ISSN 0010-5082, Combustion, Explosion, and Shock Waves, 2020, Vol. 56, No. 6, pp. 629–633. © Pleiades Publishing, Ltd., 2020. Russian Text © V.V. Zamashchikov.

Mechanism of Flame Propagation above the Surface of a Flammable Liquid

V. V. Zamashchikov^a

UDC 536.46

Published in *Fizika Goreniya i Vzryva*, Vol. 56, No. 6, pp. 12–16, November–December, 2020. Original article submitted September 19, 2019; revision submitted October 4, 2029; accepted for publication December 24, 2019.

Abstract: Combustion of vapors of a flammable liquid whose temperature is below the flash point is under study. In this case, the flame propagates along the surface of the liquid due to being heated by combustion products. The velocities of an oxidizer moving towards the flame, which propagates at velocities comparable to the laminar burning rate of premixed hydrocarbon flames, are measured. The measurements show that the gas flow is laminar. There is a correlation established between the flash point of a flammable liquid and the flame propagation velocity. On the basis of the data obtained, it is assumed that the main mechanism of formation of a flammable mixture ahead of the combustion front is a diffusion mechanism.

Keywords: diffusion combustion, flash point, flammable liquid, liquid phase controlled flame propagation.

DOI: 10.1134/S0010508220060027

INTRODUCTION

Combustion of flammable liquids is widely used in daily life. The main chemical transformations occur in the gas phase after the oxidizer is mixed with liquid vapor. The type of combustion and the very possibility of this process depend on vapor concentration in a resulting mixture. An important case is where a homogeneous mixture of air and vapor is formed with a partial pressure equal to the saturated vapor pressure, which depends on the temperature of the liquid. In this case, after initiation, the combustion wave both propagates and does not propagate through this mixture. However, in the second case, a combustion wave may propagate along the liquid surface (flame propagation controlled by the liquid phase) due to heating of the liquid by combustion products. According to [1, 2], under certain conditions, a precursor (i.e., the flame propagation controlled by the liquid phase) propagates first, followed by the formation of the main flame above the liquid surface (this becomes possible because the latter is heated by combustion products). In a narrow chan-

^aVoevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences,

Novosibirsk, 630090 Russia; albor@kinetics.nsc.ru.

nel, combustion initiation is followed by the formation of a diffusion flame at the cut, and the flame separates from it and propagates along the channel [3]. As shown in [3], this occurs only if the flow rate of the oxidizer moving toward the flame is greater than a certain value, and the flame velocity strongly depends on the flow rate of the oxidizer.

Flame propagation in the case where the saturated vapor pressure is lower than the partial fuel pressure corresponding to the lower concentration limit is an important issue. Flame propagation requires that a flammable mixture is formed ahead of the combustion front. At the initial temperature of the liquid, its vapors are not sufficient to form a flammable mixture. However, vapors can enter a pre-flame region from a region located behind the flame, in which many of them are located because the liquid is heated by the combustion products. In addition, a temperature gradient arises along the surface of the liquid, forming a heat flux through the liquid into the pre-flame region, and this heat flux may be both conductive and convective due to the movement of the liquid. Heating the liquid ahead of the combustion front increases the propellant concentration in the gas mixture in this region.

At low flame propagation velocities (less than $\approx 30 \text{ cm/s}$, convective heat transfer plays an important role. Thus, in [4, 5], the wave formation on the liquid surface ahead of the flame front with a vortex flow of the liquid is observed. In this case, the flame velocity changes periodically (pulsating regime), but its average value remains constant. Air is used as an oxidizing agent. In [6], conditions for a transition from a pulsating regime to a uniform one are obtained by numerical simulation. The problem is solved in the presence of an oncoming air flow. The correlation between the formation of a vortex ahead of the flame front and a change in the flame velocity is described in [7, 8]. According to [7-10], the formation of a vortex is associated with uncompensated capillary forces arising due to the temperature gradient along the surface of the liquid (the Marangoni effect). The liquid heated by the combustion products is transferred to the pre-flame region [11–13], thereby increasing the vapor flux into the gas phase. Thus, heat and hydrodynamic waves move in the liquid together with the flame. Their characteristic size depends on the flame velocity.

