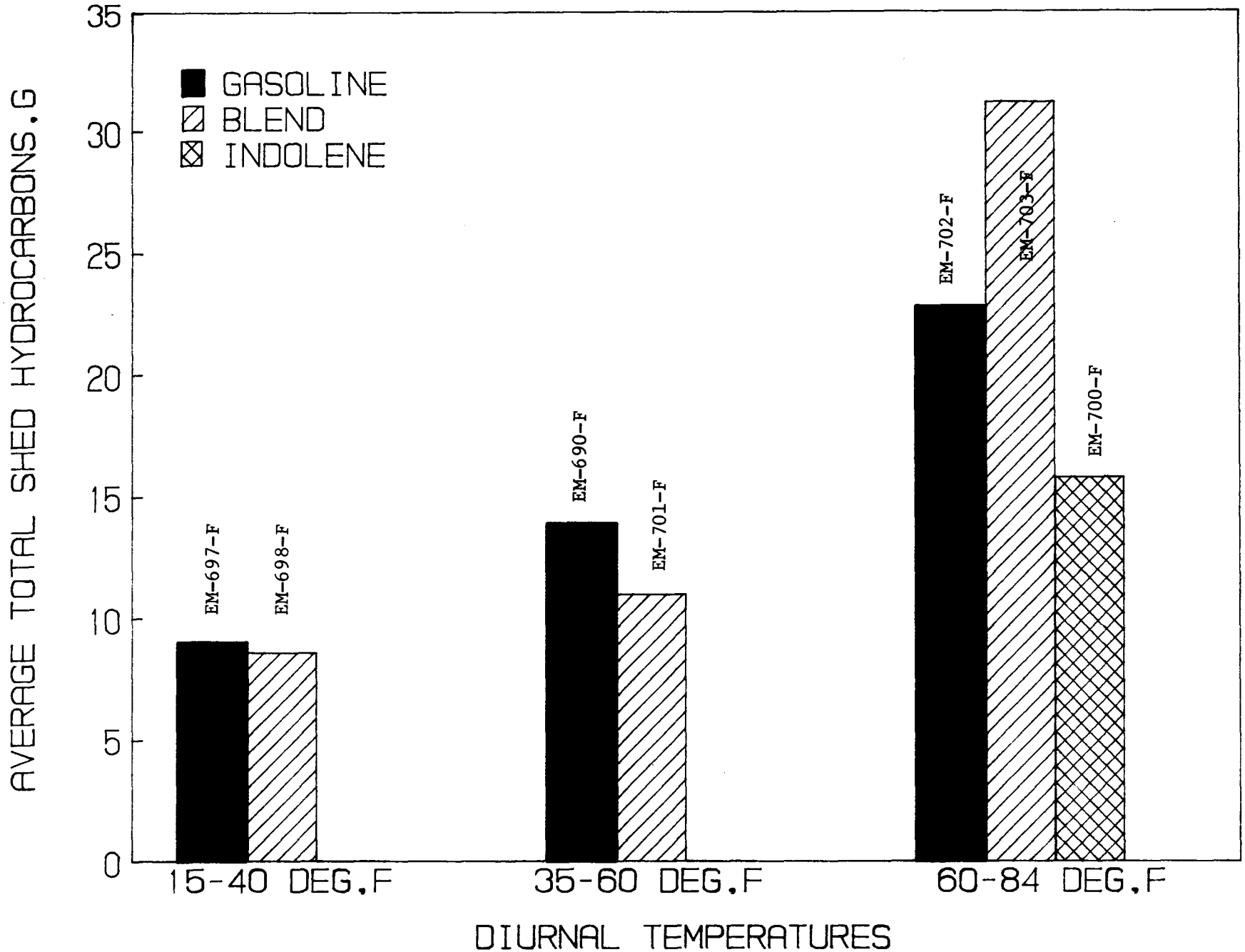

FIGURE 10. TOTAL SHED HYDROCARBON RESULTS GROUPED AS TO DIURNAL TEMPERATURE RANGE

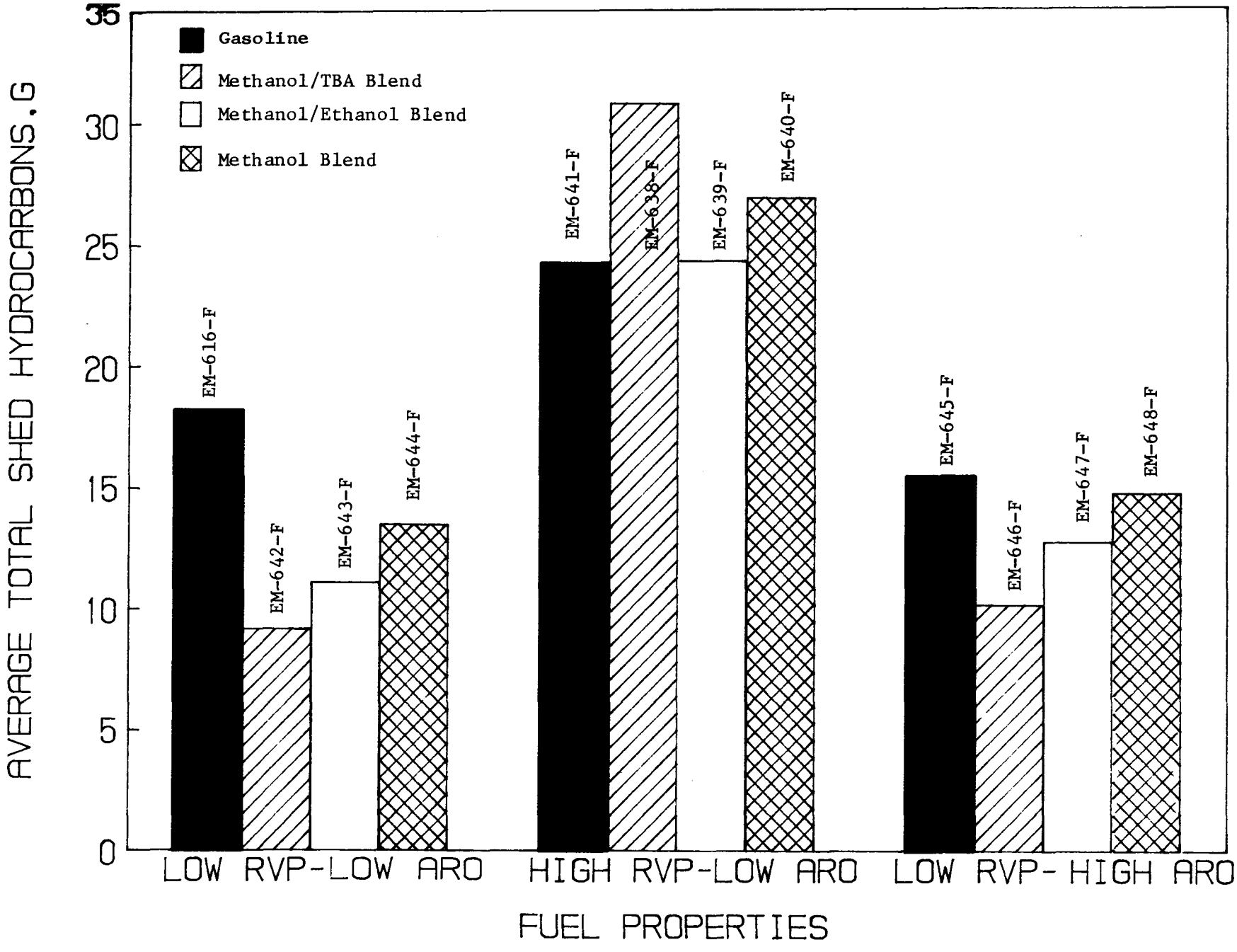

FIGURE 11. TOTAL SHED HYDROCARBON RESULTS GROUPED AS TO RVP AND AROMATIC CONTENT OF THE TEST FUEL

TABLE 7. INDIVIDUAL HYDROCARBONS AS PERCENTAGE OF TOTAL NON-OXYGENATED HYDROCARBONS, WORK ASSIGNMENT 18 STUDY

Fuel Code	EM-697-F	EM-690-F	EM-702-F	EM-700-F	EM-703-F	EM-701-F	EM-698-F
Volatility Class	E	D	C	(Indolene)	C	D	E
Methanol, Vol%	—	—	—	—	5.0	5.0	5.0
Ethanol, Vol%	—	—	—	—	2.5	2.5	2.5
RVP, psi	14.0	12.0	10.9	9.2	11.5	13.2	15.0
	Average Evaporative Results, percent of total HC						
Benzene	0.2	0.6	0.8	0.1	0.9	1.0	0.4
Toluene	2.0	0.8	0.8	2.7	0.9	1.0	1.1
Isobutane	20.4	14.5	13.5	3.0	10.3	12.1	20.9
n-Butane	36.3	36.3	33.0	51.3	30.0	32.0	39.0
Isopentane	16.3	19.0	21.4	21.5	23.8	18.7	18.2
Pentane	2.3	8.3	9.3	4.9	11.4	8.4	3.5
Cyclopentane	0.3	0.6	0.7	0.3	0.7	0.6	1.0
C_6 Saturates	2.9	8.4	9.0	6.1	12.6	9.0	3.2
2,4-dimethylpentane	0.1	0.2	0.2	1.5	0.3	0.3	0.2
C_4 Olefins	4.3	2.8	3.2	2.2	2.4	3.6	4.3
C_{5-6} Olefins	9.4	9.1	9.1	4.7	11.6	9.2	10.1

oxygenated hydrocarbons than their corresponding base fuels (light end removal during blend preparation and/or dilution by alcohol addition), however, many of the higher boiling C_5 and C_6 compounds were generally present in higher percentages in the alcohol blend vapors than in the base gasoline vapors. The percentage of olefins in the SHED non-oxygenated hydrocarbons was found to be relatively high (7-14%), possibly a result of higher concentrations of fuel olefins in the C_4 to C_6 fuel fraction as compared to the entire fuel.

Butane and isobutane SHED levels in the Work Assignment 12 study were found to be directly related to the butane and isobutane levels in the fuels. Fuels EM-642-F, EM-643-F, and EM-644-F were prepared by bubbling nitrogen through fuel EM-616-F to remove the lower-boiling hydrocarbons (such as n-butane and isobutane) before blending with the alcohols. The resulting lower levels of butane and isobutane in these fuels are reflected by the lower levels of butane and isobutane in the SHED tests. In addition, the ratio of butane to isobutane in these fuels appears to have been altered in the bubbling process, because the ratio of butane to isobutane in the SHED was higher for fuels EM-642-F, EM-643-F, and EM-644-F (3 to 1) than for the base fuel, EM-616-F (2 to 1). Isobutane is more volatile than butane (n-butane b.p., 0°C; isobutane b.p. -12°C), and its preferential loss in the bubbling process is expected. Fuel EM-641-F was prepared