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Background

Over the last eighteen months Carson Associates has designed, provided project management, technical support, and analytical support to a demonstration of low percentage methanol-gasoline blends by the Bank of America. This activity was part of a more comprehensive program by the Bank which is also evaluating autos which use highly concentrated methanol fuel. The supporting fueling facilities are common to both aspects of the total program. This automotive operation, therefore, yields considerable insight into the problems of widespread introduction of methanol into an automotive fuel market which is dominated by conventional hydrocarbon fuels -- gasoline and diesel fuel -- and is likely to continue to be for many years yet.

Conservative projections for the 1988 - 1990 period of the plant gate selling price of methanol on an equal energy basis are favorable to methanol.[1,2] Based on work done by Ford, Volkswagon, and M.A.N., among others, it also appears that engine efficiencies can be greater using methanol than gasoline or diesel fuel.[3,4,5] The Environmental Protection Agency has been investigating emissions from methanol engines and has made favorable public commentary.[6] The raw material base exists to make methanol in quantities which could eventually supplant gasoline, coal being foremost among them for the foreseeable future.[7] For these and other reasons, automotive methanol is a subject of great interest.

However, it is unlikely that methanol will attain widespread use as an automotive fuel unless an economically viable way to gradually introduce it can be devised. This paper discusses some aspects of such a use.

The Preparation and Non-Linear Effects of Low Percentage Methanol-Gasoline Blends

It is known that, when blended in small proportions in gasoline, methanol introduces certain beneficial effects into the combustion process of internal combustion engines. These are counterbalanced by a low tolerance to pressure characteristics, and activity toward metals and elastomers as the methanol concentration is increased.

Figure 1 indicates the basic facility design use to provide both dry, low percentage blends and highly concentrated methanol fuel to the Bank of America fleet. Dry methanol fuel stored in one tank is mixed with dry unleaded gasoline from the other by a blending pump. For demonstration purposes, the blending pump was modified to accurately dispense blends of 2, 4, 8, 12, and 18 percent methanol in gasoline as well as straight unleaded gasoline and methanol fuel. Flame arrestors are provided in the vents to the methanol fuel tank to prevent any externally initiated flame from travelling through the tube into the methanol-air mixture above the fuel. This is a variance to conventional hydrocarbon fuel practice because the in-tank methanol-air mixture will usually sustain combustion whereas hydrocarbon fuel-air mixtures usually will not.

The water concentration history of the methanol fuel is depicted in Figure 2 for the two stations which supported the demonstration. The reductions indicated are due to improved mixing and handling procedures. When blended with gasoline the water concentration was even further reduced by the dilution of the methanol fuel. The gasoline, of course, is not completely anhydrous; it has a typical water concentration of about 120 parts per million . Consequently, the water concentration of the 2 percent blend is maintained at less than 135 parts per million. At this water concentration level no problems were encountered with phase separation during the demonstration even though operation was often conducted near the low temperature limit of this particular system of blended fuels. No cosolvent alcohols were used.

The selection of the blend percentage range of 2 to 18 percent was a compromise between pump design and a desire to investigate blends with a substantial direct gasoline displacement effect as well as those in which the octane boosting effect would predominate. The blends are characterized by decreasing energy density and increasing octane rating as the percentage of methanol is increased. The kinematic viscosity, which determines the volumetric rate of flow through the carburetor, changes very little as methanol is added, so that the volume of blend entering the cylinder during the intake stroke is essentially the same as for the base gasoline. However, this volume of blend cannot physically consume the same amount of air as does the gasoline. This is often called a leaning effect, but can equally validly be viewed as provision of excess oxygen by chemical means.

The salient features of the blended fuel system are summarized in Table 1 in terms of increased pump octane (R+M/2) and excess oxygen. The octane rating tests were performed by a recognized commercial laboratory using the standard ASTM procedures. The increase in pump octane rating is logarithmic in nature, so no attempt has been made to arbitrarily assign a blending octane number (which is defined by a simple linear blending algorithm) to methanol. Based on an extrapolation of the logarithmic curve, the pump octane for pure methanol would be 120.5. This value lies within the range of those reported in the literature.[8]

Table 1 - SALIENT BLEND CHARACTERISTICS

Blend Percent	0	2	4	8	12	18
Pump Octane	88.3	89.4	90.4	91.7	93.1	95.3
Excess Oxygen, %	-	1.5	3.1	6.2	9.3	14

The excess oxygen numbers are calculated from the basis of the stoichiometric fuel-air ratio for the base gasoline. While the provision of 1.5 percent excess oxygen by a 2 percent blend may seem small, it provides a greatly increased probability that the last few unreacted fuel molecules of burning mixture contained in a cylinder will come in contact with unreacted oxygen before being ejected out the exhaust valve. This results in significant decreases in emissions of carbon monoxide and unburnt hydrocarbons when the engine is tuned to operate at stoichiometric conditions on gasoline.

The effects of the increased octane and excess oxygen on energy economy and emissions are seen in Figure 3 which summarizes the results of driving cycle tests (CVS-75) of the type used by the EPA to certify compliance of new model cars with federal emissions and fuel economy requirements. These tests were performed by the Automotive Laboratory of the University of Santa Clara using fuel supplied by the Bank of America rather than the standard engineering test gasoline called indolene for which the emission standards were derived.

Currently regulated emissions are shown in the top blocks, aldehyde emissions in mid-page, while energy economy is shown below. The left hand set of graphs was generated by an older car which is equipped with a conventional carburetor, a "two-way" catalytic converter which reduced pollutant "two ways" by oxidizing unburnt carbon monoxide and hydrocarbons, and a conventional vacuum actuated spark advance mechanism. The right hand set of graphs is from a new car equipped with a "feedback" fuel control (a sophisticated carburetor) which maintains the fuel-air ratio very close to stoichiometric. The purpose of this feature is to create ideal operating conditions for an additional catalytic converter intended to reduce oxides of nitrogen (so that the system now reduced pollutant "three ways", hence the nickname "three-way converter"). Because this reduction converter functions best with minimum oxygen, a sensor has been installed near the exhaust valves which generates a signal which in turn is converted by a microprocessor into a control signal to regulate the carburetor jet openings. The three-way car is also equipped with a ping detecting spark control device which automatically advances the spark setting to the ping limit to extract the maximum energy from each piston stroke. Introduced into California in 1980, the three-way system becomes mandatory across the United States in the 1981 model year.

The patterns of controlled emissions versus increased methanol percentage are similar for the two cars in that a small amount of methanol decreases unburnt hydrocarbons and carbon monoxide significantly, while oxides of nitrogen remain relatively constant. Energy economy increases in both cases, peaking at a 15 percent increase for the two-way car and a 20 percent increase for the three-way car.

Aldehydes were tested to see if any significant increase occurred. While aldehydes are not regulated, formaldehyde is a component of smog and is under environmental review. The test used is primarily sensitive to formaldehyde. Aldehyde emissions decrease for the newer car and, after an initial increase, also for the older. But the maximum for the older car is less than that for the newer car on gasoline. Thus there seems to be little reason to expect that aldehyde emissions will increase with increased blend usage.

