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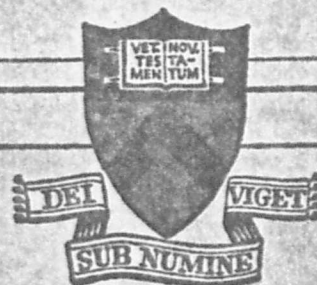
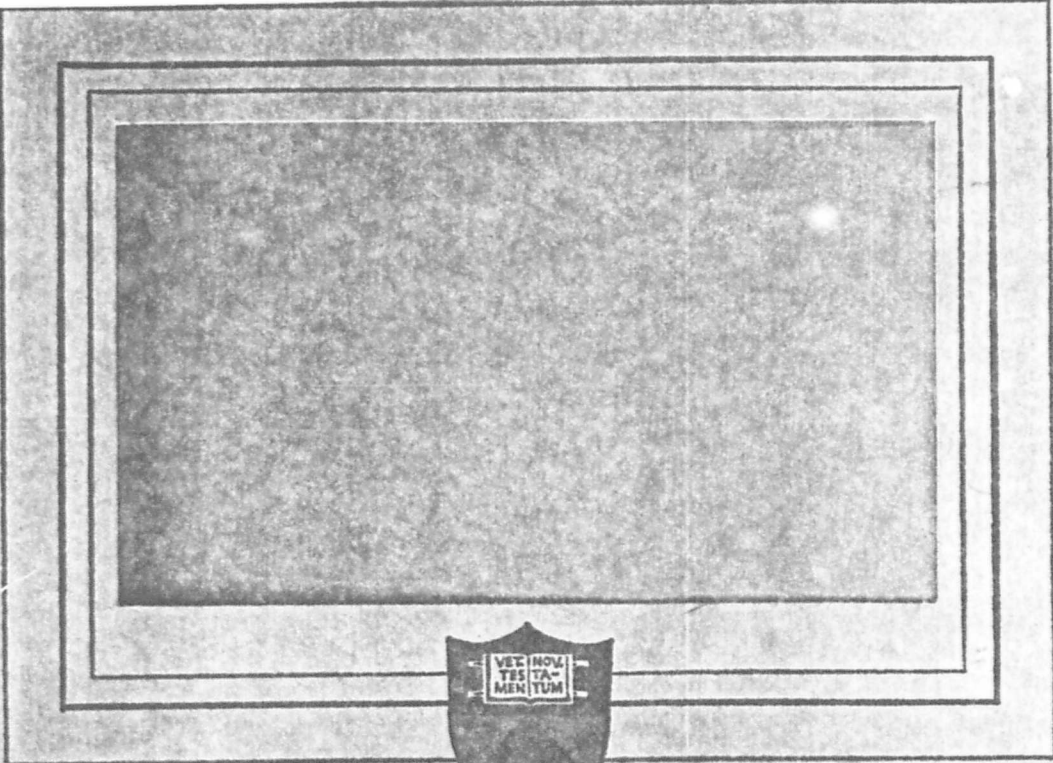
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SOME THOUGHTS AND EXPERIMENTS ON
LIQUID FUEL FLAME SPREADING, STEADY BURNING
AND IGNITABILITY IN QUIESCENT ATMOSPHERES

by

Irvin Glassman and James G. Hansel

Aerospace and Mechanical Sciences Laboratory

Report No. 841

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Physics of Flames.

Guggenheim Laboratories for the Aerospace Propulsion Sciences
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July, 1968

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SUMMARY

The concept of the liquid flash point is shown to be important in evaluating the means of propagation of a flame across a fuel surface. Gas phase phenomena control the propagation rate when the liquid temperature is above the flash point and liquid phase phenomena control when the temperature is below the flash point. Fluid motion generated by surface tension and/or buoyancy (gravity) effects plays a dominant part in this latter case. Increasing the viscosity of the fuel lowers the rate of flame propagation, but increases its ignitability, as given by model and experiment. It would be expected that the steady burning rate would be lowered as well.

The theories of flame spreading and steady burning under quiescent conditions have been reviewed critically. The new models presented have practical implications with respect to oil tanker disasters, inhibition of flame propagation by foamed plastics, and the ignitability, flame propagation and extinguishment characteristics of thickened fuels.

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Some Thoughts and Experiments on Liquid Fuel Flame Spreading
Steady Burning and Ignitability in Quiescent Atmospheres¹

by
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I. INTRODUCTION

The combustion process associated with large pools of flammable liquids can be divided into three phases: ignitability, flame spreading and steady burning. The nature of the research to be undertaken by the Combustion Research Laboratory at Princeton relates mainly to flame spreading and burning under quiescent and natural convection conditions. However, initial results on flame spreading have indicated some possible important effects concerning ignitability.

Early photographic observations by T. Eklund (1) in this laboratory were instrumental in the formulation of some preliminary models of flame spreading and subsequent thinking on burning and ignitability. The recent arrival of a copyrighted thesis (2) published in late 1966 by A. F. Roberts of Imperial College, London (now of Safety in Mines Research

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Establishment, Baxton) shows that Roberts had earlier undergone the same type of thinking, but perhaps had not extrapolated his thoughts quite as far as in the present work. Roberts' excellent work must be considered to have been first, even though some of his considerations were arrived at independently by the present authors. The models were a logical consequence of observations of simple experiments, and perhaps others have put forth similar thoughts, although a preliminary search of the literature has not revealed any very direct correspondence. This report represents a critical literature review and the current thinking of the authors on liquid fuel flame spreading, steady burning and ignitability. It further indicates the direction of effort to be followed in the Combustion Research Laboratory at Princeton.

II. THE RELATION OF THE FLASH POINT TO LIQUID POOL FLAME MODELING

Two empirical tests that are quite pertinent to the explanation of what governs the spread of a flame across a fuel surface will be discussed initially.

The first and perhaps most important is the flash point (3). The flash point is that temperature at which the liquid fuel will ignite in air when a pilot flame is passed near and at a fixed distance above the fuel surface. It is meant to specify the temperature at which the liquid can exert a vapor pressure so that a mixture of fuel vapor and air will just be within the flammability limits of the vapor mixture. Obviously the flash point will vary somewhat according to the position of the ignition source. The further the source from the liquid surface, the higher the ignition temperature. Diffusion of the vapor into the air controls the difference.

The fire point (4) is the temperature at which the liquid will not only ignite (i.e., flash), but will be sufficiently high that the ignition process will be sustained and the liquid will burn. Fundamentally it is the temperature that will create a mixture ratio near the surface so that the transfer number will be sufficiently great that the rate of energy release due to combustion will be at least equal to the rate of energy feed back necessary to evaporate the condensed liquid.

In estimating the mixture ratios mentioned above, it

would appear sufficiently accurate for purposes here to assume near the surface that the partial pressure of the fuel in air is equal to the vapor pressure.

If a fuel is at its flash point or above (really at its fire point*), and if ignited, a flame can spread over the liquid without requiring further vaporization. It is likely in such cases that phenomena in the gas phase will be controlling and the rate of spreading will be of the order of the laminar flame speed.