by the addition of n-butane to fuel EM-616-F, but no isobutane was added. This relative increase in n-butane for fuel EM-641-F is reflected in the n-butane and isobutane SHED data in Table 7. Fuels EM-638-F, EM-639-F, and EM-640-F were prepared by the addition of alcohols to base fuel EM-616-F. Fuels EM-645-F, EM-646-F, EM-647-F, and EM-648-F were prepared from a common aromatic-enriched blend stock, and gave similar levels of isobutane in the SHED. Fuel EM-645-F was enriched in n-butane to increase its RVP. This n-butane addition is once again reflected by the n-butane levels in the SHED. In Work Assignment 12, butane accounted for 18.3 to 46.5 percent of the total SHED non-oxygenated hydrocarbons, while isobutane accounted for 6.2 to 15.6 percent of the total SHED non-oxygenated hydrocarbons.

3. Alcohols

Methanol, methanol/ethanol, and methanol/TBA blends with gasoline were evaluated in the Work Assignment 12 study, while only methanol/ethanol blends were evaluated in the Work Assignment 18 study. In the Work Assignment 12 study, the higher-RVP fuels were found to give higher levels of methanol in the diurnal SHED tests than the lower-RVP fuels. The high-RVP fuels EM-638-F, EM-639-F, and EM-640-F gave SHED methanol levels ranging from 3.2 to 4.5 grams/test. The low-RVP fuels EM-642-F, EM-643-F, EM-644-F, EM-646-F, EM-647-F, and EM-648-F, gave SHED methanol levels ranging from 0.5 to 2.2 grams/test. All these fuels contained approximately 5 percent methanol. Methanol was detected in the SHED vapors for the testing of all three gasoline/alcohol blends in the Work Assignment 18 study. As was the case for the total hydrocarbons, the SHED methanol levels increased with increasing diurnal test temperatures despite a decrease in fuel volatility.

Levels of ethanol and TBA in the diurnal tests were much lower than the corresponding levels of methanol in Work Assignment 12 evaluations. As was the case for methanol, the higher-RVP fuel, EM-638-F, gave higher TBA levels than the lower RVP fuels, EM-642-F and EM-646-F (0.3 g/test vs 0.2 and 0.2 g/test). The relationship between ethanol levels in the SHED and the fuel RVP was less apparent

than for the other two alcohols. As was noted for SHED total hydrocarbon levels, variations in fuel aromatic content did not appear to alter the alcohol levels as significantly as the RVP. In Work Assignment 18 evaluations, ethanol was detected only during the SHED testing of fuel EM-703-F at 60-84°F. This result indicates that higher fuel temperatures are needed to vaporize appreciable qualities of ethanol into the SHED.