Evaporative emissions were also evaluated for the two cars. These emissions are simply fuel vapors which are emitted from the auto after it has been driven or has become hot from being parked outside on a summer day. The current standard is 2 grams for each test which combines a simulated hot day cycle and cooling down after a driving cycle test. Because of effects which will be discussed later, a three-way car showed three times the standard but in turn was three times better than the older car's test with gasoline. There are relatively simple changes which can be made to car design to counteract these emissions, and the fuel can also be made less volatile.

Synopsis of Fleet Test Fuel Economy Findings

With some reservations, the laboratory results were used as a guide to the expectation of performance of fleet cars in everyday use. For instance, it is known that many later two-way cars were tuned lean to improve the poor nitrogen oxides performance evidenced by the laboratory tests of the two-way car. With such cars, drastic reductions in emissions do not occur with the addition of methanol, nor does the energy economy increase. However, performance is not degraded unless the mixture becomes overly lean for smooth firing.

On the other hand, the closely controlled carburetion and spark setting characteristics of the three-way car leads to the expectation of repeatable emissions and energy economy performance. As is the case with actual road performance of new cars versus the EPA certified fuel economies, it would not be expected that fuel economies obtained in actual use would match those certified by EPA because of the more demanding nature of everyday driving as compared to the carefully programmed driving cycle tests. For the road tests fuel economy (miles per gallon) was measured rather than energy economy (miles per mission Btu) because the prime interest was on determining economy of operation. Because the energy density of these blends is not greatly different from that of the base gasoline, little change is introduced in qualitative extrapolation of results using fuel economy instead of energy economy.

These expectations were in fact upheld in a road test performed from November 1980 through January 1981. Over 180,000 miles were driven by 93 cars in performance of routine Bank duties. For the most part, the cars were driven by the same drivers over the same routes during formal data collection as they had been before. Table 2 shows the experimental structure used. Figure 4 shows the aggregate fuel economy results (total miles/total gallons) obtained for the two-way cars, the three-way cars, and for the blend fleet overall.

Table 2 -- BASIC EXPERIMENTAL STRUCTURE

	0	2	4	8	12	18	Totals
Two-way Cars	34	6	11	6	3	2	62
Three-way Cars	10	9	10	1	1	-	31
Totals	44	15	21	7	4	2	93

Two-way cars show a slight increase in fuel economy for the 2 and 4 percent blends, but a slight decrease for blends overall. Three-way cars show an increase of about 13 percent for all blends. This increase is attributed to the ping detecting spark advance mechanism being able to consistently exploit the potential energy in the fuel-air mixture on each power stroke. Note the decrease in fuel economy of the control cars as compared to their pre-test performance. This is attributed to the seasonal change from summer to winter gasoline at the beginning of the data collection period. The winter grade gasoline had 5 percent less energy per unit volume than the summer grade. This is usual commercial practice and results from approximately doubling the C4 and C5 hydrocarbon fraction in the gasoline to raise the vapor pressure for cold weather starting.

Because the blends achieved equal or improved fuel economy and are cheaper per gallon, fuel costs of operation were reduced about a cent per mile for the blend vehicles as compared to the controls. This resulted in a positive return on investment when blend use was extrapolated over the next ten years. Depending on the assumptions made for the rate of increase of blend use, the maximum number of cars to operate on blends, the incremental capital costs, and some nine other variables, the savings to the Bank of America should fall between 1.5 and 4.5 million dollars over the decade.

Vapor Pressure Characteristics

Because the tests were performed in the mild winter climate of California, improved driveability was reported for the blends. This is due to both higher octane and higher vapor pressure for the blends than for the base gasoline. This result repeats the experience of the Imperial Chemical Industries in England in the late 1920's when a similar blend was successfully marketed for several years.[9] Such favorable driveability results would probably not have occurred in very warm weather since it is known that the vapor pressure characteristics of methanol/gasoline blends are non-ideal and can lead to vapor lock, excessive evaporative emissions, and undesireable in-tank pressures in those conditions. However, little existed in the technical literature describing the basic mechanisms of such vapor pressure reactions. Therefore a modest project was instituted to better understand these reactions. As a consequence, a non-linear predictive technique was developed based on ASTM distillation curves for the base gasoline which proved useful in predicting the vapor pressure and composition of the blends.

The nature of the non-linearity can be seen in Figure 5. At 20 degrees Centigrade, the vapor pressure of gasoline is seen to be greater than that of pure methanol, but the vapor pressure of the blends exceeds that of either as shown in the characteristically plateau-shaped central region of the graph. Also illustrative are the ASTM distillation curves of a gasoline and various blends of ethanol and methanol shown in Figure 6. From such behavior it becomes apparent that the polar alcohol molecules form low boiling azeotropes with the lighter hydrocarbons in the gasoline. This is indicated by the lower distillation curves for the blends and the constant temperature plateaus very nearly at the boiling points of the respective alcohols until reaching percentages distilled well in excess of the combined alcohol and light hydrocarbon fractions.

Potential Uses of the Modified Azeotropic Characteristics

These different azeotropic properties, currently disregarded or considered outside of the scope of refiners' activities, can conceivably be of use for fuel blending and energy conservation purposes. In blending auto fuel, for instance, the addition of methanol permits use of higher percentages of heavy hydrocarbons for a given vapor pressure at a given temperature. This should reflect in an increased yield of auto fuel from the heavier crudes which are becoming more and more common. For instance, Figure 7 illustrates a blend of hydrocarbons and methanol which should prove very satisfactory for hot weather use.

Some initial work has been done by Southwest Research Institute under Department of Energy sponsorship in assessing unorthodox blends as emergency fuels.[10] They have published fuel economy, emissions, and driveability results for a number of blends which included such elements as naptha, kerosene, and diesel fuel as well as gasoline and alcohols. In some cases there appeared to be a synergism which yielded significantly higher miles per gallon in unmodified engines than expected on the basis of the fuel's energy density. Such results should be thoroughly investigated and understood as they could have significance well beyond their technical aspect.

Vapor Pressure Tailoring at the Refinery or by Azeotropic Distillation

Vapor pressure tailoring of the base blending gasoline could be done most simply at the refinery level. The C4-C5 stream now blended into unleaded gasoline could be easily diverted into other chemical process streams. In particular, the C4's can be converted to isobutene for production of methyl tertiary butyl ether (MTBE), another methanol containing octane boosting additive which exhibits little water sensitivity. Isobutene is forecast to be the limiting factor in MTBE production. The remainder of the C4-C5 stream could be used for the hydrocarbon starting fraction for methanol fuel used in carbureted cars.

Replacement of the C4-C5 fraction by a few percent of methanol would be sufficient to raise the vapor pressure to the original value. It would also provide sufficient octane boost to exceed the octane rating of the original gasoline. Because of the cost advantages of methanol relative to similar uses of tertiary butanol or ethanol, some refiners may use this concept for blends customized with methanol in some locations and MTBE or methanol and tertiary butanol in others, depending on climate and geography. ARCO and CONOCO are likely candidates for such strategies because of their deep backgrounds and interest in methanol.

