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## AN INVESTIGATION OF THE FORMATION AND VENTING OF FLAMMABLE MIXTURES FORMED WITHIN LIQUID FUEL VESSELS



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### ABSTRACT

The paper describes results of a parametric study obtained while using an analytical model described earlier (Bunama and Karim, 1997b) investigating the combined effects of mass, energy and momentum transfer with variable transport and thermodynamic properties on the formation of fuel vapour-air mixtures above a stagnant liquid fuel surface within the confines of a vertical cylindrical vessel. This was done mainly to examine the establishment of the formation of flammable mixtures and their changes in size and location with time within liquid fuel tanks that are partially empty. The effects of changes in the ambient and wall temperatures, presence of liquid on the walls and vessel geometry were considered. Moreover, the results of a corresponding experimental investigation are presented. Much of the data relates to the high volatility fuel n-pentane that represents the lighter fuel fractions in commercial fuels which through their early evaporation contribute much to the fire hazards in fuel tanks.

### INTRODUCTION

The subject of ensuring the safety of fuel storage and handling facilities in gas turbine installations remains of paramount importance. Transient changes in key influencing parameters, such as temperature and fuel vapour concentration distributions that commonly occur as a matter of course in liquid fuel containers may increase the fire hazard. Moreover, the question of limiting the release of fuel vapour components into the immediate surroundings of fuel containers is equally of increasing significance and concern. Numerous interacting parameters that result from the transient changes in the local conditions or specific features of design, control the phenomena involved in a complex and often unknown manner. There is a need to understand better the nature of these processes and identify the potential and extent of fire hazards so as to develop effective guidelines for their control. Full

scale testing of fuel tanks to assess their fire hazard or evaporative emissions, apart from being too expensive and time consuming is specific to a set of configurations. It would not account adequately for the contribution of numerous influencing factors to the associated transient phenomena involved. Obviously, comprehensive models that can describe reliably the events that take place within liquid fuel tanks can serve as a useful tool for dealing with the corresponding issues of fire hazards and safety.

Fire hazards within liquid fuel tanks that are partially empty relate closely to the transient processes of vaporization and convective mixing of the vapour produced off the liquid fuel surfaces with the overlaying atmosphere of air. Of particular concern is the possible formation of a flammable atmosphere within such containers for part of the time and the subsequent slow release of fuel vapour into the outside atmosphere when the tank is left either fully or partially open to the outside. There is a need to establish whether a flammable region will be formed within a tank and how it may develop in size and location with time. Moreover, how much time is needed subsequently to render the whole contents of the vessel too rich in fuel vapour, to fail supporting a flame.

Analytical studies of the transport processes involving the simultaneous presence of differences in temperature and variations in concentration in confined spaces in which a lighter gas is overlaying a heavy vapour tends to be few since they are computationally demanding (Cussler, 1992). Markham and Rosenberger (1980) used a two dimensional model and considered the concentration and velocity profiles of liquid vapour of a molecular weight greater than air (Benzene). Their study was limited to a steady state, constant property and isothermal mass transfer.

Bunama and Karim (1997a) modeled the formation and mixing of liquid fuel vapour with the over laying air within a vertical circular cylindrical tanks. The diffusive flow of air towards the interface from a higher concentration at the ambient, produces a

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balancing outward convective flow of air and vapour away from the interface. This results in an enhanced diffusion and accelerated spread of the vapour.

The negative solutal buoyancy and cooling at the interface both tend to act as suppressants to the flow field, but convective transfer tends to have a noticeable role, especially at the early stages of the diffusion process when the space above the liquid surface is not yet saturated with the vapour. Moreover, a local positive thermal buoyancy occurring near the vessel walls such as due to a higher wall temperature relative to a cooler interface, enhances the mass transfer processes. In order to understand and describe such complex transient formation of fuel vapour-air mixtures typically within the confines of a cylindrical vessel, a comprehensive analytical model that includes the effects of convection, temperature gradients and variations in transport properties was described by Bunama and Karim (1997b).

The present contribution describes results of a parametric study obtained while using this analytical model, with the objective of investigating the combined effects of convection, energy transport and variable properties on the formation of fuel vapour-air mixtures above a liquid fuel surface within the confines of a vertical cylindrical container. The effects of changes in ambient and wall temperatures, presence of liquid traces on the walls and vessel geometry on the transient formation of these mixtures can be made. In parallel with the analytical model the results of a corresponding experimental investigation is made. The relatively high volatility n-Pentane was chosen to represent the lighter fuel fractions in commercial fuels that through their early evaporation contribute to much of the initial fire hazards within fuel tanks.

