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PHYSICAL PROPERTIES OF GASOLINE/METHANOL MIXTURES

By

B. H. Eccleston

F. W. Cox

Date Published—January 1977

Bartlesville Energy Research Center
Energy Research and Development Administration
Bartlesville, Oklahoma

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PHYSICAL PROPERTIES OF GASOLINE/METHANOL MIXTURES

by

B. H. Eccleston¹ and F. W. Cox²

ABSTRACT

Experimental work was done to relate selected physical properties of gasoline/methanol solutions, containing contaminant levels of water, to compositional and physical properties of the blending gasoline.

Water tolerance, octane number, vapor pressure, and distillation data are presented for eight gasolines and for their methanol solutions at methanol levels up to 20 wt-pct. The water tolerances of these fuels were strongly dependent upon temperature, methanol concentration, and gasoline composition. To cover a wider range of compositional effects, water tolerance measurements were made at selected methanol levels on a variety of individual hydrocarbons, refinery stocks, and gasolines selected for specific compositional characteristics. These selections provided a sufficient range of property variation for the data to permit useful water-tolerance/gasoline composition correlations.

The results presented in this report supplement and expand published data on water tolerances of gasoline/methanol mixtures. It is shown that an estimate can be made of the water tolerance of a gasoline/methanol mixture when the composition of the gasoline is known in sufficient detail. Portions of the D-86 distillation curves of gasoline/methanol mixtures can be estimated from a knowledge of the base gasoline distillation curves. In the region of 5 to 20 pct methanol content, vapor pressures can be estimated from those of the gasolines. The blending octane numbers resulting from the study agree well with previously published values.

The referenced material and their associated bibliographies are intended to serve as a source of information regarding previous work on methanol and methanol/gasoline solutions for use as automotive fuel.

¹Project leader.

²Research chemist.

INTRODUCTION

Methyl alcohol (methanol) is recognized as a material that could be made available to supplement traditional automotive fuels (1-6).³ It could be used essentially pure, requiring engine modifications, or mixed as a minor component with gasoline and used with few or no engine modifications.

In mixture with gasoline, methanol gives the advantage of some improvement in the octane number and in some systems can result in improved lean-mixture combustion. On the debit side, methanol gives serious problems associated with separation from gasolines in the presence of small amounts of water. Contamination with water would be very difficult to prevent because of the hygroscopic nature of methanol and the current storage and transportation practices used in marketing gasoline. Other physical properties of gasolines, such as vapor pressure and distillation characteristics, can be materially influenced by the presence of methanol. While the foregoing is well known, the quantitative effects are not documented with sufficient data for reliable assessment of their impact on the potential and problems of methanol as a motor fuel blending agent.

The report presents data obtained from a study of the physical properties of refinery gasoline blending stocks, individual hydrocarbons, and a variety of gasolines both blended for this study and chosen from a variety of fuel stocks. Measurements were made on the hydrocarbons alone and on their mixtures with methanol in the presence of contaminant levels of water. The data related to solution stability permit a better understanding of hydrocarbon compositional effects on water tolerances of gasoline/methanol mixtures and provide an insight into the compositional and temperature requirements for gasoline/methanol compatibility. The data for vapor pressure, distillation, and octane number substantiate previously published data (6a, 6b) as well as extend knowledge in these areas by demonstrating the possibility of estimating certain physical property changes upon addition of methanol to gasolines. An associated report (7) provides results of studies made to obtain information on the characteristics of methanol and gasoline/methanol blends used as fuel for multicylinder engines.

EXPERIMENTAL FUELS

For the initial phase of this study, specifications were established for the octane number, aromatic content, and volatility of each of eight base gasolines to be used as blending stock. The base gasolines were to be composed of refinery stocks or hydrocarbon mixtures representative of products which are readily available using current refining technologies. In addition, these gasolines were to:

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

1. Be lead-free,
2. represent two different octane levels meeting roughly the octane levels of current (a) lead-free and (b) regular grade gasolines,
3. provide a range of aromaticity sufficient to demonstrate the compositional influence of aromatics upon gasoline/methanol miscibility, and
4. have vapor pressures and distillation characteristics similar to those of summer grade regular gasolines.

The eight base gasolines, meeting target specifications as closely as feasible, were obtained from a single supplier. Inspection data (table 1) and a list of the blending stocks and proportions used in preparation of the gasolines (table 2) were furnished by the supplier. The eight gasolines were formulated to provide aromatic content at four levels (15, 20, 25, and 30 vol pct) for each of two motor octane numbers, 83 and 89 MON.

Using the base gasolines, we prepared 36 gasoline/methanol mixtures to complete the list of special fuels to be used for the physical properties study. Of the 36 mixtures, 20 were prepared from the 83 MON gasolines at 3, 5, 10, 15, and 20 wt-pct methanol (5 methanol levels x 4 aromatic levels) and 16 were prepared from the 89 MON gasolines at 5, 10, 15, and 20 wt-pct methanol (4 methanol levels x 4 aromatic levels). Special attention was given to accuracy in preparing the blends, and precautionary measures were taken to prevent the sample from taking up water or otherwise becoming contaminated.

The physical properties of the base gasolines and their methanol mixtures were such that, in most cases, reasonably well defined methanol effects could be established. Nonetheless, the ranges of compositional and physical properties represented by the eight base blending stocks were found to be too limited to produce sufficient data in all areas of the physical properties study. In particular, the water tolerance range was rather narrow,

TABLE 1. - Inspection properties of the eight special 83 and 89 motor octane number gasolines (Data from fuel supplier)¹

	83M Series gasolines				89M Series gasolines			
	15A	20A	25A	30A	15A	20A	25A	30A
Composition, FIA, vol pct:								
Aromatics.....	16	22	26	33	15	19	25	29
Olefins.....	10	10	10	11	1	3	3	4
Paraffins and naphthenes.....	74	68	64	56	84	78	72	67
Octane number:								
Motor.....	82.9	82.1	82.1	82.2	89.5	88.0	88.0	88.4
Research.....	91.3	89.5	90.7	90.9	97.4	96.3	98.0	97.0
Gravity, °API.....	64.8	60.8	56.5	45.3	67.5	66.2	59.8	59.1
Reid vapor pressure, lb....	9.4	7.5	7.2	8.1	8.9	10.4	7.6	7.3
Distillation, °F:								
IBP.....	95	101	97	99	99	95	95	101
10 pct.....	120	139	136	132	127	115	133	165
30 pct.....	150	184	182	175	162	155	179	216
50 pct.....	186	219	220	221	192	206	223	235
70 pct.....	229	250	247	250	215	234	255	258
90 pct.....	299	303	300	311	233	280	305	314
End point.....	378	382	394	410	325	352	367	371

¹The code assigned the eight special fuels is AM-BA-CME. The underlined letters (A, B, C) represent digits which designate respectively: the nominal motor octane number, the targeted vol pct aromatic content, and the methanol level (wt pct).

TABLE 2. - Blendstocks used in preparing the 83M and 89M series gasolines

Blending stocks, vol pct	83M Series gasolines				89M Series gasolines			
	15A	20A	25A	30A	15A	20A	25A	30A
Toluene.....	-	-	-	5	-	-	-	-
Mixed xylenes.....	-	3	7	5	-	11	12	10
C-9 Aromatics.....	-	-	-	-	-	-	8	10
Heavy platformate....	4	6	8	10	15	-	-	-
Comm. isopentane....	8	6	2	12	15	20	12	-
Diisopropyl.....	-	-	-	-	10	-	-	-
Comm. isohexanes....	-	-	-	5	-	-	-	-
Issoctane.....	8	-	13	-	12	15	14	3
H.F. light alkylate..	10	17	-	5	12	-	10	6
H.F. heavy alkylate..	-	-	-	2	-	-	-	-
Comm. n-butane.....	4	3	4	4	5	5	4	9
Comm. n-pentane.....	8	6	11	5	-	-	-	-
Comm. n-heptane.....	-	-	-	3	-	-	-	-
Soltrol, 10 ¹	-	-	-	-	8	10	-	26
Soltrol, 50 ²	-	8	5	-	5	-	-	-
70 pct Cyclopentane..	15	-	-	-	12	5	10	-
98 pct Cyclohexane..	-	8	9	5	-	-	-	-
Hougebrand gasoline..	43	43	41	39	6	34	30	36

¹Essentially 100 pct branched chain saturated hydrocarbons.

²Essentially 100 pct aliphatic hydrocarbons.

and the hydrocarbon compositions were too complex to permit a direct assessment of compositional effects. When it became apparent that both basic and broad-range information was necessary to gain an understanding of composition/miscibility relationships, other fuels were included as experimental materials. These were:

1. 31 Individual hydrocarbons,
2. 11 refinery gasoline blending stocks,
3. 8 conventional full-boiling range gasolines,
4. 12 special purpose full-boiling range gasolines (the range of compositional and volatility variations among these gasolines greatly exceed differences typical of conventional gasolines), and
5. two gasolines used in the engine test segment (7) of this project.

A detailed list of the experimental materials is provided in table 3.

PHYSICAL PROPERTIES MEASUREMENTS

The physical properties of gasolines and gasoline/methanol mixtures measured for this study were as follows:

1. Miscibility (cloud point temperature) of the mixtures in the presence of contaminant quantities of water,
2. distillation characteristics,
3. vapor pressure (Reid and micro methods), and
4. antiknock quality (motor and research octane numbers).

To aid in applying the physical property measurements to methanol effects, the compositions of the base gasolines and several of the other hydrocarbon samples were determined. These detailed hydrocarbon analyses were made using established gas-liquid chromatographic (GLC) procedures (8). Examples of the GLC analyses and tables giving fuel composition by hydrocarbon type are presented in appendix A.

The miscibilities of gasoline/methanol/water mixtures were determined using cloud point temperature as a function of water concentration which allowed the miscibility of each gasoline/methanol mixture to be viewed as the water tolerance of the mixture at a particular temperature. The relationship was determined for each weighed mixture by noting the temperature at which a cloud or haze formed in the vigorously stirred, single-phase solution as it was slowly cooled in a clear, coolant-jacketed cell. Incremental water additions were made to establish data points over the temperature range, -15° F (limited by coolant equipment capacity) to 75° F (limited to a large extent by sample volatility). Initial and final water content were determined using a coulometric Karl Fischer procedure (9). The detailed procedure for water tolerance measurement is given in appendix B.

Distillation characteristics, vapor pressure, and octane number were measured by standard ASTM methods (10). The ambient temperature, dry air chamber procedure for Reid vapor pressure (RVP) was used to minimize contact

TABLE 3. - Materials evaluated--their code numbers, descriptions, and type of data generated

Code	Description	Physical properties measured				Calculated estimates of water tolerance	Hydrocarbon composition
		Solubility relationships	Vapor pressure	D-86 Distillation	Octane values		
PHYSICAL PROPERTIES PROJECT GASOLINES							
1	83M - 30A	x	x	x	x	x	x
2	89M - 25A	x	x	x	x	x	x
3	83M - 25A	x	x	x	x	x	x
4	89M - 20A	x	x	x	x	x	x
5	89M - 30A	x	x	x	x	x	x
6	89M - 15A	x	x	x	x	x	x
7	83M - 20A	x	x	x	x	x	x
8	83M - 15A	x	x	x	x	x	x
INDIVIDUAL HYDROCARBONS							
1-P	Cyclopentane (commercial)	x	-	-	-	-	x
2-P	n-Pentane	x	-	-	-	-	x
3-P	2,3-Dimethylbutane	x	-	-	-	-	-
4-P	Isohexanes (commercial)	x	-	-	-	-	x
5-P	3-Methylpentane	x	-	-	-	-	-
6-P	n-Heptane (commercial)	x	-	-	-	-	x
7-P	2,2,4-Trimethylpentane	x	-	-	-	-	-
8-P	Methylcyclohexane	x	-	-	-	-	-
1-O	2-Methyl-2-butene	x	-	-	-	-	-
2-O	2-Methyl-1-butene	x	-	-	-	-	-
3-O	1-Pentene	x	-	-	-	-	-
4-O	Cyclopentene	x	-	-	-	-	-
5-O	1-Hexene	x	-	-	-	-	-
6-O	4-Methyl-trans-2-pentene	x	-	-	-	-	-
7-O	2,3-Dimethyl-2-butene	x	-	-	-	-	-
8-O	2-Heptene (mixed iso)	x	-	-	-	-	-
9-O	Cyclohexene	x	-	-	-	-	-
10-O	2,4,4-Trimethyl-1-pentene	x	-	-	-	-	-
11-O	1-Octene	x	-	-	-	-	-
1-A	Benzene	x	-	-	-	-	-
2-A	Toluene	x	-	-	-	-	-
3-A	m-Xylene	x	-	-	-	-	-
4-A	Ethylbenzene	x	-	-	-	-	-
5-A	o-Xylene	x	-	-	-	-	-
6-A	Isopropylbenzene	x	-	-	-	-	-
7-A	n-Propylbenzene	x	-	-	-	-	-
8-A	sec-Butylbenzene	x	-	-	-	-	-
9-A	1,3,5-Trimethylbenzene	x	-	-	-	-	-
10-A	1,2,3-Trimethylbenzene	x	-	-	-	-	-
11-A	n-Butylbenzene	x	-	-	-	-	-
12-A	Triethylbenzenes	x	-	-	-	-	-
REFINERY STOCKS							
1-R	Heavy platformate	x	-	-	-	x	x
2-R	Platformate	x	-	-	-	x	x
3-R	Fluid cat cracked	x	-	-	-	x	-
4-R	Reformate	x	-	-	-	-	x
5-R	Cat cracked	x	-	-	-	x	x
6-R	Housebrand gasoline	x	-	-	-	x	x
7-R	Aromatic naphtha	x	-	-	-	-	-
8-R	Straight run	x	-	-	-	-	x
9-R	Heavy straight run	x	-	-	-	x	-
10-R	Cat poly	x	-	-	-	-	x
11-R	H.F. alkylate	x	-	-	-	x	x
FULL RANGE GASOLINES							
1-G	91 Octane no lead Indolene No. 1	x	-	-	-	-	x
2-G	91 Octane no lead Indolene No. 2	x	-	-	-	-	x
3-G	Vehicle study trial blend	x	-	-	-	-	-
4-G	Mileage accumulation trial blend	x	-	-	-	-	-
5-G	Vehicle study gasoline	x	-	-	-	x	x
6-G	No lead pump No. 1	x	-	-	-	-	x
7-G	Mileage accumulation gasoline	x	-	-	-	x	x
8-G	No lead pump No. 2	x	-	-	-	-	-
9-G	No lead pump No. 3	x	-	-	-	-	-
10-G	No lead pump No. 4	x	-	-	-	-	-
VOLATILITY PROJECT GASOLINES							
1-V	42 Vol pct aromatic	x	-	-	-	-	x
2-V	30 Do.	x	-	-	-	-	x
3-V	64 Do.	x	-	-	-	-	x
4-V	59 Do.	x	-	-	-	-	x
5-V	55 Do.	x	-	-	-	-	x
6-V	60 Do.	x	-	-	-	-	x
7-V	25 Do.	x	-	-	-	-	x
8-V	30 Do.	x	-	-	-	-	x
9-V	11 Do.	x	-	-	-	-	x
10-V	13 Do.	x	-	-	-	-	x
11-V	6 Do.	x	-	-	-	-	x
12-V	2 Do.	x	-	-	-	-	x
HYDROCARBON MIXTURES							
1-B	0.072 Benzene-0.928 Isooctane	x	-	-	-	x	x
2-B	0.377 Benzene-0.671 Isooctane	x	-	-	-	x	x
3-B	0.237 Toluene-0.763 Isooctane	x	-	-	-	x	x
4-B	0.453 Toluene-0.547 Isooctane	x	-	-	-	x	x
5-B	0.650 Toluene-0.350 Isooctane	x	-	-	-	x	x
6-B	0.832 Toluene-0.168 Isooctane	x	-	-	-	x	x

of the gasoline/methanol mixtures with water. The micro vapor pressure (MVP) method also avoided contact with water and, in addition, permitted continual observation of the mixture to ensure that phase separation did not occur during the measurement. The MVP procedure was modified in that the sample was air saturated at 60° F and maintained at this temperature in the charging bulb.

RESULTS AND DISCUSSION

Water Tolerance of Hydrocarbon/Methanol Solutions

When a vigorously stirred single-phase gasoline/methanol solution is cooled, the first indication of phase separation is the formation of tiny, dispersed methanol-rich droplets. The suspended droplets give the mixture a cloudy (or hazy) appearance and, for this reason, the temperature at which the droplets become visible is referred to as the "cloud point." As far as phase separation is concerned, no engine performance problems should occur with a gasoline/methanol fuel until the dispersed, methanol-rich droplets coalesce and settle as a distinctive lower phase. However, without agitation, coalescence usually takes place within a few minutes once the solution is cooled to the cloud point. For this study, the cloud point is defined as the lowest practical temperature at which a solution containing only hydrocarbon, methanol, and contaminant water can exist as a single-phase solution under static conditions.

The fraction of water that can be tolerated in a single phase, gasoline/methanol/water solution is dependent largely upon three variables:

1. The temperature of the solution,
2. the composition of the gasoline, and
3. the fraction of methanol.

A change in the water tolerance of the system can be expressed in terms of any one of these three variables at constant values for the remaining two. The composition of gasolines cannot be adequately expressed as a single variable and the relationship between water tolerance and methanol level is complex. On the other hand, the change in water tolerance of each mixture with respect to a corresponding change in solution temperature from 0° to 70° F was found to be accurately expressed mathematically by quadratic equations. Solution temperature (at the cloud point) was, therefore, chosen as the variable to be used to indicate the ability of each gasoline, hydrocarbon, or hydrocarbon mixture to dissolve contaminant portions of water at particular methanol levels. In this case, a lower cloud point temperature at a given water level represents a greater water tolerance when comparing hydrocarbon/methanol/water solutions. For the purposes of this report, curves constructed by plotting cloud point temperature versus water concentration will be referred to as "water tolerance curves."

Comparison of experimental data for several hydrocarbons and hydrocarbon mixtures reveals some definite patterns:

1. At a given methanol level, the slope $\frac{dT}{d(H_2O)}$ of the water tolerance curve is inversely related to the water tolerance of the solution. This pattern is evident in figures 1 through 3 where curves of various hydrocarbon/5 pct methanol solutions have been plotted from appendix C data. The difference in slope can easily be observed by comparing solutions with substantially differing water tolerances. Figure 4 shows this relationship to be a general trend for hydrocarbon/5 pct methanol solutions. The values for this curve were obtained from figures 1 through 3 and appendix C equation constants. Water tolerance at 60° F was read directly from the water tolerance curves, and the slope of the curve was calculated as the first derivative (at 60° F) of the curve equation. The relative positions of the plotted points may change somewhat for data sets at temperatures other than 60° F, but the inverse relationship holds for the experimental temperature range. Curves similar to figure 4 were not constructed for the 10, 15, and 20 wt-pct methanol levels. Fewer data were collected at these methanol levels, and values for midrange water tolerances were not available. Available data, however, show that the slope decrease for an incremental water tolerance increase becomes less drastic as the methanol level is raised to 20 pct.

2. For any single hydrocarbon or hydrocarbon mixture, the slope of the water tolerance curve decreases as the methanol level is increased. A typical plot of 3, 5, 10, 15, and 20 wt-pct methanol is shown for gasoline 5-G in figure 5. The effect of higher methanol levels is also shown in this figure.

3. The solubilities of methanol and water in hydrocarbons are such that at very low water concentrations (less than 0.035 wt-pct), there is a direct relationship between methanol level in the range, 5 to 20 wt-pct, and cloud point temperature in the range, 0 to 70° F. At this low water level, as the methanol level of the hydrocarbon/methanol/water system is increased from 5 pct, the phase separation temperature is also increased (or the water tolerance of the solution at a given temperature is decreased). For water concentrations within the range, 0.035 to 0.080 pct, the water tolerance curves for the 5 to 20 wt-pct methanol level cross, and at water concentrations above 0.080 pct, addition of methanol from 5 pct decreases the phase separation temperature (or increases the water tolerance of the solution). This effect is apparent in the curves of figures 6 and 7. Curves for lower methanol levels cross at lower water concentrations. Solutions having low water tolerances display only the direct relationship between methanol level and phase separation temperature (within the experimental temperature limits), and only the inverse relationship applies when water tolerances are high. These two extremes are illustrated in figure 5 by the paraffinic straight run, 9-R, and the aromatic heavy platformate, 1-R, respectively.

The trends included in the preceding discussion are generally applicable to hydrocarbon/methanol/water systems. The solutions may contain a single hydrocarbon, mixtures within a particular hydrocarbon class, or mixtures of the hydrocarbon classes. The generalizations should not, however, be extended beyond the experimental limits.

FIGURE 1. - Water Tolerance of Gasolines with 5 Pct Methanol.

FIGURE 2. - Water Tolerance of Refinery Stocks and Non-typical Gasolines with 5 Pct. Methanol.

FIGURE 3. - Water Tolerance of Individual Hydrocarbons with 5 Pct Methanol.

FIGURE 4. - Relationship of Curve Slope to Water Tolerance for 5 Wt Pct Methanol Mixtures.

FIGURE 5. - Water Tolerance at Various Methanol Levels for Broad-Range Hydrocarbon Mixtures.