B. High-Temperature Tests (160 ± 10°F)

Duplicate high-temperature SHED tests were conducted in the Work Assignment 12 investigation with 12 gasolines and gasoline-alcohol blends. These tests were conducted to simulate vehicle hot-soak losses, and used 125 ml of fuel heated with a 160°F water bath. Average test results are tabulated by fuel RVP and aromatic content in Table 8. Individual test results are presented in Appendix B. As was the case for the diurnal tests, the higher-RVP fuels, in general, gave higher levels of total hydrocarbons. As expected, however, the total hydrocarbon levels correlated more closely with the distillation curves (heating the fuel to 160°F in the flask is actually a partial distillation of the fuel, with the fraction of the fuel boiling below 160°F being "distilled" into the SHED). Fuel EM-645-F, which has only 16% of its volume distilling below 160°F, gave the lowest total hydrocarbon level; while fuel EM-639-F, which has 39% of its volume distilling below 160°F, gave the highest total hydrocarbon level. A linear regression plot of the total SHED hydrocarbons versus the volume of fuel distilling below 160°F for each of the twelve test fuels gave an r^2 value of 0.91. In contrast, a linear regression plot of SHED hydrocarbons versus RVP gave an r^2 of only 0.3.

Butane and isobutane levels in the SHED were, as in the diurnal tests, dependent on their concentration in the fuel. The ranges of butane (1.0 to 4.5 grams) and isobutane (0.2 to 1.0 grams) found in the high temperature SHED tests were not as large as for the diurnal tests (1.6 to 10.3 for butane and 0.5 to 4.1 for isobutane) due to the smaller quantities of fuel used in the tests.

The levels of alcohols in the high-temperature SHED tests were higher for the higher-RVP fuels (3.9 to 4.2 g methanol/test, 0.6 g ethanol/test, and 1.3 g TBA/test) than for the lower-RVP fuels (1.7 to 3.3 g methanol/test, <0.01 to 0.2 g ethanol/test, and 0.3 to 0.9 g TBA/test). For the higher-RVP fuels, it appears that the amount of methanol found in the SHED is almost equivalent to the amount of methanol in the 125 ml of test fuel. Fuels EM-638-F, EM-639-F, and EM-640-F all contain approximately 5% (EM-638-F contains 4.75%) by volume methanol, or 6.25 ml of methanol. Assuming that methanol has a density of 0.79 g/ml, each test fuel contains approximately 4.9 grams of methanol per 125 ml of fuel. The average SHED methanol value for fuels EM-638-F, EM-639-F, and EM-640-F (4.0 grams) accounts for more than 80% of the fuel methanol. The average SHED methanol value for the lower-RVP fuels (2.5 grams) accounts for only approximately 60% of the fuel methanol. The levels of ethanol and TBA in the SHED were much lower than the levels of methanol in the SHED, accounting for only 1% to 26% of the fuel ethanol and 6% to 28% of the fuel TBA. Changes in the amounts of alcohol in the SHED as a result of variations in fuel aromatic content were more variable and of much smaller magnitude than changes resulting from variations in fuel RVP.

TABLE 8. AVERAGE HIGH TEMPERATURE EVAPORATIVE EMISSIONS

Fuel	Low RVP-Low Aromatic			
Fuel Code	EM-616-F	EM-642-F	EM-643-F	EM-644-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	9.2	8.5	8.4	9.2
Percent Fuel Distilled at 160°F (D-86)	26	31	32	27
	Evaporative Results, g/test			
Butane	2.6	1.0	1.0	1.1
Isobutane	1.0	0.2	0.3	0.3
Methanol	ND[a]	2.5	3.3	2.6
Ethanol	NR[b]	NR	<0.1	NR
TBA	NR	0.9	NR	NR
Total Non-oxygenated HC[c]	8.1	15.0	14.9	12.3
Total Hydrocarbons[d]	8.1	18.3	18.1	14.9

Fuel	High RVP-Low Aromatic			
Fuel Code	EM-641-F	EM-638-F	EM-639-F	EM-640-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	11.6	11.6	11.9	12.0
Percent Fuel Distilled at 160°F (D-86)	30	37	39	34
	Evaporative Results, g/test			
Butane	4.5	2.5	2.6	2.8
Isobutane	0.9	0.8	0.8	1.0
Methanol	0.2	3.9	3.9	4.2
Ethanol	NR	NR	0.6	NR
TBA	NR	1.3	NR	NR
Total Non-oxygenated HC	15.8	17.1	18.9	15.4
Total Hydrocarbons	16.0	22.2	23.5	19.5

Fuel	Low RVP-High Aromatic			
Fuel Code	EM-645-F	EM-646-F	EM-647-F	EM-648-F
Methanol, vol. %	--	4.75	5.00	5.00
Ethanol, vol. %	--	--	2.50	--
TBA, vol. %	--	4.75	--	--
RVP, psi	9.4	8.8	9.1	9.6
Percent Fuel Distilled at 160°F (D-86)	16	24	28	24
	Evaporative Results, g/test			
Butane	2.4	1.5	1.6	1.4
Isobutane	0.4	0.5	0.5	0.5
Methanol	ND	1.7	2.6	2.1
Ethanol	NR	NR	0.2	NR
TBA	NR	0.3	NR	NR
Total Non-oxygenated HC	5.9	9.9	11.5	9.8
Total Hydrocarbons	5.9	11.9	14.2	11.8

[a]ND - none detected, less than 0.02 g/test
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

IV. QUALITY ASSURANCE

The Quality Assurance (QA) guidelines addressed in the QA reports for Work Assignments 12 and 18 of EPA Contract 68-03-3192 were followed in performing the work for this program. Quality assurance associated with fuel handling, SHED procedures, and sample analyses are described in the following paragraphs.

All fuel containers used in the program were kept well sealed and stored in a refrigerated facility (40°F) adjacent to the Emissions Laboratory high bay test area (location of SHED) until needed. All necessary fuel transfers were performed while the fuel was at or near 40°F to minimize any loss of fuel vapors. The gasoline/alcohol blends were prepared from the base gasolines at the Energy Conversion and Combustion Technology facility. All blending and associated fuel handling was conducted in their refrigerated facility (also at 40°F). Fuel samples of each gasoline or gasoline/alcohol blend were taken for RVP determinations from the same containers as the fuel used in the SHED tests.

The SHED bag sampling technique used in this program for the analysis of alcohols was validated in the Work Assignment 12 study. The validation experiments were conducted to determine the magnitude of alcohol losses during typical SHED tests. The effect of humidity on alcohol sampling was also investigated in the validation experiments. The test sequence followed in these experiments is summarized in Table 9.