It was shown then that the employment of relatively simple transient mass transfer modeling approaches that are based on one dimensional fixed property simulation produced results that were significantly different from those obtained when more comprehensive modeling approaches are employed. These involved three dimensional simulation that accounts for changes in the local temperature and properties arising from the effects of continued fuel vaporization, heat transfer and the resulting fuel vapour diffusion into the overlaying air. These later approaches were shown to produce results that tend to be in much better agreement with the limited experimental results available.

Another important related feature that has serious safety implication to fuel containers is the fact that when an ignition source is introduced into the space within a fuel tank and a fire flash develops, then the consumption by fire of much of the fuel vapour present would not ensure necessarily safety from subsequent flashes (Karim and Zhang, 1992). As long as some liquid fuel remains present somewhere within the tank that is in communication with the outside atmosphere, then given time, a flammable region will develop once more, albeit, in the presence of some vitiated air. This can lead in the presence of an ignition source to yet another fire spread that consumes part of the fuel vapour developed. This repeated fire flashing resulting from the continued formation of flammable regions and their consumption by fire is much too complex to be simulated analytically reliably and a resort to experimentation at present is needed for its examination.

## ANALYTICAL FORMULATION

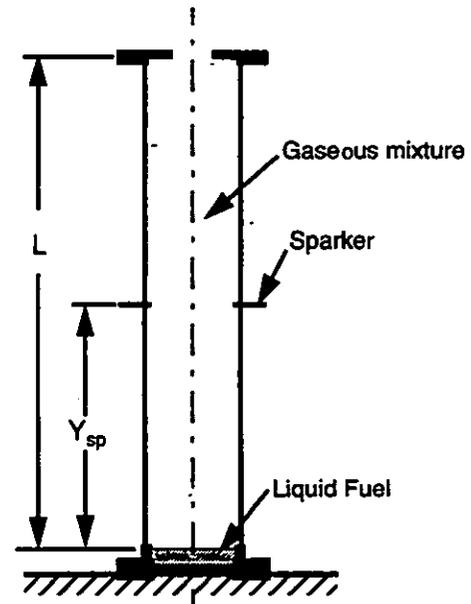


Fig. 1. Schematic representation of the cylindrical vessel arrangement considered in the experiments and modeling.

The system examined, as shown schematically in Fig. 1., is an open-topped vertical cylindrical vessel of radius ( $R$ ). The lower part of the vessel contains a stagnant liquid fuel to a shallow depth at atmospheric pressure. The upper part of length ( $L$ ) is assumed initially to contain air or air plus traces of the vapour at an initial uniform known concentration. The vessel side walls can be either dry or wetted uniformly to various extents with a liquid film. The transfer processes are initiated by assuming that surface of the stagnant liquid becomes exposed promptly to the air above it. With time, the evaporation processes proceed with the resulting vapour diffusing upwards towards the open top. Some air enters from the surrounding atmosphere and diffuses downwards towards the lower air concentration at the gas/liquid interface. Hence, a varying concentration gradient becomes established with time along the vessel axis. A steady state condition may be eventually reached. The two parts are considered initially to be each at a uniform temperature which can be either equal or different from the surrounding ambient temperature. Also, the side walls of the vessel can be at a temperature either similar to that of the ambient or higher.

As some of the liquid evaporates, the supply of the latent heat of vaporization from the surface of the liquid cools down the interface which results in the establishment of temperature gradients within both the liquid and the overlying space in the vessel. These gradients of concentration and temperature control directly the transfer process and affect significantly the transport and thermodynamic properties of the mixture. Accordingly, the spatial and time variations of temperature and concentration profiles, could be determined.

The governing equations for this axisymmetric two-dimensional system are the coupled unsteady momentum, species and energy conservation equations for the gaseous phase. The thermodynamic and transport properties were taken to be variable and their equations were solved simultaneously along with the conservation equations. The energy equation for the liquid phase is also included to determine the temperature distribution in the liquid. The tank was assumed to be axisymmetrically cylindrical and vertical. A full statement of these governing equation together with the corresponding boundary conditions have been described elsewhere (Bunama and Karim, 1997). The numerical procedure followed for their solution was also described. Throughout changes in the properties of the local mixture due to changes in temperature and concentration were accounted for.

