

## LPG 가연성 혼합물에 대한 고형 금지제의 억제 효과

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## Inhibitory Effect of Solid Inhibitors on LPG Combustible Mixtures

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**요약.** 액화석유가스-공기 불꽃에 대한 2가지 열적 금지제(즉, 돌가루, 탄산칼슘)의 억제효과를 연구하였다. 이를 위해 이들 금지제를 가하기 전과 후 가연성 혼합물의 가연성 한도를 측정하여 조사하였다. 그 결과, 탄산칼슘이 돌가루에 비해 억제 효과가 우수하였다.

**주제어:** 불꽃 금지제, 가연성 한도, 고형 금지제, 액화석유가스

**ABSTRACT.** An experimental rig was constructed in order to study the inhibitory effects of two thermal inhibitors namely; stone and calcium carbonate, on Liquefied Petroleum Gas -air flames. This was achieved by measuring the flammability limits of the combustible mixtures before and after the addition of these inhibitors. It was found that calcium carbonate has superior inhibitory effect on the combustible mixture under investigation while, Stone has a lower inhibitory effect than that of calcium carbonate.

**Keywords:** Flame inhibitors, Flammability limits, Solid inhibitors, Liquefied petroleum gas

### INTRODUCTION

A worldwide ban on the production of the principal halogenated fire suppressants, including halogen 1301 ( $\text{CF}_3\text{Br}$ ), has created a need for new, environmentally acceptable fire suppressants; however, an agent with all the desirable properties of  $\text{CF}_3\text{Br}$  is proving difficult to find. Understanding the inhibition mechanisms of known, effective flame inhibitors will help direct this search.

Solid compounds have been found to be substantially more effective flame inhibitors than halogen-containing compounds.<sup>1,2</sup> Dewtte *et al.*<sup>3</sup> have found out that dust particles when uniformly distributed in flow of flammable gas mixture, exhibit a marked inhibition effect on flame.

Reinelt and Linteris<sup>4</sup> studied the flame inhibition effect of iron pentacarbonyl on premixed flames by measuring the burning velocity and on counter flow diffusion flames by measuring the extinction strain rate. In premixed flames,  $\text{Fe}(\text{CO})_5$  and at low concentrations, reduced the burning velocities up to 100 times more effectively than  $\text{CF}_3\text{Br}$  and showed a strong dependence on both the fuel-air equivalence

ratio and oxygen mole fraction. However, at high concentration of  $\text{Fe}(\text{CO})_5$  there was no additional reduction of the burning velocity. In diffusion flames,  $\text{Fe}(\text{CO})_5$  was again shown to be more effective at the lowest concentrations, but the inhibition effect did not level off at higher mole fractions as it did in premixed flames.

Further work was carried out to find alternative inhibitors. Gilman *et al.*<sup>5</sup> found that the flammability limits of a wide variety of polymers were dramatically reduced in the presence of relatively small concentrations of silica gel and potassium carbonate ( $\text{K}_2\text{CO}_3$ ). The heat peak rate was reduced by 68% without significantly increasing the smoke or carbon monoxide levels during the combustion.

Babushok<sup>6</sup> focused on his study on the inhibition cycles, which regenerated the inhibitor. This leads to the definition of an idealized or perfect cycle. It was demonstrated that for such an inhibitor in a stoichiometric methane-air flame, additive levels in 0.001 - 0.01 mole percent range would lead to a decrease in flame velocity by an approximate value of 30% of the original one. This high inhibitory effect corresponded roughly to the behavior of metallic inhibitors, such

as  $\text{Fe}(\text{CO})_5$  which is known to be two orders of magnitude more effective than currently used suppressants. This correspondence between the behavior of a perfect inhibitor and  $\text{Fe}(\text{CO})_5$  lead to the conclusion that the only gas-phase processes can account for its inhibitive power.

Rumminger *et al.*<sup>7</sup> investigated the flame inhibition mechanism of iron pentacarbonyl in premixed and counter-flow diffusion flames of methane, oxygen, and nitrogen. For premixed flames numerical predictions of burning velocity were compared with experimental measurements, also for counter-flow diffusion flames, numerical prediction of extinction strain rate were compared with experimental results for addition of inhibitor to the air and fuel stream. The numerical predictions agreed reasonably well with experimental measurements at low inhibitor mole fraction, while at higher mole fraction the simulation over predicted inhibition. The over prediction was suggested to be due to condensation of iron-containing compounds since calculated super-saturation ratios Fe and FeO are significantly higher than unity in some regions of the flame. These results led to the conclusion that the inhibition occurred primarily by homogenous gas-phase chemistry.