TABLE 9. SHED VALIDATION EXPERIMENTS

Step	Sequence
1	SHED purged and checked for alcohol background
2	20 g of 50 vol. % methanol/50 vol. % TBA placed in a clean beaker
3	Beaker placed in the SHED and heated at a rate such that all the alcohol was evaporated within 60 minutes
4	Heating blankets placed in the SHED to simulate the presence of a vehicle
5	After all of the alcohol had been vaporized, a bag sample was obtained from the SHED and analyzed for methanol and TBA concentrations
6	Percent recovery determined for methanol and TBA
7	SHED purged
8	SHED checked for background methanol and TBA
9	Steps 1-6 repeated at higher relative humidity

This test sequence was conducted in duplicate, and the results reported to the Project Officer before any SHED testing with fuel was conducted. Table 10 lists the results of this testing. Methanol recoveries were found to be on the order of 98 ± 8 percent, while TBA recoveries were lower at 82 ± 11 percent. Increases in SHED humidity did not result in decreases in alcohol recoveries. In fact, the reverse was found, with higher alcohol recoveries occurring in the higher relative humidity tests.

SHED and bag cart (for FID total hydrocarbons) calibrations were performed using procedures and equipment specified in the Federal Register, and are available for inspection. The reliability of the SHED bag sampling system was checked by introducing a known concentration of propane (for total hydrocarbon analysis) into the sampling port on the inside of the SHED and collecting a bag sample for analysis. A 670 ppmC propane standard was introduced into the probe inlet, collected in a SHED sample bag, and analyzed using a FID total hydrocarbon analyzer. This analysis gave a total hydrocarbon reading of 667 ppmC, which is within 0.5% of the standard concentration. In a second check, a 380 ppmC propane standard gave 380, 381, and 378 ppmC when analyzed at the SwRI bag cart on three separate test days.

For the quantification of butane and isobutane in the Work Assignment 12 investigations, butane standards, named using the SwRI bag cart HC FID analyzer and published FID response factors, were run at the beginning and end of each test day. The GC-FID instrument for the analysis of butane and isobutane gave good day-to-day repeatability. The peak area for a 102.5 ppmC butane standard gave only a 4 percent variation over an 8-day period (all injections). To check the reliability of the SHED bag sampling system for butane, two butane standards named as 110 and 167 ppmC, were introduced at the SHED sampling point and were found to contain 117 and 170 ppmC, respectively, when analyzed along with other butane test samples.

For analysis, alcohol samples were collected in water and stored in polypropylene sample bottles until the appropriate analyses could be conducted. Alcohol standards and samples have been found to be stable for several months when well sealed in polypropylene sample bottles. In Work Assignment 12, alcohol samples were found to decrease in concentration by only 5 percent when stored for a six-month period. The alcohol analyses for Work Assignment 18 were generally conducted within two to four weeks of sample collection in water.

For Work Assignment 12, methanol analyses of the diurnal and high-temperature tests with fuels EM-638-F, EM-639-F, EM-640-F, EM-641-F, EM-642-F, and EM-643-F were completed immediately after the samples were collected. Due to program time constraints, only the first bubbler of each test bubbler set (two bubblers are used to collect each alcohol sample with the first bubbler containing approximately 90% of the total sample) was analyzed immediately after collection for methanol for the diurnal and high-temperature tests with fuels EM-644-F, EM-646-F, EM-647-F, and EM-648-F. The second bubbler of each set and the associated background samples (both bubblers in each set) as well as all of the samples generated in the tests with fuels EM-616-F and EM-645-F were analyzed for methanol approximately six months after sample collection. All ethanol and TBA analyses for tests conducted with fuels EM-642-F and EM-646-F were also conducted at this time. TBA analyses for tests conducted with fuel EM-638-F were conducted in part during both time periods. Diurnal test samples (Tests 1 and 2,

TABLE 10. VALIDATION RESULTS FOR ALCOHOL BAG SAMPLING TECHNIQUE AT VARYING RELATIVE HUMIDITY LEVELS

	Alcohol Evaporated, g		Alcohol Recovered, g		Recovery, %	
	Methanol	TBA	Methanol	TBA	Methanol	TBA
SHED Background	--	--	ND	ND	--	--
63% Relative Humidity	10.90	10.88	10.71	8.54	98	78
SHED Background	--	--	0.11	0.06	--	--
SHED Background	--	--	0.04	0.06	--	--
68% Relative Humidity	10.05	a	8.89	a	88	a
SHED Background	--	--	0.07	0.07	--	--
SHED Background	--	--	--	ND	--	--
70% Relative Humidity	--	10.16	--	6.81	--	67
SHED Background	--	--	--	0.03	--	--
SHED Background	--	--	ND	ND	--	--
85% Relative Humidity	10.03	b	9.80	b	98	b
SHED Background	--	--	0.06	0.06	--	--
SHED Background	--	--	0.02	ND	--	--
86% Relative Humidity	10.04	10.01	10.82	8.89	108	89
SHED Background	--	--	0.34	0.08	--	--
SHED Background	--	--	--	ND	--	--
90% Relative Humidity	--	10.14	--	9.32	--	92
SHED Background	--	--	--	0.08	--	--
				Average	98 ± 8	82 ± 11

[a] Test results atypically high, 116% recovery; experiment repeated at 70% relative humidity
[b] Test results atypically low, 40% recovery; experiment repeated at 90% relative humidity

Bubblers 1 and 2) and high-temperature bubbler 1 samples from Test 1 (both sample and background) were analyzed immediately after collection, with the remainder of the samples being analyzed at the later date.

To check the stability of actual samples in Work Assignment 12, four samples analyzed in September, 1985 were reanalyzed in March, 1986. The results of these analyses are listed below:

Sample	Test Type	Fuel	Test No.	Bubbler (1 or 2)	Sept. Analysis µg/ml	March Analysis µg/ml	Percent Difference
1	Diurnal	EM-642-F	2	1	61	64	+4.9
2	High-Temp.	EM-643-F	1	1	264	241	-8.7
3	High-Temp.	EM-643-F	2	1	297	270	-9.1
4	Diurnal	EM-647-F	1	1	230	212	-7.8
						Average	-5.2±6.7%

These analyses show that during the period between September, 1985 and March 1986 the concentration in the bubblers decreased, on the average, approximately 5 percent. These results should be taken into consideration when comparing results for samples analyzed during the two time periods. In most cases, this decrease in concentration should not greatly affect the methanol results as the majority of the bubbler 1 samples, which contain 90% of the sample, were analyzed in September.

Injection repeatability for each of the alcohol standards used to bracket the test samples was determined during both work assignments. This repeatability was determined by averaging standard areas from an uninterrupted series of standard injections actually used to bracket sample runs (one standard, two samples, one standard, two samples, etc.).