### ANALYTICAL RESULTS AND DISCUSSION

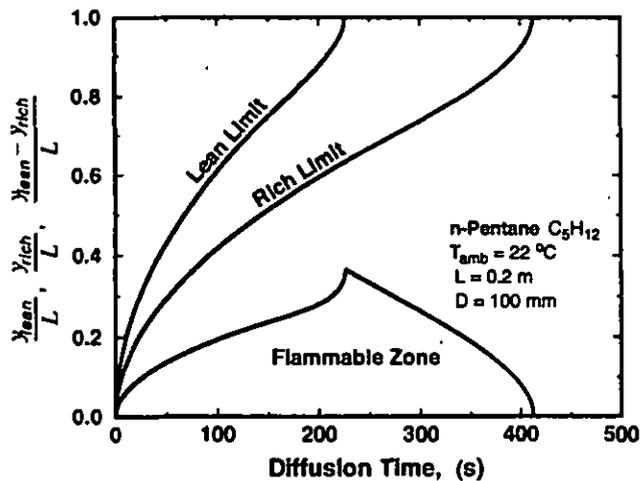
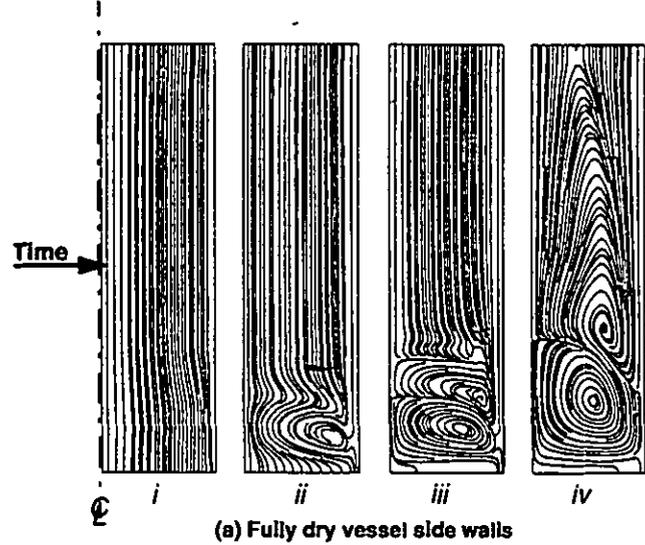


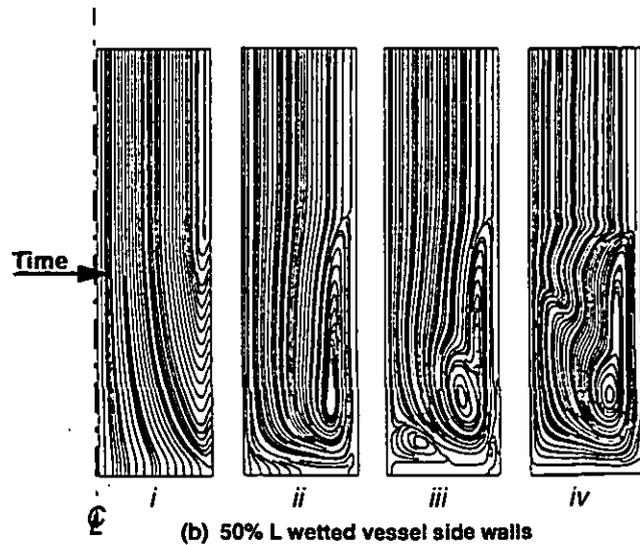
Fig. 2. Predicted lean and rich flammability limits boundary displacement with time and the resulting flammable zone.