Water tolerance curves for the eight base gasolines at various methanol levels are given in figures 6 and 7. An idea of the compositional range represented by these gasolines may be obtained by referring to table 2. A critical analysis of these curves reveals that a general (nonspecific) knowledge of the composition of several different gasolines is not sufficient to determine composition/water-tolerance relationships. The statement that the water tolerance of a gasoline is largely determined by the aromatic content is, to some extent, true; but increasing aromaticity will not necessarily increase the water tolerance especially if other adjustments in gasoline composition must be made to remain within appropriate physical property limits. Overall, figures 6 and 7 show a tendency for the water tolerance to increase with aromaticity, but two obvious exceptions may be observed by comparing 83M-15A to 83M-20A, and 89M-20A to 89M-30A. The differences in aromatic content are 7.8 and 10.6 mole pct, respectively, but the water tolerances are very nearly the same. Detailed information on aromatic content of the gasolines is provided in appendix A.

Regardless of the inconclusive evidence from experiments with the base gasolines, the orderly manner in which changes occur among the various hydrocarbon mixtures and methanol levels suggests the possibility that water tolerance or cloud point temperature can be estimated for particular hydrocarbon mixtures and methanol levels if sufficient compositional data are available. Generally speaking, it is well known that the water tolerance of gasoline/methanol mixtures may be substantially increased by the addition of low molecular weight aromatics such as benzene, toluene, or xylene. Actually, considering the hydrocarbons as three major classes, aromatics have the greatest water tolerance at a particular methanol level, olefins are intermediate, and paraffins have the least water capacity. A homologous series within a hydrocarbon class shows a decreasing water tolerance with increasing molecular weight. A good example of this is the series: benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene (figure 3). On the other hand, the water tolerance of isomers may differ considerably--for example, isopropylbenzene and 1,2,3-trimethylbenzene in figure 3-- showing that at least one variable other than molecular weight is involved with the water tolerance of hydrocarbon/methanol solutions. The search for a single variable related to water tolerance revealed that, within a hydrocarbon class, a reasonably smooth transition occurs with respect to hydrocarbon boiling point. Figure 8 illustrates the relationship, at two solution temperatures, for several hydrocarbons from each of the three major classes. These curves were constructed from the individual hydrocarbon data given in appendix C. Subtle differences in molecular structure within the broad classes of hydrocarbons undoubtedly cause water tolerance variations; but data scatter, especially that of the olefins, is thought to be largely the result of contamination. Regardless of data scatter, the curves in figure 8 indicate that the water tolerance of a single hydrocarbon/5 pct methanol solution can be estimated within 0.02 wt-pct from the hydrocarbon boiling point alone.

If no water solubility interaction (deviation from ideal solution) occurs when two or more hydrocarbons are mixed, and the water tolerance of the individual hydrocarbons can be estimated, then it should be possible to estimate

FIGURE 6. - Water Tolerance of 83M Gasolines at Various Methanol Levels.

FIGURE 7. - Water Tolerance of 89M Gasolines at Various Methanol Levels.

FIGURE 8. - Relationship of Hydrocarbon/5 Pct Methanol to Hydrocarbon Boiling Point.

the water tolerance of a mixture of known composition. In the absence of solubility interactions, the water tolerance of a solution (W_s) of n number of components becomes the sum of the water tolerance of each component ($W_1, W_2, W_3 \dots W_n$) adjusted for its fractional part ($F_1, F_2, F_3 \dots F_n$) of the total solution so that:

$$W_s = \sum_{i=1}^n W_i F_i \quad (1)$$

Though discussed here as the water tolerance of solution components (1, 2, 3-- n); this expression can be applied equally well to other physical properties of solutions. Strict adherence to ideal solution theory requires the use of molar units, but practical applications of the study results are emphasized and, when variations of the equation are used throughout this report, units are chosen for convenience. "Ideality" is loosely interpreted as "additivity" of the solution components regardless of the property being discussed or the units used.

The effect of the presence of a second hydrocarbon would likely be more pronounced if the water tolerances of the two hydrocarbons were widely separated and, since olefins are normally the minor constituent of gasolines, benzene/isooctane and toluene/isooctane mixtures were used as indicators of the feasibility of water tolerance estimation. The water tolerances of hydrocarbon/5 pct methanol solutions were determined experimentally for the three individual hydrocarbons and for six hydrocarbon mixtures of various known compositions. The curves (figure 9) constructed from the experimental data (appendix C) show the relationship of the experimental water tolerance of the mixtures to those calculated by equation (1) using mole fraction as the representative portion of each hydrocarbon. Since the methanol level is constant at 5 pct, the hydrocarbon fractions are based only on the hydrocarbon portion of the hydrocarbon/methanol/water solutions (water concentration is too low to be significant).

Several tentative conclusions were derived from figure 9:

1. There is a degree of interaction between the two hydrocarbons that causes the actual water tolerances of the mixtures to deviate from the water tolerances calculated assuming no interaction;
2. the degree of deviation is directly related to the difference in water tolerance of the individual hydrocarbons, (that is, benzene/isooctane deviation is greater than toluene/isooctane);
3. the minor component of the hydrocarbon pair has less influence upon the water tolerance of the mixture than is expected by assuming no interaction; and
4. in order to estimate the water tolerance of mixtures containing a component whose individual water tolerance approaches zero, the water tolerance curve must be smoothly extended through zero into negative water concentration values.

FIGURE 9. - Solubility Interaction Effects on Water Tolerance of Hydrocarbon Mixtures Containing 5 Pct Methanol.

In this case, the quadratic equation for isooctane derived from the experimental data was extrapolated. The unrealistic "negative water concentration" is convenient for relating the cloud point temperature to a quantity useful in estimating the water tolerance of hydrocarbon mixtures containing significant amounts of components whose water tolerances approach zero within the experimental temperature range. In figure 9, the crossover of the estimated and experimental curves for 0.6503 and 0.8322 mole fraction toluene is probably caused by experimental error in establishing the toluene curve.

The inferences drawn from the two-hydrocarbon systems discussed above are not to be taken as definitive of all hydrocarbon mixtures, but they do indicate that a reasonable estimate, at least at the 5 pct methanol level, can be made of the water tolerance of hydrocarbon mixtures (gasolines) if the composition is known. The interaction between benzene and isooctane is too great (for example, 0.032 wt-pct water for 0.33 mole fraction of benzene at 70° F) for meaningful water tolerance estimates without a correction, but benzene is normally present in gasolines at very low concentrations. On the other hand, toluene and isooctane show a maximum difference between the experimental and estimated values of about 0.01 wt-pct water.

The value of an estimate depends upon the effort required and the intended purpose. For this program, development of a method for estimating the water tolerance of hydrocarbon mixtures in the presence of methanol is intended to aid: (1) those who wish to formulate hydrocarbon/methanol mixtures having acceptable water tolerances, and (2) those to whom the detailed mixture composition is readily available. For these purposes, estimation accuracy has been sacrificed, to some extent, for the sake of simplicity. For instance, at least a third order equation would be necessary to correct mathematically for the interaction effect of the toluene/isooctane hydrocarbon pair (figure 9) and, judging from the interaction difference between the two pairs of hydrocarbons tested, the constants of the correction equation would vary with hydrocarbon composition.

Ten gasolines (including the eight specially blended for this study) and seven refinery stocks were chosen to test the validity of water tolerance estimates which ignore the deviation due to hydrocarbon interaction. Detailed hydrocarbon analyses of the gasolines and stocks were available (appendix A), and the water tolerance relationships had already been established for various methanol levels up to 20 wt-pct. Hydrocarbon analyses for the eight base gasolines are given in detail in table A-1. The summary for the remaining materials (table A-2) was condensed from equally detailed data.

As figure 8 shows, hydrocarbons within a class follow a pattern for water tolerance that is related to their boiling points. The gasolines and refinery stocks were considered as three-component systems (containing paraffins, olefins, and aromatics) and the average boiling point ($\bar{T}_B$) in °F of each class was used to determine the water tolerance of that class as a separate entity. $\bar{T}_B$ was calculated as a part of the detailed gasoline analysis by multiplying the boiling point (T_B) of each component of a class by its mole fraction within that class and then adding the weighted boiling points.

Using the three average boiling points, the water tolerance of each hydrocarbon class was read from the 60° F curves in figure 8. Equation (1) was then used to calculate an estimated water tolerance for 5 pct methanol solutions of each of the gasolines and stocks at 60° F so that:

$$W_S = W_A F_A + W_O F_O + W_P F_P \quad (1a)$$

where,

W_S = water tolerance of the solution (gasoline/5 pct methanol) at 60° F

W_A, W_O, W_P = water tolerances of the individual hydrocarbon classes (from figure 8) at 60° F

F_A, F_O, F_P = mole fractions of the hydrocarbon classes within the gasoline (from table A-2)

The estimates were all within 0.015 wt-pct water of the experimental values.

The method of estimation described above is workable and straightforward, but curves similar to those in figure 8 are necessary for each solution temperature of interest. An alternate method, which employs only mathematical calculations, has been devised to minimize the time and effort required for estimations covering solution temperatures in the range 0 to 70° F. Curves similar to those in figure 8 were constructed at 10° F intervals from 0° to 70° F, and expressions for the water tolerance of each class of hydrocarbons were derived in the following manner.

The ranges of the average boiling points of the hydrocarbon classes in gasolines are relatively narrow. For instance, the water-tolerance range of the 17 gasolines and refinery stocks is broad (0.010-0.227 wt-pct), but the average boiling points for the classes within these mixtures are:

1. Aromatics (237°-304° F)
2. Olefins (106°-181° F)
3. Paraffins (142°-238° F)

Linear curve fits within these limits vary only slightly from the best overall curves (see figure 8). From the slope-intercept formulas (for example, for aromatics: $W_A = m\bar{T}_{BA} + b$) of the linear series for each class at 10° F solution temperature intervals, expressions were derived to relate the change in the constants (m, b) over the experimental temperature range to the solution temperatures (T_S). These expressions were then substituted back into the original slope-intercept formulas, and each was reduced. The final expressions for the water tolerance of the hydrocarbon classes are:

$$W_A = [T_S^2(1.971 - 0.00306\bar{T}_{BA}) + T_S(189.5 - 0.4263\bar{T}_{BA}) - 101.8\bar{T}_{BA} + 38590]10^{-5} \quad (2)$$

$$W_O = [0.5964T_S^2 + T_S(117.3 - 0.337\bar{T}_{BO}) - 73.83\bar{T}_{BO} + 15440]10^{-5} \quad (3)$$

$$W_P = [T_S^2(0.5467 - 0.0009137\bar{T}_{BP}) + T_S(75.13 - 0.161\bar{T}_{BP}) - 23.66\bar{T}_{BP} + 1967]10^{-5} \quad (4)$$

and again equation (1a)

$$W_S = W_{AFA} + W_{OFO} + W_{PFP} \quad (1a)$$

gives the estimated water tolerance of the hydrocarbon/5 pct methanol mixture. $\bar{T}_{BA}$, $\bar{T}_{BO}$, and $\bar{T}_{BP}$ in equations (2), (3), and (4) refer to the average boiling point of the hydrocarbon class for which the water tolerance is being calculated.

Equations (2), (3), (4), and (1a) were applied to the 10 gasolines, seven refinery stocks, and six two-component hydrocarbon mixtures discussed earlier. The results, compared to the experimental values, are given in table 4. Note that the hydrocarbon mixtures in the table include broad ranges for both water tolerance and composition. The absolute differences between the water tolerance and experimental values are reasonable. Seventeen of the 23 mixtures agree within 0.010 wt-pct water, and in only one case (a benzene/isooctane mixture) is the disagreement substantially above 0.013 wt-pct water (this was expected from the initial two-component work).

TABLE 4. - Calculated water tolerance estimates
for 5 wt pct methanol mixtures

Code No. ¹	Sample properties for water tolerance estimates			Water tolerance data								
	Hydrocarbon class	Mole fraction in sample	Average boiling point, °F	Method of evaluation ²	Values at intervals of 10° F							
					0	10	20	30	40	50	60	70
PHYSICAL PROPERTIES PROJECT GASOLINES												
1	Paraffin	0.548	148	EST	0.0387	0.0455	0.0539	0.0637	0.0747	0.0874	0.1014	0.1168
	Olefin	.084	166	EXP	.0346	.0420	.0499	.0584	.0679	.0785	.0908	.1064
	Aromatic	.369	261	DIFF	.0041	.0035	.0040	.0053	.0068	.0089	.0106	.0104
2	Paraffin	0.6888	155	EST	0.0132	0.0192	0.0264	0.0348	0.0445	0.0552	0.0673	0.0805
	Olefin	.0261	167	EXP	.0197	.0265	.0338	.0418	.0505	.0605	.0724	.0878
	Aromatic	.2850	296	DIFF	-.0065	-.0073	-.0074	-.0070	-.0060	-.0053	-.0051	-.0073
3	Paraffin	0.648	162	EST	0.0218	0.0281	0.0357	0.0445	0.0547	0.0661	0.0786	0.0924
	Olefin	.063	154	EXP	.0177	.0250	.0328	.0412	.0503	.0604	.0718	.0854
	Aromatic	.290	273	DIFF	.0041	.0031	.0029	.0033	.0044	.0057	.0068	.0070
4	Paraffin	0.7661	142	EST	0.0103	0.0165	0.0237	0.0321	0.0417	0.0523	0.0642	0.0770
	Olefin	.0274	149	EXP	.0146	.0216	.0292	.0372	.0460	.0557	.0667	.0797
	Aromatic	.2065	285	DIFF	-.0043	-.0051	-.0055	-.0051	-.0043	-.0034	-.0015	-.0027
5	Paraffin	0.6555	174	EST	0.0124	0.0183	0.0253	0.0336	0.0430	0.0537	0.0655	0.0786
	Olefin	.0316	165	EXP	.0138	.0207	.0284	.0364	.0452	.0549	.0659	.0788
	Aromatic	.3129	299	DIFF	-.0012	-.0024	-.0031	-.0028	-.0022	-.0012	-.0004	-.0002
6	Paraffin	0.8128	150	EST	0.0130	0.0193	0.0268	0.0354	0.0450	0.0559	0.0678	0.0809
	Olefin	.0043	160	EXP	.0116	.0185	.0259	.0339	.0426	.0523	.0635	.0770
	Aromatic	.1829	241	DIFF	.0014	.0008	.0009	.0015	.0024	.0036	.0043	.0039
7	Paraffin	0.681	170	EST	0.0146	0.0206	0.0280	0.0364	0.0460	0.0567	0.0687	0.0818
	Olefin	.081	163	EXP	.0079	.0148	.0221	.0301	.0388	.0486	.0602	.0747
	Aromatic	.239	273	DIFF	.0067	.0058	.0059	.0063	.0072	.0081	.0085	.0071
8	Paraffin	0.747	144	EST	0.0100	0.0163	0.0235	0.0320	0.0414	0.0520	0.0637	0.0765
	Olefin	.082	161	EXP	.0082	.0146	.0214	.0288	.0370	.0462	.0572	.0713
	Aromatic	.171	276	DIFF	.0018	.0017	.0021	.0032	.0044	.0058	.0065	.0052

See footnotes at end of table.

TABLE 4. - Calculated water tolerance estimates--Continued
for 5 wt pct methanol mixtures

Code No. ¹	Sample properties for water tolerance estimates			Water tolerance data								
	Hydrocarbon class	Mole fraction in sample	Average boiling point, °F	Method of evaluation ²	Values at intervals of 10° F							
					0	10	20	30	40	50	60	70
BENZENE/ISOOCTANE ^{4, 6}												
2-B	Paraffin	0.6734	211	EST	0.0472	0.0544	0.0630	0.0731	0.0845	0.0973	0.1116	0.1273
	Olefin	-	-	EXP	.0202	.0282	.0366	.0457	.0557	.0668	.0795	.0947
	Aromatic	.3266	176	DIFF	.0270	.0262	.0264	.0274	.0288	.0305	.0321	.0326
1-B	Paraffin	0.9285	211	EST	-0.0132	-0.0081	-0.0022	0.0045	0.0123	0.0208	0.0302	0.0404
	Olefin	-	-	EXP	-.0213	-.0163	-.0109	-.0051	.0013	.0085	.0169	.0275
	Aromatic	.0715	176	DIFF	.0081	.0082	.0087	.0096	.0110	.0123	.0133	.0129
TOLUENE/ISOOCTANE ⁶												
6-B	Paraffin	0.1678	211	EST	0.1203	0.1297	0.1413	0.1550	0.1712	0.1894	0.2099	0.2326
	Olefin	-	-	EXP	.1298	.1410	.1530	.1659	.1799	.1953	.2127	.2333
	Aromatic	.8322	231	DIFF	-.0095	-.0113	-.0117	-.0109	-.0087	-.0059	-.0028	-.0007
5-B	Paraffin	0.3497	211	EST	0.0875	0.0957	0.1059	0.1180	0.1320	0.1479	0.1656	0.1852
	Olefin	-	-	EXP	.0931	.1025	.1125	.1234	.1352	.1484	.1634	.1816
	Aromatic	.6503	31	DIFF	-.0056	-.0068	-.0066	-.0054	-.0032	-.0005	.0022	.0036
4-B	Paraffin	0.5475	211	EST	0.0517	0.0588	0.0675	0.0777	0.0894	0.1206	0.1175	0.1338
	Olefin	-	-	EXP	.0472	.0554	.0641	.0736	.0840	.0958	.1096	.1270
	Aromatic	.4525	231	DIFF	.0045	.0034	.0034	.0041	.0054	.0068	.0079	.0068
3-B	Paraffin	0.7634	211	EST	0.0126	0.0185	0.0255	0.0337	0.0429	0.0534	0.0649	0.0777
	Olefin	-	-	EXP	.0054	.0122	.0195	.0273	.0358	.0452	.0559	.0686
	Aromatic	.2366	231	DIFF	.0072	.0063	.0060	.0064	.0071	.0082	.0090	.0091

See footnotes at end of table.

TABLE 4. - Calculated water tolerance estimates--Continued
for 5 wt pct methanol mixtures

Code No. ¹	Sample properties for water tolerance estimates			Water tolerance data									
	Hydrocarbon class	Mole fraction in sample	Average boiling point, °F	Method of evaluation ^a	Values at intervals of 10° F								
					0	10	20	30	40	50	60	70	
REFINERY STOCKS													
1-R	Paraffin	0.0833	238	EST	0.1341	0.1438	0.1559	0.1704	0.1873	0.2066	0.2282	0.2522	
	Olefin	-	-	EXP	.1340	.1480	.1630	.1780	.1930	.2100	.2270	.2450	
	Aromatic	.9167	237	DIFF	.0001	-.0042	-.0071	-.0076	-.0057	-.0034	.0012	.0072	
2-R	Paraffin	0.5436	172	EST	0.0372	0.0439	0.0520	0.0615	0.0725	0.0849	0.0988	0.1142	
	Olefin	.0017	181	EXP	.0333	.0412	.0500	.0597	.0700	.0810	.0940	.1085	
	Aromatic	.4547	274	DIFF	.0039	.0027	.0020	.0018	.0025	.0039	.0048	.0057	
3-R ³	Paraffin	0.4282	143	EST	0.0379	0.0450	0.0533	0.0628	0.0736	0.0856	0.0988	0.1132	
	Olefin	.3661	106	EXP	.0346	.0420	.0499	.0584	.0679	.0785	.0908	.1064	
	Aromatic	.2057	302	DIFF	.0033	.0030	.0034	.0044	.0057	.0071	.0080	.0068	
5-R	Paraffin	0.5070	171	EST	0.0238	0.0301	0.0376	0.0464	0.0564	0.0675	0.0799	0.0935	
	Olefin	.2395	125	EXP	.0193	.0262	.0342	.0433	.0533	.0640	.0760	.0900	
	Aromatic	.2535	304	DIFF	.0045	.0039	.0034	.0031	.0031	.0035	.0039	.0035	
6-R	Paraffin	0.5818	200	EST	0.0178	0.0237	0.0309	0.0393	0.0489	0.0597	0.0717	0.0851	
	Olefin	.1050	142	EXP	.0060	.0140	.0210	.0300	.0380	.0480	.0590	.0730	
	Aromatic	.3132	289	DIFF	.0118	.0097	.0099	.0093	.0109	.0117	.0127	.0121	
9-R ⁵	Paraffin	0.8271	211	EST	-0.0042	0.0010	0.0073	0.0145	0.0227	0.0319	0.0421	0.0534	
	Olefin	-	-	EXP	-.0110	-.0045	.0020	.0090	.0180	.0260	.0360	.0490	
	Aromatic	.1729	261	DIFF	.0068	.0055	.0053	.0055	.0047	.0059	.0061	.0044	
11-R ⁶	Paraffin	0.9982	200	EST	-0.0275	-0.0229	-0.0175	-0.0114	-0.0045	0.0031	0.0114	0.0204	
	Olefin	.0018	149	EXP	-.0265	-.0215	-.0162	-.0106	-.0044	.0030	.0100	.0200	
	Aromatic	-	-	DIFF	-.0010	-.0014	-.0013	-.0008	-.0001	.0001	.0014	.0004	

See footnotes at end of table.

TABLE 4. - Calculated water tolerance estimates--Continued
for 5 wt pct methanol mixtures

Code No. ¹	Sample properties for water tolerance estimates			Water tolerance data								
	Hydrocarbon class	Mole fraction in sample	Average boiling point, °F	Method of evaluation ²	Values at intervals of 10° F							
					0	10	20	30	40	50	60	70
ENGINE TEST GASOLINES												
4-G	Paraffin	0.6926	156	EST	0.0222	0.0287	0.0364	0.0453	0.0554	0.0668	0.0793	0.0932
	Olefin	.0458	138	EXP	.0160	.0240	.0310	.0390	.0480	.0580	.0710	.0850
	Aromatic	.2616	260	DIFF	.0062	.0047	.0054	.0063	.0074	.0088	.0083	.0082
7-G ⁶	Paraffin	0.5654	166	EST	0.0256	0.0320	0.0396	0.0486	0.0587	0.0702	0.0830	0.0970
	Olefin	.1050	126	EXP	.0166	.0241	.0320	.0405	.0497	.0599	.0716	.0854
	Aromatic	.3296	281	DIFF	.0090	.0079	.0076	.0081	.0090	.0103	.0114	.0116

¹ Refer to table 3 for sample description.