Flynn<sup>8</sup> investigated the effect of sodium and chlorine as chemical inhibitors on a methane/air flame. It was found out that the inhibition index of sodium was larger than that of chlorine.

Siow and Laurendeau,<sup>9</sup> studied the flame inhibition behavior of di-Me Me Phosphonate (DMMP) and tri-Me Phosphate on methane/air opposed flame. The obtained results were found to be higher than the predicted ones, leading to the need for further improvements in the understanding of the chemical kinetics controlling DMMP inhibition.

Nogueira and Fisher<sup>10</sup> studied the impact of dimethyl methylphosphonate (DMMP) in a premixed methane/oxygen/ $\text{N}_2$ -Ar flame in a flat flame burner slightly under atmospheric pressure at two different equivalence ratios: rich and slightly lean.  $\text{CH}_4$ , CO,  $\text{CO}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$  profiles were obtained with a Fourier Transform Infrared (FTIR) spectrometer. Gas samples are analyzed in FTIR, were extracted from the reaction zone using a quartz microprobe with choked flow at its orifice. Flame calculations were performed with two existing detailed chemical kinetic mechanisms for organophosphorus combustion. DMMP addition caused all profiles except that of  $\text{CH}_3\text{OH}$  to move further away from the burner surface, which can be interpreted as a consequence of a reduction in the adiabatic flame speed. Experimentally, the magnitude of the shift was 50% for his near-stoichiometric flame than for the rich flame. Experimental  $\text{CH}_3\text{OH}$  profiles were four to seven times

higher in the doped flames than in the undoped ones. The magnitude of its effect is not predicted in the calculations, suggesting a need for further mechanism development. Otherwise, the two mechanisms are reasonably successful in predicting the effects of DMMP on the flame.

The laminar flame speed was measured experimentally and calculated numerically for a premixed propane/air flame at 1 atm, under a range of equivalence ratios, undoped and doped with dimethyl methylphosphonate (DMMP) by Jayaweera *et al.* A detailed investigation of the catalytic cycles involved in the recombination of key flame radicals was made for two equivalence ratios, fuel lean and fuel rich. The chemical kinetic model indicated that the  $\text{HOPO}_2 \leftrightarrow \text{PO}_2$  inhibition cycle is more important in the lean flame than the rich. The OPCs are similarly effective across the range, demonstrating the robustness of OPCs as flame suppressants. In addition, it is shown that the phosphorus compounds are most active in the high-temperature region of the flame.

In this work new solid materials will be tested as inhibitors for an LPG-air flame, this combustible mixture is the main domestic source of energy used in Jordan. The solid inhibitor are calcium carbonate and stone, which are both non-toxic inert, and available almost free of charge.

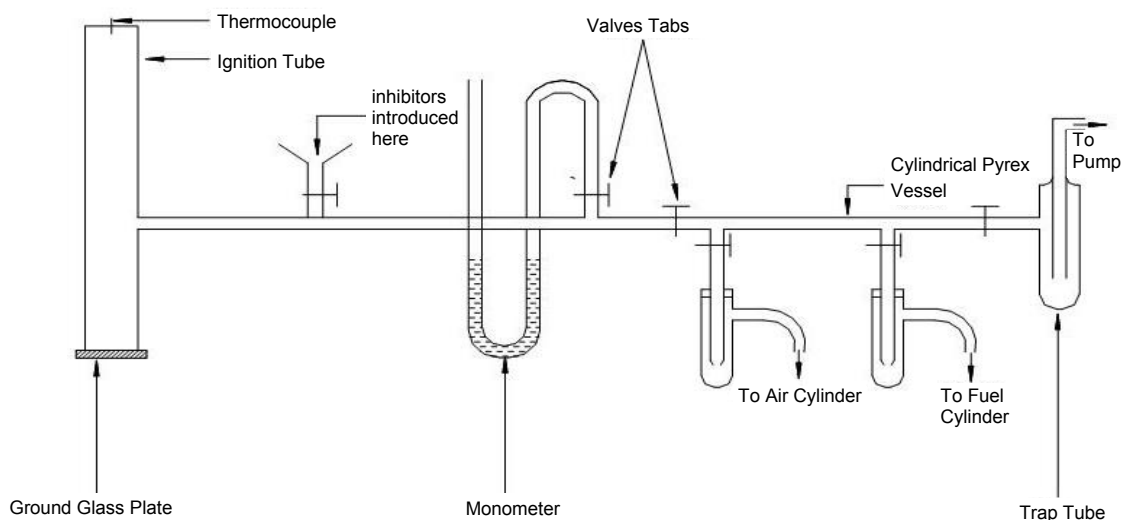
## EXPERIMENTAL SETUP

The limits of flammability may be determined in a tall vertical tube of certain specified dimensions, and under the variety of system and conditions, namely: upward propagation, downward propagation, electric spark ignition, pilot flame ignition, atmospheric pressure, pressures above and below atmospheric.