One knows, however, that a liquid below its flash point will sustain a spreading flame and subsequently burn. The logical process of sustaining the spreading flame is to have the liquid ahead of the flame heated to its flash point, so that when the flame arrives at that position it will be sustained. The methods by which the liquid ahead of the flame may be heated are: conduction through the gas ahead of the flame, radiation from the flame to the forward fuel surface, and heating from the flame and combustion gases behind the flame through the liquid. Estimates of the thermal conductivities of the gas mixture and the liquid indicate that it is a very good assumption to ignore conduction in the gas phase. Most models of flame spreading consider only the latter two mechanisms, and for non-luminous, small flames, radiation

*The fire point is more apparatus dependent than the flash point and since it is only of the order of a few degrees higher than the flash point, reference will be made mostly to the flash point.

may be neglected as well.

As mentioned before, liquids at or above their flash point will support a spreading rate of the order of the laminar flame speeds. Liquids below their flash points will have spreading rates less than the laminar flame speeds because they must be heated to the flash point through the liquid ahead of the propagating flame. One then would expect an important, but milder, variation of spreading rate with temperature when the initial temperature of the liquid is below the flash point.

It is interesting now to give consideration to the spreading rate when the initial liquid temperature (T_L) is above the flash point (T_{LFL}). Recall that the flash point is thought to give a mixture ratio near the liquid surface that corresponds to the lean flammability limit. As the temperature is raised the partial pressure near the surface, which as mentioned before is taken as a good approximation for purposes here to be the vapor pressure of the liquid at the specified liquid temperature, rises. Thus as the temperature is raised, the air-fuel mixture ratio near the surface moves from the lean inflammability limit towards the stoichiometric ratio and then to fuel rich mixture ratios. Then, one would expect that the spreading velocity would increase sharply from the value at the flash point (T_{LFL}) and reach a maximum for the liquid temperature which gives a vapor pressure corresponding to the fuel fraction required for a

stoichiometric mixture in air. This liquid temperature related to the stoichiometric condition in the vapor is specified as T_{LST} . Since T_{LST} is very much below the saturation temperature (T_{SAT}), it is possible to continue to raise the liquid temperature. Temperatures above T_{SAT} give fuel rich conditions near the surface. However, because the partial pressure of fuel above the liquid decreases with distance, there is always some point above the liquid surface where a stoichiometric mixture exists. A flame propagating through a stratified air-fuel mixture system will be led by that part of it which flashes through the stoichiometric zone. Thus one can conclude that as the temperature is raised from T_{LFL} to T_{LST} , that the flame spreading velocity will increase sharply, but that above T_{LST} there will essentially be no change in the flame spreading velocity (V_F). If the Lewis number is equal to one, that is, if the mass diffusivity (D) equals the thermal diffusivity (α), this latter statement should hold well. With this background one can draw a qualitative curve of the expected variation of V_F with T_L , as shown in Figure 1. It was found that Roberts (2) previously had given such curves and the experimental evidence to support them.

Since a truly stabilized flame can only exist when the real fire point is reached, the rapid rise in flame spreading rate designated in Figure 1 was begun a few degrees higher than T_{LFL} at the possible liquid fire point

$(T_{LFL})^*$

Thus one would expect that the maximum flame spreading rate for a liquid would be the laminar flame speed of a stoichiometric fuel vapor-air mixture at an unburned gas temperature corresponding to T_{LST} . It is assumed, of course, that there are no movements of the gases to or from a direction normal to the spreading flame front, i.e. there are no gas phase forced convection effects. All the conclusions including the last one will also hold even if radiative heat transfer from the flame to the fuel surface is considered. If, however, there can be intense radiative heating of the fuel-air gas mixture above the liquid surface, then the gas mixture can be ignited ahead of the flame and the flame speed is not the upper limit. This radiation ignition obviously could not be photolysis, but must be thermal in character. It would not seem to be important here.

These postulates would appear to be in conflict with some results on flame spreading across solid fuels. A possible explanation is as follows. Certain polymers when raised to elevated temperatures can be pyrolyzed upon

* Observations in the present experiments as well as those of Roberts show under many occasions that something which very much has the appearance of a cool flame, really a precursor flame, will precede the main propagating flame consume some vapor, disappear and reappear as the flame progresses. One could argue that these precursor flames occur when the flash point is reached, but cannot sustain combustion until the liquid is heated further to the fire point, then the flame arrives.

evaporation or sublimation as in the case of, for example, a solid propellant binder under heating. Particular fragments of the pyrolysis can be very reactive and thus act as an ignition source in the gas phase. In such cases, one would not necessarily expect the laminar flame speed to be an upper limit for the flame spreading which occurs over the solid polymer surface. It would, however, demand a strong radiative heating ahead of the flame; otherwise, the spreading rates would be much less than laminar flame propagation rates. Since most liquid hydrocarbons of interest do not pyrolyze upon evaporation, this type of ignition is not a factor and the conclusions with respect to the flame speeds hold. The authors believe, further, that the mechanism for flame spread across solid fuels must be much like that for liquids below their flash point.

III. THEORIES OF FLAME SPREADING ACROSS FUEL SURFACES IN QUIESCENT ATMOSPHERES

There are three theories* of flame spreading in quiescent atmospheres: Magee and McAlevy (5,6), Tarifa and Torralbo (7), and Roberts (2). The first two were developed for spreading with solid propellant and solid propellant materials (i.e., polymers) in mind and postulated to hold for liquids as well. Upon being informed of observations in the present study, Magee and McAlevy no longer state that their theory applies to liquids in which induced liquid convection can take place (6).

Based upon solid propellant ignition work, Magee and McAlevy propose the following model of flame spreading. "The process of ignition starts at a certain location, when it experiences a temperature increase due to the approaching flame, and responds by pyrolyzing and emitting vapors. As the vapors diffuse away from the surface they react chemically with the active component in the environment, at a site above the surface, liberating heat, and increasing the local temperature and hence the heat feedback to the surface. The advancing flame, having now moved closer to the location further accelerates the vaporization rate and thus the vapor transport rate, the heat release rate is continually accelerated by the increasing vapor flow rate

*Recently Friedman (8) reviewed the first two of these theories.

to the site of active chemical reaction, leading to a temperature "run-away" to ignition. Ignition occurs just as the flame reaches the location. Thus, flame spreading is described as continuous, diffusive, gas-phase ignition."

McAlevy and Magee further state that the reaction in the gas follows an Arrhenius kinetic rate law and has a high activation energy. Thus, there appears to be a fundamental inconsistency in their model. The vapors arising from the surface are not likely to react with the oxygen in the atmosphere if the activation energy of the reaction is high. Only, if the pyrolyzed fuel fragments are quite reactive and thus give a gas phase reaction of low activation energy, does the second sentence in the above quote seem probable. These investigators then formulate the one-dimensional equations of mass and heat diffusion for vaporized fuel at a position ahead of the flame. The equations include a reaction term in the heat equation but omit this term in the mass diffusion equation. No support is given for this apparent assumption. The authors state they solve their equations by the Semenov technique of "dimensionless group analysis." This technique appears to be no different than that given by Frank-Kamenetskii (9) for the solutions he obtains in his thermal theory of ignition. McAlevy and Magee find excellent agreement between their experiments with solid propellants and solid propellant binders in oxygen atmospheres and a parameter which evolves from their

analysis, $Y_{OX}^C P_T$, where Y_{OX} is the oxygen mole fraction, C is a constant about 2 and P_T is the total pressure. That $Y_{OX}^2 P_T$ should be an important parameter from the simplified Frank-Kamenetskii approach can readily be shown. In all such ignition theories, the rate of energy release is related to $Y_{OX} Y_{fuel} P_T$. Since in a diffusion situation it is appropriate to assume that the greatest part of the reaction will take place under stoichiometric conditions (i.e., the common diffusion flame assumption), the above expression can be written $Y_{OX}^2 i P_T$, where i is the stoichiometric ratio and is constant. This simple explanation is a possible answer to the very good experimental and "theoretical" agreement found by McAlevy and Magee. Another possible explanation will be offered later.