² EST = Estimation; EXP = Experimental; DIFF = Difference.

^{3,4} Error of water tolerance estimates are excessive and not used in mean and standard deviation calculation.

⁵ No water tolerance estimates at 20 wt pct methanol.

⁶ No water tolerance estimates at 10, 15, and 20 wt pct methanol.

By necessity, the experimental technique was altered somewhat for the evaluation of the individual hydrocarbons at 10, 15, and 20 wt-pct methanol. The aromatics and olefins were treated as they were for the 5 pct methanol estimates, but the relationship between hydrocarbon boiling point and water tolerance (figure 8) could not be established for the paraffins at the higher methanol levels. Below 70° F solution temperature, only the paraffins boiling below 160° F can form single-phase solutions with 10 wt-pct methanol and, at 15 and 20 wt-pct methanol, the boiling points of the compatible paraffins are even lower. Expressions for the water tolerance of paraffins (W_p) containing the higher methanol levels were generated by taking W_p to be the difference between the experimental water tolerance of each gasoline (W_s) and the calculated sum of the olefin and aromatic water tolerances:

$$W_p = \frac{W_s - (W_{AFA} + W_{OF0})}{F_p} \quad (1b)$$

and regression analyses of W_p (formula 1b) versus $\bar{T}_{BP}$ (the average boiling point of the paraffinic portion of a hydrocarbon mixture) for several gasolines and refinery stocks gave values for the constants (m, b) of the slope-intercept formulas ($W_p = m\bar{T}_{BP} + b$). The slope-intercept formulas were then treated as they were for the 5 pct methanol estimates.

The expressions derived for the water tolerance of the hydrocarbon classes at the various methanol levels are:

at 10 wt pct methanol--

$$W_A = [T_S^2(2.27 - 0.00226\bar{T}_{BA}) + T_S(533 - 1.37\bar{T}_{BA}) - 239\bar{T}_{BA} + 90200]10^{-5} \quad (5)$$

$$W_O = [T_S^2(1.41 - 0.0035\bar{T}_{BO}) + T_S(234 - 0.553\bar{T}_{BO}) - 196\bar{T}_{BO} + 34000]10^{-5} \quad (6)$$

$$W_P = [T_S^2(0.923 - 0.00333\bar{T}_{BP}) + T_S(205 - 0.298\bar{T}_{BP}) - 115\bar{T}_{BP} + 5110]10^{-5} \quad (7)$$

at 15 wt-pct methanol--

$$W_A = [T_S^2(4.45 - 0.00784\bar{T}_{BA}) + T_S(737 - 1.74\bar{T}_{BA}) - 472\bar{T}_{BA} + 172600]10^{-5} \quad (8)$$

$$W_O = [T_S^2(1.46 - 0.0008\bar{T}_{BO}) + T_S(434 - 1.21\bar{T}_{BO}) - 326\bar{T}_{BO} + 54700]10^{-5} \quad (9)$$

$$W_P = [T_S^2(1.78 - 0.00871\bar{T}_{BP}) + T_S(171 + 0.799\bar{T}_{BP}) - 348\bar{T}_{BP} + 25400]10^{-5} \quad (10)$$

and at 20 wt-pct methanol--

$$W_A = [T_S^2(4.67 - 0.00509\bar{T}_{BA}) + T_S(1060 - 2.31\bar{T}_{BA}) - 728\bar{T}_{BA} + 261700]10^{-5} \quad (11)$$

$$W_O = [T_S^2(3.33 - 0.0135\bar{T}_{BO}) + T_S(502 - 0.553\bar{T}_{BO}) - 533\bar{T}_{BO} + 86400]10^{-5} \quad (12)$$

$$W_P = [T_S^2(2.14 - 0.00845\bar{T}_{BP}) + T_S(523 - 0.857\bar{T}_{BP}) - 461\bar{T}_{BP} + 26700]10^{-5} \quad (13)$$

The water tolerance of the gasoline or refinery stock (W_S) is calculated at each methanol level using equation (1a).

Water tolerance estimates similar to those in table 4 were made at 10, 15, and 20 wt-pct methanol using (except as noted in the table) the same hydrocarbon mixtures. These estimates can be reproduced using equations 5 thru 13 and 1a and the sample property information in table 4; and can be compared to the experimental values from appendix C. Rather than include separate tables for the estimates at the higher methanol levels, the differences between the estimated and experimental values have been used to calculate the mean and standard deviation of error for each level:

Methanol level, wt-pct	Error of estimate, wt-pct water		
	Number of values	Mean error	Std. error of estimate
5	*4168	0.003	0.005
10	6120	0.000	.015
15	3,6106	-0.001	.021
20	3,5,6104	-0.002	.034

*3,4,5,6 Refer to table 4 footnotes.

The method of derivation for equations (7), (10), and (13) forces the mean error of estimate to be near zero at 10, 15, and 20 wt-pct methanol. The standard deviation, however, clearly shows that the precision of water-tolerance estimation deteriorates as the methanol level is raised. Analysis of the data at the four methanol levels revealed no relationship between the magnitude of water tolerance and error of estimate, but the relationship between water tolerance and hydrocarbon boiling point became less distinct as the methanol level was raised. At higher methanol levels, the increased data scatter for curves similar to those in figure 8 (which appeared to be the result of differences in molecular structure within each hydrocarbon class) made the curves less representative of the individual compounds. This could account for the decrease in precision of the estimates.

Distillation Characteristics of Gasoline/Methanol Solutions

When methanol is added to gasoline, a portion of the ASTM D86 distillation curve is substantially altered. This change in the distillation curve is the result of the formation of minimum boiling azeotropic hydrocarbon/methanol mixtures, and from the beginning of the distillation to the point of methanol depletion, the change is predictable. The fraction of the base gasoline curve which is affected depends to a large extent upon the fraction of methanol in the gasoline and the shape and position of the curve. Figure 10 shows relationships between the boiling points of individual hydrocarbons and their corresponding azeotropes. The data used to construct the curves are given in appendix D. Many (if not all) paraffins and olefins boiling below 335° F form azeotropic solutions with methanol; but, excepting benzene and toluene, the aromatics normally found in substantial quantities in gasolines do not. According to figure 10-A, as the initial distillation temperature of a gasoline increases to 176° F, the distillation temperature of a gasoline/methanol mixture will increase only to 129° F. At this point, the paraffins and olefins through C₆ have been distilled and, if the mixture contained no higher aliphatics, the azeotropic distillation curve would rise rather rapidly from 129° to 135° F where benzene/methanol boils. This, however, is not the case with gasolines, and the azeotropic distillation temperature continues to rise smoothly. This behavior is limited to azeotropic distillation temperatures below 149° F, the boiling point of methanol. The hydrocarbon boiling point corresponding to 149° F azeotropic boiling point is roughly 335° F, and hydrocarbons boiling at higher temperatures cannot form minimum boiling azeotropes with methanol. At 149° F, the gasoline/methanol distillation temperature would remain constant until the methanol had been distilled then rise rapidly to the vicinity of 280° F (assuming xylene to be present.)

The foregoing discussion presupposes excess methanol. The ratio of methanol to gasoline distilled is dependent upon the gasoline composition since, generally, the azeotropes become richer in methanol as the boiling point increases (figure 10-B). The distillation characteristics study was limited to the eight base gasolines, and the 20 wt-pct methanol maximum was not sufficient to distill all of the paraffins boiling below 335° F before the methanol was depleted.

FIGURE 10. - Relationships of Hydrocarbon/Methanol Azeotropes and Hydrocarbons.

The ASTM D86 distillation data for the eight base gasolines blended for this study are given in appendix E along with similar data for their methanol mixtures. The data for gasolines 83M-15A, 83M-20A, 89M-25A, and 89M-30A and their methanol mixtures are shown graphically in figure 11. The azeotropic distillation curves were constructed from the original gasoline curves and figure 10-A. Beyond 10 vol pct recovered distillate, the predicted curve is in good agreement with the experimental data. The shaded areas in figure 11 for 89M-30A show the approximate limits of the hydrocarbon/methanol distillations. The experimental data increments (10 vol pct recovered distillate) are too large to establish the curves in these areas.

When azeotropic distillation has removed the methanol from the solution (figure 11), a sharp increase in distillation temperature occurs. The azeotropic distillation curve then approaches the original gasoline distillation curve but remains displaced to a degree dependent upon the amount of methanol which has been added. On a volume basis, the fraction of azeotropic distillate recovered (D_A) is calculated from the fraction of the corresponding base gasoline distillate recovered (D_G) and the fractions of gasoline (F_G) and methanol (F_M) in the starting gasoline/methanol solution.

$$D_A = D_G F_G + F_M \quad (14)$$

Vapor Pressure of Gasoline/Methanol Solutions

The vapor pressure of gasoline is an important factor in startability of automotive engines at low temperatures and in susceptibility to vapor lock at high temperatures. Therefore, when considering the possibility of using methanol as a blending component in gasolines, its effect on the vapor pressure of the fuel is important.

The accepted procedure for measuring the vapor pressure of gasolines is the Reid method (ASTM 323). This method measures the pressure exerted by air-saturated gasoline at 100° F and a 4:1 vapor to liquid ratio. Phase separation becomes a hazard when this procedure is used to measure the vapor pressure of gasoline/methanol mixtures. No more water than that acquired from exposure to humid air could cause phase separation at room temperature of some mixtures tested in this program, and some of the mixtures would separate at the 32° F air-saturation temperature even without water contamination. Phase separation during the air-saturation operation would result in nonrepresentative sampling. This, or the existence of two phases during measurement, would generally give low vapor pressure values. In view of these objections, measurements were made in this laboratory using the ASTM micro vapor pressure procedure D2551-71, to supplement the Reid data. The samples for MVP were saturated with air at 60° F and measured at 100° F by mercury manometer. This procedure avoids all contact with water and, by use of appropriate drying tubes, minimizes contact of the sample with humid air. In addition, the sample is visible during the test so that any tendency to phase separation can be detected.

FIGURE 11. - Distillation Characteristics of Gasoline/Methanol Mixtures.

The operation and performance of the micro vapor pressure apparatus⁴ was evaluated using pure hydrocarbons (the MVP of methanol was also checked). An adequate vapor measure range was covered, and the results (table 5) were excellent. After the measured hydrocarbon values were corrected for air saturation, they were compared to the literature values and found to agree within 2.2 ± 6.3 mmHg. A major portion of the deviation and bias is probably due to uncertainties in the correction used for air saturation.

TABLE 5. - Vapor pressures of methanol and individual hydrocarbons

Compound	Vapor pressure, mm Hg (100° F)			
	Literature ¹	Micromethod		Difference (corrected-literature)
		Measured ²	Corrected for air saturation ³	
n-Pentane.....	805	838	801	-4
2,3-Dimethylbutane.....	383	436	391	8
3-Methylpentane.....	315	368	321	6
1-Hexene.....	311	365	319	8
n-Hexane.....	256	298	249	-7
Methylcyclopentane.....	233	278	239	6
Methanol.....	239	267	240	1
Cyclohexane.....	169	203	175	6
2,2,4-Trimethylpentane...	88	129	81	-7
n-Heptane.....	84	137	88	4

¹ ASTM Special Technical Publication No. 109A.

² ASTM D2551-71, "Vapor Pressure of Petroleum Products (Micromethod) Except 60° F Air Saturation Used In Place of Recommended 32° F."

³ *Analytical Chemistry*, v. 29, No. 8, August 1957 (50° F air saturation temperature used).

⁴ *Selected Properties of Hydrocarbons and Related Compounds*, API Research Project No. 44.

The vapor pressure of the eight base gasolines and their methanol mixtures were measured by the micro method and the values recorded in table 6. Considering only the vapor pressures of methanol (267 mmHg, table 5) and the gasolines (428-586 mmHg), one would expect methanol addition to lower the gasoline vapor pressures. However, the results of the distillations have already confirmed that gasoline and methanol do not form ideal solutions with respect to boiling point. Table 6 shows that methanol actually increases the gasoline vapor pressures by about 180 mmHg. The effect of methanol addition to the base gasolines is shown graphically in figure 12. Here the large influence of small quantities of methanol is very striking, with only 3 wt-pct accounting for more than 96 pct of the total vapor pressure increase of the 83M series gasolines. The shape of the curves and the consistency of the vapor pressure rise indicate that the vapor pressure of 5 to 20 wt-pct methanol mixtures can be reasonably estimated simply by adding 180 mmHg to the gasoline MVP; provided that the gasoline vapor pressure is within the range, 425 to 585 mmHg. (This vapor pressure range is representative of summer grade gasolines and is slightly narrower and does not quite coincide with that of normally marketed gasolines if winter grades are also considered.)

The empirical mathematical relationship of MVP and Reid vapor pressure was supplied with the MVP apparatus. This equation,

$$\text{ERVVP, psi} = 0.019(\text{MVP, mmHg}) - 0.66 \quad (15)$$

allows the measured MVP to be expressed as an "equivalent Reid vapor pressure" (ERVVP) simultaneously converting the pressure units to those commonly used with the Reid method. The MVP values for the base gasolines and their methanol mixtures have been converted to ERVVP values and added to table 6 along with the RVP values obtained from another lab. The data are compared in figure 13. The relationship given by equation (15) is represented in the figure by a

⁴ Manufacturers Engineering and Equipment Corp., Model G Dual Head Micro Vapor Pressure Apparatus.

TABLE 6. - Vapor pressures of 83M and 89M gasolines
and their blends with methanol

Gasoline	Methanol, wt pct					
	0	3	5	10	15	20
MICRO VAPOR PRESSURE, mm Hg						
83M-15A	534	698	710	707	711	705
20A	424	588	596	602	595	597
25A	424	590	598	605	605	603
30A	455	613	622	630	634	633
89M-15A	519	-	697	700	699	694
20A	586	-	762	761	756	753
25A	448	-	628	630	630	628
30A	444	-	616	615	623	612
EQUIVALENT REID VAPOR PRESSURE, LB ¹						
83M-15A	9.49	12.60	12.83	12.77	12.85	12.74
20A	7.40	10.51	10.66	10.78	10.65	10.68
25A	7.40	10.56	10.70	10.84	10.84	10.80
30A	7.99	10.99	11.10	11.31	11.39	11.37
89M-15A	9.20	-	12.58	12.64	12.62	12.53
20A	10.47	-	13.82	13.80	13.70	13.65
25A	7.85	-	11.27	11.31	11.31	11.37
30A	7.78	-	11.04	11.03	11.12	10.97
REID VAPOR PRESSURE, LB ²						
83M-15A	9.5	11.7	11.5	11.6	12.0	11.8
20A	7.0	9.0	9.4	9.7	9.6	9.8
25A	7.1	9.2	9.8	10.0	10.0	9.9
30A	8.0	10.0	10.2	10.4	10.7	10.6
89M-15A	10.2	-	13.0	12.8	12.8	12.9
20A	10.3	-	12.5	12.5	12.6	12.8
25A	7.8	-	10.3	10.2	10.1	10.3
30A	7.7	-	10.2	10.0	9.9	10.2

¹ Equivalent Reid, psi = 0.019 (MVP, mmHg) - 0.66.
² ASTM D323 (dry bomb).

FIGURE 12. - Effect of Methanol Addition on the Vapor Pressure of Gasolines.

FIGURE 13. - Comparison of Micro and Reid Vapor Pressures to Equivalent Reid Vapor Pressure.

dashed line and, excepting 89M-15A, the gasolines are in good agreement with the expected values. The averaged values for the gasoline/methanol mixtures, however, consistently show a 1.0 psi difference in the results obtained by the two methods. Though the bias for the mixtures appears to be real, neither the mechanism nor the measurement method responsible for its occurrence was established by this study.

The physical properties of an ideal solution may be calculated by summing the contributions of the individual components. Equations (1) and (1a), for example, can be transformed for general application by substituting the desired physical property for the water tolerance terms. When the expression does not hold for a property of a solution, the solution is said to be "non-ideal" with respect to that property. For solutions which can be considered as binary, "blending values" are sometimes used to express the effect of mixing upon the properties. The blending value is usually assigned to the minor component of the system; the minor component assumed to be responsible for all the deviation of the solution from ideality. In this manner, the actual, rather than theoretical, properties of the solution can be calculated. This is especially useful when preparing nonideal mixtures such as gasoline/methanol.

Considering gasoline/methanol mixtures to be binary and methanol to be the minor component, an expression for the blending vapor pressure of methanol (BVP_M) can be derived from equation (1):

$$BVP_M = \frac{VP_S - VP_G F_G}{F_M} \quad (16)$$

where, subscripts S, G, and M are solution, gasoline, and methanol, respectively. The units for the component fractions (F) would normally be moles, but weight is used here for convenience. However, the reported values may be converted to a molar or volume basis from the information given in appendix A. The similar densities of methanol (0.79 g/ml) and gasolines (0.71 to 0.75 g/ml) produce similar volume and weight fractions, but mole fraction will differ considerably from these because of the large difference in molecular weights (methanol is 32.04 and gasoline averages are 95 to 105). Ideal solution vapor pressures and methanol blending vapor pressures were calculated for the base gasolines and their methanol mixtures. Average values are given in table 7. There is a certain amount of variation among the values for different gasolines, but averages are adequately representative of the group since the range of initial vapor pressure for the gasolines is narrow (424 to 586 mmHg). The extent of departure from ideality with respect to vapor pressure is indicated by the large differences between the ideal and measured vapor pressures and by the large blending vapor pressures (as

TABLE 7. - Average deviation of vapor pressures from ideality
(Base gasolines and their methanol mixtures)

	Methanol, wt pct						
	0	3	5	10	15	20	100
MICRO VAPOR PRESSURE, mmHg							
Measured.....	479	622	654	656	657	653	267
Calculated as ideal solution.....	479	473	468	458	447	437	267
Deviation from ideal..	0	149	186	198	210	216	0
METHANOL BLENDING VAPOR PRESSURE, psi							
From ERVP data.....	-	111	75	42	31	25	-
From RVP data.....	-	77	57	33	25	21	-

compared to 5.2 psi for air saturated methanol). The bias between micro and Reid vapor pressure measurements of gasoline/methanol mixtures (discussed earlier in connection with figure 13) appears in this table as a difference between the methanol blending vapor pressures calculated from ERVP and those calculated from RVP.

Antiknock Quality of Gasoline/Methanol Solutions

Antiknock quality or octane number is a property important to the use of fuels in internal combustion engines. In general, the fuel for a spark-ignited internal combustion engine must possess a minimum level octane number for the engine to perform satisfactorily and, as a rule, the greater the octane number the more efficiently an engine can be designed or adjusted to deliver power and economy. Conversely, the higher the octane number required, the more costly the hydrocarbon portion of the fuel is to produce in terms of processing energy requirements.

Methanol has been reported to have octane values (2, 5) of from 86 to 92 motor octane number (MON) and 106 to 115 research octane number (RON). These octane values are excellent in comparison to the majority of individual hydrocarbons in gasolines. In addition, methanol and gasoline form nonideal mixtures with respect to octane number just as for many other properties. This nonideal behavior results in an additional benefit in that the actual increase in octane value resulting from the addition of methanol is greater than expected from the amount added and the octane values of the methanol and gasoline taken separately. It is necessary to use a higher value, known as blending octane value, to estimate the effect of methanol addition to a gasoline. The blending octane values for methanol resulting from this study averaged 94 to 95 blending MON and 131 blending RON when added to the base gasolines: at least 2 to 3 MON and 16 RON above the reported values for pure methanol.

The octane numbers for the eight base gasolines and their methanol mixtures are given in table 8. From these data and equation (16) (with vapor pressure replaced by octane number), blending octane values were calculated and are recorded in table 9. Close inspection of the data in tables 8 and 9 at each methanol level shows that no trend exists for octane number and aromatic content of the gasolines. In fact, the differences between octane numbers for the various aromatic levels of a gasoline when mixed with methanol are largely the result of octane number differences between the aromatic levels of the gasolines alone. This indicates that the change in octane value upon addition of methanol to gasoline is independent of fuel composition per se. This independence allows the octane values obtained at the four aromatic levels to be averaged. The average octane values from table 8 have been plotted versus methanol level in figure 14. From 0 to 20 wt-pct methanol, the relationship is essentially linear. Judging from the octane values of the gasolines and that of methanol, one would expect results similar to those shown by the curves. The greater methanol influences (larger octane number increases with methanol addition) reflect greater differences between the base gasoline and methanol octane values. Note the greater octane increase

TABLE 8 . - Octane values for the 83M and 89M series
gasoline and their methanol blends

Gasoline	Methanol, wt pct						Pct methanol vs octane ¹	
	0	3	5	10	15	20	Slope	Intercept
MOTOR OCTANE								
83M-15A	83.4	83.8	84.1	² 85.3	85.3	85.8	0.120	83.4
20A	² 81.2	83.0	83.0	84.2	84.5	85.2	.135	82.6
25A	82.8	83.0	83.2	84.0	84.9	85.4	.140	82.6
30A	82.9	83.1	83.1	84.4	85.3	85.3	.142	82.8
Average	83.0	83.2	83.4	84.2	85.0	85.4	.130	82.9
89M-15A	90.0	-	90.5	90.4	90.7	90.7	0.032	90.1
20A	88.9	-	89.2	89.1	89.7	89.9	.050	88.9
25A	88.5	-	88.6	88.9	89.2	89.2	.040	88.5
30A	88.5	-	88.7	89.0	88.9	88.9	.020	88.6
Average	89.0	-	89.3	89.4	89.6	89.7	.034	89.1
RESEARCH OCTANE								
83M-15A	90.3	91.9	92.6	95.0	96.8	98.1	0.394	90.6
20A	89.3	90.3	91.4	93.0	95.6	96.7	.385	89.3
25A	90.3	91.0	92.4	94.4	96.3	98.1	.401	90.2
30A	91.0	92.3	93.1	94.7	96.9	98.5	.374	91.1
Average	90.2	91.4	92.4	94.3	96.4	97.9	.390	90.3
89M-15A	97.3	-	99.1	100.8	102.6	104.3	0.350	97.3
20A	96.3	-	98.3	99.8	101.3	102.8	.320	96.5
25A	97.4	-	99.0	100.2	101.5	102.8	.266	97.5
30A	96.5	-	98.5	100.1	101.5	102.9	.316	96.7
Average	96.9	-	98.7	100.2	101.7	103.2	.312	97.0

¹ Within methanol concentration limits 3 to 20 wt pct. Octane = slope (pct methanol) + intercept.

