

The Effect of Ullage on the Flash Point and Lower Flammability Limit Temperatures of JP-5 Jet Fuels

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ABSTRACT

From theoretical considerations it can be shown that the relative size of the free-space ("ullage") above a liquid fuel mixture can be a significant factor in the flammability properties of such a system. A simple apparatus has been used to test the effect of ullage on flash point and lower flammability limit temperatures of JP-5 jet fuels. Results indicate that both ullage and time to achieve equilibrium conditions are factors. In general, flammability limit temperatures decreased with decreasing ullage, the rate and magnitude of the decrease depending on the composition of the fuel. Thus, at smaller ullages, flammability hazard is increased. In one instance, the extrapolated flammability temperature of a specification JP-5 jet fuel was 26°F lower than its ASTM flash point as ullage approached zero. The data suggest that both the rate of temperature decrease with decreasing ullage, and the limiting value at zero ullage are important information in evaluating flammability properties of JP-5 fuel mixtures.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C01-03
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THE EFFECT OF ULLAGE ON THE FLASH POINT AND LOWER FLAMMABILITY LIMIT
TEMPERATURES OF JP-5 JET FUELS

INTRODUCTION

Petroleum fuels do not burn in the liquid phase. In order to burn, they must be vaporized and mixed with air. In a tank containing fuel, the free space above the liquid (ullage) represents a potential fire or explosion hazard if the fuel vapors are in a flammable concentration. Since jet fuel is stored in the skin tanks of aircraft carriers, it is mandatory for safety that the concentration of fuel vapors in the ullages of these tanks be well below the flammability range. This has led to the present military specification requirements (1) for JP-5 fuel to have a flash point of 140°F (minimum) and a value of less than 50% in the "explosiveness" test at 125°F. Helpful as these two tests are in promoting safety, they give only a partial measure of the true flammability picture in the ullage space of a tank containing fuel. It is desirable, then, to consider in more detail those properties of both pure hydrocarbons and fuels that affect flammability in ullage spaces, and the conditions needed to achieve it.

The flammability of a single pure liquid hydrocarbon in air in an enclosed space at atmospheric pressure depends on the vapor-air ratio (or vapor concentration) above the liquid and the lower and upper flammability limits of the hydrocarbon. Under equilibrium conditions the concentration of vapor above a liquid depends on the vaporization tendency (vapor pressure) of the liquid. Vapor pressure is temperature dependent, increasing exponentially with temperature.

Suppose that for a given hydrocarbon the temperature is relatively low, so that the vapor concentration above the liquid is too lean, and is non-flammable. At increasing temperatures, more hydrocarbon vaporizes leading to higher vapor concentrations above the liquid. Eventually a temperature will be achieved at which a flammable vapor concentration is just reached and this is the concentration at the lower flammability limit. This temperature, below which the mixture is non-flammable, is called the flash point temperature, but more properly should be referred to as the lower flash point temperature, or the lower flammability temperature limit. A corresponding temperature (the upper flash point temperature) also exists at the upper flammability limit, above which the vapor mixture is too rich and therefore, non-flammable. The region between these two limits is called the flammable temperature (or concentration) region for that hydrocarbon in air.

If, in a tank containing a liquid hydrocarbon and a free air space above, we assume (a) equilibrium conditions between the liquid and the evaporated vapor, (b) the presence of excess of liquid, and (c) uniform vapor-air composition throughout the free space, then the flammability will be a function of temperature only and will be independent of the size of the ullage above the liquid.

In the case of liquid solutions of two or more volatile components, such as jet fuels, the problem is more complicated. In the first place, the relative fuel concentrations in the vapor space above a liquid fuel mixture will depend on the relative concentrations and individual vapor pressures of the individual constituents of the liquid. Secondly, the flammability limits of a multicomponent vapor mixture and air are a function of the limit concentrations of the individual vapor components. The theoretical aspects of this problem are presently being studied and will be reported later.

The size of the free space above a liquid mixture will influence the relative amounts of vaporization (fractional distillation) of individual constituents, and hence the flammability of the vapor mixture above the liquid. The lower flash point or lower flammability limit temperatures of a fuel mixture should therefore vary with ullage. It was decided to test this concept by a simple experiment. The results are being reported now because of their implications and timeliness. Further experimental work on binary and multicomponent mixtures is in progress.