Variation in the dimension of the tube exerts some influence on the measurements. As a general rule flammability ranges widen as the tube diameter is made larger due to reduction in quenching effects by the tube walls but the changes in limit for diameters above 5 cm diameter is very small.

The apparatus used in this experiment is shown in Fig. 1, which is made from Pyrex glass.

The apparatus consists of a long cylindrical Pyrex vessel connects the parts of the apparatus, with inside diameter 20 mm and 1 m in length. Ignition tube with 7 cm in diameter where mixing and combustion occurs. The inhibitor, in a form of powder, is introduced to the apparatus through the valve nears the ignition tube, then as air flows, from the high pressure air cylinder into the apparatus it carries the inhibitors with it. A mercury manometer measures the gas partial pressures of both LPG gas and air. A vacuum pump



**Fig. 1.** The Experimental Setup.

is used to evacuate the apparatus, which introduced after a water trap tube to prevent moisture from entering the pump. Two tubes are connected to the fuel and air cylinders. To verify whether or not a mixture is able to propagate to the top of the ignition tube a thermocouple assembly is installed as shown, so a deflection on a galvanometer indicated that a certain mixture has successfully propagated to the top.

### EXPERIMENTAL PROCEDURE

The apparatus was evacuated by the vacuum pump. Then the LPG (Liquefied Petroleum Gas) was introduced into the ignition tube through the manometer to measure the required quantity. Then the required amount of air was introduced into the tube using the manometer. It is to be noted that the total sum of the partial pressure of both gases was made up to atmospheric pressure.

The mixture was introduced into the ignition tube, without adding inhibitors to determine flammability limits, and then left for a period of 45 minutes to one hour to mix by diffusion before being ignited manually using a spark located at the bottom of the tube. Having ignited the mixture and if the combustible mixture lies within the flammability limits the flame will propagate vertically inside the tube to the top end, this will be indicated by the deflection on the galvanometer of the thermocouple that is located at the top of the tube as mentioned earlier. Otherwise, and in case of no ignition the flame will not move upward inside the tube and no deflection was noted on the galvanometer scale. The limits of flammability were determined by trial and error technique, by introducing different gas mixtures until the right mixture

was found, which is indicated by no ignition condition. For each trial the apparatus was thoroughly evacuated, and then a different gas mixture was introduced until the right limits were found. After determining the flammability limits, inhibitors were added to different gas mixture to find their inhibition effect also by trial and error technique.

During this work the fuel percentages within the mixture varies between 10.4 and 14.9, all of which are within the flammability limits. While the added amount of calcium carbonate is within the range from 0.3 to 2.5 (g), and that of stone added is within the range from 0.5 to 2.0 (g).

### RESULTS AND DISCUSSION

As mentioned earlier, the flammability limits were determined by trial and error method. It was found that the flammability limits for the LPG (butane 70%, propane 30%) are within (3 to 5.8 cm of Hg) 8.96% - 17.3% (at fuel percentage) and the flame color were blue. At 17.3%, the upper flammability limit (UFL), the flame was strong with a loud noise inside the ignition tube, while at 8.96%, the lower flammability limit (LFL), the flame was weak and no noise was heard. It was found that the flammability limits for the LPG-air mixture is not wide, this is due to the fact that air contains nitrogen.