² Not used in linear regression or averages.

TABLE 9 . - Blending octane values¹

Fuel	Methanol, wt pct						Average 3 thru 20
	0	3	5	10	15	20	
MOTOR OCTANE							
83M-15A	83	97	97	³ 102	96	95	96
20A	² 81	96	91	99	95	96	95
25A	83	90	91	95	97	96	94
30A	83	90	87	98	99	95	94
Average	83	93	92	97	97	96	95
89M-15A	90	-	100	94	95	94	96
20A	89	-	95	91	94	94	94
25A	89	-	91	93	93	92	92
30A	89	-	93	94	91	91	92
Average	89	-	95	93	93	93	94
RESEARCH OCTANE							
83M-15A	90	144	136	137	134	129	134
20A	89	123	131	126	131	126	129
25A	90	114	132	131	130	129	131
30A	91	134	133	128	130	129	130
Average	90	129	133	131	131	128	131
89M-15A	97	-	133	132	133	132	133
20A	96	-	136	131	130	129	132
25A	97	-	129	125	125	124	126
30A	97	-	137	134	131	129	133
Average	97	-	134	131	130	129	131

¹ (Blending value)(Fraction methanol) + (Base gasoline value)
(Fraction base) = octane value of mixture.

² Intercept of linear regression (82.6) used to calculate
blending values and average.

³ Not used in averages.

FIGURE 14. - Effect of Methanol Addition on the Octane Value of Gasolines.

for 83M with methanol addition to the two gasolines and for RON when comparing the two rating methods.

The linear increase of octane value with methanol addition, for the range of values shown in figure 14, is convenient for formulating gasoline/methanol mixtures to octane number specifications. The linearity allows the octane value of any mixture from 0 to 20 wt-pct methanol to be determined from the octane number of the 83 to 89 MON or 90 to 97 RON gasoline and methanol blending octane numbers of 94 for MON and 131 for RON (table 9).

SUMMARY AND CONCLUSIONS

Results in this study of the physical properties of gasoline/methanol mixtures supplement previously available data in the areas of miscibility, distillation, vapor pressure, and antiknock quality. Most of the physical property data (other than the data for miscibility) contained in this report were generated from measurements of eight specially blended gasolines and their methanol mixtures. The lead-free fuels included two octane levels (83 and 89 MON), four aromatic content levels (15, 20, 25, and 30 vol pct), five methanol levels (3, 5, 10, 15, and 20 wt-pct), and vapor pressures and distillation characteristics similar to commercial gasolines. Other materials were evaluated to supply additional miscibility data.

Standard ASTM methods were used to measure distillation characteristics, vapor pressures, and octane numbers with slight variations in vapor-pressure measurement procedures to ensure that single-phase solutions were being tested. A cloud-point temperature method was developed in this laboratory to measure gasoline/methanol/water miscibility.

The complex effects of methanol upon the various physical properties of gasolines make it desirable to list the observations and conclusions resulting from the study under separate physical property headings.

Water Tolerance (Miscibility of Gasoline/Methanol/Water)

Some general observations may be made from families of water tolerance curves (cloud point temperature versus water concentration). Experimental limits are 5 to 20 wt-pct methanol and 0° to 70° F.

1. At a given methanol level, the slope of the curve is inversely related to the water tolerance of the solution,
2. for any single hydrocarbon mixture, the slope of the curve decreases as the methanol level is increased, and
3. at very low water concentrations (less than 0.035 wt-pct), hydrocarbons having intermediate water tolerances will show a direct relationship between methanol level and cloud point temperature; but at water concentrations above 0.08 wt-pct, the relationship is inverse.

The water tolerances of certain hydrocarbon/methanol mixtures containing more than a single hydrocarbon deviate from ideality in that the minor hydrocarbon component exerts less influence than is expected assuming no solubility interaction. Gasoline composition, being a much more complex mixture however, is such that valid water tolerance estimates can be made. The precision of water tolerance estimates decreases as the methanol level is raised from 5 to 20 wt-pct of the gasoline/methanol mixture.

Distillation Characteristics

When methanol is added to gasoline, the formation of minimum boiling hydrocarbon/methanol azeotropes causes a portion of the ASTM D86 distillation curve to be substantially altered. Front-end distillation temperatures are lowered, and the fraction of the curve affected greatly depends upon the fraction of methanol present and the shape and position of the base gasoline curve. Portions of the azeotropic distillation curve may be estimated from that of the gasoline-distillation curve. Front-end temperature depression (the difference between hydrocarbon and azeotropic boiling temperatures) causes the distillation curve to break sharply when the methanol is depleted. The mixture curve then approaches and follows the gasoline curve, but azeotropic removal of some higher boiling hydrocarbons at temperatures below their normal boiling points causes the mixture distillation temperature to continue to be slightly depressed.

Vapor Pressure

The vapor pressure range of the eight base gasolines (424 to 585 mmHg) was slightly narrower and did not quite coincide with that of normally marketed gasolines if both summer and winter grades are considered. The difference between these gasolines and normally marketed gasolines, however, should not be enough to cause significant deviation from the experimental evidence from which the following conclusions were drawn:

1. Addition of 5 to 20 wt-pct of methanol to gasoline increases the vapor pressure about 180 mmHg with as little as the first 3 wt-pct accounting for about 96 pct of the increase,
2. the magnitude of the gasoline vapor pressure and the composition of the gasoline has only small influences upon the methanol effect, and
3. Reid and micro vapor pressure measurements agree for gasolines, but for gasoline/methanol mixtures, RVP measurements of this study are about 1.0 psi lower than MVP measurements.

Note that the radical influence of methanol upon the vapor pressure and distillation characteristics of gasoline may require revision of established gasoline volatility/engine performance correlations for application to gasoline/methanol mixtures.

Antiknock Quality

Compared to vapor pressure and distillation characteristics, the octane value deviation of gasoline/methanol mixtures from ideality is small. A small increase in octane value obtained by methanol addition, however, may represent a substantial savings in production cost of the gasoline hydrocarbons. The average increase in octane number for 20 wt-pct methanol in 83 and 89 MON gasolines was found to be 2.6 and 0.7 MON, respectively. Measured as RON, the increases were 7.8 and 6.2 RON for 90 and 97 RON gasolines, the greater increase again for the lower octane gasoline. The methanol effect in terms of antiknock quality is:

1. Dependent upon the octane level of the gasoline, but
2. at a given octane level, independent of normal gasoline composition.

Methanol is a good octane improver, especially for low-octane gasolines. The octane increase with methanol addition up to 20 wt-pct is essentially linear for 83 to 89 MON and 90 to 97 RON gasoline. This linearity gives nearly constant blending octane numbers for methanol, and averages of 94 for MON and 131 for RON give reasonably good estimates of the octane values of mixtures containing 0 to 20 wt pct methanol.

REFERENCES

1. U.S. Environmental Protection Agency. Current Status of Alternative Automotive Power Systems and Fuels. Vol 3. Alternative Nonpetroleum-Based Fuels. Section 4--Methanol and Methanol-Gasoline Blends. EPA 460/3-74-013-C, July 1974.
2. Johnson, R. T. and R. K. Riley. Single Cylinder Spark Ignition Engine Study of the Octane, Emissions, and Fuel Economy Characteristics of Methanol/Gasoline Blends. Pres. at the SAE Automotive Engineering Congress and Exposition, Detroit, Mich., Feb. 23-27, 1976, SAE Paper No. 760377, 1976.
3. Wigg, E. E., and R. S. Lunt. Methanol as a Gasoline Extender - Fuel Economy, Emissions, and High Temperature Driveability. Pres. at the SAE Automotive Engineering Meeting, Toronto, Canada, October 21-25, 1974, SAE Paper No. 741008, 1974.
4. The Mitre Corporation. Survey of Alcohol Fuel Technology Interim Report. Report No. M74-61 Rev. 1, July 1974.
5. American Petroleum Institute. Use of Alcohol in Motor Gasoline - A Review. API Publication No. 4082, Committee for Air and Water Conservation, August 1971.
6. Methanol as an Alternate Fuel. Vol II. Compilation of Papers presented at the Engineering Foundation Conference, New England College, Henniker, New Hampshire, July 7-12, 1974
- 6a. Conference Paper 1.A.2. White, J. R., C. N. Rowe, and W. J. Koehl. Physico-Chemical Properties of Methanol Related to Fuel Use. Mobile Research and Development Corp.
- 6b. Conference Paper 1.C.1. Lindquist, R. H. and J. C. Ingamells. Methanol/Gasoline Blends - A Fuel Supplier's Viewpoint. Chevron Research Company. ny.
7. Allsup, J. R. Experimental Results Using Methanol and Methanol/Gasoline Blends as Automotive Engine Fuel. BERC/RI-76/15
8. Dimitriadis, B., C. J. Raible, and C. A. Wilson. Interpretation of Gas Chromatographic Spectra in Routine Analysis of Exhaust Hydrocarbons. BuMines/RI-7700, 1972.
9. Meyer, A. S., Jr. and C. M. Boyd. Determination of Water by Titration with Coulometrically generated Karl Fischer Reagent. Analytical Chemistry, v. 31, No. 2, February 1959, pp 215-219.
10. American Society for Testing and Materials. 1974 Annual ASTM Book of Standards, Part 23. Test for Distillation of Petroleum Products D86;

Test for Vapor Pressure of Petroleum Products (Reid Method) D 323. 1974 Annual ASTM Book of Standards, Part 24. Vapor Pressure of Petroleum Products (micromethod) (MVP) D 2551. ASTM Manual for Rating Motor Diesel and Aviation Fuels, Fourth Edition, 1974. Test for Knock Characteristics of Motor Fuels by the Research Method (RON) D 2699; Test for Knock Characteristics of Motor and Aviation-Type Fuels by the Motor Method (MON) D 2700.

APPENDIX A
DETAILED COMPOSITION OF 8 SPECIAL GASOLINES
SUMMARY OF DATA OBTAINED FROM GLC ANALYSIS

TABLE A-1. - Detailed hydrocarbon analysis

Hydrocarbon name	Fuel designation								5-G vehicle study gasoline	LA-74 ^{1/} regular no-lead gasoline
	83M-30A	89M-25A	83M-25A	89M-20A	89M-30A	89M-15A	83M-20A	83M-15A		
Propane.....	0.01	-	-	-	-	-	-	-	0.04	0.14
Isobutane.....	.08	0.09	0.07	0.11	0.21	0.09	0.07	0.09	.10	.85
Isobutylene.....	.00	.00	.00	.00	.00	-	.00	.00	.01	.11
1-Butene.....	.00	.00	.00	.00	.00	-	.00	.00	.01	.11
n-Butane.....	3.76	4.98	4.85	6.99	11.98	5.84	4.35	5.35	5.69	4.32
t-2-Butene.....	-	-	-	-	-	-	-	-	.12	.33
Neopentane.....	.06	.16	.08	.13	.37	.18	.07	.08	-	-
C-2-butene.....	.02	-	.02	.09	-	-	.02	.02	.08	.28
3-M-1-butene.....	.02	.01	.03	.02	.01	.00	.03	.03	.03	.14
Isopentane.....	14.70	13.96	5.75	25.85	2.28	16.66	10.09	11.26	3.61	10.75
1-Pentene.....	.27	.22	.19	.12	.10	.02	.24	.25	.14	.58
2-M-1-butene.....	.27	.15	.26	.13	.12	.03	.30	.29	.19	.77
2-M-1,3-Butadiene.....	.00	.01	.00	.04	.00	-	.00	.00	.00	-
n-Pentane.....	6.00	1.52	12.65	1.58	.47	1.28	7.70	10.48	12.25	6.62
t-2-Pentene.....	.53	-	.56	.22	.23	-	.58	.63	.64	-
C-2-pentene.....	.37	.11	.42	.15	.14	.03	.40	.47	.34	.60
2-M-2-butene.....	.68	.27	.69	.29	.35	.05	.76	.76	.49	1.59
3,3-Dimethylbutene.....	.00	.00	.01	.00	.00	-	.01	.00	.00	-
2,2-Dimethylbutane.....	.67	.52	.03	.29	.03	.62	.04	.79	1.82	.31
Cyclopentene.....	.10	.04	.11	.04	.05	.01	.12	.12	.06	.22
4-Methyl-1-pentene.....	.03	.01	.03	.01	.02	.00	.04	.04	.02	.10
3-Methyl-1-pentene.....	.03	.01	.03	.01	.02	.00	.04	.04	.02	.10
4,MC-2-pentene.....	.02	-	.03	-	.01	-	.05	-	.03	-
2,3-Dimethyl-1-butene.....	.06	-	.05	-	.01	-	.05	-	.03	-
Cyclopentane.....	.07	10.04	.09	5.45	.03	11.33	.07	14.78	.05	.86
2,3-Dimethylbutane.....	.53	1.02	.14	.43	.53	7.05	.50	.93	3.31	1.28
2-Methylcyclopentane.....	2.72	1.62	.66	.93	.55	1.92	.89	2.48	7.69	4.80
2-Methyl-1-pentene.....	.14	.05	.14	.05	.06	.02	.15	.15	.07	.20
3-Methylpentane.....	1.23	.81	.41	.50	.34	.97	.50	1.41	3.25	3.35
1-Hexene.....	.35	.19	.17	.11	.08	.02	.21	.22	.36	-
Unknown C ₆ olefin.....	.54	-	.12	-	.06	-	.25	.19	-	-
Cyclo-3-hexene.....	.08	.03	.08	.03	.03	.00	.08	.09	.05	.27
trans-3-Hexene.....	.13	.05	.15	.05	.06	.00	.16	.15	.06	-
3-Methylcyclopentene.....	-	-	-	.05	-	-	.08	.06	.06	-
2-Methyl-2-pentene.....	.32	.12	.33	.07	.15	.02	.28	.29	.13	-
3-Methylcyclopentene.....	.25	.09	.26	.09	.11	.02	.29	.29	.13	-
n-Hexane.....	.58	.28	.54	.23	.27	.11	.59	.67	1.22	3.79
4,4,DM-1-pentene.....	-	-	-	-	-	-	.14	-	.12	-
trans-2-Hexene.....	-	.07	-	.06	.07	.03	-	-	-	.74
cyclo-2-Hexene.....	.17	.06	.17	.06	.08	.01	.19	.19	.09	-
3,MT-2-pentene.....	.21	.07	.22	.08	.09	.01	.25	.24	.11	.34
44DMT2pentene.....	-	.00	-	.00	.00	.00	-	-	.00	-
Methylcyclopentane.....	.33	.19	.28	.18	.23	.03	.27	.30	.38	2.63
33DM-1-pentene.....	.12	-	.16	-	-	-	.22	.18	-	-
2,2-Dimethylpentane.....	.10	.07	.14	.05	.08	.01	.14	.07	.08	.25
2,3-Dimethyl-2-butene.....	.05	-	.03	-	-	-	.05	.05	-	-
Benzene.....	.37	.13	.38	.12	.15	.06	.40	.40	.27	.98
2,4-Dimethylpentane.....	.50	1.31	.26	.57	1.52	1.53	1.26	.82	1.88	.84
223,DMbutane.....	.01	.02	.02	.01	.03	.03	.03	.02	.02	.11
24DM-1-pentene.....	.01	-	.01	.00	.00	-	.01	.01	.01	-
1,MCYpentene.....	.32	.12	.32	.12	.15	.02	.34	.35	.17	.49
2,4,DM-2-pentene.....	.01	.00	.01	.00	.00	.00	.01	.01	.00	.02
3-Ethyl-1-pentene.....	.01	.00	.01	.00	.00	.00	.01	.01	.00	.02
3-Methyl-1-hexene.....	.01	.00	.01	.00	.00	.00	.01	.01	.00	.02
2,3,DM-1-pentene.....	.01	.00	.01	.00	.01	.01	.01	.01	.00	-
2,MT-3-hexene.....	.02	.01	.01	.01	.01	.00	.02	.02	.01	-
5-Methyl-1-hexene.....	.02	.01	.01	.01	.01	.00	.02	.02	.01	-
Unknown C ₇ olefin.....	-	.02	-	.01	.03	.00	-	-	.01	.09
3,3-Dimethylpentane.....	-	-	-	-	-	-	-	-	-	.63
Cyclohexane.....	5.91	.12	11.89	.01	.15	.02	10.62	.20	.08	-
4-Methyl-1-hexene.....	-	-	-	.08	-	-	-	-	.07	.05
4,MC-2-hexene.....	.08	.01	.07	.01	.01	-	.06	.05	.01	-
4,MT-2-hexene.....	.08	.01	.07	.01	.01	-	.06	.05	.01	-
5,MT-2-hexene.....	.06	.01	.06	.01	.01	.00	.07	.04	.01	.05
Cyclohexene.....	.05	.02	.05	.02	.03	.00	.05	.05	.03	-
2-Methylhexene.....	.92	.84	.84	.60	8.74	4.43	.99	.92	.28	1.84
1,1-DMCYpentane.....	-	-	-	-	-	-	.39	-	-	-
2,3-Dimethylpentane.....	.88	2.65	.39	2.89	-	-	2.03	1.41	5.25	1.00
3-Methylhexane.....	1.08	.91	.92	.66	1.29	.29	1.05	1.00	.92	2.04
1,C-3-DMCYpentane.....	-	.13	-	.12	.06	.04	-	-	.09	.51
2-Methyl-1-hexene.....	.17	.03	.12	.01	.01	.01	.14	.14	.07	-
3,4,DMT-2-pentene.....	.17	.03	.12	.01	.01	.01	.14	.14	.07	-
1,T-3-DMCYpentane.....	.18	.13	.11	.10	.17	.03	.11	.14	.08	.51
1-Heptene.....	.08	.03	.07	.02	.04	.01	.08	.07	.07	-
2,E-1-pentene.....	.07	.03	.07	.02	.04	.01	.08	.07	.07	-
3-Ethylpentane.....	.18	.08	.09	.06	.11	.02	.10	.11	-	.31
3,MT-2-hexene.....	.14	.03	.08	.02	.04	.01	.11	.06	-	-

^{1/} The West Coast gasoline composition from California Air Resources Board, Feb. 1975.