EXPERIMENTAL

A large test tube (19.5 cm., 4 cm. diameter, 171 ml.) containing varying amounts of fuel was immersed in a carefully controlled constant temperature bath, and allowed to equilibrate with occasional shaking from time to time. The tube, (Fig. 1) which was fitted with a teflon stopper containing two metal rods arranged as a spark gap in the free space above the liquid, was sparked, and ignition if any was noted. At a given ullage, the lowest temperature for positive ignition was recorded. This was done for three JP-5 jet fuels, and a sample of pure n-undecane.

RESULTS

The results for two jet fuels and pure n-undecane are shown in Figure 2, in which the lower flammability temperature limit is plotted against ullage. Ullage is calculated from the ratio of the volume of the vapor space to the total volume (liquid plus vapor), the result expressed as percent. Standard closed cup Pensky-Martens flash point temperatures (2) are also shown in the figure (triangles) for comparison. Ullage for the ASTM apparatus is approximately 39%.

The curve for n-undecane is a horizontal straight line showing negligible change of lower flammability temperature limit (t_L) with ullage, and the ASTM flash point temperature falls on this line. This is as would be expected for a single pure hydrocarbon. The JP-5 fuels, however, behave somewhat differently, tending to show decrease in t_L (downward slope to the left) with decrease in ullage. The curve for JP-5 fuel No. 424 suggests a slight slope, and increasingly greater slopes were exhibited by No. 437,

(not shown in graph), and No. 417 respectively. The ASTM flash points of two of the three jet fuels (No. 424 and 437) do not meet the minimum requirement of 140°F (60°C) of the military specification (1), and are in all three cases higher than the respective t_L values. That the flash points (t_F) are higher than the t_L values is not unexpected since the latter were determined under equilibrium conditions.

The data suggest composition differences among the three jet fuels (small concentrations of more volatile components) which result in t_L variations with ullage. From the point of view of fire and explosion hazards, the results imply that the flash point alone is not a very dependable measurement of hazard, since it is shown that ignition may be possible below the flash point temperature. The data also indicate that the relative size of the vapor space above the liquid in the test chamber may influence the results which will be obtained. Since t_L values decrease with decreased ullage, the data suggest that the limiting value for these temperatures should be at minimum ullage. The curves were therefore extrapolated to zero ullage to observe what these minimum temperatures would be in the cases of the three fuels which were studied. The results are shown in Table I. It can be seen that experimental lower flammability limit temperatures (t_L) were obtained for the three fuels which were lower than the ASTM flash point temperatures (t_F) by 5, 7 and 11°F (3, 4, and 6.5°C), and the minimum extrapolated values (t_L') were lower by 5, 16, and 26°F (3, 9, and 14.5°C) respectively for fuels Nos. 424, 437, and 417.

Another interesting concept which is suggested by the data, is that the relative fire hazard of a given fuel is not necessarily indicated by a single isolated value, whether it be an ASTM flash point temperature, or a lower flammability temperature limit. It would seem that more than one measurement is necessary at different ullages in order to obtain the slope of the curve. The importance of slope is shown in Fig. 1. For example, with the t_L values and the ASTM flash point temperature for jet fuel No. 424 are greater than those of fuel No. 417, suggesting that the former is a safer fuel. However, because of its greater slope at decreasing ullage, the curve of fuel No. 417 crosses and passes the curve of No. 424, and extrapolates to a lower minimum value. Thus, in an almost full tank, fuel No. 417 would be the more hazardous fuel.

CONCLUSIONS

The data suggest that both ullage and time to reach equilibrium conditions are important factors in the determination of minimum flash point type temperature measurements for jet fuels and similar complex mixtures. From the viewpoint of fire safety, the smaller the ullage, and the closer to equilibrium conditions, the lower and more meaningful will these temperature values be. It also is suggested from the data, that, in the inspection of a JP-5 fuel for

safety, it might be desirable to make two or more determinations at different but small ullages, in order to determine the slope, and hence, the lowest flammability temperature as ullage approaches zero.