Figure 2. shows typically for n-Pentane vaporization and spread into air, how the calculated lean limit boundary of the developed flammable zone progresses along the vertical cylindrical vessel, with unwetted side walls with time. This fuel lean boundary is always well a head of the rich limit boundary that is on the side of the fuel surface. It can be seen that after a certain time from the commencement of the exposure of the liquid fuel surface to the air, the lean limit progression reaches the outlet of the tank. After the elapse of some further time, the rich flammability limit boundary arrives at the outlet. This will render the whole contents of the vessel too rich to support a flame initiated from an ignition source somewhere within the tank. Moreover, a flame anywhere just outside will be unable to lead to a flame flashing within the tank. The corresponding variation in the size of the flammable zone with time is also shown. It indicates a gradual growth in size throughout the time period when the lean limit concentration progresses upwards towards the open end of the tank. Beyond this period, the size of the flammable zone decreases somewhat more rapidly as the rich limit progresses upwards towards the open end. Beyond this time the flammable zone disappears altogether from the tank and remains usually so afterwards.

Accordingly, on this basis it can be seen that during the development of the flammable zone within the tank, there is a time when only an ignition source within the tank can lead to a flame flash. But, once the lean flammability limit concentration boundary reaches the outlet of the tank then an ignition source just outside the tank outlet can also produce a flame flash within the tank contents.



(a) Fully dry vessel side walls



(b) 50% L wetted vessel side walls

Fig. 3. Typical streamline distributions at different time intervals for two cases of side vessel walls wetting conditions, with n-pentane diffusing into air.

The exposure of a liquid fuel surface within a vertical cylindrical container will involve in time the spread of fuel vapour upwards into the air due to the combined effects of diffusion and convection. Flammable mixtures will be formed and spread, while varying in size and location, at rates depending on the physical properties of the liquid, the initial concentration of fuel vapour in the air, geometrical configurations and initial temperatures of the liquid, walls and air. These flammable mixtures can be generated

very rapidly initially at locations immediately above the initial liquid fuel-air interface. Later on, as much fuel vapour diffusion takes place, the flammable region not only grows in size considerably but also tends to move upwards bounded by a too fuel rich zone on the side of the liquid fuel surface and a too fuel lean region on the upper air side. Obviously, the phenomena involved will be modified at any location not only by the changes in density and concentration but also by the fact that the local temperature is likely to be changing as a result of the thermal requirements associated with evaporation and heat transfer. This will tend to cool the temperature of the liquid surface and the vapour-air layers above the liquid surface as well as setting a temperature gradient within the liquid. Accordingly, as indicated earlier, our modelling of these processes in full while accounting for these changes provide a much better agreement between calculated and measured fuel concentrations corresponding to the lean limit progression in the vessel with time. The corresponding predicted concentrations and their changes with time on the basis of constant temperature and property values displayed a significant deviation from those of the experiment (Bunama, et al., 1995).

Figure 3a,b. shows a typical development of the calculated streamline distribution with time both for a dry cylinder side wall and when wetted uniformly with a fuel to the extent of 50% of the cylinder height. It can be seen that a very diverse flow regime is developed with time controlled through the interaction of the solutal and thermal buoyancy forces. This multidimensional behavior of the flow field would result in a complex flammable region which justifies the need for the detailed model used, to predict the flammable region development in space and time. The time required for the flammable region to sweep out of the vessel is reduced very markedly with the increased level of fuel wetting of the side walls. It would also represent an increased level of hazard and especially in case of an ignition source or a flame existing just outside that can lead to a flash fire within the vessel.

Changes in the initial temperature of the system fuel, air and walls produce significant changes in the size of the flammable region and the times required for the lean and rich limits boundaries to reach the container outer rim. As can be seen in Fig. 4., reducing the temperature not only increases the size of the flammable zone but also prolongs the time needed to render the contents of the whole vessel nonflammable. Moreover, for cases when the overlaying air initially contained some fuel vapour homogeneously mixed with it at concentrations represented as % of the corresponding lean limit, it can be seen typically in Fig. 5. that although the time requirements to have the lean limit boundary arrive relatively quickly at the outlet of the vessel, the size of the flammable zone is extended very markedly while the total time required to render the contents of the vessel nonflammable is hardly affected. Thus, it can be seen from these calculated results that having full wetted walls, reduced ambient temperature or the presence of pre-evaporated fuel with the air represent increased fire flash hazards in liquid fuel containers that are partially empty while they are exposed to the outside atmosphere