TABLE A-1. - Detailed hydrocarbon analysis--Continued

Hydrocarbon name	Fuel designation								5-G vehi- cle study gasoline	LA-741/ regular no- lead gasoline
	83M-30A	89M-25A	83M-25A	89M-20A	89M-30A	89M-15A	83M-20A	83M-15A		
1,T-2-DMCPentane.....	0.18	0.08	0.09	0.06	0.11	0.02	0.10	0.11	-	0.31
C3Heptane.....	.16	-	.19	-	-	-	.33	.40	0.20	.16
3,MT-3-hexene.....	.07	-	.05	-	-	-	.09	.13	-	-
2,Methyl-2-hexene.....	.08	-	.05	-	-	-	.10	.14	-	-
3,Methylcyclo-3-hexene	.07	-	.05	-	-	-	.09	.13	-	-
3,Ethyl-2-pentene.....	.03	.08	.05	.09	.11	.04	.04	.07	.02	-
trans-2-Heptene.....	.12	.08	.10	.08	.10	-	.10	.11	.06	.04
3,Methylcyclo-2-hexene	.17	-	.09	-	-	-	.08	.13	.05	-
n-Heptane.....	1.80	.98	.97	.70	1.24	1.44	1.07	1.00	.87	1.85
2,2,4-TRIMPentane.....	1.74	17.40	12.02	21.53	22.78	17.71	5.16	9.94	8.00	1.57
2,3-DM-2-pentene.....	.07	.06	.06	.06	.08	-	.06	.07	.03	.06
cis-2-Heptene.....	.07	.06	.06	.06	.08	-	.06	.07	.03	.06
Unknown C ₈ olefin.....	.30	.03	.14	.06	.07	.02	.20	.16	.01	.30
1,C-2-DMCPentane.....	.06	.05	.04	.05	.08	.01	.03	.05	.06	.17
Methylcyclopentane.....	.45	.13	.21	.11	.18	.03	.23	.24	.19	.39
2,2-Dimethylhexane.....	.39	.12	.19	.10	.16	.03	.20	.21	.17	.34
2,5-DMT-3-hexene.....	.03	.01	.02	.01	.01	.00	.02	.03	.01	-
2,5-Dimethylhexane.....	.25	.43	.20	.49	.80	.46	.65	.43	.67	.50
Ethylcyclopentane.....	.16	-	.12	-	-	-	-	-	-	-
2,4-Dimethylhexane.....	.38	.53	.33	.60	1.03	.65	.89	.51	.86	.39
2,2,3-trimethylpentane	.04	.11	.03	.11	.22	.15	.17	.08	.16	.08
1,T-2-C-4-TMCPentane...	.10	.05	.09	.04	.07	.02	.10	.09	.07	.17
Toluene.....	17.25	1.89	10.42	1.49	2.39	15.37	9.63	7.15	16.01	6.55
3,3-Dimethylhexane.....	-	-	-	-	-	-	.07	-	-	-
1,T-2-C-3-TMCPentane...	.18	.07	.04	.06	.11	-	.04	.04	-	.69
2,3,4-Trimethylpentane	.67	1.42	1.18	.84	2.02	2.17	3.20	.94	1.52	.60
2,3,3-Trimethylpentane	.33	.87	.74	.40	1.12	1.45	2.17	.58	.94	.44
1,1,2-TMCPentane.....	.47	-	.69	-	-	-	-	.58	.05	-
2,3-Dimethylhexane.....	-	.55	-	.30	.69	.88	1.50	-	.72	.68
2-Methylheptane.....	.65	.36	.80	.30	.46	.28	.69	.60	.35	.32
4-Methylheptane.....	.33	.18	.40	.15	.23	.14	.34	.30	.20	.14
3,4-Dimethylhexane.....	.13	.10	.17	.06	.13	.18	.31	.15	1.06	-
3-Methylheptane.....	.94	.54	1.14	.44	.68	.39	.99	.86	.52	.93
2,2,5-Trimethylhexane...	.34	.28	.62	.12	.28	1.03	1.84	.56	.01	.28
1,T-4-DMCYhexane.....	-	-	-	-	-	-	-	-	-	.15
1,1-DMCYhexane.....	-	-	-	-	-	-	-	-	-	.15
1-Octene.....	.04	-	-	-	-	-	-	.04	-	-
1,C-3-DMCYhexane.....	.13	.09	.12	.08	.11	.04	.14	.13	.18	-
trans-4-Octene.....	.13	-	.14	-	-	-	.15	.14	-	-
1,MT-3-ECYPentane.....	.03	.03	.04	.03	.04	.01	.04	.05	.06	.10
2,2,4-Trimethylhexane...	.09	.05	.07	.08	.06	.03	.09	.09	.16	.19
Cycloheptane.....	-	-	-	.02	-	.02	-	-	.01	.07
1-M-1-ECYPentane.....	.01	.01	.01	.01	.01	.00	.01	.01	-	-
Unknown C ₈ olefin.....	.34	.14	.35	.09	.19	.02	.37	.33	.04	.03
Unknown C ₈ paraffin...	-	-	.04	.01	.00	.00	-	-	-	.05
1-C-2-C-3-TMCPentane...	-	-	-	-	-	-	-	-	.05	-
trans-2-Octene.....	.08	-	.08	-	-	-	.09	.09	-	-
n-Octane.....	.75	.48	.73	.29	.61	.21	.79	.72	.84	.77
1-C-4-DMCYhexane.....	-	-	-	-	-	-	-	-	-	.11
1-T-3-DMCYhexane.....	.05	.02	.05	.02	.03	.01	.05	.05	.04	-
2,4,4-Transmethylhexane	.01	.01	.02	.00	.01	.03	.05	.02	.01	-
Isopropylcyclopentane...	.01	.00	.00	.00	.00	-	.00	.01	.00	-
2,3,5-Transmethylhexane	.05	.05	.13	.02	.05	.18	.34	.09	.07	.03
2,2-Dimethylheptane...	.02	.02	.02	.01	.02	.00	.02	.02	.02	.27
2,4-Dimethylheptane...	.04	.04	.05	.03	.05	.03	.07	.05	.07	.07
2,2,3-Transmethylhexane	.04	.04	.05	.03	.05	.03	.07	.05	.07	.07
2,2-DM-3-Epentane.....	.01	.01	.01	.01	.01	.00	.01	.02	.01	.02
2-M-4-Ehexane.....	.01	.01	.01	.01	.01	.00	.01	.02	.01	.02
2,6-Dimethylheptane...	.08	.05	.08	.03	.05	.03	.10	.09	.07	.11
n-Propylcyclopentane...	.03	.02	.02	.02	.02	.00	.03	.03	.02	.04
Ethylcyclohexane.....	.08	.06	.09	.04	.06	.04	.13	.09	.20	-
2,5-Dimethylheptane...	.07	.05	.08	.04	.05	.03	.11	.08	.03	-
3,5-Dimerhylheptanc...	.07	.05	.08	.04	.05	.03	.11	.08	.03	-
Ethylbenzene.....	1.25	1.52	1.32	1.47	1.56	.19	1.19	.99	.94	1.42
1,1,3-TMCPentane.....	.05	.03	.04	.03	.03	.01	.06	.06	.03	.09
2,3,3-transmethylhexane	.02	.02	.02	.02	.02	.00	.03	.02	.01	.04
1,C-3-C-5-TMCPentane...	.05	.02	.04	.02	.01	-	.08	.08	.03	-
2-M-3-Ehexane.....	.00	.01	.01	.00	.00	.01	.02	.00	.00	-
Propylxylene.....	2.12	4.29	2.57	4.18	3.49	.40	1.56	.80	1.05	1.62
m-Xylene.....	5.41	8.31	6.53	8.73	8.16	1.01	4.16	1.74	2.48	4.28
2,3-Dimethylheptane...	-	-	-	-	-	-	-	-	.12	-
3,4-Dimethylheptane...	.22	-	-	-	-	.05	.17	.14	.14	.15
4-Methyloctane.....	.21	.22	.19	.19	.25	.04	.22	.20	.22	.20
2-Methyloctane.....	.22	.19	.21	.16	.22	.04	.24	.22	.23	.25
3-Ethylheptane.....	.06	.07	.05	.07	.08	.01	.06	.06	.06	.07
3-Methyloctane.....	.24	.21	.27	.17	.25	.08	.34	.25	.31	.26
Orthoxylene.....	3.18	2.49	3.28	2.37	2.43	.69	2.06	1.04	1.33	2.24

1/ The West Coast gasoline composition from California Air Resources Board, Feb. 1971.

TABLE A-1. - Detailed hydrocarbon analysis--Continued

Hydrocarbon name	Fuel designation								5-G vehi- cle study gasoline	LA-74 ^{1/} regular no- lead gasoline
	83M-30A	89M-25A	83M-25A	89M-20A	89M-30A	89M-15A	83M-20A	83M-15A		
2,2,4, TMheptane.....	0.28	-	0.19	-	-	-	0.40	0.06	0.06	-
2,2,6, TMheptane.....	.05	.07	.15	.03	.06	.12	.31	.04	.09	-
2,2,5 TMheptane.....	.05	.07	.15	.03	.06	.12	.31	.04	.09	-
Unknown C ₉ olefin....	.48	.11	.23	.08	.09	.02	.26	.24	.14	0.09
Unknown C ₉ paraffin..	.06	.07	.04	.13	.12	.03	.05	.05	-	.22
2,5,5, TMheptane.....	.03	.04	.09	.01	.03	.07	.18	.03	.06	.03
2,4,4, TMheptane.....	.03	.04	.09	.01	.03	.07	.18	.03	.06	.03
Isopropylbenzene.....	.07	.52	.08	.06	.62	.00	.10	.03	.02	.04
Nonane.....	.23	.19	.23	.15	.26	.03	.26	.24	.27	.28
3,3,5, TMheptane.....	.01	.01	.02	.01	.01	.01	.04	.01	.02	.04
2,4,5, TMheptane.....	.03	.02	.05	.01	.02	.04	.11	.02	.04	.02
2,3,5 TMheptane.....	.03	.02	.05	.01	.02	.04	.11	.02	.04	.02
Unknown C ₁₀ olefin...	-	-	-	.01	.01	.00	-	-	-	-
Unknown C ₁₀ paraffin..	.19	.18	.20	.11	.22	.06	.26	.26	.22	.25
n-Propylbenzene.....	.20	1.51	.20	.11	2.01	.03	.20	.18	.17	.40
2,2,3,3, TETRAMhexane.	.03	-	.03	.02	-	.01	.03	.03	.03	.03
2,6, DMoctane.....	.03	-	.03	.02	-	.01	.03	.03	.03	.03
1, Methyl-3-benzene...	.61	2.30	.63	.33	3.04	.09	.68	.62	.62	1.49
1, Methyl-4-benzene...	.30	.91	.30	.16	1.21	.04	.32	.31	.28	.75
3,3,4, TMheptane.....	.07	.06	.02	.02	.07	.03	.05	.03	.05	.04
3,4,4, TMheptane.....	.06	.06	.01	.02	.07	.03	.04	.03	.05	.04
3,4,5, TMheptane.....	.06	.06	.01	.02	.07	.03	.04	.03	.05	.04
1, Methyl-2-ethylbenzene	.15	.62	.19	.12	.84	.03	.19	.18	.19	.53
5, Mnonane.....	.05	-	.03	-	-	-	.03	.03	.02	-
4, Mnonane.....	.05	-	.06	.04	-	.01	.06	.06	.06	.09
1,3,5, TMbenzene.....	.32	.58	.33	.20	.78	.05	.36	.35	.35	.93
2, Mnonane.....	-	-	-	-	-	-	-	-	.04	.12
TERTbutylbenzene.....	-	-	-	-	-	-	-	-	.01	-
3Mnonane.....	.04	.02	.00	.01	.02	.01	.01	.02	.10	-
Unknown C ₁₀ paraffin..	.25	.19	.09	.10	.23	.05	.13	.14	.04	.02
1,2,4, TMbenzene.....	.89	1.52	.91	.50	2.00	.15	1.00	.90	.97	2.72
SECbutylbenzene.....	.04	.05	.03	.02	.06	.00	.03	.05	.03	-
Isobutylbenzene.....	.04	.05	.03	.02	.06	.00	.03	.05	.03	-
1-M-3, isopropylbenzene	-	.10	.01	-	.13	-	.00	.01	.00	-
n-Decane.....	.14	.07	.10	.06	.10	.02	.11	.10	.10	.19
1,2,3, TMbenzene.....	.09	.17	.09	.05	.22	.02	.10	.09	.09	.28
1-M-4, isopropylbenzene	.09	.15	.08	.04	.20	.01	.09	.09	.08	.25
1-M-2, isopropylbenzene	.07	.08	.06	.03	.09	.00	.07	.07	.05	.15
Indane.....	.07	.08	.07	.03	.10	.01	.07	.08	.05	.17
Unknown C ₁₁ alkylate.	.14	.01	.05	.01	-	.00	.06	.05	-	.04
Unknown C ₁₀ aromatic.	-	-	-	-	-	-	.01	-	-	-
1,3, Diethylbenzene...	.05	.09	.05	.02	.12	.01	.05	.07	.04	.17
1, M,3, n-propylbenzene	.12	.10	.12	.06	.13	.02	.13	.12	.10	.31
n-Butylbenzene.....	-	.03	.04	.02	.04	.00	.04	.04	.04	.14
1,2, Diethylbenzene...	-	-	-	-	-	-	-	-	.01	.11
1-M-4, n-propylbenzene	-	-	-	-	-	-	-	-	.01	.11
1,4, Diethylbenzene...	.08	.12	.08	.04	.17	.01	.08	.08	.06	-
Unknown C ₁₁ paraffin..	.04	.07	.04	.03	.10	.00	-	.01	.06	-
1-M-2, n-propylbenzene	.03	.03	.03	.02	.04	.00	.04	.04	-	.10
1,3, DM,5, ethylbenzene	.18	.15	.12	.07	.19	.02	.15	.13	.12	.37
2-M-Indane.....	.02	.00	-	.00	.01	-	-	-	.00	.07
1,4, DM,2, ethylbenzene	.03	.01	.03	-	.01	-	.08	.04	.03	.22
1-M, Indane.....	.06	.06	.09	.03	.09	.01	.08	.06	.06	.14
1-M-3-TERTbutylbenzene	.09	.03	.05	.02	.04	.00	.03	.06	.03	-
1,3, DM,4, ethylbenzene	.08	.08	.07	.04	.11	.01	.07	.09	.09	.24
1,3, DM,2, ethylbenzene	.08	.11	.07	.04	.14	.01	.08	.08	.07	.22
1,2, DM,4, ethylbenzene	.08	.11	.07	.04	.14	.01	.08	.08	.07	.22
Unknown C ₁₁ paraffin..	-	-	-	-	-	-	.00	-	.01	-
Unknown C ₁₁ olefin	.04	.13	.03	.02	.11	.00	.01	.03	-	-
1,2, DM,3, ethylbenzene	.03	-	.09	-	-	-	.05	.04	.02	-
n-undecane.....	.03	.06	.03	.02	.08	.00	.04	.03	.03	.14
1,2,4,5, TETRAMbenzene	.05	.06	.05	.03	.07	.01	.06	.06	.05	.19
1,2,3,5, TETRAMbenzene	.11	.09	.10	.05	.12	.01	.12	.10	.10	.33
Unknown C ₁₂ paraffin..	.02	-	.01	-	-	-	.01	.01	.01	.06
Isopentylbenzene.....	.05	-	.03	.02	.03	.00	.06	.05	.03	.14
Unknown C ₁₁ aromatic.	.01	.02	.01	.01	.06	-	.01	.01	-	-
5-M, Indane.....	.07	.03	.08	.03	.04	.00	.08	.08	.05	.19
4-M, Indane.....	.01	.01	.01	.01	.01	.00	.01	.01	-	.04
n-pentylbenzene.....	.03	.01	.04	.01	.02	-	.02	.03	.02	.09
1,2,3,4, TETRAMbenzene	.02	.02	.02	.01	.02	.00	.02	.03	.02	.11
Tetralin.....	.00	.00	.00	.00	.01	-	.01	.01	.00	.10
Unknown C ₁₂ paraffin..	-	-	-	-	-	-	-	-	.01	.11
Unknown C ₁₁ aromatic.	.03	-	.03	-	-	-	.03	.02	-	-
Napthalene.....	.06	.04	.07	.02	.06	.00	.07	.07	.03	.30
1,3, DM,5, TERTbutylbenzene	.01	.01	.01	.00	.01	-	.01	.01	.01	.05
Unknown C ₁₂ paraffin..	.07	-	.02	-	-	-	.03	.03	.01	.10
Unknown C ₁₂ aromatic..	-	.02	-	.02	.04	-	.07	.06	.03	.43
n-dodecane.....	.01	.00	.01	.01	.00	-	.02	.02	.01	.04

^{1/} The West Coast gasoline composition from California Air Resources Board, Feb. 1975.

TABLE A-2. - Molecular weight, boiling point, and hydrocarbon analysis

Fuel	Whole fuel Calc. avg. mole. wt.	Normal Paraffins					Branched Paraffins				Cyclic Paraffins				Total Paraffins			
		Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F	
		Mole	Volume			Mole	Volume			Mole	Volume			Mole	Volume			
PROJECT GASOLINES																		
1	93	12	13	77	111	33	36	92	152	9	8	90	139	54	57	88	148	
2	97	8	7	73	91	49	54	99	172	11	8	73	130	68	69	92	155	
3	95	20	18	73	98	30	36	106	194	15	13	87	134	65	67	92	162	
4	93	9	9	68	72	60	65	94	154	7	5	75	135	76	79	89	142	
5	102	15	11	67	68	49	55	109	205	2	2	99	207	66	68	99	174	
6	91	9	7	69	78	61	68	97	165	12	9	71	123	82	84	90	150	
7	96	14	14	75	103	40	46	103	191	13	11	87	182	67	71	94	170	
8	90	18	17	73	97	39	45	98	170	17	13	74	134	74	75	86	144	
COMMERCIAL HYDROCARBON MIXTURES																		
1-P	73	0	0	-	-	21	27	86	-	79	73	70	-	100	100	73	-	
4-P	86	6	6	86	-	94	94	86	-	0	0	-	-	-	-	-	-	
6-P	100	39	40	100	-	25	26	100	-	36	34	-	-	100	100	100	-	
REFINERY STOCKS																		
1-R	95	1	1	-	-	5	7	114	240	3	3	112	229	9	11	114	238	
2-R	116	17	17	86	152	33	37	98	182	4	4	90	180	54	58	94	172	
4-R	101	16	16	85	-	36	40	102	-	2	2	87	-	54	58	96	-	
5-R	95	7	7	86	149	36	39	96	171	8	7	96	195	51	53	95	171	
6-R	103	10	10	94	181	43	47	106	204	5	5	100	211	58	62	103	200	
8-R	81	43	43	75	-	34	37	86	-	19	20	86	-	97	97	81	-	
10-R	105	3	2	51	-	25	22	82	-	2	2	110	-	30	26	81	-	
11-R	107	1	1	58	31	99	99	107	201	0	0	-	-	100	100	107	200	
FULL RANGE GASOLINES																		
1-G	91	28	24	70	-	33	37	97	-	5	5	88	-	64	66	85	-	
2-G	95	17	17	75	-	43	46	101	-	6	5	88	-	66	68	93	-	
5-G	93	25	21	73	98	42	46	97	175	2	2	100	213	67	69	89	149	
6-G	94	11	9	66	-	48	52	100	-	4	4	92	-	63	65	94	-	
7-G	97	12	12	80	125	40	45	98	176	3	3	94	192	57	60	94	166	
VOLATILITY PROJECT GASOLINES																		
1-V	93	18	16	70	-	39	44	97	-	5	4	82	-	62	64	88	-	
2-V	94	18	15	69	-	49	56	101	-	5	4	83	-	72	75	92	-	
3-V	92	16	16	74	-	20	22	87	-	5	5	83	-	41	43	81	-	
4-V	88	25	25	66	-	22	22	75	-	4	3	80	-	51	50	71	-	
5-V	88	27	25	66	-	24	24	76	-	4	4	81	-	55	53	72	-	
6-V	95	17	16	75	-	24	26	89	-	5	4	83	-	46	46	84	-	
7-V	86	28	25	66	-	45	51	96	-	5	4	81	-	78	80	82	-	
8-V	92	20	17	69	-	45	48	93	-	6	5	84	-	71	70	85	-	
9-V	88	7	5	67	-	82	84	88	-	2	2	104	-	91	91	87	-	
10-V	88	29	25	67	-	55	58	95	-	7	7	86	-	91	90	85	-	
11-V	88	3	3	68	-	91	93	88	-	< 1	< 1	89	-	94	96	87	-	
12-V	84	2	2	70	-	96	96	84	-	< 1	< 1	86	-	98	98	84	-	

NOTE. - See Table 3 for fuel identification.

TABLE A-2. - Molecular weight, boiling point, and hydrocarbon analysis--Continued

Fuel	Benzene		Toluene		C8 and Greater Aromatics				Total Aromatics			
	Percent		Percent		Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F
	Mole	Volume	Mole	Volume	Mole	Volume			Mole	Volume		
PROJECT GASOLINES												
1	0	0	20	17	17	17	110	301	37	34	101	261
2	0	0	2	2	27	26	112	301	29	28	111	296
3	0	0	10	9	19	18	111	299	29	27	104	273
4	0	0	2	2	19	17	108	290	21	19	107	285
5	< 1	< 1	2	2	29	27	114	306	31	29	112	299
6	0	0	15	13	3	3	112	298	18	16	95	241
7	0	0	10	8	14	14	113	306	24	22	104	273
8	0	0	7	6	10	10	116	313	17	16	105	276
COMMERCIAL HYDROCARBON MIXTURES												
1-P	0	0	0	0	0	0	-	-	0	0	-	-
4-P	0	0	0	0	0	0	-	-	0	0	-	-
6-P	0	0	0	0	0	0	-	-	0	0	-	-
REFINERY STOCKS												
1-R	0	0	81	78	10	11	110	286	91	89	94	237
2-R	5	4	13	11	28	27	-	-	46	42	104	274
4-R	2	1	11	-	32	-	-	-	45	42	107	-
5-R	1	1	4	4	23	21	-	-	25	26	113	304
6-R	1	1	8	6	23	22	116	312	32	29	109	289
8-R	3	3	0	0	0	0	-	-	3	3	84	176
10-R	0	0	0	0	0	0	-	-	0	0	-	-
11-R	0	0	0	0	0	0	-	-	0	0	-	-
FULL RANGE GASOLINES												
1-G	3	-	9	-	20	-	-	-	32	30	105	-
2-G	1	-	7	-	18	-	-	-	26	25	108	-
5-G	0	0	17	15	11	12	113	309	28	27	100	260
6-G	1	-	3	-	14	-	-	-	18	18	114	-
7-G	3	2	9	7	21	22	-	-	33	31	107	281
VOLATILITY PROJECT GASOLINES												
1-V	15	11	4	-	19	-	-	-	38	36	102	-
2-V	15	10	1	-	12	-	-	-	28	25	99	-
3-V	5	3	25	-	29	-	-	-	59	57	99	-
4-V	1	1	8	-	40	-	-	-	49	50	105	-
5-V	1	1	9	-	35	-	-	-	45	47	107	-
6-V	6	-	19	-	29	-	-	-	54	53	105	-
7-V	9	6	< 1	-	13	-	-	-	22	20	99	-
8-V	1	1	2	-	21	-	-	-	24	25	117	-
9-V	< 1	< 1	4	-	5	-	-	-	9	9	104	-
10-V	2	1	1	-	6	-	-	-	9	10	117	-
11-V	< 1	< 1	2	-	2	-	-	-	5	4	107	-
12-V	< 1	< 1	1	-	1	-	-	-	2	2	-	-

NOTE. - See Table 3 for fuel identification.