The results of the Work Assignment 12 injection repeatability determinations are presented below:

Standard	Concen. ppm	Number of Analyses in Uninterrupted Sequence	Average Area	Standard Deviation in Area	Percent Deviation
Methanol	791	14	23069	775	3.4
	79.1	7	33707	2296	6.8
	39.6	8	129.5(peak height, mm)	5.2 (peak height, mm)	4.0
Ethanol	78.9	12	28615	921	3.2
TBA	78.9	4	23915	385	1.6
	39.5	8	31556	1201	3.8

Sample peak heights were found to be more reliable than peak areas when using the 39.6 ppm methanol standard, and were therefore used in place of the area to calculate sample concentrations. A linearity check for peak heights in the 0.4 to 39.6 ppm range was conducted and found to be acceptable, with $r^2 = 0.993$ for the plotted line.

Injection repeatability was found to be somewhat better in Work Assignment 18 studies than in Work Assignment 12 studies, with the percent deviation less than five percent for all of the alcohol standards and less than two percent for the higher concentration standards. The results for the Work Assignment 18 injection repeatability determinations are presented below:

Standard	Conc. ppm	Number of Analyses in Uninterrupted Sequence	Average Area	Standard Deviation in Area	Percent Deviation
Methanol	7.91	9	3407	170	4.7
	15.8	5	5865	269	4.6
	79.1	5	10452	130	1.2
	791	3	13308	70	0.5
Ethanol	15.8	11	5553	56	1.0
	78.9	5	14465	132	0.9

For the GC-FID analysis of the C_1-C_3 hydrocarbons, benzene, and toluene, standard samples from a compressed gas cylinder containing known concentrations of methane, ethylene, ethane, acetylene, propane, propylene, benzene, and toluene were run at the beginning and end of each test day to bracket samples analyzed that day. In all, 10 sets of standard analyses (total of 20 analyses) were conducted during the course of the program. With the exception of acetylene, the day-to-day repeatability (as percent deviation for the 20 analyses) ranged from 4.9% for methane to 8.6% for toluene. The repeatabilities for the standards run on the same day were generally 1 to 1.5% better for each of the individual hydrocarbons. The day-to-day repeatability for the acetylene standard was not good, and has been used in this program only as a means to determine the presence or absence of acetylene in the SHED samples. Acetylene was not detected in any of the samples analyzed.

For the GC-FID analysis of the C_4-C_6 hydrocarbons and 2,4-dimethylpentane, a standard bag containing 13 individual hydrocarbons (isobutane, n-butane, isopentane, pentane, 2,2-dimethylbutane, cyclopentane, 2-methylpentane, 3-methylpentane, hexane, methylcyclopentane, 2,4-dimethylpentane, and benzene) in the approximate ratio observed in the SHED samples was run at the beginning and end of each test day to bracket the samples. This standard bag was named against a known propane standard using the SwRI bag cart (total hydrocarbons) and found to contain 995 ppmC. The summation of all the peak areas in the individual hydrocarbon analysis divided by the bag cart ppmC gave the average GC response factor (area per ppmC) which was used to calculate an individual hydrocarbon sample concentration. The percent deviation for standards run on the same day was, on the average, 6.1% (total area basis).

APPENDIX A

DIURNAL EVAPORATIVE EMISSIONS

TABLE A-1. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-616-F (WORK ASSIGNMENT 12)

Methanol, vol. %	--
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.2

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	5.9	4.6	5.3
Isobutane	3.0	2.3	2.7
Methanol	ND[a]	ND	ND
Ethanol	NR[b]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[c]	18.3	18.0	18.2
Total Hydrocarbons[d]	18.3	18.0	18.2

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-2. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-642-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	8.5

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.5	1.7	1.6
Isobutane	0.5	0.6	0.6
Methanol	0.4	0.6	0.5
Ethanol	NR[a]	NR	NR
TBA	0.2	0.2	0.2
Total Non-oxygenated HC[b]	8.2	8.8	8.5
Total Hydrocarbons[c]	8.8	9.6	9.2

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-3. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-643-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	—
RVP, psi	8.4

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.9	1.9	1.9
Isobutane	0.7	0.7	0.7
Methanol	0.5	0.9	0.7
Ethanol	<0.1	ND[a]	< 0.1
TBA	NR[b]	NR	NR
Total Non-oxygenated HC[c]	10.4	10.4	10.4
Total Hydrocarbons[d]	10.9	11.3	11.1

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-4. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-644-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.2

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.0	2.3	2.2
Isobutane	0.7	0.8	0.7
Methanol	2.1	2.3	2.2
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	10.5	12.0	11.3
Total Hydrocarbons[c]	12.6	14.3	13.5

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-5. DIURNAL EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-641-F (WORK ASSIGNMENT 12)

Methanol, vol. %	--
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	11.6

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	10.7	9.8	10.3
Isobutane	3.3	2.9	3.1
Methanol	0.4	0.3	0.4
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	25.2	22.6	23.9
Total Hydrocarbons[c]	25.6	22.9	24.3

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-6. DIURNAL EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-638-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	11.6

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	8.7	7.8	8.3
Isobutane	4.3	3.9	4.1
Methanol	3.3	3.4	3.4
Ethanol	NR[a]	NR	NR
TBA	0.4	0.3	0.3
Total Non-oxygenated HC[b]	29.6	24.7	27.2
Total Hydrocarbons[c]	33.3	28.4	30.9

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-7. DIURNAL EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-639-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	--
RVP, psi	11.9

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	10.7	9.8	10.3
Isobutane	2.9	3.6	3.3
Methanol	2.6	3.7	3.2
Ethanol	ND[a]	0.2	0.1
TBA	NR[b]	NR	NR
Total Non-oxygenated HC[c]	19.4	22.8	21.1
Total Hydrocarbons[d]	22.0	26.7	24.4

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-8. DIURNAL EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-640-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	—
TBA, vol. %	—
RVP, psi	12.0

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	7.6	6.0	6.8
Isobutane	3.5	2.9	3.2
Methanol	4.6	4.4	4.5
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	21.8	23.2	22.5
Total Hydrocarbons[c]	26.4	27.6	27.0

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-9. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-645-F (WORK ASSIGNMENT 12)

Methanol, vol. %	—
Ethanol, vol. %	—
TBA, vol. %	—
RVP, psi	9.4

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	7.0	7.3	7.2
Isobutane	1.4	1.5	1.5
Methanol	0.1	< 0.1	0.1
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	15.4	15.5	15.5
Total Hydrocarbons[c]	15.5	15.5	15.5

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-10. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-646-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	8.8

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.4	2.6	2.5
Isobutane	1.1	1.2	1.2
Methanol	1.0	1.1	1.1
Ethanol	NR[a]	NR	NR
TBA	0.2	0.2	0.2
Total Non-oxygenated HC[b]	8.5	9.3	8.9
Total Hydrocarbons[c]	9.7	10.6	10.2