In [14], experiments are carried out in the presence of an oncoming oxidizer flow. The use of oxygenenriched air as an oxidizer allows one to change the flame velocity in a wide range. When oxygen is used as an oxidizer, the flame velocities turn out to be comparable to normal velocities for hydrocarbon–oxygen mixtures (a laminar burning rate of <1 m/s). According to [14], with an increase in the flame velocity, the characteristic size of the heat wave decreases, and it is shown by the estimates given in [14] that the mass transfer generated by capillary forces is unlikely in this case. In this regard, the question of the diffusion flame propagation mechanism at high velocities is relevant. The experiments performed in this study are aimed at elucidating this mechanism.

EXPERIMENT

Experiments are carried out in a horizontal rectilinear channel 4 mm in width and 42 mm in height. The side walls are made of quartz plates. The schematic diagram is shown in Fig. 1. The oxidizer is fed through a closed end. Oxygen-enriched air is used as an oxidizing agent. A mixture of air with oxygen is convectively stirred in a mixer with a preparation accuracy of 0.6%. The oxidizer flow rate is controlled using Smart Trak 2 Sierra Instruments and equal to 1 liter/min in the experiments. The flammable liquid is poured into the bottom of the channel. Combustion is initiated through the open end. The PIV method (Polis Company SigmaPro) is used to measure the gas velocity profile. The PIV Zamashchikov



Fig. 1. Schematic diagram of the device.

laser beam enters the channel through a window at its closed end. Then TiO₂ particles with a size of about 2 μ m are added to the oxidizing agent. The light scattered by the particles was recorded by a video camera. Another high-speed video camera records the self-glow of the flame. A thermocouple is placed at the open end, and its signal triggers the PIV equipment and the high-speed video camera. The flame velocity is measured with an accuracy of 7%. The gas velocity is measured with an accuracy of 10%.

RESULTS AND DISCUSSION

Because the liquid is heated by the combustion products, a temperature gradient arises along its surface. As a result, a heat flux is formed into the preflame region. It is assumed in [6-8] that the main heat transfer mechanism is capillary, i.e., heat is transferred via surface tension forces. However, according to [14]. this mechanism is unlikely at high flame velocities. In the present study, this is verified with the help of experiments carried out with flammable liquids of various dynamic viscosities. It is obvious that the mass transfer due to capillary forces depends on the viscosity of the liquid. The data for the flammable liquids used in the experiment are given in the table. Oxygen is used as an oxidizing agent. It can be seen from the table that the viscosity of *n*-butanol is almost three times larger than that of decane, while the flame velocity is also higher too. If it is assumed that the mass transfer is due to capillary forces, then the velocity should decrease with increasing viscosity. The dependence of the velocity on the viscosity is not observed, while the dependence on the flash point is clear. This dependence is shown in Fig. 2. It is seen that, as the flash point becomes larger, the flame velocity decreases. An exception is formic acid, which can be explained by its interaction with the channel walls. The resulting dependence indicates that the flash point is a key parameter in the flame propagation mechanism.

If it is assumed that the liquid is heated up ahead of the flame front, then the formation of a flammable

Substance	Formula	Viscosity at 20°C, kg/(m $\cdot s)$	Flame velocity, m/s	Flash point, °C
n-Butanol	C_4H_9OH	$2.95 \cdot 10^{-3}$ [15]	2.35	35 [16]
Decane	$\mathrm{C}_{10}\mathrm{H}_{22}$	$0.907 \cdot 10^{-3}$ [15]	1.47	47 [16]
Dodecane	$\mathrm{C}_{12}\mathrm{H}_{26}$	$1.492 \cdot 10^{-3} \ [15]$	0.80	77 [16]
Glycerol	$\mathrm{C_{3}H_{8}O_{3}}$	1.48 [15]	0.02	198 [16]
Amyl alcohol	$C_5H_{11}OH$	$4.1 \cdot 10^{-3} \ [17]$	1.29	48 [16]
Formic acid	HCOOH	$1.6 \cdot 10^{-3} (25 \ ^{\circ}\text{C}) \ [17]$	0.027	60 [16]





Fig. 2. Flame velocity versus the flash point.