TABLE A-2. - Molecular weight, boiling point, and hydrocarbon analysis--Continued

Fuel	1-Alkenes				Internal Alkenes				Total Olefins			
	Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F	Percent		Molecular weight	Boiling point, °F
	Mole	Volume			Mole	Volume			Mole	Volume		
PROJECT GASOLINES												
1	2	2	82	140	7	7	91	173	9	9	89	166
2	1	1	78	210	2	2	94	186	3	3	89	167
3	1	1	82	132	5	5	86	159	6	6	85	154
4	0	0	-	-	0	0	-	-	3	2	68	100
5	0	0	-	126	0	0	-	173	3	3	88	165
6	0	0	-	-	0	0	-	-	0	0	-	-
7	2	1	82	133	7	6	89	170	9	7	88	163
8	2	2	83	140	7	7	88	166	9	9	87	161
COMMERCIAL HYDROCARBON MIXTURES												
1-P	0	0	-	-	0	0	-	-	0	0	-	-
4-P	0	0	-	-	0	0	-	-	0	0	-	-
6-P	0	0	-	-	0	0	-	-	0	0	-	-
REFINERY STOCKS												
1-R	0	0	-	-	0	0	-	-	0	0	-	-
2-R	0	0	-	-	0	0	-	-	0	0	-	-
4-R	0	0	-	-	0	0	-	-	1	1	98	-
5-R	6	5	75	105	18	16	79	132	24	21	78	125
6-R	2	2	78	122	8	7	83	147	10	9	82	142
8-R	0	0	-	-	0	0	-	-	0	0	-	-
10-R	3	3	85	-	67	71	116	-	70	74	115	-
11-R	0	0	-	-	0	0	-	-	0	0	-	-
FULL RANGE GASOLINES												
1-G	1	1	76	-	3	3	73	-	4	4	74	-
2-G	2	2	76	-	6	5	75	-	8	7	75	-
5-G	1	1	83	140	4	3	80	137	5	4	81	138
6-G	4	3	73	-	15	14	81	-	19	17	79	-
7-G	2	2	75	108	8	7	79	132	10	9	78	126
VOLATILITY PROJECT GASOLINES												
1-V	0	0	-	-	0	0	-	-	< 1	< 1	-	-
2-V	0	0	-	-	0	0	-	-	0	0	-	-
3-V	0	0	-	-	0	0	-	-	< 1	< 1	-	-
4-V	0	0	-	-	0	0	-	-	0	0	-	-
5-V	0	0	-	-	0	0	-	-	0	0	-	-
6-V	0	0	-	-	0	0	-	-	< 1	< 1	-	-
7-V	0	0	-	-	0	0	-	-	0	0	-	-
8-V	4	4	79	-	1	1	75	-	5	5	-	-
9-V	1	1	74	-	1	1	71	-	2	2	73	-
10-V	0	0	-	-	0	0	-	-	0	0	-	-
11-V	1	1	76	-	< 1	< 1	74	-	1	1	75	-
12-V	0	0	-	-	0	0	-	-	< 1	< 1	70	-

NOTE. - See Table E for fuel identification.

APPENDIX B--DETERMINATION OF CLOUD POINT AND WATER CONTENT OF HYDROCARBON/METHANOL MIXTURES

Generally, the correlation of cloud point temperature and water content was accomplished in three major steps:

1. Determination of the water content of the mixture components (hydrocarbon and methanol),
2. mixing of the components in the desired proportions, and
3. determination of the cloud point at incremental water levels.

Errors within one of these steps produce characteristic changes in the results. An incorrect initial water determination produces a curve shift along the water level axis, significant errors in the hydrocarbon/methanol ratio change the curve slope, and erratic cloud-point determination or water addition results in data scatter.

The precision and repeatability in establishing the relationship is, to an extent, operator dependent. The sharpness of cloud formation depends upon methanol concentration, becoming increasingly difficult to see at lower methanol levels. The cloud continues to form (over a temperature range of about 1 to 3° F) as the solution temperature is lowered, and inconsistent end point readings can be a source of error. The rate of solution cooling can also effect the end point determination and, especially at low methanol levels and reasonable temperature-change rates, the point of cloud formation does not necessarily coincide with the point of cloud disappearance. Vigorous stirring of some hydrocarbon/methanol mixtures causes the solution to have a slightly cloudy appearance even though only a single phase exists. For this reason, it is advantageous always to read the cloud point at the first definitive change in cloudy appearance.

Apparatus

1. Balance with four-decimal-place accuracy for sample weighing
2. Photovolt Aquatest II for water measurement
3. Dual sidearm, coolant-jacketed cloud point test cell (Wheaton Water Jacketed Celstir, 25 ml)
4. Finned-disk magnetic stirring bar and magnetic stirrer
5. Thermocouple operated potentiometric temperature indicator
6. Circulating coolant bath with capability to about -20° F (Neslab RTE-8 Circulating Bath)
7. Dry nitrogen supply

8. Common laboratory items as needed for equipment operation, sample handling, and glassware cleaning

Sample Preparation

The initial water content of premixed hydrocarbons (gasolines and refinery stocks) has been considered to be intractable since treatment to remove water is likely to alter the hydrocarbon composition. However, water can be sufficiently removed from individual hydrocarbons and methanol with relative ease. Two methods of water removal were used for this study: (1) by passing the hydrocarbon or methanol through a column of oven-dried "Linde" type 3A molecular sieve and (2) by distillation. At times, more than a single treatment was necessary.

Individual hydrocarbons with contaminants which slowly reacted with the Aquatest reagent were washed with water and then distilled. This situation was most common with olefins and was indicated by the inability of the instrument to reach a definite end point for an exceptionally long time period. Treatment of these hydrocarbons usually resulted in substantially lower water tolerances.

Procedure

1. Set up the cloud point cell according to figure B-1.

2. Purge the cell with dry nitrogen for at least 5 minutes to remove all moisture.

3. While the cloud point cell is being purged, determine the initial water content of the hydrocarbon and methanol by delivering appropriately sized, weighed aliquots to the Aquatest II¹ from a clean, dry, valved syringe. Record the water content of each.

4. Repeat step 3 until successive samples of both hydrocarbon and methanol agree.

5. In a clean, dry, valved syringe, accurately weigh a volume of the hydrocarbon which, when combined with the desired weight of methanol gives a total volume of 15 to 20 ml. Record the weight of hydrocarbon and syringe.

FIGURE B 1. - Cloud Point Cell.

¹Operating Manual, Aquatest II, Photovolt, 115 Broadway, New York 10010.

6. Discontinue nitrogen purge of the cloud point cell, deliver the hydrocarbon to the cell, and immediately reweigh and record the weight of the syringe.

7. Calculate the weight of hydrocarbon and then the volume of methanol needed to give the desired dry methanol level in the hydrocarbon/methanol/water mixture.

8. Accurately weigh the desired volume of methanol in a clean, dry, valved syringe, deliver the methanol to the cloud point cell, reweigh the syringe, and calculate the weight fractions of methanol and water in the hydrocarbon/methanol/water mixture.

9. Stir the mixture vigorously and, with a light source a few inches to the left or right and slightly to the rear of the cell, observe the clear-cloudy state of the mixture (the most sensitive method is by light scatter of a cloudy mixture). If a clear, single-phase solution is observed, proceed to step 10. If the mixture is cloudy or obviously two-phase, gently warm the cell and contents until a clear, single-phase solution exists or to about 75° F. If two phases are still present at 75° F, it may be possible to obtain data after removing water from the hydrocarbon and/or methanol and beginning with a new, dry sample (see "sample preparation").

10. Open the valve from the circulating coolant bath so that the solution in the cell is cooled rather rapidly and note the approximate temperature at which the solution clouds, then shut off the coolant flow and allow the mixture to warm to a single-phase solution. (This step is unnecessary if the approximate cloud point is already known.)

11. Circulate coolant through the cell so that the contents are cooled at a rate of 5° F/min or less and record the temperature at which the cloudiness appears. Go to step 12. If the solution does not cloud before the lower temperature limit is reached, add a known portion of water, recalculate the water concentration, and when the mixture clears, repeat the cooling process.

12. From this point, incremental portions of water are added (delivery from a 10 µl syringe is convenient) and new cloud-point temperatures obtained until the temperature range is covered. (After each water addition and before each cloud point is read, be sure the cell contents are warmed sufficiently to obtain a clear, single-phase solution.)

13. When the final cloud point temperature is recorded, allow the cell contents to clear and add a weighed amount of the solution to the Aquatest II to verify the final water content.

APPENDIX C

TABULAR DATA--PHASE SEPARATION TEMPERATURES AND CORRESPONDING
WATER CONTENT FOR VARIED CONCENTRATIONS OF METHANOL IN
GASOLINES AND OTHER HYDROCARBONS

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data

<i>Methanol, wt pct</i>	<i>Cloud pt., °F</i>	<i>Water, wt pct</i>		<i>Methanol, wt pct</i>	<i>Cloud pt., °F</i>	<i>Water, wt pct</i>	
<u>83M-15A</u>				<u>83M-15A</u>			
3.0	1.5	0.0154	$K_2 = -25089^*$ $K_1 = 3485$ $K_0 = -45.4$	20.0	48.5	0.0245	$K_2 = 2.50^*$ $K_1 = 173$ $K_0 = 44.3$
"	21.0	.0223		"	54.5	.0582	
"	35.0	.0292		"	66.0	.1255	
"	57.0	.0430		"	72.0	.1591	
"	69.5	.0533					
				<u>83M-20A</u>			
5.0	27.0	0.0264	$K_2 = -8207^*$ $K_1 = 1762$ $K_0 = -13.9$	3.0	4.0	0.0180	$K_2 = -18147^*$ $K_1 = 3005$ $K_0 = -44.0$
"	43.5	.0403		"	19.5	.0247	
"	63.5	.0612		"	44.0	.0381	
"	70.0	.0716		"	62.5	.0515	
				"	69.5	.0582	
10.0	39.0	0.0278	$K_2 = -982^*$ $K_1 = 556$ $K_0 = 24.6$	5.0	11.0	0.0156	$K_2 = -6913^*$ $K_1 = 1620$ $K_0 = -12.4$
"	46.5	.0415		"	29.5	.0293	
"	63.5	.0825		"	50.5	.0498	
"	74.0	.1099		"	68.0	.0703	
				"	71.0	.0772	
15.0	47.0	0.0295	$K_2 = -197^*$ $K_1 = 284$ $K_0 = 38.8$	10.0	38.0	0.0228	$K_2 = -455^*$ $K_1 = 482$ $K_0 = 27.2$
"	52.5	.0502		"	47.0	.0428	
"	66.5	.1053		"	64.0	.0827	
"	73.0	.1329		"	74.5	.1094	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water, wt pct			Methanol, wt pct	Cloud pt., °F	Water, wt pct		
83M-20A					83M-25A				
15.0	46.0	0.0208	} K ₂ = 0.0* K ₁ = 249 K ₀ = 40.9		10.0	18.0	0.0182	} K ₂ = -810* K ₁ = 570 K ₀ = 8.0	
"	53.0	.0476			"	41.5	.0641		
"	66.0	.1014			"	58.0	.1035		
"	73.0	.1282			"	73.0	.1428		
20.0	48.5	0.0196	} K ₂ = -250* K ₁ = 220 K ₀ = 44.3		15.0	28.0	0.0189	} K ₂ = -146* K ₁ = 285 K ₀ = 22.6	
"	56.5	.0595			"	40.5	.0658		
"	68.0	.1258			"	58.0	.1326		
"	72.0	.1523			"	70.5	.1861		
83M-25A									
3.0	-11.5	0.0167	} K ₂ = -18493* K ₁ = 3173 K ₀ = -58.6		20.0	31.0	0.0186	} K ₂ = -46* K ₁ = 190 K ₀ = 27.4	
"	6.5	.0234			"	43.0	.0841		
"	33.5	.0369			"	59.5	.1756		
"	53.5	.0504			"	70.5	.2408		
"	69.0	.0639							
					83M-30A				
5.0	- 0.5	0.0174	} K ₂ = -5518* K ₁ = 1603 K ₀ = -26.7		3.0	- 2.0	0.0272	} K ₂ = -20617* K ₁ = 3533 K ₀ = - 82.4	
"	25.5	.0372			"	14.0	.0337		
"	58.5	.0701			"	37.5	.0469		
"	68.5	.0833			"	61.5	.0666		
"	73.0	.0899							

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water, wt pct				Methanol, wt pct	Cloud pt., °F	Water, wt pct			
83M-30A						89M-15A					
5.0	- 7.5	0.0302	$\left. \begin{array}{l} K_2 = -5873^* \\ K_1 = 1803 \\ K_0 = -55.3 \end{array} \right\}$			5.0	20.0	0.0259	$\left. \begin{array}{l} K_2 = -6363^* \\ K_1 = 1634 \\ K_0 = -18.1 \end{array} \right\}$		
"	4.5	.0369				"	44.5	.0471			
"	21.0	.0502				"	58.5	.0612			
"	48.0	.0770				"	68.5	.0753			
"	64.0	.0970				"	73.5	.0824			
"	72.5	.1103									
10.0	- 2.5	0.0283	$\left. \begin{array}{l} K_2 = -896^* \\ K_1 = 638 \\ K_0 = -19.6 \end{array} \right\}$			10.0	32.5	0.0266	$\left. \begin{array}{l} K_2 = -874^* \\ K_1 = 572 \\ K_0 = 17.9 \end{array} \right\}$		
"	5.5	.0414				"	50.0	.0621			
"	29.5	.0872				"	62.5	.0905			
"	56.5	.1525				"	76.0	.1259			
"	70.0	.1916									
15.0	4.0	0.0238	$\left. \begin{array}{l} K_2 = -230^* \\ K_1 = 332 \\ K_0 = -3.7 \end{array} \right\}$			15.0	40.0	0.0272	$\left. \begin{array}{l} K_2 = -294^* \\ K_1 = 316 \\ K_0 = 31.6 \end{array} \right\}$		
"	14.5	.0565				"	52.0	.0690			
"	42.0	.1546				"	63.0	.1107			
"	58.5	.2198				"	74.5	.1594			
"	62.5	.2394									
20.0	5.5	0.0223	$\left. \begin{array}{l} K_2 = -140^* \\ K_1 = 234 \\ K_0 = 0.3 \end{array} \right\}$			20.0	44.0	0.0223	$\left. \begin{array}{l} K_2 = -115^* \\ K_1 = 203 \\ K_0 = 39.5 \end{array} \right\}$		
"	19.5	.0870				"	54.5	.0772			
"	32.5	.1517				"	65.5	.1389			
"	44.5	.2163				"	74.5	.1936			
"	48.5	.2421									

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water wt pct		Methanol, wt pct	Cloud pt., °F	Water, wt pct	
89M-20A				89M-25A			
5.0	19.0	0.0283	$\left. \begin{array}{l} K_2 = -5890^* \\ K_1 = 1631 \\ K_0 = -22.5 \end{array} \right\}$	5.0	-12.0	0.0125	$\left. \begin{array}{l} K_2 = -7245^* \\ K_1 = 1807 \\ K_0 = -32.8 \end{array} \right\}$
"	43.0	.0491		"	20.0	.0327	
"	63.0	.0698		"	48.0	.0596	
"	72.5	.0837		"	73.0	.0933	
10.0	20.0	0.0102	$\left. \begin{array}{l} K_2 = -875^* \\ K_1 = 572 \\ K_0 = 14.3 \end{array} \right\}$	10.0	16.0	0.0114	$\left. \begin{array}{l} K_2 = -852^* \\ K_1 = 576 \\ K_0 = 9.6 \end{array} \right\}$
"	41.5	.0516		"	37.0	.0516	
"	57.0	.0861		"	58.0	.0985	
"	73.0	.1275		"	73.0	.1386	
15.0	32.0	0.0133	$\left. \begin{array}{l} K_2 = -228^* \\ K_1 = 304 \\ K_0 = 28.0 \end{array} \right\}$	15.0	27.0	0.0094	$\left. \begin{array}{l} K_2 = -202^* \\ K_1 = 301 \\ K_0 = 24.2 \end{array} \right\}$
"	46.0	.0622		"	42.5	.0636	
"	59.0	.1111		"	58.5	.1246	
"	74.0	.1739		"	73.0	.1855	
20.0	37.5	0.0137	$\left. \begin{array}{l} K_2 = -105^* \\ K_1 = 203 \\ K_0 = 34.8 \end{array} \right\}$	20.0	31.0	0.0090	$\left. \begin{array}{l} K_2 = -142^* \\ K_1 = 214 \\ K_0 = 29.1 \end{array} \right\}$
"	51.0	.0825		"	44.5	.0762	
"	63.0	.1512		"	57.0	.1433	
"	74.5	.2199		"	67.5	.2103	
				"	72.0	.2371	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt. pct	Cloud pt., °F	Water, wt. pct		Methanol, wt. pct	Cloud pt., °F	Water, wt. pct	
<u>89M - 30A</u>				<u>Cyclopentane (commercial)</u>			
5.0	- 2.5	0.0121	$K_2 = -5704^*$ $K_1 = 1602$ $K_0 = -20.8$	4.98	15.5	0.0039	$K_2 = -5389^*$ $K_1 = 1314$ $K_0 = 10.5$
"	25.5	.0322		"	23.5	.0104	
"	53.5	.0590		"	38.5	.0234	
"	65.0	.0724		"	51.0	.0363	
"	70.0	.0791		"	62.0	.0493	
	73.0	.0824		"	71.5	.0623	
10.0	22.0	0.0110	$K_2 = -683^*$ $K_1 = 533$ $K_0 = 16.2$	10.05	45.5	0.0049	$K_2 = -683^*$ $K_1 = 463$ $K_0 = 43.3$
"	42.0	.0516		"	48.5	.0114	
"	59.5	.0921		"	57.0	.0311	
"	75.0	.1327		"	65.0	.0508	
				"	72.5	.0705	
15.0	35.5	0.0103	$K_2 = -209^*$ $K_1 = 299$ $K_0 = 32.5$	14.91	54.5	0.0057	$K_2 = -263^*$ $K_1 = 264$ $K_0 = 53.1$
"	49.0	.0573		"	56.5	.0121	
"	63.0	.1111		"	62.5	.0378	
"	74.5	.1580		"	69.0	.0635	
				"	74.5	.0891	
20.0	38.5	0.0109	$K_2 = -101^*$ $K_1 = 205$ $K_0 = 36.3$	20.02	57.5	0.0066	$K_2 = 49^*$ $K_1 = 146$ $K_0 = 56.4$
"	50.5	.0720		"	59.0	.0185	
"	63.0	.1397		"	64.5	.0541	
"	74.5	.2074		"	70.0	.0897	
				"	75.5	.1252	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>			<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		
<u> n-Pentane </u>					<u> 2,3-Dimethylbutane </u>				
5.05	6.0	0.0035	} K ₂ = -8060* K ₁ = 1655 K ₀ = 1.2		5.21	33.5	0.0093	} K ₂ = -5410* K ₁ = 1318 K ₀ = 21.7	
"	20.5	.0115			"	42.5	.0169		
"	40.5	.0276			"	65.5	.0397		
"	57.5	.0436			"	72.0	.0473		
"	71.5	.0596							
<u> Isohexanes (commercial) </u>					<u> Isohexanes (commercial) </u>				
9.90	37.5	0.0048	} K ₂ = -715* K ₁ = 541 K ₀ = 35.0		5.19	24.0	0.0039	} K ₂ = -7346* K ₁ = 1482 K ₀ = 18.7	
"	42.0	.0128			"	35.5	.0116		
"	54.0	.0369			"	53.0	.0270		
"	69.0	.0691			"	74.5	.0500		
"	76.0	.0852							
15.16	50.5	0.0060	} K ₂ = -229* K ₁ = 291 K ₀ = 48.9		9.87	55.0	0.0049	} K ₂ = -2118* K ₁ = 584 K ₀ = 52.2	
"	53.0	.0138			"	59.0	.0122		
"	63.5	.0525			"	75.5	.0484		
"	75.5	.0990							
20.04	55.5	0.0072	} K ₂ = -91* K ₁ = 191 K ₀ = 54.2		15.04	68.5	0.0062	} K ₂ = --* K ₁ = 280 K ₀ = 66.8	
"	58.5	.0226			"	72.5	.0205		
"	65.5	.0612							
"	75.0	.1152							