The methanol-aided azeotropic distillation would seem to be of use in refinery applications where accelerated low temperature separation of light hydrocarbons is desired.

As an alternative to refinery blending, the light hydrocarbon fraction can be removed from commercial unleaded gasoline by simple azeotropic distillation. A pilot scale flash distillation facility with minimum fractionation capability would be adequate for the purpose. The level of difficulty is not significantly different than that involved in the operation of an ethanol still.

The extent of tailoring the blending characteristics of commercial unleaded gasoline by this method is illustrated in Figures 8 and 9. These data were generated by means of the following equation:

$$L = \frac{\pi F1}{\pi + P1\ K1\ (V/L)} + \frac{\pi F2}{\pi + P2\ K2\ (V/L)} + \frac{\pi Fn}{\pi + Pn\ Kn\ (V/L)} \qquad (1)$$

Where:

F is the percent of each constituent. (The fraction)
P is the vapor pressure of each constituent at the ditillation temperature in millimeters of Mercury.
π is the pressure at which the azeotropic distillation in the vapor phase.
V is the percent composition of the constituent in the vapor phase.
L is the percent composition of the constituent in the liquid phase.
K is the constant for non-linear vapor pressure elevation when methanol is added.[11]

The equation contains two variables, V and L, which must be determined by means of an iterative trial-and-error process. Successive values of V and L are assumed which cause convergence to a unique set of fractions. The data as displayed in Figures 8 and 9 indicate the relative amounts of light hydrocarbons which can be removed from an unleaded gasoline or a methanol-gasoline blend by azeotropic distillation. It is apparent that the light ends can be removed with a 20 percent cut at 120°F over a wide range of C4-C5 contents. Smaller amounts of heavier hydrocarbons are removed at the same time. This is characteristic of azeotropic distillation and is an important determinant in yielding a distillate cut which is storable at room temperatures.

The compositions of the distillate cuts are given in Figure 10. The vapor pressure characteristics of such distillate cuts are similar to aviation gasoline and similar storage facilities would be adequate. This blend might be useable as aviation fuel or in a similar application where high volatility is desired.

Conclusion

This paper has touched upon aspects of the utility of methanol blended with gasoline and sketched the nature of the non-linear vapor pressure phenomena associated with such blends. It is the author's belief that widespread use of blends would be beneficial in terms of energy conservation, improved air quality, and greater yields of transportation fuel from low grade crudes. Further, the use of a mixed strategy of simple methanol blends, blends which use methanol and cosolvent alcohols, and MTBE can permit a wide variety of vapor pressure tailoring strategies for varying geographic and climatic conditions. Also, some processing efficiency improvements seem feasible.

The use of methanol in this way can promote the commercial introduction of neat methanol automotive fuel by increasing its availability for fleet use and development of more advanced engines pending the commercial introduction of price competitive methanol derived from coal.