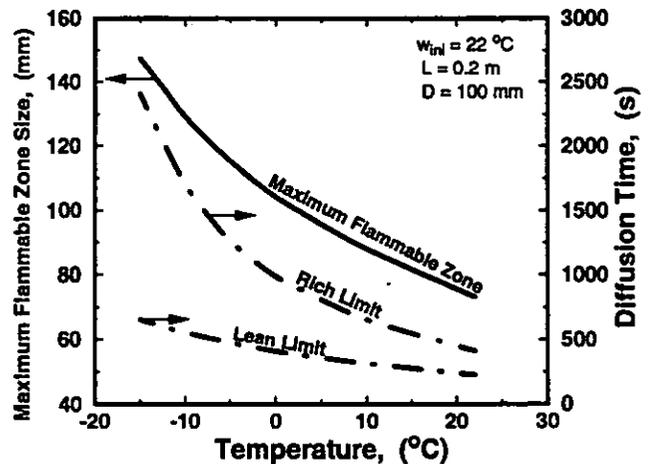


Fig. 4. Effects of the initial temperature of fuel, air and vessel walls on the maximum flammable zone size and on the arrival times of the lean and rich flammability boundaries at the vessel outer rim.

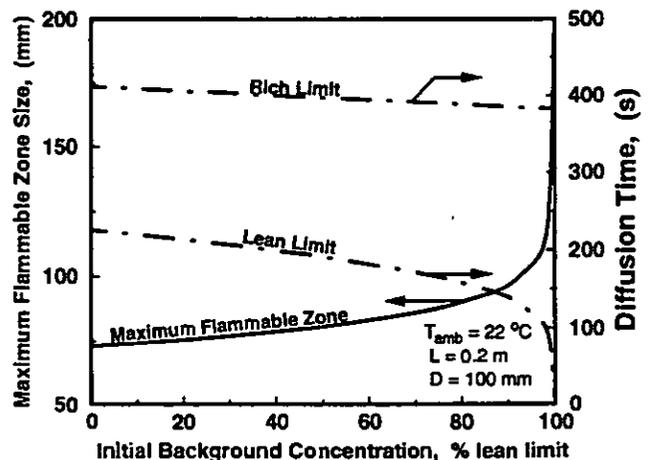


Fig. 5. Effects of the presence of initial fuel traces in the overlaying air on the maximum flammable zone size and on the arrival times of the lean and rich flammability boundaries at the vessel outer rim.

The vaporization, convective diffusion and flame spread phenomena were examined experimentally within smooth circular long vertical glass cylinders of varying lengths of up to 3.00 m and with different diameters varying from 25 mm to 100 mm. The typical tube arrangement is similar to that shown schematically in Fig. 1. These cylinders which were either fully open to the atmosphere or partially closed with a circular central aperture, contained initially only air. Some liquid fuel was introduced promptly at the base of the cylinder without contaminating the air with fuel vapour. The procedure employed to achieve this was through having to remove the base of the vessel while introducing the fuel in a shallow tray of a similar diameter so as to produce suddenly at the required time a vessel with a pool of liquid fuel at its base. This procedure was shown to be effective and produced repeatable

results. The temperature of the liquid fuel could be made different from that of the overlaying atmosphere by external jacketing with ice or hot water. Of particular concern was the establishing at any specific location within the vessel the minimum time required to form a flammable region. This was determined through the mounting of horizontal ignition electrodes along a diameter within the tank at the location of interest and finding out through intermittent deliberate sparking whether a propagating flame can be initiated then or not. This approach could establish the minimum time requirements to produce a flammable mixture at any location. A similar procedure can be followed to determine whether after a certain time period the concentration of the diffusing fuel vapour in the space within the tank becomes sufficiently high at that location that no flame can propagate.

Much of the work carried out involved the use of the relatively volatile fuel n-pentane. The passage of an electric spark for this local flammability testing was ensured not to affect the diffusional processes. The period between the passage of consecutive sparks was typically varied between two to twenty seconds depending on the lapse of time from the commencement of the diffusion. Also, the characteristics and energy of these intermittent sparks used to monitor the first development of a propagating flame was strictly controlled since using highly energetic sparks could ignite mixtures and produce a localized flame flashes within mixtures that may not be wholly flammable. Prolonged application of the spark during the early stages of the diffusion was unnecessary and was also avoided.