During the experimental work, it is to be noted that, away from the flammability limits, the flame was ignited with strong pressure wave and a loud noise; it was of blue color and propagated all the way to the top of the tube with an "umbrella shape". However and as the flammability limits were approached, the flame was noticed to be of weak pre-

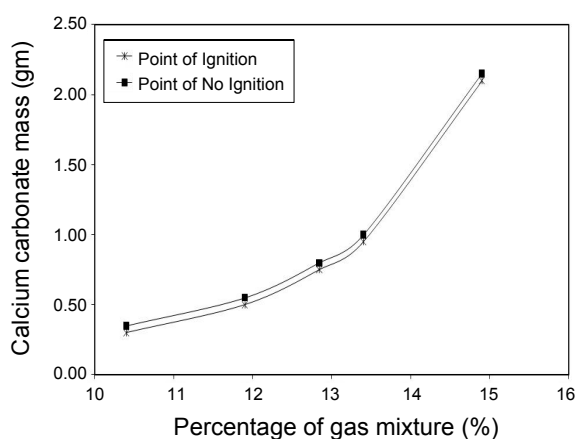


Fig. 2. Points of Ignition and No Ignition using Calcium Carbonate.

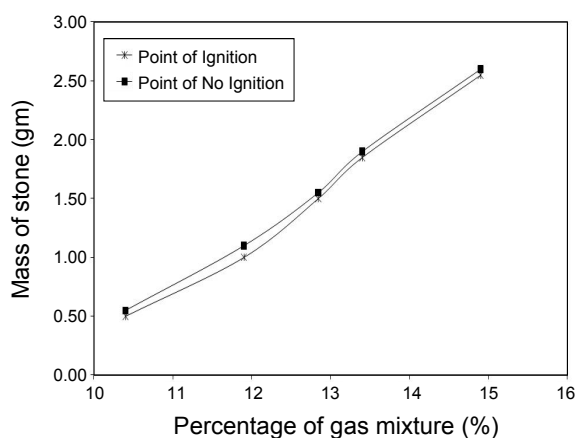


Fig. 3. Points of Ignition and No Ignition using Stone.

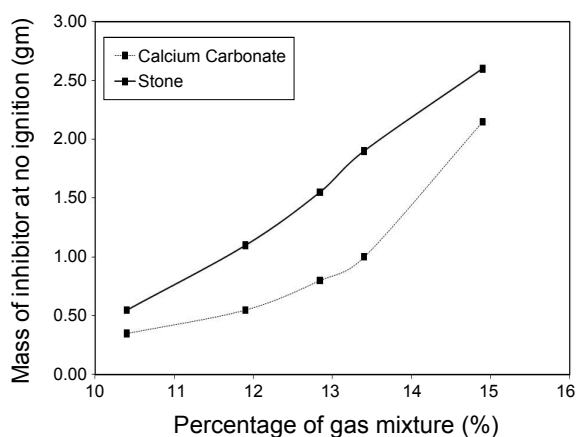


Fig. 4. Comparison of Points of No Ignition using Calcium Carbonate and Stone.

ssure wave, low noise, and orange color and did not reach the upper part of the tube.

The inhibitory effects of calcium carbonate and stone represented in Figs. 2 and 3.

Fig. 2, represents the amount of calcium carbonate required to be added to inhibit the combustible mixture with certain fuel concentration. Two curves are shown; one represents the points at ignition, while the other one represents the points of no ignition. Within the region to the right of the line joining the no ignition points, ignition is impossible, while it is possible within the region to the left of line joining the points of ignition. Fig. 3 shows the same two lines behavior when stone is added to the combustible mixtures.

Fig. 4 shows a comparison between the inhibitory effects of both inhibitors.

The figure shows that the inhibition effect of calcium carbonate is more pronounced than that of stone. This pronounced inhibitory effect of calcium carbonate over stone may be attributed to the endothermic degradation that undergoes under high temperature producing calcium oxide and carbon dioxide, this degradation removes heat from the surrounding, thus cooling the material and increase the inhibitory effect.

Further, carbon dioxide acts as diluents for the combustible gases, lowering their partial pressures and the partial pressure for oxygen, and hence slowing the reaction rate.

It may be noted that the slope of the calcium carbonate curve is steeper at low concentration of this inhibitor than for larger amount. However, the slope of the curve representing the inhibition effect of stone is almost the same for all amounts of stone added.

## CONCLUSIONS

In an effort to construct a paradigm for flame inhibition by solid compounds, an experimental investigation was made for studying their inhibitory effects on premixed fuel-air flames. The fuel was LPG (Liquefied Petroleum Gas), which contained 70% butane and 30% propane.

The solid inhibitors were calcium carbonate ( $\text{CaCO}_3$ ) and stone, which was firestone (flint). The experiment showed that calcium carbonate acted as a better inhibitor than stone. Both inhibitors raised the lower flammability limit when added to the mixture, as the amount of inhibitor increased there was a distinct raise in the Lower flammability limit.

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