Roberts' model considers the flame to be a strip source of heat moving across the surface of the liquid. Notice that the source of heat is at the surface. The two-dimensional equations of heat conduction are written for the liquid state. The flame spreading rate is given by the condition that the flame reaches a certain point when the temperature of that point reaches the flash point (T_{LFL}). Of great interest here is that Roberts observed the flow of liquid ahead of the flame front and wrote of possible convective currents in the propagating direction.

He thus solved the two-dimensional heat conduction equation for an essentially anisotropic medium. Even though he omitted the mathematical convective term in the heat equation he obtained an excellent qualitative correlation between his analytical results and experiments.

Tarifa and Torralbo modeled the problem more correctly in considering the flame to be a surface discontinuity with combustion gases behind the discontinuity. The heat transfer to the fuel ahead of the flame is considered to come from two paths: (1) radiation from the flame to the fuel ahead and (2) convection and radiation from the combustion gases behind the flame to the liquid and then conduction through the liquid. Path (2) is considered faster than conduction of heat ahead of the flame because of the low thermal conductivity of gases. The propagation condition is the same as that of Roberts except Tarifa calls the required surface temperature, the ignition temperature. For liquid fuels he uses the flash point temperature and simplifies the problem by dealing only with large flames in which radiation is the only mode of heat transfer. His models are stated correctly mathematically; however, his treatment of the liquid case is limited in the sense he considered only radiation and did not consider the anisotropy in the liquid. This latter effect is believed to be a major one.

Both Roberts and Tarifa inherently assume that the time required for vaporization, diffusive mixing, and combustion is small compared to the time required to heat the fuel to the flash point. They have, in essence, mathematically uncoupled the gas phase from the liquid phase conditions.

There appears to be sufficient evidence to support the general concepts of the Tarifa and Roberts' models. By the general concepts it is meant that the heat is transferred through the liquid and when the temperature on the surface reaches the flash point, the flame can be considered to have traveled to that point. Since the flash point is related to the lean flammability limit, it offers another possible explanation to the correlating factor $Y_{OX}^2 P_T$ that McAlevy and Magee found. It would be most interesting to determine by literature search or experiment how the inflammability limit varies with oxygen mole fraction and total pressure. Since it is obvious that the flammability limits broaden with increasing Y_{OX} and P_T , so then the flash point must decrease with Y_{OX} and P_T . If the T_{LFL} decreases, the propagation rate must increase. The trend is there, it remains to be determined whether this trend can be correlated with $Y_{OX}^C P_T$ where the constant C is a number near 2.

IV. SOME NEW EXPERIMENTS ON FLAME SPREADING--
THE EFFECTS OF VISCOSITY AND SURFACE TENSION

In preliminary experiments to estimate flame propagation rates across kerosene surfaces, it was decided to use only films of the fuel as economic and safety measures. As Tarifa had done, these films were floated on water.* During the observations of the flame spreading process it was noticed, as Roberts apparently had, that the liquid ahead of the flame moves in the same direction as the flame. This observation was verified by noting the movement of styrofoam chips floating on the fuel surface during the flame propagation experiments. It was then speculated that convective currents, or more truly cells, were established in the direction of propagation. An iron oxide powder, was then dispersed on the kerosene-water interface (probably supported by interfacial surface tension). During an actual experiment, one readily could observe the styrofoam chips to move in the direction of the flame, and the powder under the surface to move in the opposite direction. The powder moved much slower than the chips. Since quantitative effects were not sought, no efforts as yet have been made to refine this type of experiment. Obviously the thickness of the fuel film and the interface play a part in the particle movements.

*The container used was a metal tray 6 in. wide, 48 in. long and 1 in. deep.

Nevertheless, it was concluded that convective currents were established in the direction of the flame propagation and were a most important factor in determining the propagation rate. This conclusion was supported by two other experiments. An early one, in which the fuel was absorbed in metal and refractory wicks, was designed originally to verify Tarifa's model that conduction through the liquid was important. Roberts thesis was not available at the time. It was reasoned that the metal wick had a higher thermal conductivity and thus the flame should propagate at a faster rate. The flame established in a plane on the wick with an ignition source propagated so slowly across the metal wick that it could be considered trivial with respect to regular fuel propagation rates. The liquid in the refractory wick was transferred, in essence, to a stationary flame through capillary action. In the second group of experiments a barrier was placed in the experimental trough. The height of the barrier was such that it almost pierced the fuel-air surface; i.e., the fuel just wetted the top of the barrier. Barriers of thermal conductivity equal to (cardboard) and greater than (steel and glass) the fuel were used. In this experiment the flame would propagate at its normal speed until it would reach the barrier and then stop. All barrier materials performed in the same way. If allowed to burn for awhile, the fuel on the other side of the barrier would eventually ignite

and propagation begin again. If the barrier were lowered a little below the fuel surface, the flame propagated normally and crossed the barrier. Thus it was concluded that if convective cells did exist their height was small.

There are two possible means by which a convective cell could be established. Either by surface tension induced flows (Marangoni effect) (10) or buoyancy effects (gravity flows). One should recall the early experiments of dispersing particles on the surface of water and observing them race from the point at which a drop of detergent (or any surface tension reducing agent) is placed on the surface. Since surface tension decreases with temperature, the flame could act as the "detergent" in a propagation experiment. Whether surface tension or buoyancy effects or both determine the convective movements in these flame experiments, it was realized that these effects could be reduced by increasing the viscosity of the fuel. This logic is supported by the fact that the viscous forces oppose the surface tension induced and buoyancy forces in a convective system as represented by the Grashof number (ratio of buoyancy forces to viscous forces) and the Marangoni number (ratio of the surface tension induced forces to the viscous forces)*. The

*

$$\text{Gr} = \frac{\beta \Delta T g h^3}{\nu^2}$$

$$\text{Ma} = \frac{\sigma h}{\mu}$$
 where
 β = volumetric coefficient of thermal expansion
 k = thermal conductivity
 ν = viscosity
 ΔT = temp. gradient
 σ = surface tension
 h = height
 ρ = density

Marangoni number is sometimes called the Thompson number (10).

Experiments were then performed with kerosene in which thickening agents (particularly Vistanex*, a polyisobutylene of molecular weight $\sim 200,000$) were added in small percentages. Such thickening agents are not expected to alter the vapor pressure of the kerosene and indeed thickened fuels had the same flash point as the unthickened fuels. It is not known how they affect the surface tension. Both the vapor pressure and surface tension of a thickened source will be measured in future experiments. As expected, it was found that, as the viscosity of the fuel was increased, the flame propagation decreased. The effect was significant, as shown in Figures 2 and 3. Examination of Figures 2 and 3 did show that the depth of the fuel does affect the results with pure kerosene and with the thickened fuels. This result also is consistent with the convective cell concept.

Whether simply adding a surface tension reducing agent will alter the flame propagation rate cannot be assessed at this time. The Marangoni number contains the gradient of the surface tension (σ) with respect to temperature (T), i.e. $d\sigma/dT$, and not the absolute value of the surface tension. Experiments with surface tension altering agents will be tried.

*Vistanex is the trade-mark used by the Enjay Chemical Company.