## EXPERIMENTAL RESULTS AND DISCUSSIONS

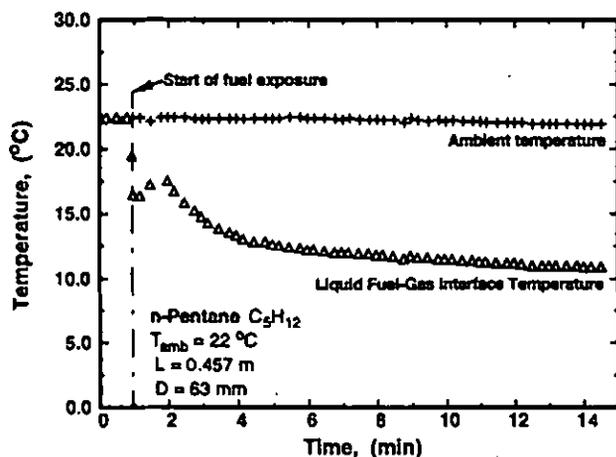


Fig. 6. Variation of the minimum time needed to achieve the required lean limit concentration at different heights above the liquid fuel-gas interface for two different temperatures.

Figure 6. shows experimentally how the temperature around the base of the fuel tank changes with time when initially the whole liquid and apparatus were at the same temperature as that of the air. It can be seen for a typical case that a significant drop in temperature of the liquid fuel surface of around 10 °C, is produced due to the effects of liquid fuel vaporization. Moreover, the walls of the base of the tank undergo similarly cooling as a result of heat transfer.

The progress of the lean limit concentration along the tube with time when established experimentally on the basis of the time to the first successful flame flash at a specified location from a periodic electric spark as described earlier, is shown in Fig. 7. for two initial ambient temperatures of 22°C and 2.5 °C. The slower progress of the lean flammability limit front at the lower temperature is evident. However, following a first flame flash while leaving the fuel vessel and the whole system undisturbed, the time needed to produce a second flame flash, as can be seen in Fig. 8. tends to increase approximately linearly with locations above the fuel surface. Moreover, this time period for any location along the vessel appears to be approximately of the same order as the time needed to form a flammable mixture the first time. Evidently the effects of vitiation with combustion products were counter-balanced by the heating due to energy release effects aiding both the fuel vaporization and the diffusional processes of fuel vapour and fresh air. It can also be seen that doubling the height of the vessel while keeping the diameter the same, reduced this time period between two consecutive flame flashes substantially. This is probably due to the reduced contribution of the dilution of the atmosphere within the larger capacity vessel and the greater availability of unconsumed air that can descend faster to replace the products of combustion and produce a flammable zone once more. Similarly, a colder ambient and fuel liquid temperature of 2.5 °C generated more quickly a flammable mixture at any location. The faster convective processes as a result of the much increased buoyancy forces speed up the scavenging of the products of combustion and their displacement by a heavier fresh air. The unconsumed fuel vapour adjacent to the surface of the liquid within the too rich region will provide some of the fuel vapour needed more readily as it becomes a little warmer and more agitated by the flashing flame propagation and subsequent diffusional processes. Moreover, the size of the flammable zone and consequently mixture requirements, are reduced significantly with the lowering of the temperature.

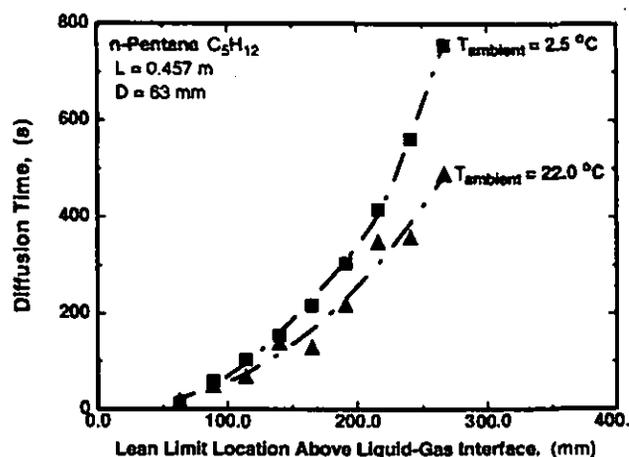


Fig. 7. Variation of the minimum time needed to achieve the required lean limit concentration at different heights above the liquid fuel-gas interface for two different temperatures.