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Figure 1

PROTOTYPICAL DISPENSING FACILITY

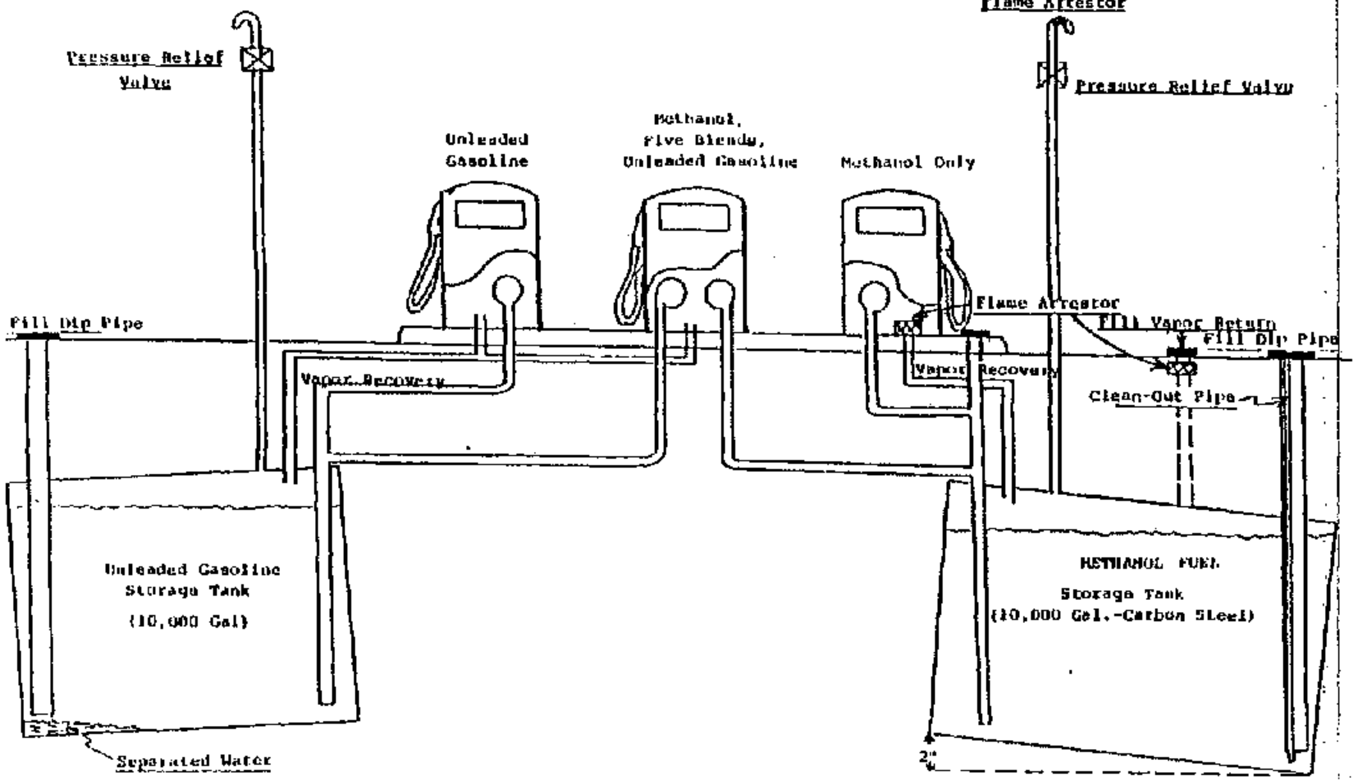


Figure 2

WATER CONTAMINATION HISTORY FOR SAN FRANCISCO, LOS ANGELES, AND DUBLIN MX STORAGE TANKS

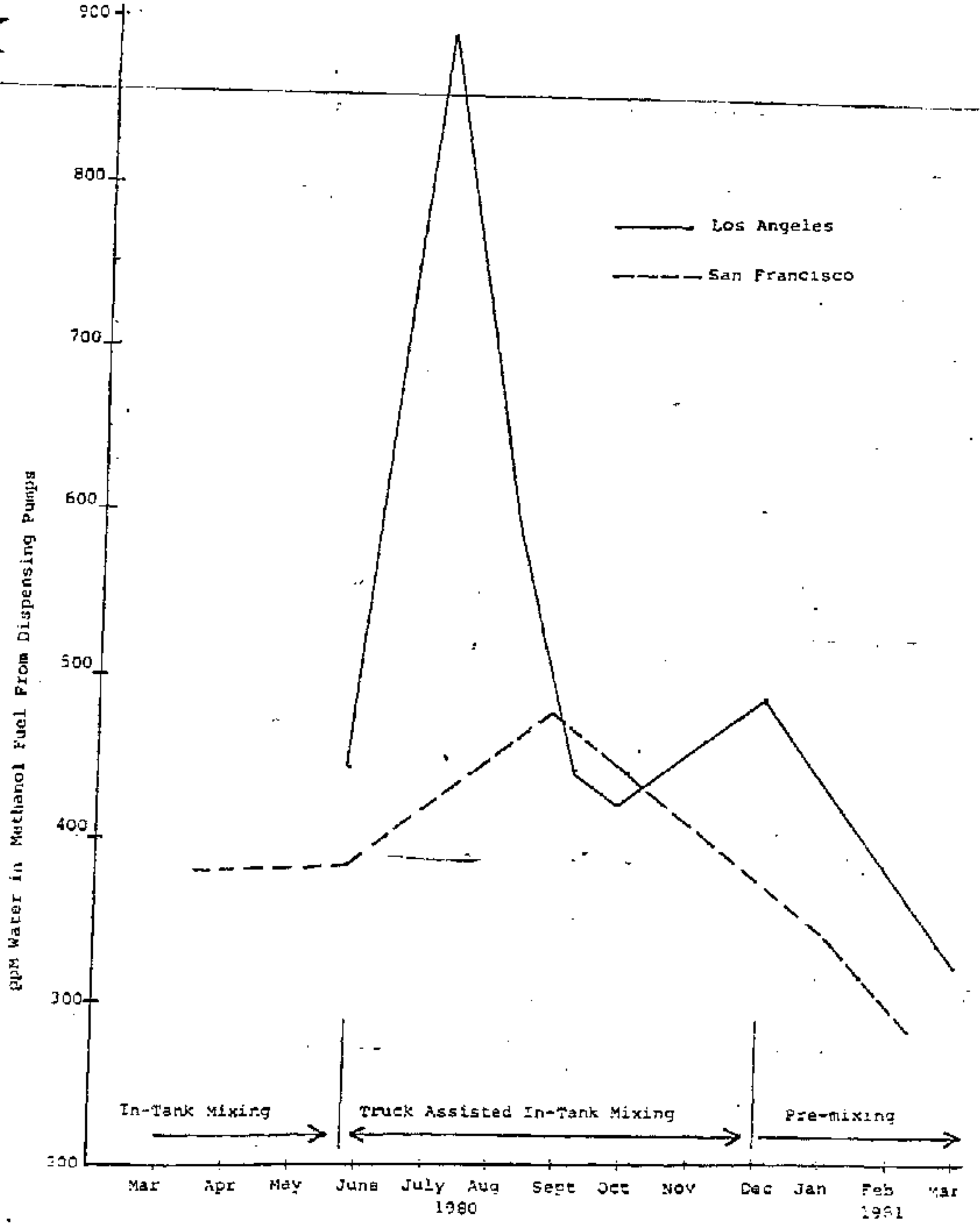
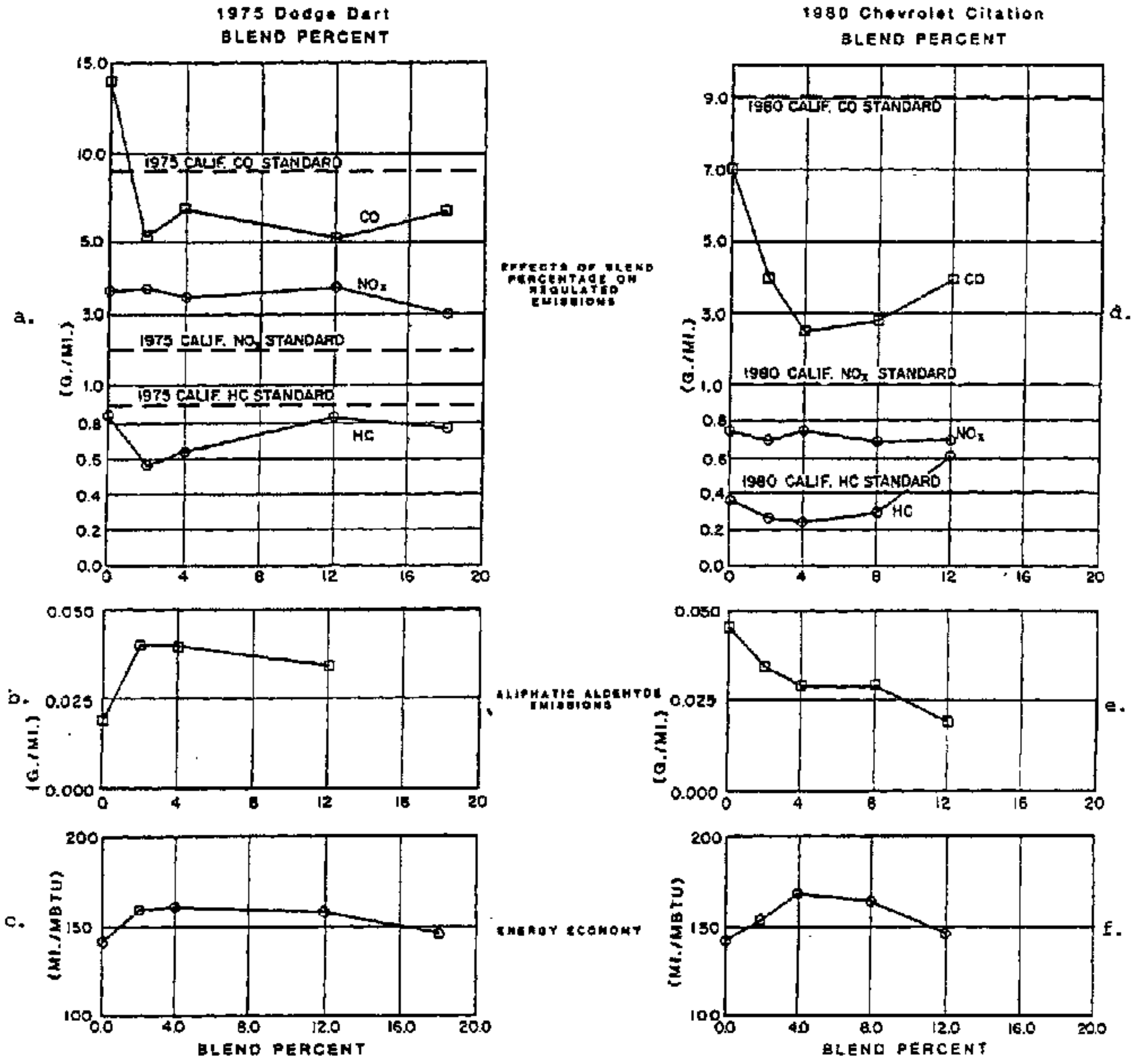