V. IGNITABILITY

In performing the experiments with the thickened fuels, the ignitability characteristics of these fuels were noted and found to be consistent with the concepts of convective fluid movements postulated in the previous section. Again the experiments were preliminary, not refined, but revealing.

It was required to ignite pure kerosene in the spreading experiments by first pouring a small amount of a low flash point fuel (usually hexane) at one end of the tray and then igniting with a secondary source. However with the thickened fuels, a low flash point fuel was not required for ignition. A pilot flame can be used as the initial ignition source. When this flame is directed at the pure kerosene surface, one observes the surface liquid to move away from the heat source, and ignition does not occur. As in the discussion of flame spreading, it is apparent that heat is convected away from the ignition source and ignition cannot occur. When the fuel is thickened, there is less convection, more heat is retained at the source and ignition occurs with a simple pilot flame. Again one can actually observe the slower surface currents in the thickened fuels.

The thickened fuels then act very much like thick wicks. A thick wick ignited at one edge will not propagate to the other. As mentioned earlier, fuel will flow to the edge which has been ignited. Convective currents are not

possible in such wicks. If there is any propagation, it is only that the wick can become heated by conduction. One can ignite kerosene in a wick with a pilot flame, but not without the wick, unless the kerosene is thickened. Thus thickening the fuel increases its ignitability, but reduces the rate of flame spreading across its surface.

VI. STEADY BURNING

There exist too much data on the burning of pools of liquid fuels to discuss all the work in this area. What will be discussed is the early work (1957) of Blinov and Khudiahov (11), as reported by Hottel (12), and considered by most authors to be one of the most significant since it was in essence the first to show the effect of pool size on burning rate. Also, the recent work of Akito and Yumato (13) with segmented circular pools and the work of Blackshear (14,15) on fuel soaked wicks will be reviewed briefly.

Although all the vast literature in this area may not have reviewed, the authors do not recall any one stating the possible difference in the burning rate of fuels in pans and in horizontal fuel soaked wicks in the context of the part that hydrodynamic effects actually play. It has been well established that in large pools of liquids the burning takes place at the edge of the retaining pan. Although there is evaporation of the fuel in the center of the pool, appreciable combustion does not take place until the fuel reaches the edge of the hollow cone flame formed above the pool, and thus the amount evaporated from the center is appreciably less thick than that at the edge. Many have realized that there is a likely flow in the liquid from the more dense center to the pan edge. This point apparently was considered as a simple buoyancy effect (gravity flow).

However when one considers that the surface tension is less at the pan edge than in the center, there could be a surface tension induced flow away from the pan edge on the surface with a return flow below the surface as discussed in previous sections. These hydrodynamic currents could be important to the burning rate and it appears well worthwhile to establish experiments which will permit observation of these currents.

It would seem then that experimental results with fuel-soaked horizontal wicks should yield different results than pools. Blackshear states "the fuel consumption rates in wick burning are found to be nearly the same as in comparable burning experiments in which liquid fuels burn in horizontal pans (14,15)." Without knowing the extent of the convective effects it is difficult to say how they will alter burning rates, nevertheless one feels compelled to say that Blackshear's statement cannot be explicitly correct for large pools. Experiments to be carried out by the present investigators will determine the difference between the burning rate of a fuel in a pool with and without level control, where there is a forced liquid flow, the same fuel in a wick of the same size as the pool, and lastly of a fuel in a pool with various amounts of thickener and surface tension agents. With this background, no further comment will be made on wick experiments.

Fundamentally there have been only two approaches to determine the burning rate of liquid pools. There have been many models and theories dealing with the flame plume. Recall the fundamental problem in determining the burning rate of a condensed fuel in a quiescent gaseous atmosphere. Only the spherical-symmetric problem is tractable. The one-dimensional or cylindrical symmetric systems cannot be solved (16,17). In order to solve these problems, one must impose a convective condition in the atmosphere in order to establish a "boundary-layer thickness" or "stagnant film" which determines the distance between the conditions of the free atmosphere and the condensed plane surface. Using methods developed by Spalding (18), it can be shown (19) that the burning rate for stagnant film conditions can be written as

$$G = \frac{\rho D}{\delta} \ln(1+B) = \frac{k}{c_p} \cdot \frac{1}{x} \ln(1+B) \quad (1)$$

Where G is mass flux, δ is the boundary layer or stagnant film thickness and B is the transfer number. This expression may be written in terms of the Nusselt number (Nu) as follows:

$$\frac{G \times C_p}{k \ln(1+B)} = Nu \quad (2)$$

Where x is the critical dimension of the system.

The Nusselt number may be determined from either the Reynolds

or Grashof number depending upon whether the convective atmosphere is forced or natural. As will be discussed shortly, Spalding (20) has adopted this approach to explain the diameter effect on the burning rate of liquid pools and this work is considered one of the two fundamental efforts mentioned earlier.

The second is due to Hottel (12) who developed a semi-qualitative approach from reviewing the work of Blinov and Khudiahov (11). The Hottel developments have recently been modified by Akito and Yumato to correlate with their experimental results.

The Hottel approach is best developed by first discussing the experimental results of Blinov and Khudiahov. Their results". . . indicate that as the pan diameter increases, the flame structure, for any of the fuels, changes from a conical steady flame (1.1 cm pans) to a pulsating-tip flame, of maximum frequency about 18-20 cycles per second (3 cm pans). Further increase in pan diameter reduces the pulsations, but the unstable portion of the flame shifts downward until, for a 15 cm. pan, the entire flame is changing continuously in structure everywhere; and with 1.3 meter pans the random turbulent motion is fully established (12)."

Figure 4 taken from Reference 12 reveals that Blinov and Khudiahov results show a decrease in burning rate with pan diameter in the laminar region, a variation in burning rate through a transition region, and a burning rate independent

of pan diameter in the turbulent region. Since the work of Blinov and Khudiahov, others have verified experimentally the diameter effect of the burning rate.

Hottel attempted to correlate the results of the Russian investigators by an expression

$$\frac{q}{(\pi d^2)/4} = \frac{k_s(T_p - T_w)}{d} + \sigma(T_p - T_w)^4 - \sigma F(T_p^4 - T_w^4)(1 - e^{-kd}) \quad (3)$$

which simply states that the heat flux to the liquid per unit surface area is equal to the heat gained from the pan rim, the convection from the flame, and the radiation from the flame, respectively. k , the thermal conductivity, σ the convective coefficient, F , the view factor and k , Beer's extinction coefficient were all assumed constant, although it was stated that they are not likely to be constant. The expression was said to explain the diameter effect since for small d 's the first term is the only one of importance. At large d 's the first term is negligible, the second is constant and the third term will dominate and it is constant because $k d$ is so large. This argument is very qualitative and the fact that such an expression can be fitted to experimental data may be purely fortuitous when one considers the number of physical constants which are in essence handled as arbitrary constant terms adjusted according to the experimental

conditions.

Akita and Yumato (13) made some relative minor modifications to the Hottel expression, by writing k and $\bar{\sigma}$ as a function of d and dropping the radiation term. Since these authors dealt with non-luminous methanol flames, the last modification was certainly valid. They claim good agreement with their data, but again such agreement is fortuitous because of the presence of the large number of physical constants, which again are handled as arbitrary constant terms.