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-11. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-647-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	--
RVP, psi	9.1

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.9	3.0	3.0
Isobutane	1.4	1.5	1.5
Methanol	2.5	1.5	2.0
Ethanol	0.1	0.1	0.1
TBA	NR[a]	NR	NR
Total Non-oxygenated HC[b]	10.7	10.6	10.7
Total Hydrocarbons[c]	13.3	12.2	12.8

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-12. DIURNAL EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-648-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.6

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	3.2	3.5	3.4
Isobutane	1.5	1.7	1.6
Methanol	1.8	2.3	2.1
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	12.5	13.0	12.8
Total Hydrocarbons[c]	14.3	15.3	14.8

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-13. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-697-F (WORK ASSIGNMENT 18)

Volatility Class	E
Methanol, Vol %	--
Ethanol, Vol %	--
RVP, psi	14.0

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	<0.01[a]	ND[b]	<0.01
Ethylene	<0.01	ND	<0.01
Ethane	ND	<0.01	<0.01
Acetylene	ND	ND	ND
Propane	0.20	0.18	0.19
Propylene	0.02	0.01	0.01
Benzene	0.03	0.02	0.02
Toluene	0.24	0.12	0.18
Isobutane	1.92	1.75	1.84
n-Butane	3.44	3.10	3.27
Isopentane	1.56	1.38	1.47
Pentane	0.22	0.20	0.21
2,2-Dimethylbutane	0.01	0.02	0.01
Cyclopentane	0.03	0.02	0.03
2,3-Dimethylbutane	0.04	0.04	0.04
2-Methylpentane	0.10	0.08	0.09
3-Methylpentane	0.05	0.04	0.04
Hexane	0.02	0.02	0.02
Methylcyclopentane	0.03	0.09	0.06
2,4-Dimethylpentane	0.01	0.01	0.01
C_4 Olefins	0.38	0.40	0.39
C_5-C_6 Olefins	0.90	0.79	0.85
Alcohols			
Methanol	ND[c]	ND	ND
Ethanol	NR[d]	NR	NR
Total Non-oxygenated HC[e]	9.5	8.5	9.0
Total Hydrocarbons[f]	9.5	8.5	9.0

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, <0.001 g/test
[c] none detected, for methanol and ethanol, < 0.01 g/test
[d] not required
[e] Total FID hydrocarbons corrected for alcohol content
[f] Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-14. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-690-F (WORK ASSIGNMENT 18)

Volatility Class	D
Methanol, Vol %	--
Ethanol, Vol %	--
RVP, psi	12.0

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	0.02	0.03	0.02
Ethylene	ND[a]	<0.01[b]	<0.01
Ethane	0.02	0.03	0.03
Acetylene	ND	ND	ND
Propane	0.25	0.38	0.31
Propylene	0.02	0.03	0.03
Benzene	0.07	0.12	0.09
Toluene	0.09	0.13	0.11
Isobutane	1.52	2.50	2.01
n-Butane	3.58	6.51	5.04
Isopentane	1.87	3.41	2.64
Pentane	0.83	1.49	1.16
2,2-Dimethylbutane	0.08	0.10	0.09
Cyclopentane	0.06	0.12	0.09
2,3-Dimethylbutane	0.08	0.14	0.11
2-Methylpentane	0.31	0.56	0.43
3-Methylpentane	0.14	0.31	0.23
Hexane	0.13	0.24	0.18
Methylcyclopentane	0.09	0.17	0.13
2,4-Dimethylpentane	0.02	0.04	0.03
C_4 Olefins	0.24	0.54	0.39
C_5-C_6 Olefins	0.87	1.64	1.26
Alcohols			
Methanol	ND[c]	ND	ND
Ethanol	NR[d]	NR	NR
Total Non-oxygenated HC[e]	10.6	17.1	13.9
Total Hydrocarbons[f]	10.6	17.1	13.9

[a]none detected, for individual hydrocarbons, <0.001 g/test
[b]<0.01, less than 0.005 g/test and greater than 0.001 g/test
[c]none detected, for methanol and ethanol, < 0.01 g/test
[d]not required
[e]Total FID hydrocarbons corrected for alcohol content
[f]Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-15. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-702-F (WORK ASSIGNMENT 18)

Volatility Class	C
Methanol, Vol %	--
Ethanol, Vol %	--
RVP, psi	10.9

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	<0.01[a]	0.01	<0.01
Ethylene	ND[b]	ND	ND
Ethane	0.01	0.02	0.01
Acetylene	ND	ND	ND
Propane	0.31	0.34	0.33
Propylene	0.02	ND	0.01
Benzene	0.18	0.18	0.18
Toluene	0.18	0.18	0.18
Isobutane	3.02	3.14	3.08
n-Butane	7.48	7.55	7.52
Isopentane	4.88	4.84	4.86
Pentane	2.22	1.99	2.11
2,2-Dimethylbutane	0.15	0.16	0.15
Cyclopentane	0.15	0.14	0.15
2,3-Dimethylbutane	0.22	0.23	0.22
2-Methylpentane	0.84	0.78	0.81
3-Methylpentane	0.21	0.34	0.27
Hexane	0.39	0.39	0.39
Methylcyclopentane	0.22	0.22	0.22
2,4-Dimethylpentane	0.06	0.03	0.05
C_4 Olefins	0.75	0.74	0.74
C_5-C_6 Olefins	2.08	2.07	2.08
Alcohols			
Methanol	ND[c]	ND	ND
Ethanol	NR[d]	NR	NR
Total Non-oxygenated HC[e]	23.1	22.4	22.8
Total Hydrocarbons[f]	23.1	22.4	22.8

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, < 0.001 g/test
[c] none detected, for methanol and ethanol, < 0.01 g/test
[d] not required
[e] Total FID hydrocarbons corrected for alcohol content
[f] Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-16. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-700-F (WORK ASSIGNMENT 18)

Volatility Class	(Indolene)
Methanol, Vol %	--
Ethanol, Vol %	--
RVP, psi	9.2

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	<0.01[a]	<0.01	<0.01
Ethylene	<0.01	<0.01	<0.01
Ethane	0.02	0.02	0.02
Acetylene	ND[b]	ND	ND
Propane	0.16	0.15	0.15
Propylene	0.02	0.03	0.03
Benzene	0.02	0.02	0.02
Toluene	0.22	0.28	0.25
Isobutane	0.51	0.46	0.48
n-Butane	8.23	7.99	8.11
Isopentane	3.46	3.33	3.40
Pentane	0.80	0.77	0.78
2,2-Dimethylbutane	0.12	0.12	0.12
Cyclopentane	0.05	0.05	0.05
2,3-Dimethylbutane	0.29	0.28	0.28
2-Methylpentane	0.26	0.26	0.26
3-Methylpentane	0.15	0.14	0.15
Hexane	0.09	0.08	0.08
Methylcyclopentane	0.08	0.07	0.08
2,4-Dimethylpentane	0.15	0.13	0.14
C_4 Olefins	0.36	0.34	0.35
C_5-C_6 Olefins	0.78	0.71	0.75
Alcohols			
Methanol	ND[c]	ND	ND
Ethanol	NR[d]	NR	NR
Total Non-oxygenated HC[e]	16.2	15.3	15.8
Total Hydrocarbons[f]	16.2	15.3	15.8