Figure 3

Characteristic Emissions & Energy Economy Effects



TWO-WAY

THREE-WAY

Figure 4

AGGREGATE FUEL ECONOMY PERFORMANCE FOR BLEND CARS

(mpg/#cars)

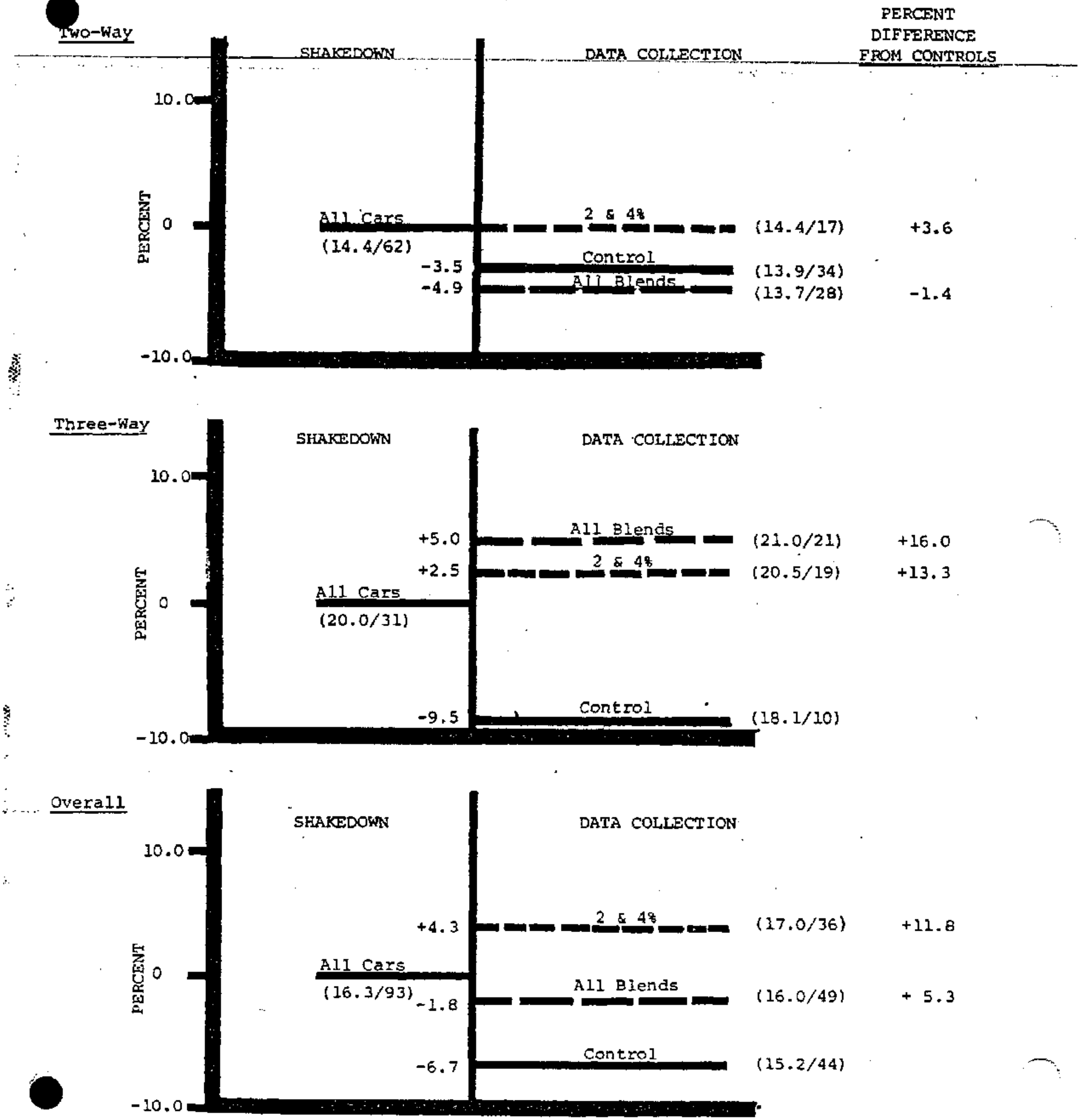
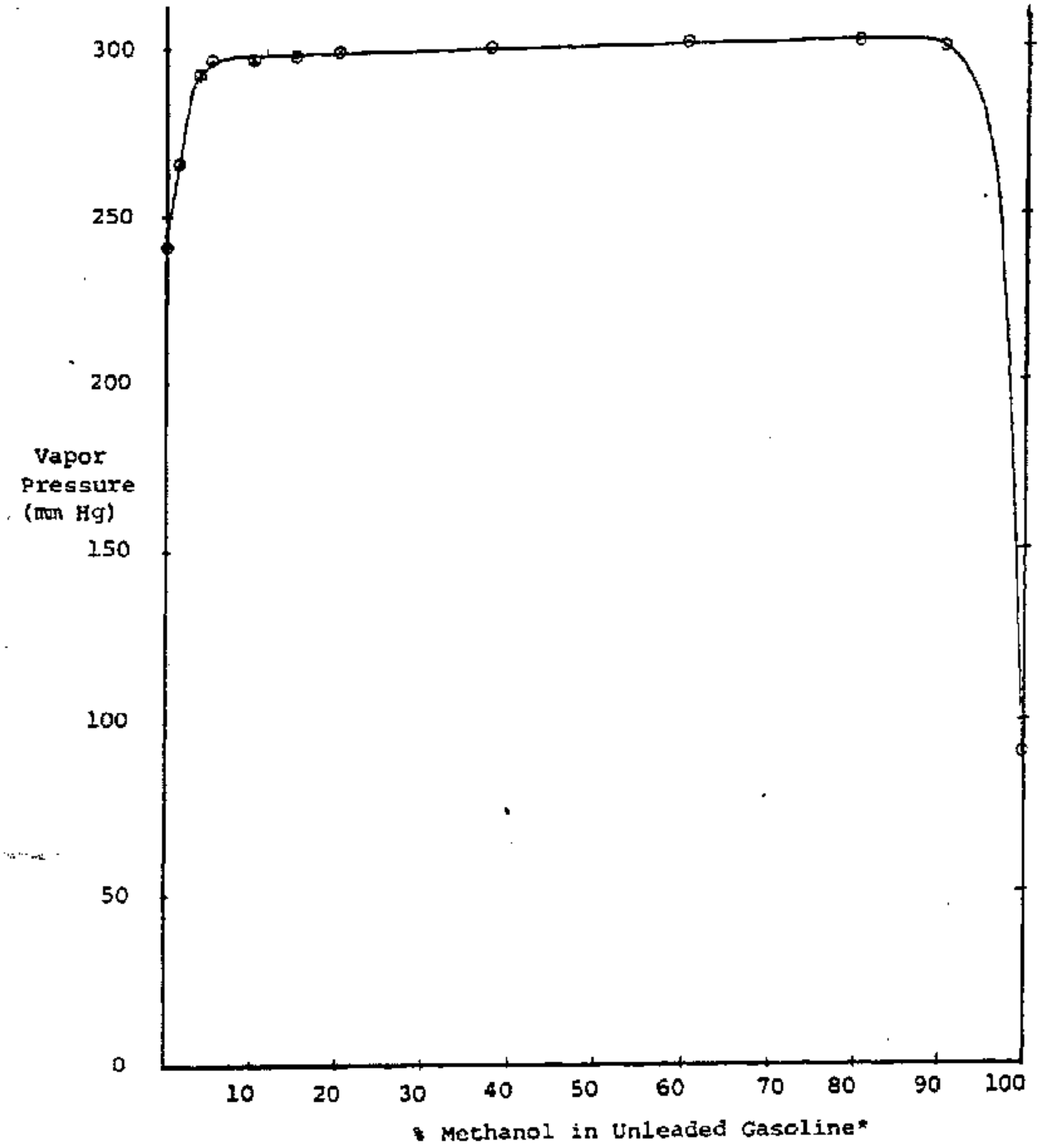