Spalding (20) has suggested that his work on burning rates in free convection both with vertical flat plates and spherical surfaces could also be adapted to the horizontal pan or wick. The expression for the pan burning rate which then develops from the previous expression given in terms of a stagnant film and the Nusselt number is

$$\frac{r d}{(k/c_p)} = AB^{3/4} [gd^3/\nu^2]^n \quad (4)$$

where A is a constant and n is the coefficient to the Grashof number. r is the linear regression rate, B is the transfer number as before, and ν is the kinematic viscosity. The Grashof number in the above expression does not contain a density difference. In flames burning in air the density of the flame zone is about one-seventh to one-fifth that of

the surrounding air which suggests that an adequate approximation of the buoyancy force in the flame zone is to assume the density to be vanishingly small, thus permitting writing the Grashof number as shown.

For laminar conditions, heat transfer experiments show A and n to be 0.45 and $\frac{1}{4}$ respectively; for turbulent conditions they take the values of 0.117 and $1/3$. Thus one sees immediately that for the turbulent condition, $n = 1/3$, Spalding's expression gives \dot{r} independent of d . For laminar conditions, \dot{r} should be proportional to $d^{-1/4}$. Akita and Yumato results experimentally predict $n = 0.20$, which does not appear too bad, although they deem it unsatisfactory. Blackshear and Murthy (14) found $n = \frac{1}{4}$ and $n = 1/3$ respectively for burning on vertical wicks for the small and large size condition respectively. Others have supported the Spalding approach. (21,22). Apparently there are other factors to be considered under the small diameter condition.

Additional evidence may be offered to support the semi-empirical approach of Spalding. Burgess, Grumer, and Wolfhard (23) relate the liquid burning rate (linear regression rate, \dot{r}) at large tray diameter to two physical properties of the fuel, the heat of combustion in air (Q) and the heat of vaporization (L_v , which includes the heat capacity term from ambient temperature to the saturation temperature), by plotting \dot{r} as a function of Q/L_v . They argue that the percent of heat radiated to the surface from the flames of many

different fuels (methanol, UDMH, hydrocarbons and liquid hydrogen) are approximately equal and that the burning rate must then be proportional to the heat of combustion. Since experiments show the burning rate to be inversely proportional to the heat of evaporation, they contend that the burning rate should be inversely proportional to L_v/Q . This conceptual reasoning is said to be expressed in more detail in reports of the Fire Research Station at Boreham Wood, England. Burgess, et. al., find a good linear correlation and state "the approach to linearity...is somewhat disconcerting in view of the crude reasoning in which the correlation is based."

The Q/L_v and \dot{r} can be correlated in another manner. Q/L_v as calculated by Burgess, et. al., is the transfer number B for the fuel burning in air. Spalding's formulation suggests $G = \rho \dot{r} \sim B^{3/4}$. Since the densities of most of the hydrocarbon type fuels are the same, one would expect $\dot{r} \sim B^{3/4}$. Figure 5 gives a plot of $\log \dot{r}$ vs $\log B$. Although it was difficult to pick data from Burgess' figure, the linearity found in Figure 5 is even better than that found in Reference 23, in that the liquid hydrogen aligns more closely. The slope obtained is, however, 0.9 somewhat higher than 0.75 suggested.

It was at first thought that the hydrogen agreement was fortuitous, since its liquid density is much less than the others. However there is the gas phase term k/c_p ($=D_p$)

in Spalding's expression and an estimate of this term indicates that it is appreciably lower for hydrogen and very nearly compensates for the liquid density factor. Because omitted terms are self-compensating, the agreement is not as fortuitous as might be expected.

Equation 4 and Figure 4 show the consumption rate to be independent of pan size when the pan is large. Recall that the significance of this trend is that the natural convective field has become turbulent. Further, the fact that the convective heat transfer is independent of the critical dimension and that a radiant component would also be independent of the size of the horizontal pan makes it difficult to assess the relative importance of these two modes of heat transfer. However, it has been shown by one of the authors and detailed in a student thesis (19) that when the radiative mode must be accounted for in problems of heat and mass transfer, only the transfer number need be modified in most cases. The effective transfer number with radiation becomes

$$B_{\text{eff}} = \frac{B}{1 - \frac{R}{r L_v}}$$

where R is the radiant flux.

One must question the extent of the radiant flux in flames of the fuels listed in Figure 5. The luminosity of

hydrocarbon flames are certainly much greater than that of either the alcohol or hydrogen. Yet, the linear regression rate appears to correlate with B and not B_{eff} .

Some of Akita and Yumato other experiments (13) are worth reviewing in a little more detail. They performed a series of tests in circular pans which were divided into three concentric rings of equal area. They found that the burning rate is the largest in the outer ring which is next to the flame base (at pan edge) and the rate decreases with the distance in from the outer rim. As the vessel gets larger, this effect decreases. Also of interest is that the average burning rate of the three concentric zone is generally less than the burning rate found in vessels not subdivided and of equivalent size of each of the sub-divisions. These results would seem to support the strong influence of liquid convection in burning experiments.

In conclusion, the experiments suggested earlier in this section, in which the burning rate of thickened fuels would be measured, and the currents of pure and thickened liquids observed, seem very valid and should give further understanding of the burning of liquid fuels. It is important, as well, to reflect on the experiments in which the experimental burning rate is determined by the rate of feed to keep the surface at a stationary height with respect a container rim. Practically all the published data for

the steady burning of liquids were obtained by this technique or some modification of it. Knowing that the hydrodynamics in the liquid can play a part in determining the burning rate, one must question whether such experiments will give the same results as stagnant pools. For this reason the present investigation will attempt to measure burning rates with stagnant pools and with liquid level control.

VII. CONCLUSIONS

The flame propagation rate of liquid fuels is determined by gas phase phenomena when the temperature of the fuel is greater than its flash point and by liquid phase phenomena when the fuel is at a temperature less than its flash point. The maximum flame propagation rate across a liquid surface is the laminar flame speed of the stoichiometric fuel vapor-air mixture at the liquid temperature which gives a vapor pressure sufficiently high to form a stoichiometric mixture, i.e. T_{LST} . For the $T_L < T_{LFL}$, in which liquid phenomena control, the important heat transfer mode is apparently a convective fluid motion in direction of the flame propagation. This fluid motion is generated by surface tension and/or buoyancy (gravity) effects. Increasing the viscosity of the fuel, then lowers the rate of flame propagation and burning, but increases its ignitability. The effects of surface tension are yet to be determined.

It is apparent that hydrodynamic considerations are important, (if not the most important) factors in determining the ignitability, burning and flame spreading rate of pools of liquid fuels at temperatures below their flash point. In fact, they establish the difference between the combustion of large pools of liquid and small liquid droplets. Their relative importance to a large, sooty flame where radiation ahead of the flame may be a major mode of heat transfer, is yet to be evaluated.

VIII. PRACTICAL IMPLICATIONS

If the modeling described in the previous sections is correct and if the experimental observations have been interpreted properly, then it is possible to speculate as to the applicability of the results to certain practical problems. But, first, the reader must be reminded that much remains to be verified.

The problem which arises when oil tankers meet disasters and affect neighboring land areas is best exemplified by the so-called "Torrey Canyon" incident. Efforts to burn the oil from the Torrey Canyon on the water just off the coast of southern England met with failures. To the best of the authors' knowledge, flares, torches, bombs, etc., were tried, but to no avail. From the work presented here one could analyze the difficulty. The temperature of the ocean is such that one is sure that the oil was below its flash point. More than likely, the oil, as well, has a flash point well above standard conditions. One then concludes that propagation must be controlled through the liquid phase. As discussed in the body of the report, if the oil slick is thin, then propagation is difficult and not likely. The thin slick permits the ocean to be a large heat sink and also alters the "convective" situation necessary for propagation. Thus, a region ignited by the flare or other device does not spread. The manner by which one possibly should proceed would be to spray or coat the oil

with a volatile hydrocarbon (gasoline, for example) that has a low flash point, i.e., one below the ambient conditions (say the ocean temperature). Since the flame for such compounds propagates in the gas phase, it is a simple procedure to ignite at one location and have the flame propagate rapidly across all the coated area. Once ignited in this fashion, the oil should burn.