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, <0.001 g/test
[c] none detected, for methanol and ethanol, <0.01 g/test
[d] not required
[e] Total FID hydrocarbons corrected for alcohol content
[f] Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-17. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-703-F (WORK ASSIGNMENT 18)

Volatility Class	C
Methanol, Vol %	5.0
Ethanol, Vol %	2.5
RVP, psi	11.5

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	<0.01[a]	ND[b]	<0.01
Ethylene	ND	ND	ND
Ethane	<0.01	<0.01	<0.01
Acetylene	ND	ND	ND
Propane	0.14	0.17	0.15
Propylene	0.01	0.01	0.01
Benzene	0.22	0.26	0.24
Toluene	0.22	0.27	0.24
Isobutane	2.57	3.17	2.87
n-Butane	7.63	9.16	8.39
Isopentane	6.10	7.20	6.65
Pentane	2.91	3.45	3.18
2,2-Dimethylbutane	0.21	0.25	0.23
Cyclopentane	0.14	0.24	0.19
2,3-Dimethylbutane	0.29	0.34	0.32
2-Methylpentane	1.12	1.40	1.26
3-Methylpentane	0.67	0.79	0.73
Hexane	0.57	0.69	0.63
Methylcyclopentane	0.32	0.39	0.35
2,4-Dimethylpentane	0.07	0.11	0.09
C_4 Olefins	0.73	0.61	0.67
C_5-C_6 Olefins	3.22	3.29	3.25
Alcohols			
Methanol	2.49	3.28	2.89
Ethanol	0.17	0.44	0.31
Total Non-oxygenated HC[c]	25.5	30.5	28.0
Total Hydrocarbons[d]	28.2	34.2	31.2

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, <0.001 g/test
[c] Total FID hydrocarbons corrected for alcohol content
[d] Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-18. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-701-F (WORK ASSIGNMENT 18)

Volatility Class	D
Methanol, Vol %	5.0
Ethanol, Vol %	2.5
RVP, psi	13.2

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	ND[a]	ND	ND
Ethylene	ND	ND	ND
Ethane	< 0.01[b]	< 0.01	< 0.01
Acetylene	ND	ND	ND
Propane	0.14	0.16	0.15
Propylene	0.01	ND	0.01
Benzene	0.10	0.10	0.10
Toluene	0.10	0.09	0.10
Isobutane	1.20	1.32	1.26
n-Butane	3.06	3.60	3.33
Isopentane	1.82	2.07	1.94
Pentane	0.82	0.92	0.87
2,2-Dimethylbutane	0.07	0.06	0.07
Cyclopentane	0.06	0.07	0.06
2,3-Dimethylbutane	0.08	0.09	0.08
2-Methylpentane	0.32	0.34	0.33
3-Methylpentane	0.14	0.27	0.21
Hexane	0.14	0.16	0.15
Methylcyclopentane	0.09	0.10	0.10
2,4-Dimethylpentane	0.02	0.03	0.03
C_4 Olefins	0.34	0.40	0.37
C_5-C_6 Olefins	1.00	0.92	0.96
Alcohols			
Methanol	0.40	0.75	0.58
Ethanol	ND[c]	ND	ND
Total Non-oxygenated HC[d]	10.0	10.7	10.4
Total Hydrocarbons[e]	10.4	11.5	11.0

[a] none detected, for individual hydrocarbons, <0.001 g/test
[b] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[c] none detected, for methanol and ethanol, <0.01 g/test
[d] Total FID hydrocarbons corrected for alcohol content
[e] Sum of alcohols and non-oxygenated hydrocarbons

TABLE A-19. DIURNAL EVAPORATIVE EMISSIONS, FUEL EM-698-F (WORK ASSIGNMENT 18)

Volatility Class	E
Methanol, Vol %	5.0
Ethanol, Vol %	2.5
RVP, psi	15.0

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Individual Hydrocarbons			
Methane	<0.01[a]	ND[b]	<0.01
Ethylene	ND	ND	ND
Ethane	<0.01	<0.01	<0.01
Acetylene	ND	ND	ND
Propane	0.14	0.11	0.13
Propylene	0.01	0.01	0.01
Benzene	0.03	0.02	0.03
Toluene	0.14	0.05	0.09
Isobutane	0.81	1.60	1.71
n-Butane	3.42	2.98	3.20
Isopentane	1.67	1.31	1.49
Pentane	0.38	0.19	0.29
2,2-Dimethylbutane	0.01	0.01	0.01
Cyclopentane	0.14	0.02	0.08
2,3-Dimethylbutane	0.05	ND	0.03
2-Methylpentane	0.10	0.08	0.09
3-Methylpentane	0.07	0.04	0.06
Hexane	0.04	0.01	0.03
Methylcyclopentane	0.04	0.04	0.04
2,4-Dimethylpentane	0.02	0.01	0.02
C_4 Olefins	0.39	0.31	0.35
C_5-C_6 Olefins	1.00	0.65	0.83
Alcohols			
Methanol	0.34	0.40	0.37
Ethanol	ND[c]	ND	ND
Total Non-oxygenated HC[d]	8.5	7.8	8.2
Total Hydrocarbons	8.8	8.2	8.5

[a] <0.01, less than 0.005 g/test and greater than 0.001 g/test
[b] none detected, for individual hydrocarbons, <0.001 g/test
[c] none detected, for methanol and ethanol, <0.01 g/test
[d] Total FID hydrocarbons corrected for alcohol content
[e] Sum of alcohols and non-oxygenated hydrocarbons

APPENDIX B

HIGH TEMPERATURE EVAPORATIVE EMISSION RESULTS

TABLE B-1. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-616-F (WORK ASSIGNMENT 12)

Methanol, vol. %	--
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.2
Percent Fuel Distilled at 160°F (D-86)	26

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.2	3.2	2.6
Isobutane	0.8	1.2	1.0
Methanol	ND[a]	ND	ND
Ethanol	NR[b]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[c]	8.1	8.0	8.1
Total Hydrocarbons[d]	8.1	8.0	8.1

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-2. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-642-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	8.5
Percent Fuel Distilled at 160°F (D-86)	31

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.1	1.0	1.0
Isobutane	0.2	0.2	0.2
Methanol	2.7	2.3	2.5
Ethanol	NR[a]	NR	NR
TBA	0.8	0.9	0.9
Total Non-oxygenated HC[b]	15.9	14.0	15.0
Total Hydrocarbons[c]	19.4	17.2	18.3