Figure 5

METHANOL/UNLEADED GASOLINE EQUILIBRUIM VAPOR PRESSURE



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* Base Gasoline taken from Bank of America, Maple Ave., Service Facility, 7/31/80

Figure 6

DISTILLATION CURVE

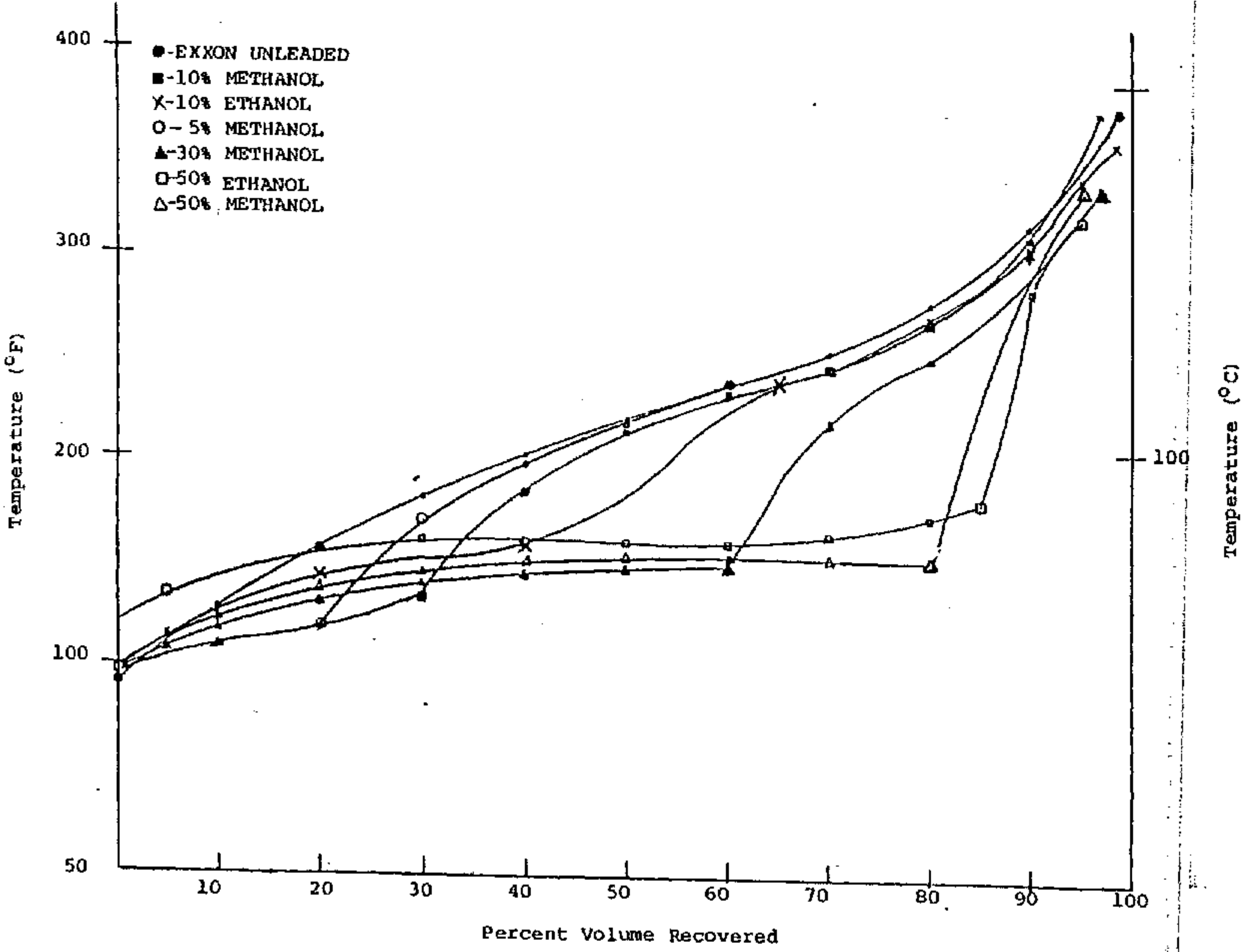