The use of foamed plastics to inhibit the propagation of condensed phase flames in closed spaces (i.e. a partially empty fuel tank) deserves some comment. If the plastic does not completely fill a volume; that is a gap can exist, then the effectiveness of the foam depends upon whether the fuel under consideration is above or below its flash point. The foam would prevent propagation near any gaps if the ambient temperature is below the flash point, but may be completely ineffective if the ambient temperature is above the flash point and propagation can take place through the gap in the vapor phase. This situation is very similar to the spreading problem when wicks are used and has been discussed in the body of the report.

Although thickened fuels no doubt have slower flame spreading rates than pure fuels, the thickened fuels would appear to be ignited more readily by hot projectiles, or for that matter any ignition source.

Related to the concept of ignitability, one may also

speculate about the merits of thickened fuels from the point of view of pool fire extinguishment techniques using water. In fire-fighting practice, moderately sized pools of burning liquids whose flash point are above normal environmental temperatures, may be extinguished by driving the flame across surface with the aid of water (and thus steam). The water cools the liquid surface by direct contact and also creates motion within the fuel to bring cooler fuel to the surface. In this regard the technique is directly opposite to the process of flame spreading. The thickening of a fuel inhibits the fuel motion; thus, it would appear that, other factors being equal, a large, thickened-fuel fire may be more difficult to extinguish with water.

IX. ACKNOWLEDGMENTS

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FIGURE CAPTIONS

1. The flame spreading rate (\sqrt{F}) in air across liquid fuel surfaces as a function of the bulk liquid temperature, T_L . (T_{LFL} is the liquid flash point, T_{LFI} is the liquid fire point, and T_{LST} is that temperature of the liquid which gives a sufficient vapor pressure to create a stoichiometric fuel vapor-air mixture above the surface.)
2. The flame spreading rate across thickened kerosene surfaces at room temperature ($\sim 21^\circ\text{C}$) as a function of reciprocal viscosity. A 3.5 mm kerosene film floated on 7.0 mm of water.
3. The flame spreading rate across thickened kerosene at room temperature ($\sim 21^\circ\text{C}$) as a function of reciprocal viscosity. A 10.5 mm depth in metal tray, no water present.
4. Linear liquid burning velocity as a function of pan diameter. Data of Blinov and Khudiahov (11), figure from Reference 12.
5. Relationship of linear regression rate at large tray diameter to the transfer number, B. Data from Reference 23.