TABLE I

LOWER FLAMMABILITY TEMPERATURE LIMITS FOR JP-5 FUELS

JP-5 Sample Number	ASTM Flash Point (t_F , °F)	Lower Flammability Temperature Limits (t_L , °F)			
		Exper. Min. (t_L'')	Difference ($t_F - t_L''$)	Extrap. Min.* (t_L')	Difference ($t_F - t_L'$)
424	138	133	5	133	5
437	138	131	7	122	16
417	146	135	11	120	26

* $t_L' = \lim_{V \rightarrow 0} t_L$, (where V = Ullage)

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- (2) American Society of Testing Materials, Flash Point by Pensky-Martens Closed Tester, ASTM D93-61, (1961).

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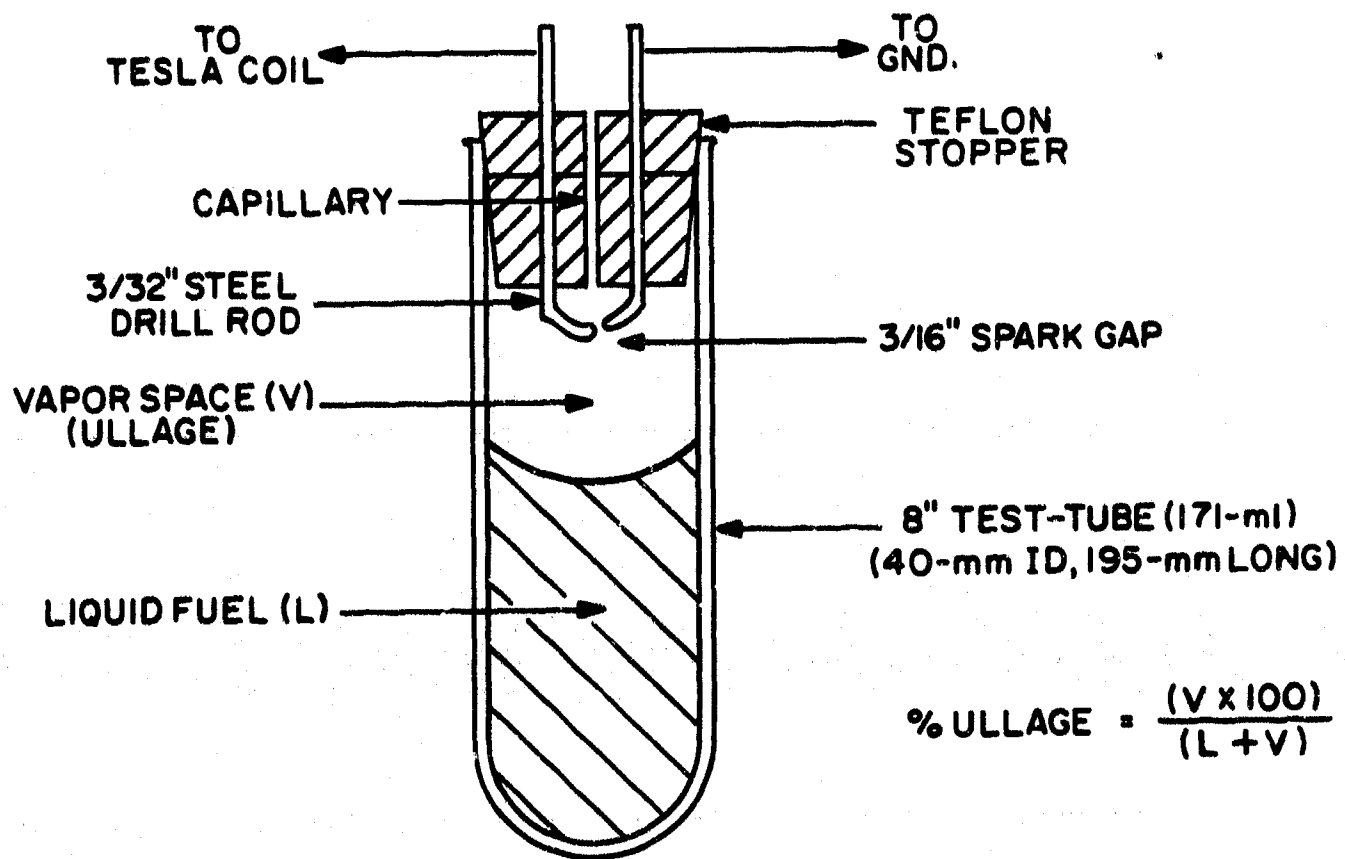