Figure 7

ILLUSTRATIVE HOT WEATHER METHANOL/GASOLINE COMPOSITION

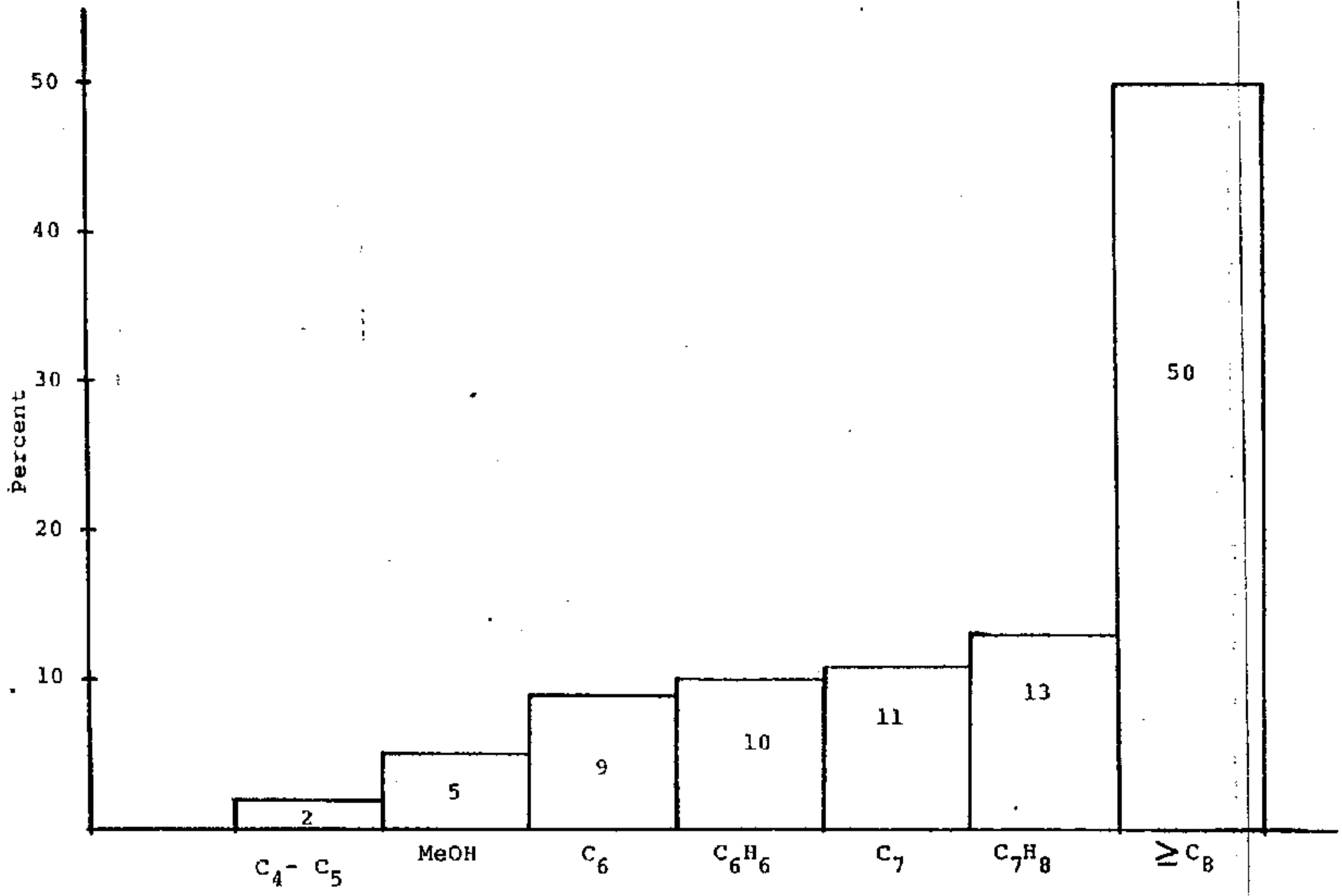


Figure 8

ASTM DISTILLATION OF LIGHT ENDS FROM TWO UNLEADED GASOLINE COMPOSITIONS

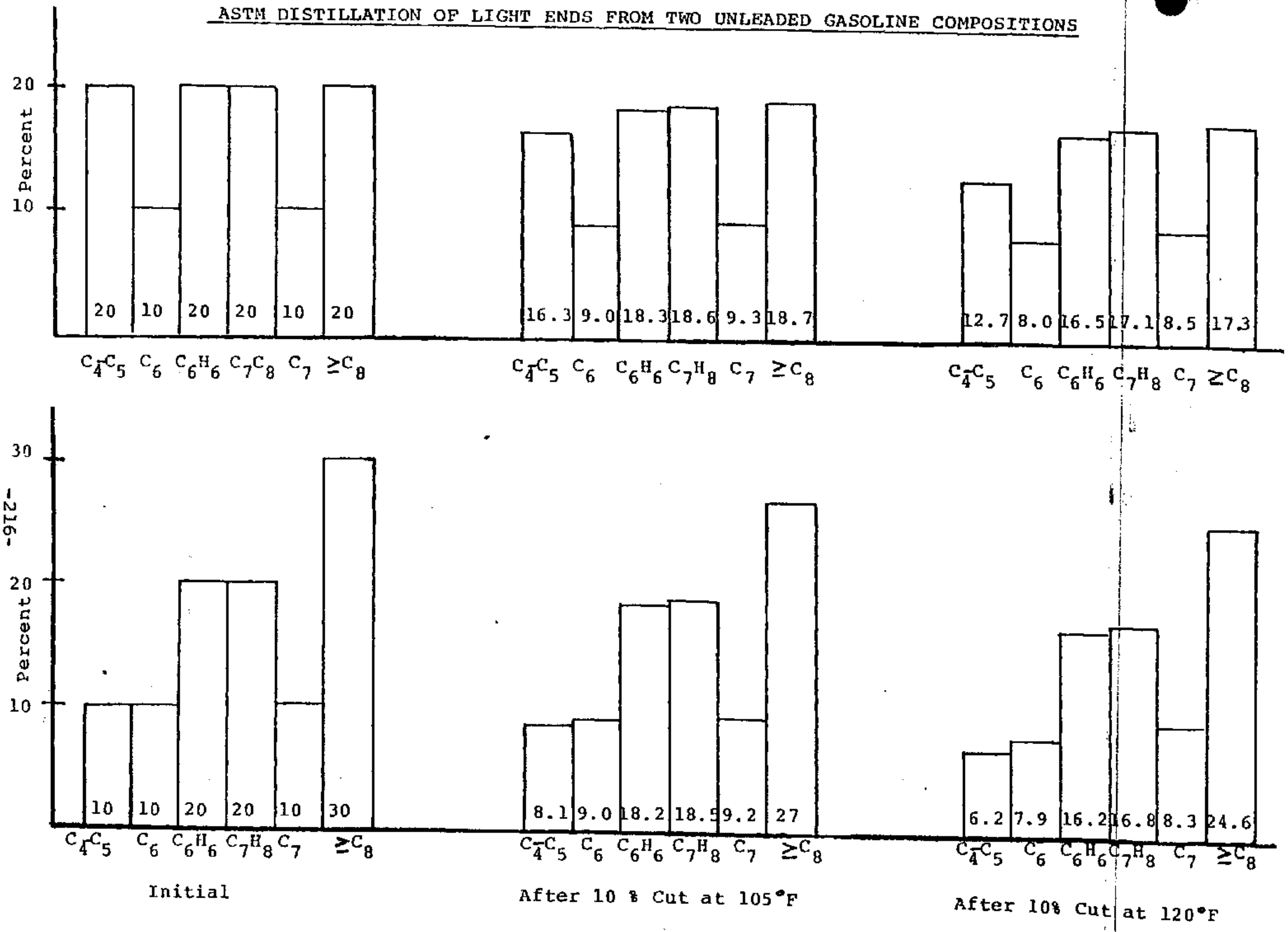
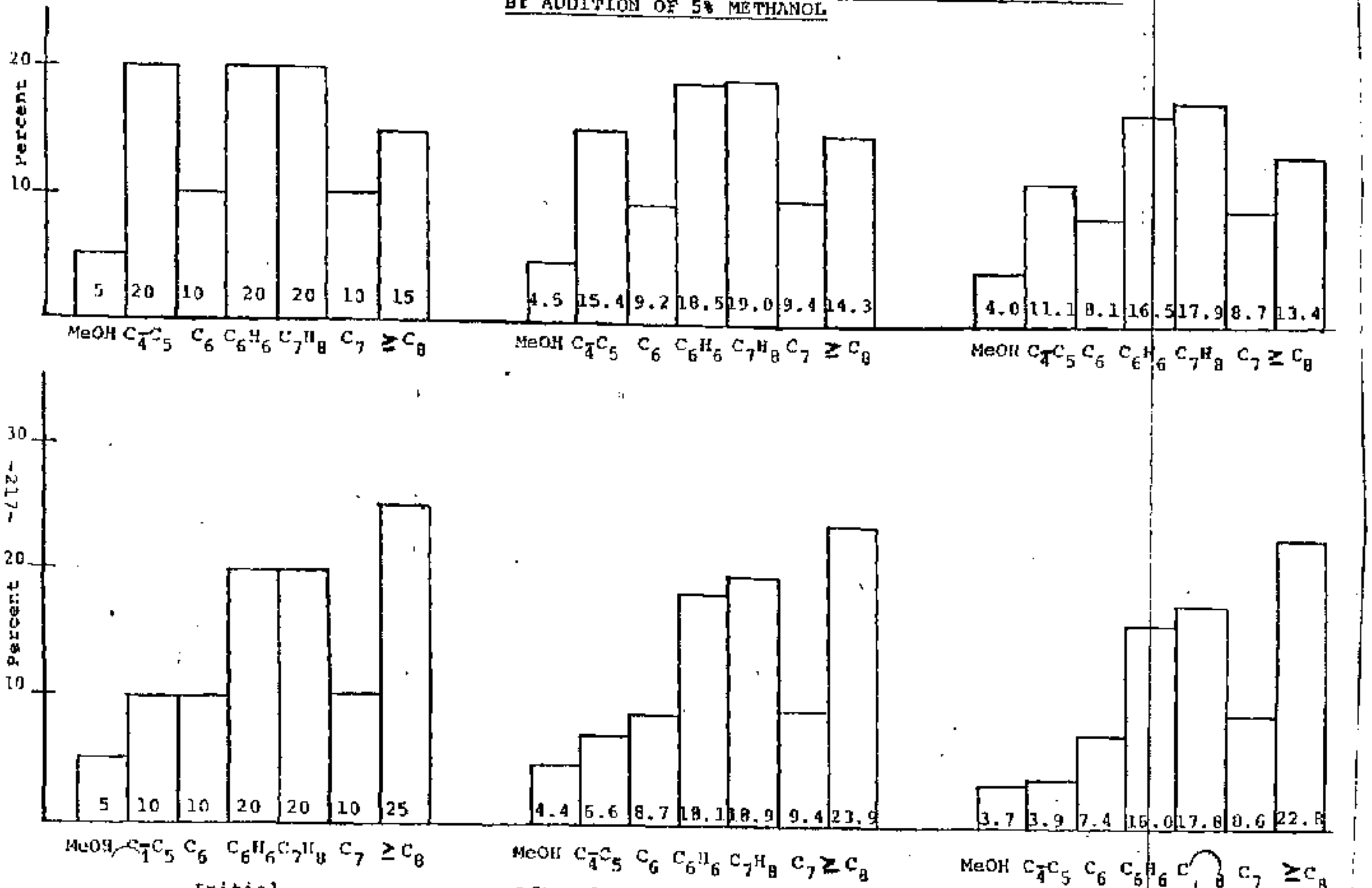