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-3. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-643-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	--
RVP, psi	8.4
Percent Fuel Distilled at 160°F (D-86)	32

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.1	0.8	1.0
Isobutane	0.3	0.2	0.3
Methanol	2.8	3.7	3.3
Ethanol	<0.1	ND[a]	<0.1
TBA	NR[b]	NR	NR
Total Non-oxygenated HC[c]	15.5	14.2	14.9
Total Hydrocarbons[d]	18.3	17.9	18.1

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-4. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - LOW AROMATIC FUEL EM-644-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.2
Percent Fuel Distilled at 160°F (D-86)	27

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.1	1.1	1.1
Isobutane	0.2	0.3	0.3
Methanol	2.5	2.7	2.6
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	13.3	11.3	12.3
Total Hydrocarbons[c]	15.8	14.0	14.9

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-5. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-641-F (WORK ASSIGNMENT 12)

Methanol, vol. %	--
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	11.6
Percent Fuel Distilled at 160°F (D-86)	30

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	4.4	4.6	4.5
Isobutane	0.9	0.9	0.9
Methanol	0.3	< 0.1	0.2
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	15.1	16.5	15.8
Total Hydrocarbons[c]	15.4	16.5	16.0

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-6. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-638-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	11.6
Percent Fuel Distilled at 160°F (D-86)	37

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.4	2.5	2.5
Isobutane	0.8	0.8	0.8
Methanol	3.6	4.1	3.9
Ethanol	NR[a]	NR	NR
TBA	1.6	0.9	1.3
Total Non-oxygenated HC[b]	16.8	17.3	17.1
Total Hydrocarbons[c]	22.0	22.3	22.2

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-7. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-639-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	--
RVP, psi	11.9
Percent Fuel Distilled at 160°F (D-86)	39

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.7	2.5	2.6
Isobutane	0.9	0.8	0.8
Methanol	3.6	4.2	3.9
Ethanol	0.9	0.4	0.6
TBA	NR[a]	NR	NR
Total Non-oxygenated HC[b]	19.9	17.9	18.9
Total Hydrocarbons[c]	24.4	22.5	23.5

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-8. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, HIGH RVP - LOW AROMATIC FUEL EM-640-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	12.0
Percent Fuel Distilled at 160°F (D-86)	34

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.8	2.7	2.8
Isobutane	1.0	1.0	1.0
Methanol	4.3	4.0	4.2
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	16.1	14.6	15.4
Total Hydrocarbons[c]	20.4	18.6	19.5

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-9. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-645-F (WORK ASSIGNMENT 12)

Methanol, vol. %	--
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.4
Percent Fuel Distilled at 160°F (D-86)	16

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	2.4	2.4	2.4
Isobutane	0.4	0.4	0.4
Methanol	ND[a]	ND	ND
Ethanol	NR[b]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[c]	5.9	5.8	5.9
Total Hydrocarbons[d]	5.9	5.8	5.9

[a]ND - none detected, less than 0.02 g
[b]NR - not required
[c]Total FID hydrocarbons corrected for alcohol content
[d]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-10. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-646-F (WORK ASSIGNMENT 12)

Methanol, vol. %	4.75
Ethanol, vol. %	--
TBA, vol. %	4.75
RVP, psi	8.8
Percent Fuel Distilled at 160°F (D-86)	24

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.5	1.5	1.5
Isobutane	0.5	0.5	0.5
Methanol	1.3	2.0	1.7
Ethanol	NR[a]	NR	NR
TBA	0.3	0.4	0.3
Total Non-oxygenated HC[b]	9.4	10.4	9.9
Total Hydrocarbons[c]	11.0	12.8	11.9

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-11. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-647-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	2.50
TBA, vol. %	--
RVP, psi	9.1
Percent Fuel Distilled at 160°F (D-86)	28

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.6	1.6	1.6
Isobutane	0.5	0.5	0.5
Methanol	2.5	2.6	2.6
Ethanol	0.2	0.2	0.2
TBA	NR[a]	NR	NR
Total Non-oxygenated HC[b]	10.3	12.6	11.5
Total Hydrocarbons[c]	13.0	15.4	14.2

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TABLE B-12. HIGH TEMPERATURE EVAPORATIVE EMISSIONS, LOW RVP - HIGH AROMATIC FUEL EM-648-F (WORK ASSIGNMENT 12)

Methanol, vol. %	5.00
Ethanol, vol. %	--
TBA, vol. %	--
RVP, psi	9.6
Percent Fuel Distilled at 160°F (D-86)	24

	Evaporative Results, g/test		
	Test 1	Test 2	Average
Butane	1.4	1.3	1.4
Isobutane	0.5	0.5	0.5
Methanol	1.8	2.3	2.1
Ethanol	NR[a]	NR	NR
TBA	NR	NR	NR
Total Non-oxygenated HC[b]	9.3	10.2	9.8
Total Hydrocarbons[c]	11.1	12.5	11.8

[a]NR - not required
[b]Total FID hydrocarbons corrected for alcohol content
[c]Sum of alcohols and non-oxygenated hydrocarbons

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
460/3-87-001		

4. TITLE AND SUBTITLE	5. REPORT DATE
VAPOR GENERATION OF FUELS	August 1987
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Lawrence R. Smith	Work Assignment B-7

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southwest Research Institute 6220 Culebra Road San Antonio, Texas 78284	11. CONTRACT/GRANT NO. 68-03-3353

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency 2565 Plymouth Road Ann Arbor, MI 48105	Final (4-9-87/6-87) 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report combines the data from two previous work assignments (Work Assignments 12 and 18 of Contract 68-03-3192) conducted at Southwest Research Institute for the Environmental Protection Agency, and analyzes the resulting data set. When possible, the combined results have been generalized in order to draw conclusions. In Work Assignment 12, vapors from twelve gasolines and gasoline/alcohol blends were analyzed for butanes, total hydrocarbons, methanol, and appropriate cosolvent alcohols. The analyses were conducted in duplicate for each fuel at FTP diurnal SHED temperatures (60-84°F) and at typical hot soak temperatures (160±10°F). The fuels were prepared with different levels of aromatic content and Reid Vapor Pressure. The Work Assignment 18 study involved generating vapors from seven gasolines and gasoline/alcohol blends during simulated diurnal test conditions (15-40°F, 35-60°F, and 60-84°F). These vapors were analyzed for total hydrocarbons, alcohols, and individual hydrocarbons up to and including C_6. The Reid Vapor Pressure of the seven fuels varied from 9.2 to 15.0 psi.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Evaporative Emissions	Gasoline/alcohol blends Fuel Effects FTP SHED Tests Temperature Effects	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	76
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)