mixture in this region requires more than increasing the vapor flux from the liquid to the gas phase. The vapors should also be mixed with the oxidizing agent. As the flame velocity is sufficiently high, the mixing should be quick. It can strongly accelerate if a vortex gas motion is formed ahead of the combustion wave. The formation of such vortices is described in [9]. In order to determine the gas flow regime, the gas velocity ahead of the combustion front is measured. The *n*-butanol is used as a flammable liquid. Along with the gas velocity, the flame velocity is measured using a high-speed video camera that records the self-glow of the flame. The PIV system provides two-dimensional gas velocity profiles. In this case, the video camera records not only the laser light scattered by TiO_2 particles added to the oxidizer, but also that scattered by the combustion products at the areas with none of these particles. The superposition of the flame image obtained by a high-speed video camera on the image of the laser light scattered by the combustion products reveals



Fig. 3. Superposition of the images of the flame and the scattered laser light onto the two-dimensional gas velocity profile: oxidizer is $60 \% O_2 + air$; flame velocity is 60 cm/s.

that the contours of the flame front and the glowing (due to the scattered laser light) combustion products match. As shown by analyzing the images, there are no TiO_2 particles near the flame front.

Figure 3 demonstrates the superposition of the images of the flame and the scattered laser light on the two-dimensional gas velocity profile. At sufficiently high flame velocities, the vortex motion of the gas ahead of the front is not observed. However, there are no particles added to the gas in the immediate vicinity of the front, so the velocity is not determined here. Nevertheless, this region is small, and, considering the gas viscosity, it is unlikely that vortex motion of gas occurs in it.

There are two possible reasons for a significant decrease in the concentration of particles added to the oxidizer in the immediate vicinity of the flame front. When the oxidizer heats up, it expands and the particle concentration decreases. Moreover, the particle concentration decreases from a maximum value in the oxidizer to zero behind the combustion front where the combustion products are mixed with liquid vapors. If only a heated oxidizer is ahead of the flame, the flame is lost because the presence of a flammable mixture is necessary to maintain combustion. Thus, a decrease in the particle concentration in the immediate vicinity of the front, the presence of a flammable mixture, and the absence of the vortex motion of gas in this region indicate that a flammable mixture is formed due to the diffusion of fuel and oxidizer toward each other.

It is shown by the images obtained that the concentration of TiO₂ particles in the oxidizer also decreases near the liquid surface, while their concentration decreases even more near the surface at the combustion front. This can be explained by the fact that the near-surface liquid layer near the front is heated and, as a consequence, the vapor flux from it increases. The distance between the flame and the liquid surface is determined by two factors, namely the heat flux from the combustion front into the liquid and the absence of a flammable mixture. At a flame velocity v = 1 m/s, the characteristic thickness of the heated liquid layer is $\chi/v \approx (8 \cdot 10^{-4} \text{ cm}^2/\text{s})/(100 \text{ cm/s}) = 8 \cdot 10^{-6} \text{ cm}.$ In other words, the heat wave moving through the liquid should very slightly be ahead of the combustion wave. However, the particles vanish near the most protruding part of the flame front at a much greater distance. An explanation can be found for this if the presence of radiation heating is assumed, i.e., the light emitted by hot combustion products is absorbed by the liquid, heating it ahead of the combustion wave. Further research is required to clarify this issue.

CONCLUSIONS

It is shown by the experiments that the flame velocity does not depend on the viscosity of the flammable liquid, but depends on the flash point, which indicates that heat and mass transfer by capillary forces does not occur at sufficiently high flame velocities. In this case, the near-surface layer of the liquid ahead of the combustion front heats up even at sufficiently high flame velocities. The resulting two-dimensional oxidizer velocity profiles show that the gas flow is laminar, i.e., there is no vortex motion ahead of the combustion front, which indicates that, most likely, the main mechanism for the formation of a combustible mixture ahead of the flame front is the diffusion of fuel and oxygen vapors toward each other.