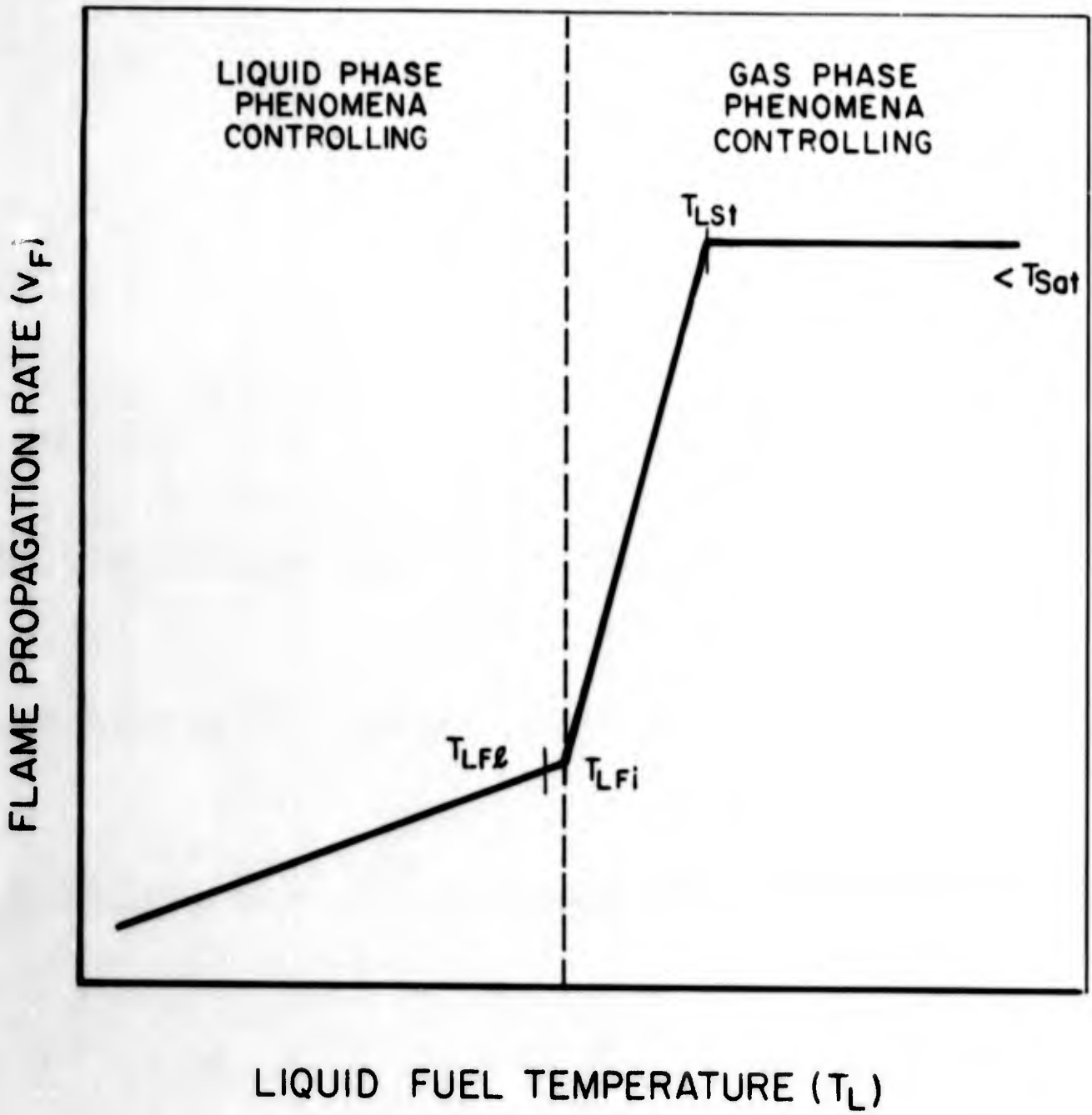


FIGURE 1

P 13 R 4120 68

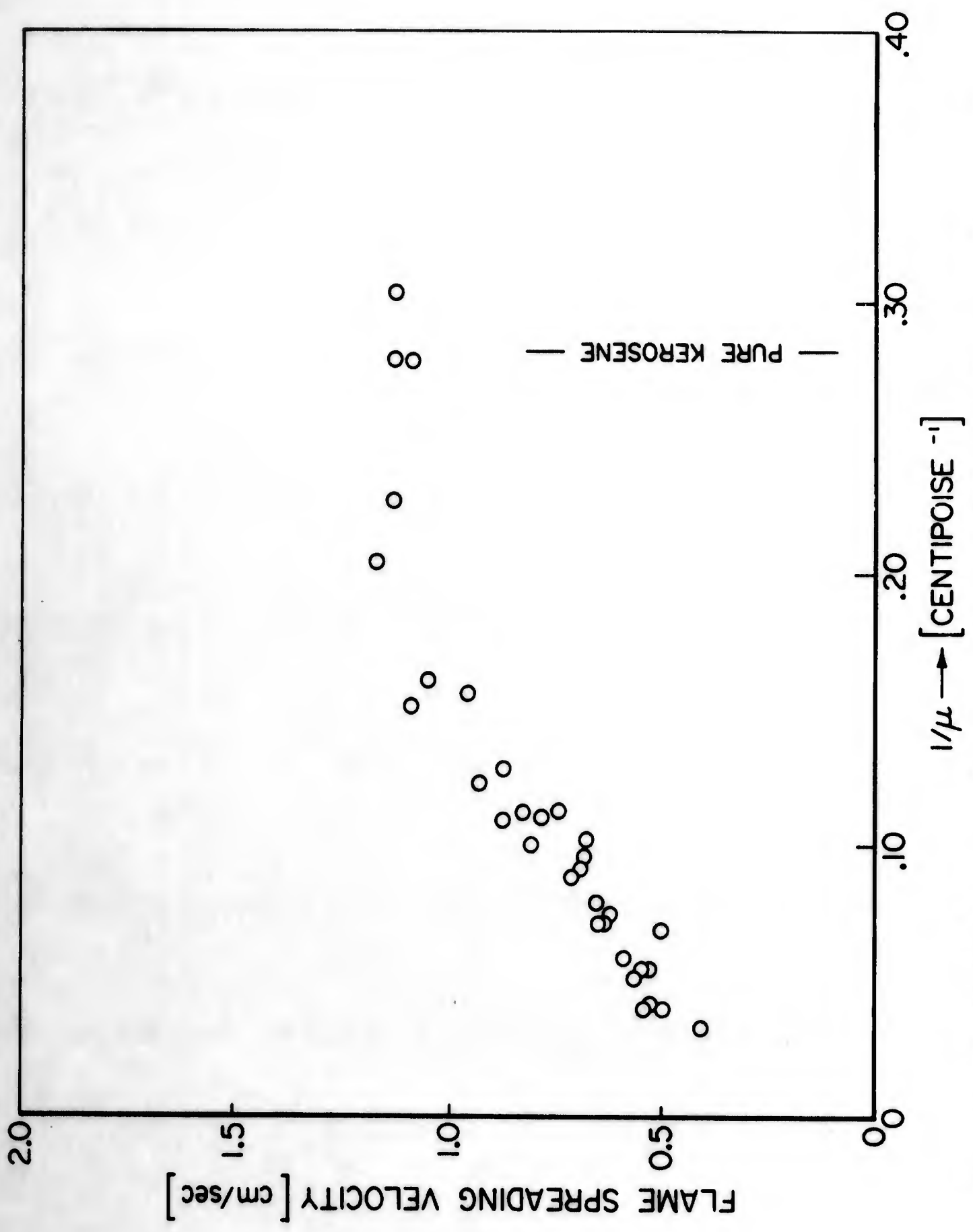


FIGURE 2

JP 13 RAZI 68