Figure 9

ACCELERATED REMOVAL OF LIGHT ENDS FROM TWO UNLEADED GASOLINE COMPOSITIONS BY ADDITION OF 5% METHANOL



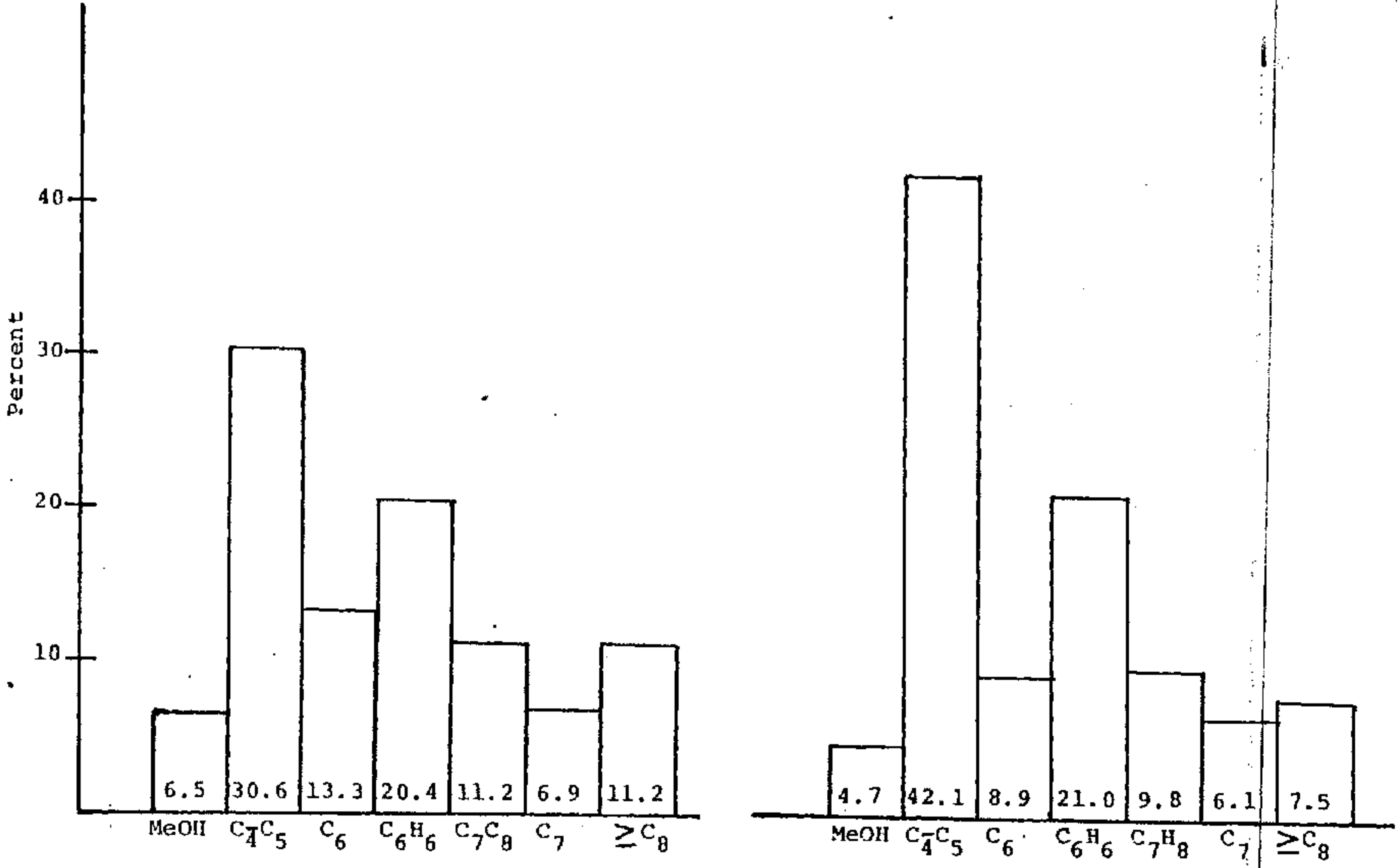
Initial

After 10% Cut at 105°F

After 10% Cut at 120°F

Figure 10

COMPOSITION OF DISTILLATE COLLECTED AFTER 20 PERCENT CUT AT 120°F



Unleaded Gasoline with Initial
10 Percent C_4-C_5 Composition

Unleaded Gasoline with Initial
20 Percent C_4-C_5 Composition