Fig. 1 - Lower flammability temperature limit apparatus

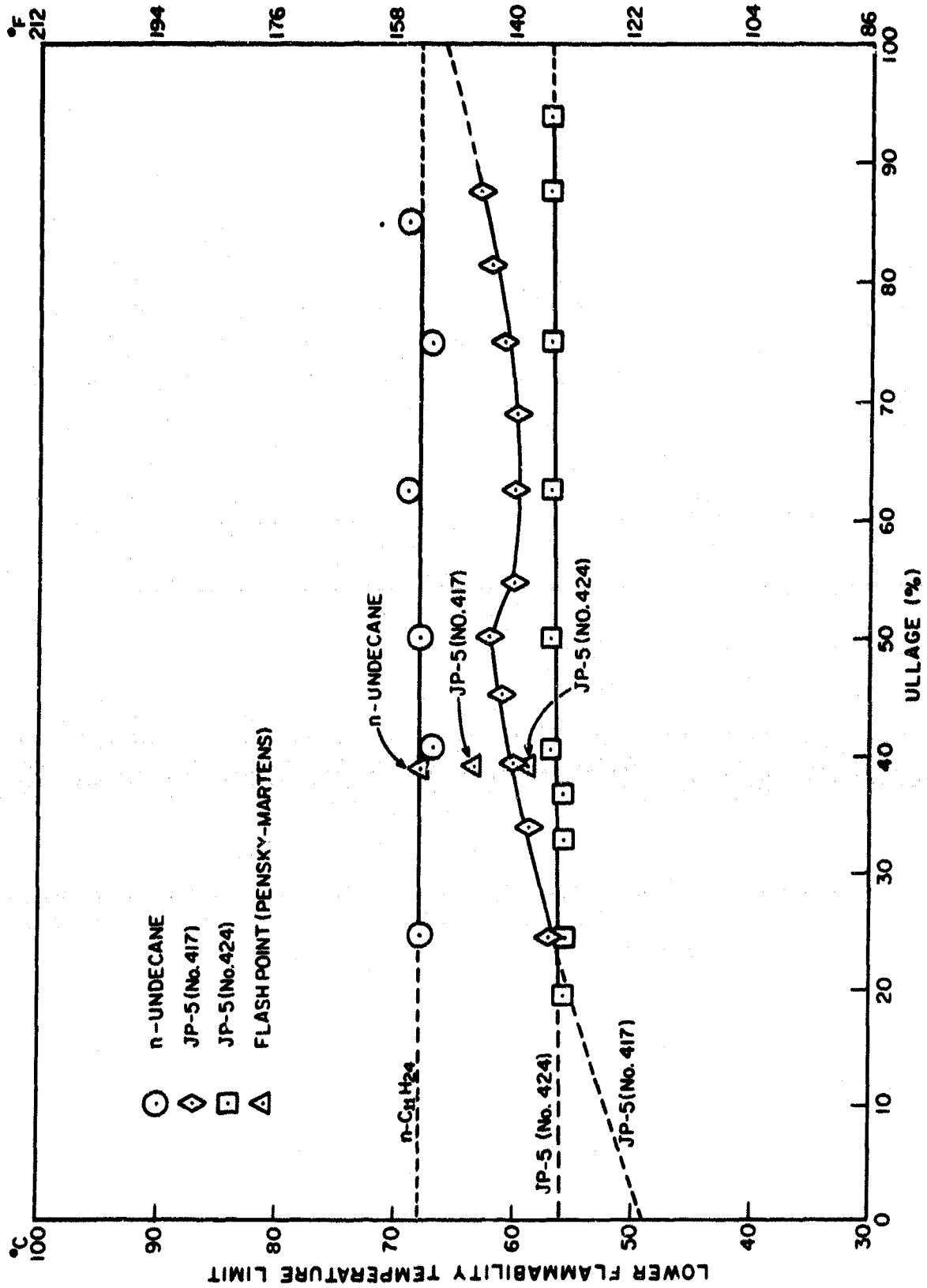


Fig. 2 - Lower flammability temperature limit versus Ullage for JP-5 jet fuels

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