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>3-Methylpentane</u>				<u>2-Methyl-2-butene</u>			
5.12	28.5	0.0030	} $K_2 = -5771^*$ $K_1 = 1328$ $K_0 = 24.6$	5.10	- 4.5	0.0903	} $K_2 = -2622^*$ $K_1 = 1481$ $K_0 = -116.7$
"	38.0	.0106		"	24.5	.1210	
"	62.5	.0334		"	52.5	.1593	
"	72.5	.0448		"	66.0	.1823	
				"	77.0	.2053	
<u>n-Heptane (commercial)</u>				<u>2-Methyl-1-butene</u>			
5.04	54.0	0.0037	} $K_2 = -10204^*$ $K_1 = 1290$ $K_0 = 49.4$	5.05	5.0	0.0989	} $K_2 = -2520^*$ $K_1 = 1454$ $K_0 = -113.8$
"	62.0	.0107		"	19.5	.1138	
"	69.0	.0177		"	43.0	.1438	
"	75.0	.0247		"	62.5	.1737	
				"	74.5	.1961	
<u>2,2,4-Trimethylpentane</u>				<u>1-Pentene</u>			
5.09	59.0	0.0041	} $K_2 = -15286^*$ $K_1 = 1416$ $K_0 = 53.5$	5.09	3.0	0.0787	} $K_2 = -3418^*$ $K_1 = 1619$ $K_0 = -102.9$
"	67.5	.0113		"	20.0	.0943	
"	74.5	.0186		"	46.5	.1256	
				"	66.5	.1568	
				"	75.0	.1724	
<u>Methylcyclohexane</u>				<u>Cyclopentene</u>			
4.97	65.5	0.0041	} $K_2 = -^*$ $K_1 = 1061$ $K_0 = 61.2$	4.95	-10.5	0.0496	} $K_2 = -2835^*$ $K_1 = 1330$ $K_0 = -68.7$
"	72.5	.0107		"	- 2.5	.0560	
				"	21.5	.0818	
				"	45.5	.1140	
				"	65.0	.1462	
				"	72.5	.1622	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>1-Hexene</u>				<u>Cyclohexene</u>			
5.04	- 5.5	0.0507	$\left. \begin{array}{l} K_2 = -4842^* \\ K_1 = 1821 \\ K_0 = -84.9 \end{array} \right\}$	5.10	9.5	0.0059	$\left. \begin{array}{l} K_2 = -3435^* \\ K_1 = 1069 \\ K_0 = 3.7 \end{array} \right\}$
"	14.5	.0655		"	16.5	.0121	
"	44.0	.0949		"	38.5	.0365	
"	66.5	.1244		"	59.5	.0671	
"	75.0	.1391		"	73.0	.0915	
<u>4-Methyl-trans-2-pentene</u>				<u>2,4,4-Trimethyl-1-pentene</u>			
5.08	- 5.0	0.0479	$\left. \begin{array}{l} K_2 = -4918^* \\ K_1 = 1785 \\ K_0 = -78.8 \end{array} \right\}$	5.11	- 2.5	0.0141	$\left. \begin{array}{l} K_2 = -6880^* \\ K_1 = 1764 \\ K_0 = -25.8 \end{array} \right\}$
"	5.5	.0554		"	8.5	.0211	
"	30.5	.0780		"	28.0	.0350	
"	56.5	.1081		"	51.0	.0559	
"	70.5	.1306		"	69.0	.0768	
"	74.0	.1382		"	74.0	.0838	
<u>2,3-Dimethyl-2-butene</u>				<u>1-Octene</u>			
5.07	- 2.0	0.0152	$\left. \begin{array}{l} K_2 = -4331^* \\ K_1 = 1378 \\ K_0 = -21.5 \end{array} \right\}$	5.05	31.5	0.0143	$\left. \begin{array}{l} K_2 = -6433^* \\ K_1 = 1471 \\ K_0 = 11.8 \end{array} \right\}$
"	16.0	.0293		"	56.0	.0354	
"	43.0	.0574		"	68.5	.0494	
"	64.5	.0855		"	74.5	.0564	
"	73.0	.0996					
<u>2-Heptene (mixed iso)</u>				<u>Benzene</u>			
5.07	0.5	0.0197	$\left. \begin{array}{l} K_2 = -5957^* \\ K_1 = 1666 \\ K_0 = -29.4 \end{array} \right\}$	5.03	53.0	0.3100	$\left. \begin{array}{l} K_2 = -745^* \\ K_1 = 834 \\ K_0 = -133.9 \end{array} \right\}$
"	21.5	.0341		"	62.5	.3387	
"	44.5	.0556		"	72.5	.3674	
"	63.0	.0771		"	74.5	.3789	
"	73.5	.0914					

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water, wt pct		Methanol, wt pct	Cloud pt., °F	Water, wt pct	
<u>Benzene</u>				<u>Toluene</u>			
10.02	39.0	0.6354	$K_2 = -119^*$ $K_1 = 355$ $K_0 = -138.2$	9.93	- 7.0	0.3309	$K_2 = -435^*$ $K_1 = 695$ $K_0 = -189.0$
"	42.5	.6525		"	- 2.0	.3425	
"	53.5	.7094		"	9.5	.3715	
"	63.5	.7663		"	29.5	.4296	
"	73.0	.8230		"	46.0	.4876	
				"	60.5	.5455	
				"	72.0	.6034	
14.99	40.0	1.1034	$K_2 = -41^*$ $K_1 = 214$ $K_0 = -145.9$	15.07	-13.0	0.5790	$K_2 = -166$ $K_1 = 453$ $K_0 = -219.0$
"	47.0	1.1597		"	- 4.5	.6080	
"	56.5	1.2439		"	9.5	.6658	
"	65.5	1.3280		"	22.5	.7236	
"	73.0	1.4008		"	33.5	.7813	
				"	53.5	.8965	
				"	66.0	.9827	
				"	74.5	1.0515	
19.90	41.5	1.6811	$K_2 = -17^*$ $K_1 = 140$ $K_0 = -145.7$	19.98	- 7.5	0.9000	$K_2 = -75^*$ $K_1 = 307$ $K_0 = -223.0$
"	50.5	1.7934		"	3.5	.9580	
"	59.0	1.9055		"	21.5	1.0737	
"	67.5	2.0174		"	37.0	1.1891	
"	73.0	2.1011		"	56.5	1.3617	
				"	68.0	1.4764	
				"	75.0	1.5566	
<u>Toluene</u>				<u>m-Xylene</u>			
5.02	5.0	0.1572	$K_2 = -1965^*$ $K_1 = 1385$ $K_0 = -163.7$	5.04	- 5.5	0.1088	$K_2 = -2527^*$ $K_1 = 1499$ $K_0 = -138.5$
"	9.5	.1629		"	5.5	.1205	
"	19.0	.1745		"	25.5	.1439	
"	30.5	.1918		"	41.5	.1673	
"	43.0	.2149		"	61.0	.2024	
"	56.5	.2437		"	73.5	.2317	
"	68.0	.2726					
"	73.0	.2898					

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Ethylbenzene</u>				<u>sec-Butylbenzene</u>			
5.07	- 0.5	0.0982	$K_2 = -2518^*$ $K_1 = 1424$ $K_0 = -116.0$	4.99	- 5.0	0.0417	$K_2 = -5436^*$ $K_1 = 1819$ $K_0 = -71.1$
"	10.0	.1099		"	11.0	.0533	
"	38.0	.1447		"	36.0	.0765	
"	58.0	.1795		"	64.0	.1112	
"	69.0	.2027		"	73.0	.1286	
"	74.0	.2143					
<u>o-Xylene</u>				<u>1,3,5-Trimethylbenzene</u>			
5.02	- 7.0	0.0800	$K_2 = -2674^*$ $K_1 = 1405$ $K_0 = -101.7$	5.03	-12.5	0.0220	$K_2 = -4351^*$ $K_1 = 1442$ $K_0 = -40.5$
"	5.0	.0915		"	- 3.5	.0277	
"	29.0	.1204		"	11.0	.0393	
"	54.5	.1609		"	28.5	.0566	
"	71.0	.1955		"	40.5	.0738	
				"	57.5	.0969	
				"	70.5	.1199	
<u>Isopropylbenzene</u>				<u>1,2,3-Trimethylbenzene</u>			
5.00	- 4.5	0.0702	$K_2 = -3819^*$ $K_1 = 1663$ $K_0 = -101.8$	4.98	- 6.0	0.0204	$K_2 = -3491^*$ $K_1 = 1250$ $K_0 = -29.6$
"	21.5	.0934		"	12.5	.0371	
"	48.0	.1281		"	37.5	.0650	
"	62.0	.1513		"	58.5	.0984	
"	72.5	.1744		"	73.0	.1262	
<u>n-Propylbenzene</u>				<u>n-Butylbenzene</u>			
4.97	- 3.0	0.0624	$K_2 = -3415^*$ $K_1 = 1497$ $K_0 = -76.6$	5.08	- 7.0	0.0257	$K_2 = -5996^*$ $K_1 = 1754$ $K_0 = -47.2$
"	16.5	.0741		"	11.5	.0374	
"	41.5	.1031		"	37.0	.0608	
"	64.5	.1379		"	61.5	.0900	
"	74.0	.1553		"	72.5	.1075	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water, wt pct		Methanol, wt pct	Cloud pt., °F	Water, wt pct	
<u>Triethylbenzene</u>				<u>Heavy platformate</u>			
4.97	24.5	0.0178	$\left. \begin{array}{l} K_2 = -5940^* \\ K_1 = 1500 \\ K_0 = -0.2 \end{array} \right\}$	20.00	- 7.5	0.7422	$\left. \begin{array}{l} K_2 = -73^* \\ K_1 = 283 \\ K_0 = -176.6 \end{array} \right\}$
"	33.0	.0242		"	- 1.0	.7721	
"	47.0	.0370		"	9.5	.8319	
"	65.5	.0562		"	29.0	.9672	
"	75.0	.0689		"	44.5	1.0845	
				"	58.5	1.2016	
				"	67.5	1.2892	
				"	73.0	1.3475	
<u>Heavy platformate</u>				<u>Platformate</u>			
5.05	1.0	0.1358	$\left. \begin{array}{l} K_2 = -811^* \\ K_1 = 939 \\ K_0 = -111.2 \end{array} \right\}$	4.90	-13.5	0.0241	$\left. \begin{array}{l} K_2 = -4753^* \\ K_1 = 1611 \\ K_0 = 49.0 \end{array} \right\}$
"	5.0	.1417		"	- 3.5	.0307	
"	14.5	.1536		"	20.5	.0504	
"	31.0	.1774		"	46.0	.0766	
"	47.0	.2070		"	70.5	.1094	
"	62.0	.2308					
"	72.5	.2485					
9.99	- 8.5	0.2851	$\left. \begin{array}{l} K_2 = -406^* \\ K_1 = 648 \\ K_0 = -160.0 \end{array} \right\}$	10.02	-11.5	0.0061	$\left. \begin{array}{l} K_2 = -897 \\ K_1 = 623 \\ K_0 = -14.8 \end{array} \right\}$
"	- 1.0	.3029		"	1.5	.0262	
"	7.0	.3207		"	23.0	.0664	
"	28.5	.3800		"	46.5	.1200	
"	46.0	.4392		"	70.5	.1869	
"	62.0	.4983					
"	73.5	.5456					
14.98	-14.5	0.4730	$\left. \begin{array}{l} K_2 = -195^* \\ K_1 = 472 \\ K_0 = -193.8 \end{array} \right\}$	14.95	2.0	0.0073	$\left. \begin{array}{l} K_2 = -251^* \\ K_1 = 332 \\ K_0 = 0.1 \end{array} \right\}$
"	-11.0	.4848		"	13.5	.0398	
"	- 5.5	.5024		"	32.5	.1046	
"	10.5	.5612		"	49.0	.1693	
"	31.0	.6492		"	63.5	.2339	
"	53.0	.7663		"	75.0	.2856	
"	67.0	.8540					
"	75.5	.9124					

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Platformate</u>				<u>Fluid cat cracked</u>			
19.91	7.5	0.0093	$\left. \begin{array}{l} K_2 = -112^* \\ K_1 = 222 \\ K_0 = 5.6 \end{array} \right\}$	20.07	17.5	0.0188	$\left. \begin{array}{l} K_2 = -120^* \\ K_1 = 228 \\ K_0 = 13.4 \end{array} \right\}$
"	22.0	.0766		"	20.5	.0314	
"	35.5	.1437		"	34.0	.0941	
"	47.5	.2108		"	46.0	.1567	
"	63.5	.3113		"	57.5	.2192	
"	74.0	.3782		"	61.0	.2379	
<u>Fluid cat cracked</u>				<u>Reformate</u>			
4.99	-14.5	0.0249	$\left. \begin{array}{l} K_2 = -5870^* \\ K_1 = 1800 \\ K_0 = -54.9 \end{array} \right\}$	4.91	-12.5	0.0297	$\left. \begin{array}{l} K_2 = -5325^* \\ K_1 = 1734 \\ K_0 = -58.0 \end{array} \right\}$
"	- 3.5	.0316		"	- 0.5	.0364	
"	15.5	.0452		"	23.5	.0565	
"	30.5	.0587		"	43.5	.0766	
"	50.0	.0790		"	59.0	.0967	
"	61.0	.0925		"	72.5	.1168	
"	70.5	.1060					
9.87	- 0.5	0.0135	$\left. \begin{array}{l} K_2 = -813^* \\ K_1 = 617 \\ K_0 = -8.2 \end{array} \right\}$	10.01	-12.0	0.0149	$\left. \begin{array}{l} K_2 = -1024^* \\ K_1 = 686 \\ K_0 = -21.2 \end{array} \right\}$
"	4.0	.0200		"	0.5	.0322	
"	15.5	.0395		"	17.5	.0610	
"	32.0	.0718		"	35.0	.0956	
"	52.5	.1171		"	50.0	.1301	
"	66.0	.1494		"	66.0	.1704	
"	73.0	.1688		"	73.5	.1934	
15.10	13.5	0.0186	$\left. \begin{array}{l} K_2 = -213^* \\ K_1 = 331 \\ K_0 = 7.7 \end{array} \right\}$	14.96	- 6.0	0.0048	$\left. \begin{array}{l} K_2 = -327^* \\ K_1 = 374 \\ K_0 = -7.3 \end{array} \right\}$
"	16.0	.0252		"	1.0	.0216	
"	30.5	.0714		"	18.0	.0718	
"	43.5	.1175		"	28.5	.1052	
"	56.0	.1637		"	41.0	.1498	
"	67.5	.2097		"	55.5	.2054	
"	74.0	.2360		"	63.5	.2388	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Reformate</u>				<u>Cat cracked</u>			
19.97	0.5	0.0055	$\left. \begin{array}{l} K_2 = -114^* \\ K_1 = 232 \\ K_0 = -0.7 \end{array} \right\}$	19.97	33.0	0.0113	$\left. \begin{array}{l} K_2 = -134^* \\ K_1 = 210 \\ K_0 = 30.6 \end{array} \right\}$
"	5.5	.0264		"	41.0	.0515	
"	10.0	.0473		"	53.5	.1183	
"	19.5	.0890		"	65.0	.1851	
"	31.5	.1516		"	73.0	.2385	
"	44.0	.2140					
"	48.5	.2400					
<u>Cat cracked</u>				<u>Housebrand gasoline</u>			
4.96	-11.0	0.0137	$\left. \begin{array}{l} K_2 = -6356^* \\ K_1 = 1700 \\ K_0 = -31.6 \end{array} \right\}$	4.93	- 2.0	0.0059	$\left. \begin{array}{l} K_2 = -6056^* \\ K_1 = 1542 \\ K_0 = -10.2 \end{array} \right\}$
"	2.0	.0204		"	8.5	.0123	
"	27.0	.0403		"	25.0	.0251	
"	52.5	.0668		"	46.0	.0444	
"	72.0	.0933		"	63.0	.0636	
				"	72.5	.0764	
10.0	15.5	0.0087	$\left. \begin{array}{l} K_2 = -666^* \\ K_1 = 533 \\ K_0 = 11.0 \end{array} \right\}$	10.03	33.0	0.0070	$\left. \begin{array}{l} K_2 = -486^* \\ K_1 = 483 \\ K_0 = 29.9 \end{array} \right\}$
"	23.0	.0228		"	36.5	.0133	
"	39.5	.0581		"	50.5	.0449	
"	58.0	.1004		"	64.0	.0766	
"	73.5	.1427		"	74.0	.1018	
15.02	27.0	0.0103	$\left. \begin{array}{l} K_2 = -272^* \\ K_1 = 314 \\ K_0 = 23.8 \end{array} \right\}$	14.96	45.5	0.0081	$\left. \begin{array}{l} K_2 = -185^* \\ K_1 = 277 \\ K_0 = 43.2 \end{array} \right\}$
"	35.0	.0367		"	48.5	.0196	
"	53.0	.1025		"	63.5	.0770	
"	64.5	.1486		"	74.5	.1229	
"	74.5	.1946					

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Housebrand gasoline</u>				<u>Straight run</u>			
20.03	51.5	0.0092	} K ₂ = -154* K ₁ = 196 K ₀ = 49.7	5.86	26.5	0.0090	} K ₂ = -738* K ₁ = 1094 K ₀ = 16.6
"	54.0	.0219		"	41.5	.0234	
"	62.0	.0660		"	55.0	.0356	
"	72.5	.1291		"	66.5	.0472	
<u>Aromatic naphtha</u>							
5.16	22.0	0.0120	} K ₂ = -5510* K ₁ = 1330 K ₀ = 6.8	15.27	62.5	0.0095	} K ₂ = 28* K ₁ = 269 K ₀ = 60.0
"	29.0	.0181		"	66.0	.0219	
"	48.0	.0364		"	72.5	.0467	
"	63.0	.0547		"	76.0	.0590	
"	74.5	.0729					
				<u>Heavy straight run</u>			
10.05	48.5	0.0130	} K ₂ = -1363* K ₁ = 548 K ₀ = 41.8	4.91	25.0	0.0058	} K ₂ = -7312* K ₁ = 1449 K ₀ = 16.9
"	52.0	.0191		"	34.0	.0124	
"	63.0	.0436		"	49.0	.0257	
"	75.0	.0743		"	62.5	.0389	
				"	72.5	.0521	
14.61	60.5	0.0159	} K ₂ = 64* K ₁ = 256 K ₀ = 56.4	10.04	58.5	0.0067	} K ₂ = -3206* K ₁ = 595 K ₀ = 54.8
"	64.0	.0296		"	62.0	.0128	
"	69.0	.0486		"	67.5	.0250	
"	75.0	.0715		"	72.5	.0373	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Heavy straight run</u>				<u>91 Octane no lead Indolene No. 1</u>			
15.04	72.0	0.0076	} K ₂ = --* K ₁ = 227 K ₀ = 70.3	5.03	- 8.5	0.0241	} K ₂ = -5163* K ₁ = 1646 K ₀ = -44.8
"	73.5	.0142		"	1.5	.0311	
				"	27.5	.0521	
				"	58.5	.0870	
				"	73.0	.1079	
<u>Cat poly</u>							
5.08	34.5	0.0034	} K ₂ = -7849* K ₁ = 1429 K ₀ = 29.9	10.62	8.0	0.0240	} K ₂ = -596* K ₁ = 554 K ₀ = -5.4
"	44.5	.0106		"	18.0	.0460	
"	60.5	.0250		"	33.0	.0746	
"	74.0	.0393		"	40.0	.0913	
				"	53.0	.1203	
				"	64.0	.1499	
10.09	73.0	0.0046	} K ₂ = --* K ₁ = 571 K ₀ = 70.4	16.71	6.0	0.0059	} K ₂ = -186* K ₁ = 287 K ₀ = 4.8
"	77.0	.0116		"	8.0	.0109	
				"	12.0	.0240	
				"	19.5	.0520	
				"	28.5	.0877	
				"	54.0	.1972	
				"	64.0	.2436	
<u>H.F. alkylate</u>							
5.01	52.0	0.0039	} K ₂ = -12486* K ₁ = 1431 K ₀ = 46.5	26.32	13.0	0.0076	} K ₂ = -232* K ₁ = 199 K ₀ = 11.8
"	60.5	.0110		"	15.0	.0163	
"	68.5	.0180		"	20.5	.0434	
"	74.5	.0251		"	26.0	.0796	
				"	35.0	.1405	
				"	42.0	.1959	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>91 Octane no. lead No. 2</u>				<u>Vehicle study trial blend</u>			
4.96	- 8.0	0.0175	$\left. \begin{array}{l} K_2 = -5491^* \\ K_1 = 1629 \\ K_0 = -34.3 \end{array} \right\}$	11.77	16.0	0.0061	$\left. \begin{array}{l} K_2 = -703^* \\ K_1 = 499 \\ K_0 = 13.9 \end{array} \right\}$
"	2.5	.0244		"	20.0	.0117	
"	28.5	.0450		"	23.0	.0179	
"	48.5	.0655		"	29.0	.0303	
"	64.5	.0860		"	39.0	.0550	
"	74.0	.0997		"	58.0	.1044	
				"	74.0	.1532	
9.56	9.0	0.0066	$\left. \begin{array}{l} K_2 = -963^* \\ K_1 = 623 \\ K_0 = 4.7 \end{array} \right\}$	20.28	30.0	0.0057	$\left. \begin{array}{l} K_2 = -81^* \\ K_1 = 204 \\ K_0 = 28.7 \end{array} \right\}$
"	14.0	.0166		"	31.0	.0111	
"	29.0	.0399		"	34.0	.0274	
"	47.0	.0778		"	39.5	.0544	
"	64.0	.1162		"	45.0	.0815	
"	78.0	.1541		"	54.5	.1339	
				"	64.0	.1869	
17.66	25.0	0.0088	$\left. \begin{array}{l} K_2 = -258^* \\ K_1 = 308 \\ K_0 = 22.4 \end{array} \right\}$	52.09	35.0	0.0106	$\left. \begin{array}{l} K_2 = 18^* \\ K_1 = 50 \\ K_0 = 34.5 \end{array} \right\}$
"	31.0	.0283		"	36.0	.0262	
"	36.0	.0453		"	37.0	.0520	
"	45.0	.0790		"	39.5	.0909	
"	67.0	.1684		"	42.0	.1563	
				"	47.0	.2208	
				"	50.0	.2873	
<u>Vehicle study trial blend</u>				<u>Mileage accumulation trial blend</u>			
5.01	-16.0	0.0109	$\left. \begin{array}{l} K_2 = -6823^* \\ K_1 = 1776 \\ K_0 = -33.0 \end{array} \right\}$	3.04	- 7.0	0.0176	$\left. \begin{array}{l} K_2 = -21167^* \\ K_1 = 3403 \\ K_0 = -60.3 \end{array} \right\}$
"	8.0	.0238		"	6.5	.0231	
"	23.0	.0368		"	20.5	.0286	
"	38.0	.0497		"	31.5	.0341	
"	50.0	.0620		"	57.0	.0507	
"	61.0	.0743		"	69.5	.0617	
"	71.0	.0879					