REFERENCES

- M. Li, S. Lu, R. Chen, et al., "Experimental Investigation on Flame Spread over Diesel Fuel near Sea Level and at High Altitude," Fuel 184, 665–671 (2016); http://dx.doi.org/10.1016/j.fuel.2016.07.060.
- J. Ji, S. Lin, C. Zhao, et al., "Experimental Study on Initial Temperature Influence on Flame Spread Characteristics of Diesel and Gasoline–Diesel Blends," Fuel **178**, 283–289 (2016); http://dx.doi.org/10.1016/j.fuel.2016.03.072.
- V. V. Zamashchikov, A. A. Korzhavin, and E. A. Chinnov, "Combustion of a Liquid Fuel in a Rectangular Channel," Fiz. Goreniya Vzryva 50 (4), 15–21 (2014) [Combust., Expl., Shock Waves 50 (4), 381–386 (2014)].
- V. V. Zamashchikov, "Flame Spread Across Shallow Pools in Modulated Opposed Air Flow in Narrow Tube," Combust. Sci. Technol. 181 (1), 176–189 (2009); http://dx.doi.org/10.1080/00102200802424484.
- V. V. Zamashchikov, "Effect of Modulations of Opposed Gas Flow Velocity on Flame Spread Rate over a Liquid Surface," Fiz. Goreniya Vzryva 45 (1), 11–17 (2009) [Combust., Expl., Shock Waves 45 (1), 8–13 (2009)].
- I. Kim and W. A. Sirignano, "Computational Study of Opposed-Force-Flow Flame Spread Across Propanol Pools," Combust. Flame. **132** (4), 611–627 (2003); http://dx.doi.org/10.1016/s0010-2180(02)00506-0.
- H. D. Ross and F. J. Miller, "Detailed Experiments of Flame Spread Across Deep Butanol Pools," Symp. (Int.) Combust. 26 (1), 1327–1334 (1996); http://dx.doi.org/10.1016/s0082-0784(96)80351-1.
- H. D. Ross and F. J. Miller, "Flame Spread Across Liquid Pools with Very Low-Speed Opposed or Concurrent Airflow," Symp. (Int.) Combust. 27 (2), 2723– 2729 (1998); http://dx.doi.org/10.1016/S0082-0784(98)80128-8.
- M. Li, C. Wang, Z. Li, S. Yang, K. Fukumoto, C. Fan, "Combustion and Flame Spreading Characteristics of Diesel Fuel with Forced Air Flows," Fuel **216**, 390–397 (2018); https://doi.org/10.1016/j.fuel.2017.11.100.
- M. Li, S. Lu, R. Chen, C. Wang, "Pulsating Behaviors of Flame Spread Across n-butanol Fuel Surface," Appl. Therm. Eng. **112**, 1445–1451 (2017); http://dx.doi.org/10.1016/j.applthermaleng.2016.10.001.
- E. Degroote and P. L. García-Ybarra, "Flame Propagation over Liquid Alcohols. Part III. Pulsating Regime," J. Therm. Anal. Calorim. 80 (3), 555–558 (2005); http://dx.doi.org/10.1007/s10973-005-0693-7.
- E. Degroote and P. L. García-Ybarra, "Flame Propagation over Liquid Alcohols. Part II. Steady Propagation Regimes," J. Therm. Anal. Calorim. 80 (3), 549–553 (2005); http://dx.doi.org/10.1007/s10973-005-0692-8.

Mechanism of Flame Propagation above the Surface of a Flammable Liquid

- E. Degroote and P. L. García-Ybarra, "Flame Propagation over Liquid Alcohols. Part I. Experimental Results," J. Therm. Anal. Calorim. 80 (3), 541–548 (2005); http://dx.doi.org/10.1007/s10973-005-0735-1.
- V. V. Zamashchikov, A. A. Korzhavin, and E. A. Chinnov, "Combustion of Liquid Fuel in the Flat Micro- and Minichannels," Int. J. Heat Mass Transfer. **102**, 470–478 (2016); http://dx.doi.org/10.1016/j.ijheatmasstransfer.2016.06.043.
- N. B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases: In Normal and Dissociated States (Hemisphere Publishing Corporation, 1975).
- A. N. Baratov, A. Ya. Korol'chenko, et al., Fire and Explosion Hazard of Substances and Materials and Means of Their Extinguishing (Khimiya, Moscow, 1990) [in Russian].
- 17. https://pubchem.ncbi.nlm.nih.gov/compound/.