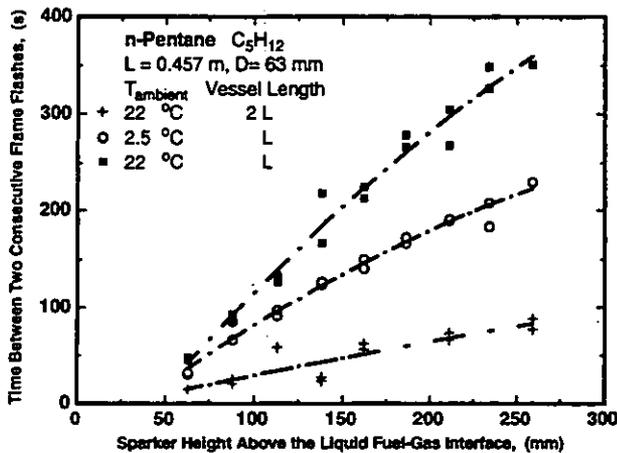


Fig. 8. The effect of changing ambient temperature and vessel length on the time interval between two consecutive flame flashes at different sparker heights above the liquid fuel-gas interface.

Figure 9. shows experimentally that changes in the diameter of the vessel with dry clean walls has only minor effects on the time needed to generate the first flame flashing. A small tendency to increase this time can be noted with larger diameter vessels, probably as a result of the reduced relative contribution of drag at the walls to the convective and diffusional processes. It was also evident that partially restricting the emergence of fuel vapour through having a partially open tank, speeds up the diffusional processes and permits a substantial reduction in the time between consecutive flame flashing, in comparison to the case of a fully open vessel. This is also reflected when a reduction in the diameter of the vessel is employed.

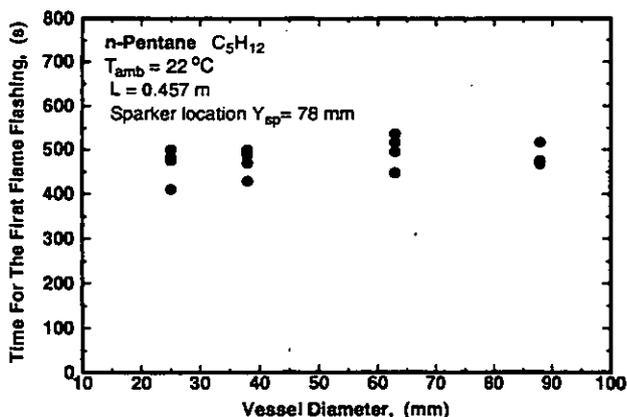


Fig. 9. Effects of changing the vessel diameter on the time of the first flame flashing at a fixed sparker location above the liquid fuel-gas interface.

Much of the results shown were obtained at this stage for the relatively volatile fuel n-Pentane. However, it would be expected that changes in the type of the fuel though will show qualitatively similar trends, quantitatively a big difference can be observed. For example, Fig. 10. shows the variation of the predicted lean flammability limits relative displacement within the vessel with time

for the three fuels benzene, n-pentane and methanol. It can be seen that as a result of the combined effects of the transfer processes involved the progress of the lean limit boundary for methanol is significantly slower than those for n-pentane and benzene. Fig. 11. shows the calculated variations of the rate of liquid fuel evaporation and subsequent rate of its emergence from the vessel with dimensionless time for the three fuels when reckoned relative to the minimum amount of fuel needed to render the whole vessel volume at the lean limit. Similar trends are evident. However, as shown in Fig. 12. experimental results obtained for various binary mixtures of the volatile n-pentane and the very much less volatile hexadecane, the minimum time requirements to produce a flammable mixture at a location around half way through the vessel increases very markedly as the volatility of the fuel mixture is reduced. This indicates that in fuel mixtures, such as commercial fuels that contain only small fractions of highly volatile components, the contents of the vessel will remain for a very substantially longer time than for n-pentane liable to fire spread and thus represents a greater fire hazard.

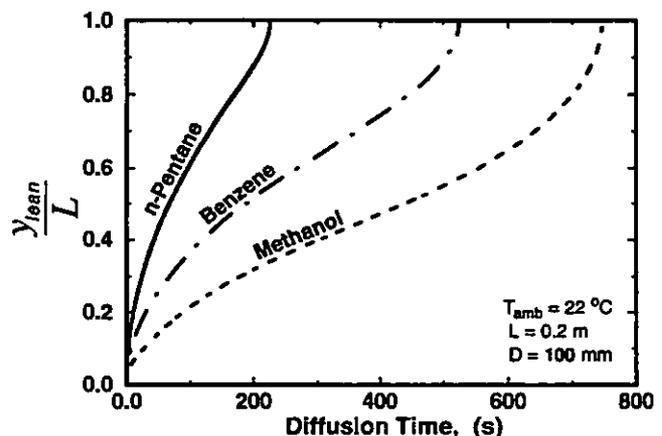


Fig. 10. Predicted lean flammability limits boundary displacement with time for n-Pentane, Methanol and Benzene.