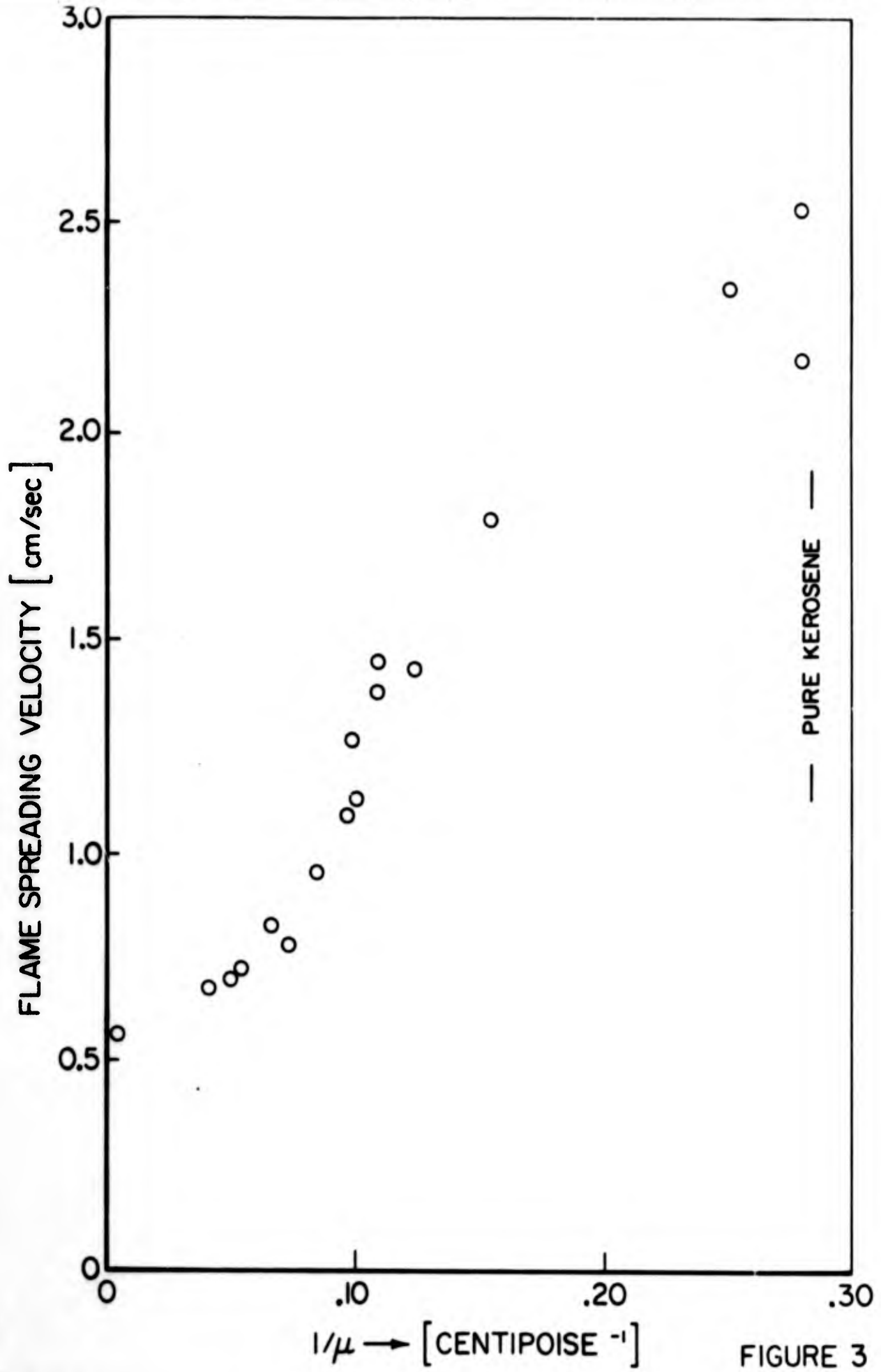


FIGURE 3

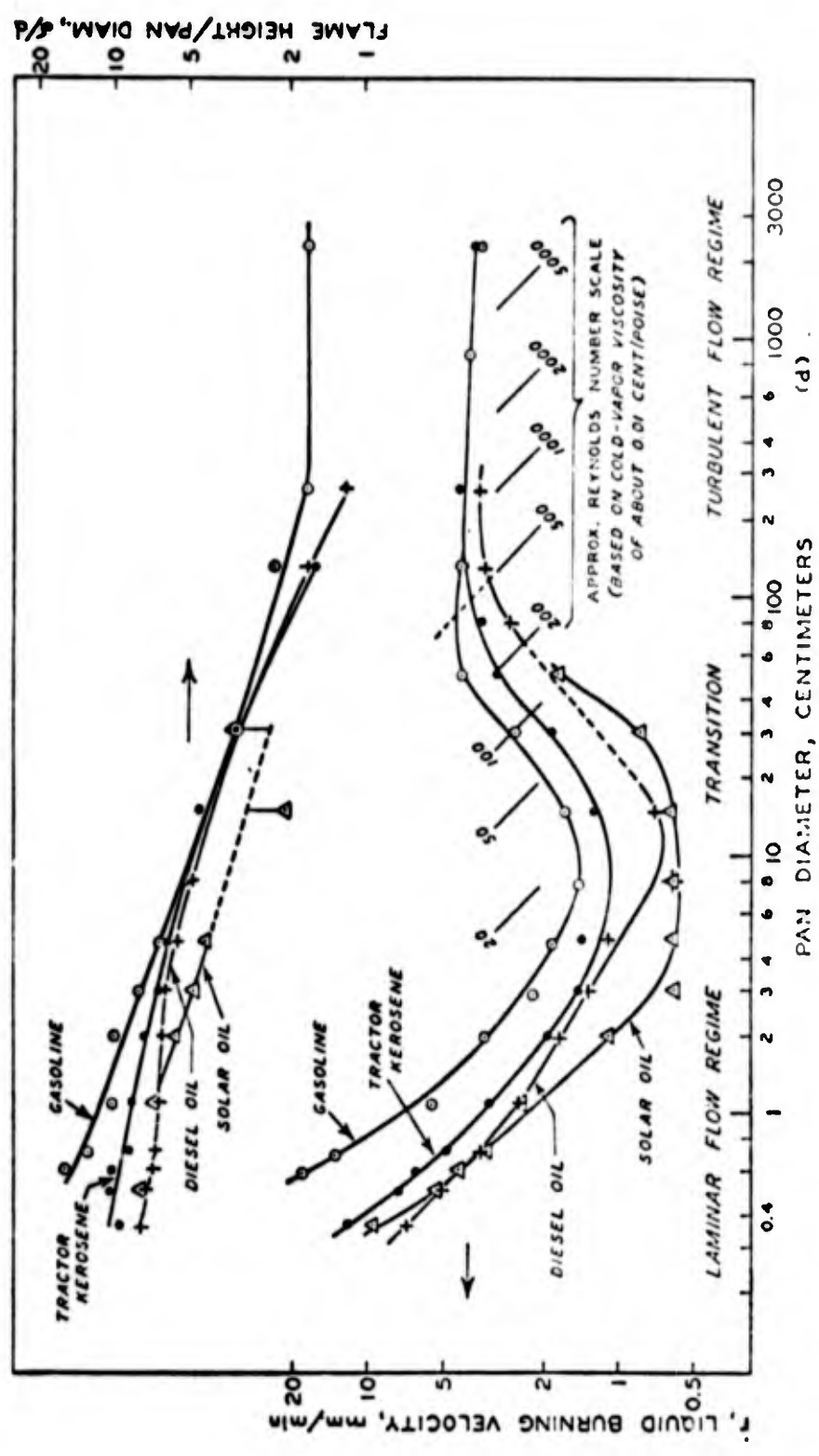


FIGURE 4

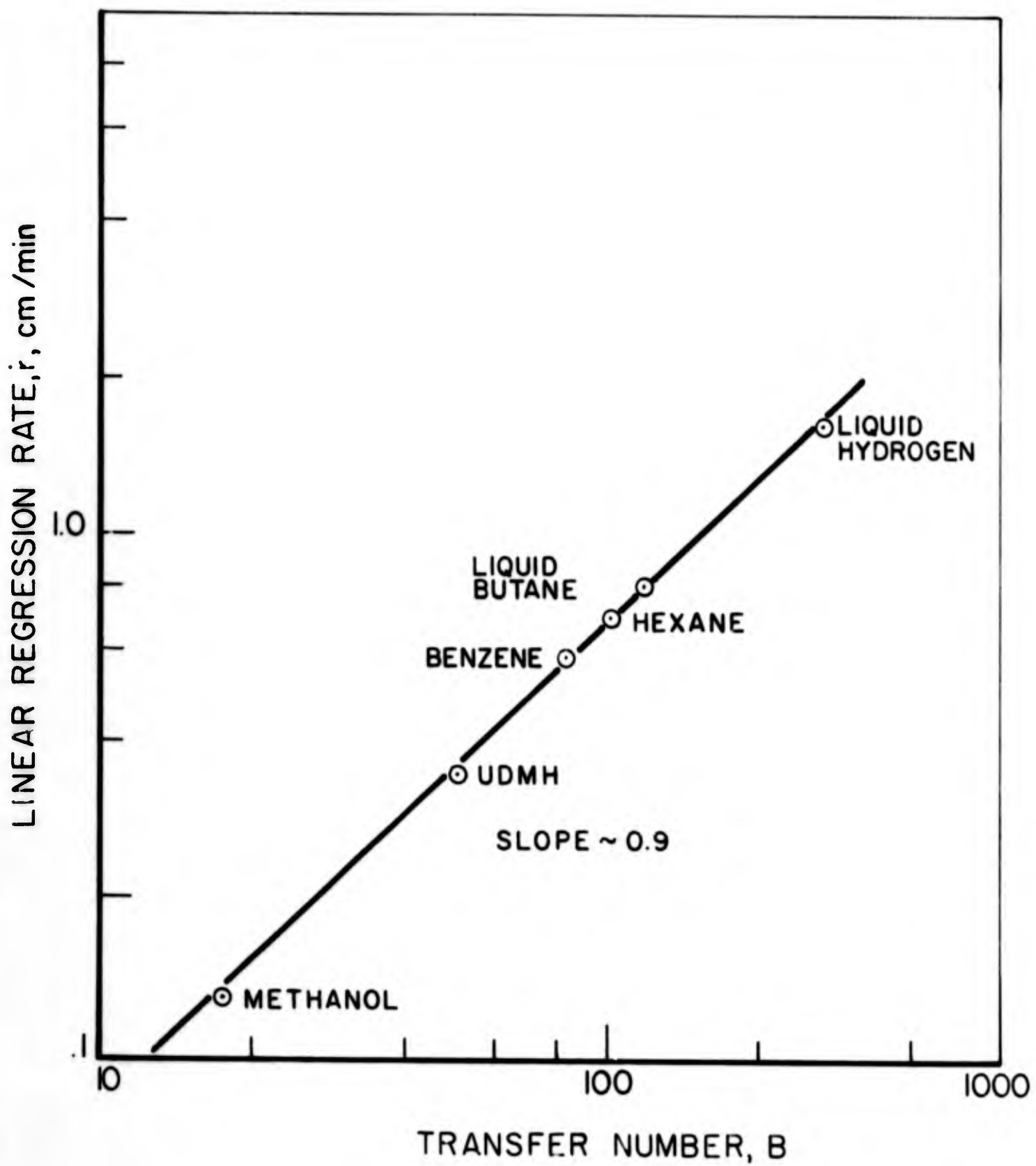


FIGURE 5