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Mileage accumulation trial blend</u>				<u>Vehicle study gasoline</u>			
5.01	- 0.5	0.0140	$\left. \begin{array}{l} K_2 = -4860* \\ K_1 = 1463 \\ K_0 = -19.6 \end{array} \right\}$	10.10	17.0	0.0073	$\left. \begin{array}{l} K_2 = -787* \\ K_1 = 551 \\ K_0 = 13.2 \end{array} \right\}$
"	9.0	.0209		"	21.0	.0142	
"	34.0	.0416		"	35.0	.0416	
"	51.5	.0623		"	53.5	.0826	
"	73.0	.0899		"	64.0	.1100	
				"	76.5	.1441	
19.98	38.5	0.0119	$\left. \begin{array}{l} K_2 = -81* \\ K_1 = 197 \\ K_0 = 36.3 \end{array} \right\}$	14.98	30.0	0.0081	$\left. \begin{array}{l} K_2 = -269* \\ K_1 = 314 \\ K_0 = 27.4 \end{array} \right\}$
"	41.5	.0260		"	32.0	.0151	
"	54.5	.0965		"	48.5	.0713	
"	67.0	.1670		"	63.0	.1274	
"	74.0	.2092		"	76.0	.1835	
<u>Vehicle study gasoline</u>							
3.07	-12.5	0.0124	$\left. \begin{array}{l} K_2 = -24666* \\ K_1 = 3479 \\ K_0 = -51.4 \end{array} \right\}$	19.93	35.5	0.0092	$\left. \begin{array}{l} K_2 = -73* \\ K_1 = 196 \\ K_0 = 33.9 \end{array} \right\}$
"	7.5	.0196		"	38.5	.0225	
"	25.0	.0268		"	51.0	.0894	
"	38.0	.0340		"	62.5	.1561	
"	58.5	.0483		"	74.0	.2227	
"	70.0	.0626					
5.03	-18.0	0.0057	$\left. \begin{array}{l} K_2 = -6498* \\ K_1 = 1682 \\ K_0 = -26.0 \end{array} \right\}$	29.90	41.0	0.0112	$\left. \begin{array}{l} K_2 = -46* \\ K_1 = 116 \\ K_0 = 39.8 \end{array} \right\}$
"	- 5.5	.0127		"	43.5	.0309	
"	6.5	.0197		"	50.5	.0967	
"	23.5	.0336		"	57.5	.1624	
"	38.5	.0476		"	62.0	.2083	
"	58.0	.0685		"	64.5	.2346	
"	73.0	.0894					

See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

Methanol, wt pct	Cloud pt., °F	Water, wt pct		Methanol, wt pct	Cloud pt., °F	Water, wt pct	
<u>Vehicle study gasoline</u>				<u>No lead pump No. 1</u>			
39.91	44.5	0.0131	$\left. \begin{array}{l} K_2 = -8^* \\ K_1 = 72 \\ K_0 = 43.6 \end{array} \right\}$	4.95	- 0.5	0.0083	$\left. \begin{array}{l} K_2 = -7917^* \\ K_1 = 1801 \\ K_0 = -14.9 \end{array} \right\}$
"	46.5	.0389		"	11.0	.0152	
"	51.0	.1035		"	30.0	.0291	
"	55.5	.1679		"	48.0	.0430	
"	60.0	.2323		"	62.5	.0568	
				"	72.5	.0707	
50.03	41.5	0.0160	$\left. \begin{array}{l} K_2 = -4^* \\ K_1 = 57 \\ K_0 = 40.6 \end{array} \right\}$	9.92	32.0	0.0093	$\left. \begin{array}{l} K_2 = -649^* \\ K_1 = 521 \\ K_0 = 27.3 \end{array} \right\}$
"	43.0	.0414		"	35.5	.0158	
"	46.5	.1047		"	48.0	.0417	
"	50.0	.1680		"	59.5	.0677	
"	53.5	.2312		"	73.0	.1001	
59.95	29.0	0.0171	$\left. \begin{array}{l} K_2 = 19^* \\ K_1 = 41 \\ K_0 = 28.3 \end{array} \right\}$	14.96	45.0	0.0092	$\left. \begin{array}{l} K_2 = -361^* \\ K_1 = 305 \\ K_0 = 42.3 \end{array} \right\}$
"	29.5	.0295		"	47.0	.0160	
"	32.0	.0913		"	58.5	.0563	
"	35.0	.1531		"	66.5	.0900	
"	37.0	.1963		"	74.5	.1236	
"	39.0	.2395					
70.07	5.5	0.0202	$\left. \begin{array}{l} K_2 = 38^* \\ K_1 = 24 \\ K_0 = 5.1 \end{array} \right\}$	19.97	50.0	0.0102	$\left. \begin{array}{l} K_2 = -74^* \\ K_1 = 191 \\ K_0 = 48.1 \end{array} \right\}$
"	6.5	.0521		"	52.5	.0228	
"	8.5	.1158		"	64.0	.0863	
"	10.5	.1794		"	75.0	.1496	
"	13.0	.2366					
"	15.5	.2937					

See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>Mileage accumulation gasoline</u>				<u>42 vol pct aromatic</u>			
5.03	0.0	0.0167	$\left. \begin{array}{l} K_2 = -5383^* \\ K_1 = 1567 \\ K_0 = -24.6 \end{array} \right\}$	4.98	-17.0	0.0905	$\left. \begin{array}{l} K_2 = -2985^* \\ K_1 = 1626 \\ K_0 = -139.0 \end{array} \right\}$
"	26.0	.0368		"	- 2.0	.1033	
"	47.0	.0569		"	16.0	.1225	
"	59.0	.0704		"	36.0	.1480	
"	69.0	.0838		"	56.5	.1799	
				"	69.5	.2053	
<u>No lead pump No. 2</u>				<u>30 vol pct aromatic (a)</u>			
9.87	50.0	0.0088	$\left. \begin{array}{l} K_2 = -1451^* \\ K_1 = 553 \\ K_0 = 45.3 \end{array} \right\}$	4.89	-12.0	0.0781	$\left. \begin{array}{l} K_2 = -3368^* \\ K_1 = 1676 \\ K_0 = -122.0 \end{array} \right\}$
"	57.5	.0232		"	3.5	.0912	
"	67.0	.0447		"	28.5	.1175	
"	73.0	.0591		"	49.0	.1438	
				"	66.0	.1700	
				"	72.0	.1832	
<u>No lead pump No. 3</u>				<u>64 vol pct aromatic</u>			
10.00	51.0	0.0058	$\left. \begin{array}{l} K_2 = -953^* \\ K_1 = 502 \\ K_0 = 48.1 \end{array} \right\}$	4.93	-16.0	0.0655	$\left. \begin{array}{l} K_2 = -3865^* \\ K_1 = 1730 \\ K_0 = -112.0 \end{array} \right\}$
"	58.0	.0203		"	- 7.0	.0719	
"	67.5	.0420		"	14.5	.0913	
"	73.5	.0565		"	37.0	.1170	
				"	56.0	.1427	
				"	70.0	.1685	
<u>No lead pump No. 4</u>				<u>59 vol pct aromatic</u>			
9.94	49.0	0.0070	$\left. \begin{array}{l} K_2 = -1340^* \\ K_1 = 542 \\ K_0 = 45.2 \end{array} \right\}$	4.96	7.5	0.0795	$\left. \begin{array}{l} K_2 = -3511^* \\ K_1 = 1601 \\ K_0 = -97.4 \end{array} \right\}$
"	52.5	.0142		"	21.5	.0929	
"	66.0	.0428		"	38.5	.1131	
"	74.5	.0643		"	58.0	.1400	
				"	72.0	.1668	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>55_vol_pct_aromatic</u>				<u>11_vol_pct_aromatic</u>			
5.06	- 6.5	0.0598	$\left. \begin{array}{l} K_2 = -3798^* \\ K_1 = 1632 \\ K_0 = -90.2 \end{array} \right\}$	5.09	- 0.5	0.0060	$\left. \begin{array}{l} K_2 = -6671^* \\ K_1 = 1612 \\ K_0 = -9.2 \end{array} \right\}$
"	10.0	.0739		"	12.0	.0134	
"	31.0	.0950		"	31.0	.0280	
"	52.5	.1231		"	54.0	.0500	
"	70.0	.1512		"	72.5	.0720	
<u>60_vol_pct_aromatic</u>				<u>13_vol_pct_aromatic</u>			
5.02	-10.0	0.0489	$\left. \begin{array}{l} K_2 = -3896^* \\ K_1 = 1583 \\ K_0 = -77.2 \end{array} \right\}$	5.05	8.5	0.0067	$\left. \begin{array}{l} K_2 = -7605^* \\ K_1 = 1591 \\ K_0 = -1.3 \end{array} \right\}$
"	6.5	.0615		"	20.0	.0139	
"	25.5	.0805		"	38.0	.0285	
"	46.0	.1058		"	59.0	.0502	
"	63.0	.1310		"	74.0	.0720	
"	73.0	.1500					
<u>25_vol_pct_aromatic</u>				<u>6_vol_pct_aromatic</u>			
5.02	- 5.0	0.0227	$\left. \begin{array}{l} K_2 = -5161^* \\ K_1 = 1614 \\ K_0 = -38.4 \end{array} \right\}$	5.07	12.5	0.0055	$\left. \begin{array}{l} K_2 = -8471^* \\ K_1 = 1644 \\ K_0 = 3.8 \end{array} \right\}$
"	5.5	.0297		"	24.0	.0130	
"	30.5	.0507		"	43.0	.0279	
"	56.0	.0787		"	65.0	.0502	
"	71.5	.0997		"	70.5	.0577	
<u>30_vol_pct_aromatic (b)</u>				<u>2_vol_pct_aromatic</u>			
5.03	- 6.5	0.0164	$\left. \begin{array}{l} K_2 = -5357^* \\ K_1 = 1587 \\ K_0 = -30.6 \end{array} \right\}$	5.16	11.0	0.0054	$\left. \begin{array}{l} K_2 = -8951^* \\ K_1 = 1705 \\ K_0 = 2.8 \end{array} \right\}$
"	4.0	.0232		"	24.5	.0129	
"	28.5	.0435		"	43.5	.0280	
"	48.5	.0638		"	59.0	.0430	
"	69.5	.0908		"	72.0	.0581	

*See footnote at end of table.

APPENDIX C

TABLE C-1. - Cloud point temperature and
water content data--Continued

<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>		<u>Methanol,</u> <u>wt pct</u>	<u>Cloud</u> <u>pt., °F</u>	<u>Water,</u> <u>wt pct</u>	
<u>.072 Mole fraction benzene/isooctane</u>				<u>.453 Mole fraction toluene/isooctane</u>			
5.06	46.5	0.0058	$\left. \begin{array}{l} K_2 = -11180* \\ K_1 = 1439 \\ K_0 = 38.6 \end{array} \right\}$	5.05	- 8.0	0.0412	$\left. \begin{array}{l} K_2 = -4862* \\ K_1 = 1724 \\ K_0 = -70.6 \end{array} \right\}$
"	55.5	.0130		"	10.0	.0550	
"	63.0	.0202		"	38.5	.0827	
"	75.0	.0346		"	60.5	.1102	
<u>.327 Mole fraction benzene/isooctane</u>				<u>.650 Mole fraction toluene/isooctane</u>			
5.03	-15.5	0.0089	$\left. \begin{array}{l} K_2 = -4817* \\ K_1 = 1493 \\ K_0 = -28.2 \end{array} \right\}$	4.97	- 9.0	0.0855	$\left. \begin{array}{l} K_2 = -3415* \\ K_1 = 1728 \\ K_0 = -131.3 \end{array} \right\}$
"	- 5.5	.0161		"	13.5	.1050	
"	13.5	.0306		"	36.5	.1311	
"	49.5	.0668		"	59.5	.1636	
"	66.5	.0886		"	74.0	.1896	
"	74.5	.1031					
<u>.237 Mole fraction toluene/isooctane</u>				<u>.832 Mole fraction toluene/isooctane</u>			
5.08	6.5	0.0100	$\left. \begin{array}{l} K_2 = -6386* \\ K_1 = 1579 \\ K_0 = -8.3 \end{array} \right\}$	5.08	- 3.0	0.1266	$\left. \begin{array}{l} K_2 = -2293* \\ K_1 = 1508 \\ K_0 = -157.1 \end{array} \right\}$
"	27.0	.0244		"	19.0	.1516	
"	43.5	.0388		"	42.0	.1828	
"	63.0	.0604		"	60.5	.2140	
"	74.5	.0748		"	72.5	.2390	

* K_2 , K_1 , K_0 are coefficients of the equation: $^{\circ}\text{F} = K_2W^2 + K_1W + K_0$
where, W = water content, wt pct.

APPENDIX D -- AZEOTROPE DATA

TABLE D-1. - Azeotropic distillation data¹

Hydrocarbon	Azeo. BP, ° F	HC BP, ° F	Fraction MeOH in azeotrope
3-Methyl-1-butene.....	67.6	72.5	0.03 wt
2-Methylbutane (isopentane).....	76.1	82.3	.04 wt
<u>n</u> -Pentane.....	87.1	97.0	.182 wt
2-Pentene.....	88.7	96.4	.141 wt
2-Methyl-2-butene.....	89.2	98.9	.07 wt
Cyclopentene.....	98.6	109.4	.204 wt
Cyclopentane.....	101.8	120.9	.14 wt
2,3-Dimethylbutane.....	113.0	136.4	.20 wt
Hexenes.....	121.1	154.4	.30 wt
Hexanes.....	122.0	154.4	.297 wt
Methylcyclopentane.....	124.3	161.6	.32 wt
Methylcyclopentene.....	127.4	168.5	.35 wt
Cyclohexane.....	129.2	176.0	.38 wt
Cyclohexene.....	132.6	181.0	.40 wt
Benzene.....	135.5	176.2	.391 wt
<u>n</u> -Heptane.....	138.4	209.2	.515 wt
Methylcyclohexane.....	138.6	213.4	.54 wt
2,2,4-Trimethylpentane (isooctane).	138.9	210.7	.53 wt
2,5-Dimethylhexane.....	141.8	228.6	.60 wt
1,3-Dimethylcyclohexane.....	<144.5	249.3	-
Octane.....	145.4	258.1	.72 wt
Toluene.....	146.8	231.3	.69 wt

¹ Azeotropic Data Advances in Chemistry Series No. 6, American Chemical Society, 1952.

APPENDIX E

DISTILLATION DATA FOR 83M AND 89M SERIES FUELS

TABLE E-1. - Distillation data for 83M-15A and 83M-20A series fuels

Gasoline..... Methanol, wt pct.....	83M-15A						83M-20A					
	0	3	5	10	15	20	0	3	5	10	15	20
Distillation, ASTM, °F:												
IBP.....	93	91	92	90	91	92	101	102	97	100	101	103
5 pct.....	111	102	102	104	105	105	129	114	112	114	115	118
10 pct.....	120	105	109	108	108	109	142	116	116	119	119	122
20 pct.....	134	118	113	114	114	114	167	155	122	126	126	130
30 pct.....	146	144	135	120	121	122	189	186	176	131	131	135
40 pct.....	165	163	160	123	126	128	208	206	202	190	136	139
50 pct.....	186	185	185	171	132	133	222	221	217	214	210	206
60 pct.....	210	211	209	203	191	191	228	234	231	229	224	225
70 pct.....	229	229	229	219	220	216	251	249	245	242	241	241
80 pct.....	256	255	255	253	245	246	270	267	262	264	262	262
90 pct.....	302	305	302	300	291	297	305	308	305	296	295	299
95 pct.....	348	352	349	349	329	348	349	347	346	341	339	340
End point.....	391	385	388	386	380	382	395	390	378	381	383	384
Recovery, vol pct.	98.0	97.5	98.0	98.0	98.0	98.5	98.5	98.0	98.0	98.0	98.0	98.0
Residual, vol pct.	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Loss, vol pct.....	1.0	1.5	1.0	1.0	1.0	1.0	0.5	1.0	1.0	1.0	1.0	1.0
Gravity, API at 60° F..	64.4	64.3	63.9	63.1	62.4	62.5	59.8	59.9	59.6	59.0	58.7	58.4

TABLE E-2. - Distillation data for 83M-25A and 83M-30A series fuels

Gasoline..... Methanol, wt pct.....	83M-25A						83M-30A					
	0	3	5	10	15	20	0	3	5	10	15	20
Distillation, ASTM, °F:												
IBP.....	95	98	102	104	101	101	95	94	94	96	97	97
5 pct.....	123	111	113	115	113	114	117	109	109	111	113	113
10 pct.....	139	115	116	121	118	119	129	112	114	116	118	117
20 pct.....	161	149	124	128	126	128	149	134	119	123	126	125
30 pct.....	184	181	175	132	133	134	171	168	160	129	132	132
40 pct.....	203	203	199	190	137	137	196	196	193	164	138	137
50 pct.....	217	217	215	216	206	140	215	216	215	214	190	141
60 pct.....	231	229	230	230	223	220	222	232	231	230	230	220
70 pct.....	244	244	246	244	237	236	247	246	247	245	244	240
80 pct.....	266	264	266	264	259	258	267	266	266	264	263	260
90 pct.....	299	295	300	300	295	293	307	302	297	304	302	299
95 pct.....	333	330	338	338	330	348	356	353	352	349	354	352
End point.....	397	382	390	384	377	375	400	399	400	396	393	391
Recovery, vol pct.	98.0	98.5	98.0	98.0	98.0	98.0	98.0	98.0	98.5	98.0	98.0	98.0
Residual, vol pct.	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0	1.0	1.0	1.0	1.0
Loss, vol pct.....	1.0	0.5	1.0	1.0	1.0	1.5	1.0	1.0	0.5	1.0	1.0	1.0
Gravity, API at 60° F..	58.5	58.3	58.3	57.8	57.2	56.7	56.8	56.8	56.6	56.1	55.9	55.2

TABLE E-3 . - Distillation data for 89M-15A and 89M-20A series fuels

Gasoline..... Methanol, wt pct.....	89M-15A					89M-20A				
	0	5	10	15	20	0	5	10	15	20
Distillation, ASTM, °F:										
IBP.....	90	94	92	94	94	86	87	89	90	90
5 pct.....	104	106	104	108	108	106	100	102	102	103
10 pct.....	124	110	110	112	112	116	105	106	107	109
20 pct.....	142	116	116	120	120	135	112	114	116	118
30 pct.....	158	146	122	126	126	154	132	122	124	127
40 pct.....	175	172	129	131	132	183	176	129	137	134
50 pct.....	192	190	184	135	136	210	208	200	138	139
60 pct.....	205	204	203	198	176	225	220	222	217	144
70 pct.....	215	208	211	210	200	236	237	235	235	228
80 pct.....	223	222	222	220	220	254	254	250	249	248
90 pct.....	236	234	234	232	230	285	282	282	282	279
95 pct.....	258	260	260	258	250	306	316	305	308	306
End point.....	306	316	306	310	311	355	348	344	342	341
Recovery, vol pct.	98.0	98.0	97.5	98.0	98.5	97.5	97.5	97.5	97.5	97.5
Residual, vol pct.	1.0	0.5	0.5	0.5	0.5	1.0	0.5	0.5	1.0	0.5
Loss, vol pct.....	1.0	1.5	2.0	1.5	1.0	1.5	2.0	2.0	1.5	2.0
Gravity, API at 60° F..	66.9	66.2	65.4	64.4	63.4	66.2	65.6	64.7	63.9	62.8

TABLE E-4 . - Distillation data for 89M-25A and 89M-30A series fuels

Gasoline..... Methanol, wt pct.....	89M-25A					89M-30A				
	0	5	10	15	20	0	5	10	15	20
Distillation, ASTM, °F:										
IBP.....	96	98	98	99	99	94	104	98	104	104
5 pct.....	121	112	112	113	112	144	122	119	122	124
10 pct.....	134	117	117	118	118	176	129	130	130	132
20 pct.....	158	122	126	127	127	210	200	138	138	140
30 pct.....	182	170	131	133	134	222	220	208	141	142
40 pct.....	208	202	187	137	138	230	230	224	227	144
50 pct.....	227	224	220	207	141	238	238	235	232	228
60 pct.....	242	238	237	234	225	249	248	246	242	240
70 pct.....	258	256	254	250	246	266	264	260	258	256
80 pct.....	280	280	275	275	271	293	292	286	284	284
90 pct.....	305	306	304	304	302	323	320	316	316	316
95 pct.....	328	324	319	318	324	364	363	344	349	356
End point.....	367	366	357	356	353	367	365	360	365	360
Recovery, vol pct.	98.0	98.5	98.0	98.5	99.0	95.5	96.0	96.0	96.0	95.5
Residual, vol pct.	0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0
Loss, vol pct.....	1.5	1.0	1.5	1.0	0.5	3.5	3.0	3.0	3.0	3.5
Gravity, API at 60° F..	59.4	59.1	58.4	57.8	57.1	58.5	58.3	57.7	57.1	56.7