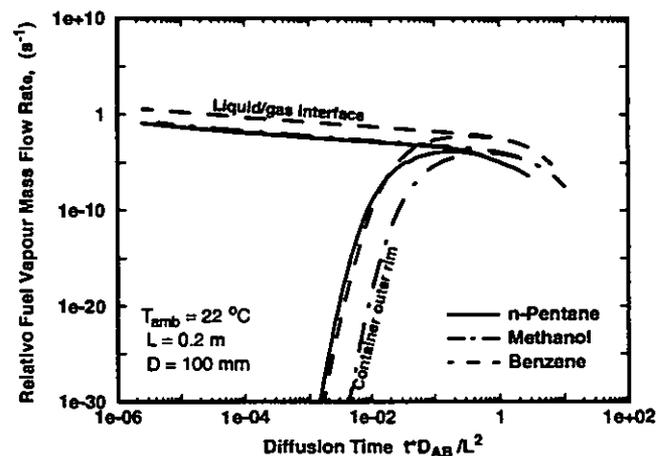


Fig. 11. Relative evaporation rate of fuel from the liquid-gas interface and fuel vapour subsequent rate of emergence at the vessel outer rim for n-Pentane, Methanol and Benzene.

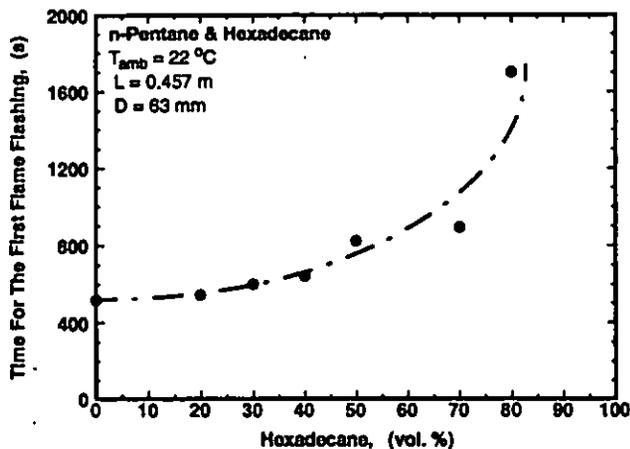


Fig. 12. Effects of adding hexadecane to n-pentane at different mixture ratios on the time for the first flame flashing.

### CONCLUSIONS

- The formation of flammable regions, their growth and decline within the confines of a vertical cylindrical tank containing initially air with unvaporized liquid fuel (n-Pentane) at the base can be established from the transient development of the local lean and rich flammability limits concentrations.
- Three time phases can be identified consecutively in this development. The first is associated with the flammable region located entirely within the vessel. The second begins after the lean limit boundary has reached the top while the rich limit boundary is still within. The third phase begins after both the lean and rich limit boundaries have arrived at the tank top rendering the whole contents too rich to support a flame.
- Some of the observations made experimentally are:
  - i - The progress of the lean limit front upwards is slowed with lowering the system temperature.
  - ii - In the presence of an ignition source a flame flash may develop. This is followed after the lapse of some time by yet another flame.
  - iii - The time interval between any reoccurring flame flashing increases approximately linearly with the height of the ignition source from the liquid fuel surface.
  - iv - The evaporation of the liquid fuel at the liquid-gas interface resulted in a local temperature drop that affected significantly the mass transport processes involved.
  - v - Changes in the diameter of the vessel, for the same height, has only a minor effect on the time needed to generate first flame flashing.
  - vi - The diffusional processes in a partially open tank tend to be somewhat faster than those in fully open tanks.
  - vii - Reducing the concentration of volatile components in liquid fuel mixtures will render the contents of a fuel tank more likely to undergo a flame flash for longer times than those rich in volatile components.

### ACKNOWLEDGEMENTS

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