

DETONABILITY OF AIR MIXTURES OF POLYETHYLENE PYROLYSIS PRODUCTS

S. M. Frolov^{1,2,3}, V. I. Zvegintsev⁴, I. O. Shamshin^{1,3}, M. V. Kazachenko^{1,5}, V. S. Aksenov^{1,2}, I. V. Biler⁶, and I. V. Semenov³

¹N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation

²National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe Sh., Moscow 115409, Russian Federation

³Scientific Research Institute for System Analysis, Russian Academy of Sciences, 36-1 Nakhimovskii Prosp., Moscow 117218, Russian Federation

⁴S. A. Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences, 4/1 Institutskaya Str., Novosibirsk 630090, Russian Federation

⁵N. E. Bauman Moscow State Technical University, 5-1 Baumanskaya 2nd Str., Moscow 105005, Russian Federation

⁶A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prosp., Moscow 119991, Russian Federation

Abstract: Based on the measured values of deflagration-to-detonation transition run-up distance and time, the detonability of air mixtures of polyethylene (PE) pyrolysis products (pyrogas) of different composition is determined in the standard pulsed detonation tube. The pyrogas was obtained in a reactor at decomposition temperatures of 650–850 °C. Chromatographic analysis of the pyrogas showed that at high decomposition temperature (850 °C), it mainly consists of hydrogen, methane, ethylene, and ethane and has a molecular weight of 5–10 kg/kmol and at low decomposition temperature (650 °C), it mainly consists of methane, hydrogen, ethylene, ethane, propane, and higher hydrocarbons and has a molecular weight of 24–27 kg/kmol. It has been shown that in the fuel–air mixtures with the equivalence ratio ranging from 0.6 to 1.6 at normal pressure, the pyrogas of PE possesses the detonability close to that of homogeneous air mixtures of ethylene and propylene. On the one hand, this indicates a high explosion hazard of PE pyrogas which can be formed, for example, in industrial and domestic fires. On the other hand, PE pyrogas can be considered as a promising fuel for solid-fuel detonation ramjets.

Keywords: detonability; standard pulsed detonation tube; granulated polyethylene; thermal pyrolysis of polyethylene; pyrogas, fuel–air mixture; deflagration-to-detonation transition; detonation ramjet

DOI: 10.30826/CE20130206

Figure Captions

Figure 1 Schematic of the standard pulsed detonation tube with measuring segments: 0 — cross section of distance count; * — ignition site; and 1–18 — positions of ionization probes and/or pressure transducers. Dimensions are in millimeters

Figure 2 Schematic of the gas generator with pyrogas sampler (a), with simultaneous pyrogas and liquid fraction sampling (b), and photograph of samplers (c)

Figure 3 Examples of records of pyrogas temperature (a) and pressure (b) (the mass of granular polyethylene is 1 g) in a closed reactor at the decomposition temperature 850 °C (upper row); also, the rates of change of temperature and pressure are shown (lower row)

Figure 4 Examples of records of pyrogas temperature (mass of granulated polyethylene 15 g) in an open reactor at decomposition temperatures 650 (a) and 750 °C (b): 1 — oven temperature; and 2 — temperature at reactor bottom. Vertical lines correspond to the time interval of pyrogas sampling for chromatography

Figure 5 Examples of records of pyrogas temperature (a) and pressure (b) and the calculated time history of the shot-mean mass flow rate of pyrogas (c) in the experiment on the standard pulsed detonation tube with $T_p = 765$ °C and $m_0 = 10$ g

Figure 6 Measured velocities of shock waves (closed circles) and flame fronts (open circles) in each shot of the standard pulsed detonation tube in the experiment of Fig. 5 ($T_p = 765$ °C and $m_0 = 10$ g). The horizontal dashed line corresponds to the typical value of the Chapman–Jouguet detonation velocity \overline{D}_{CJ} in stoichiometric mixtures of hydrocarbon fuels with air

Figure 7 Measured dependences of the shock wave (closed symbols) and flame front (open symbols) velocities on the distance from the ignition source in each shot of the standard pulsed detonation tube in the experiment of Fig. 5 ($T_p = 765^\circ\text{C}$ and $m_0 = 10\text{ g}$); the horizontal dashed line corresponds to the typical value of the Chapman–Jouguet detonation velocity \overline{D}_{CJ} in stoichiometric mixtures of hydrocarbon fuels with air: 1 – shot 2; 2 – 3; 3 – 4; 4 – 5; 5 – 7; 6 – 8; 7 – 9; 8 – 10; 9 – 11; and 10 – shot 13

Figure 8 Measured values of DDT run-up time in detonation shots of the standard pulsed detonation tube in the experiment of Fig. 5 ($T_p = 765^\circ\text{C}$ and $m_0 = 10\text{ g}$)

Figure 9 Measured dependences of the mean velocities of shock waves (closed circles) and flame fronts (open circles) in the measuring section of the standard pulsed detonation tube on the fuel-to-air equivalence ratio of the pyrogas–air mixture. The solid curve corresponds to the thermodynamic detonation velocity D_{CJ} in a homogeneous ethylene–air mixture

Figure 10 The dependence of the DDT run-up time on the fuel-to-air equivalence ratio for the gaseous mixtures of the polyethylene pyrolysis products with air: solid and dashed curves correspond to DDT run-up time in the homogeneous ethylene–air and propylene–air mixtures, respectively [7]

Table Captions

Table 1 Measurement errors of gas generator characteristics

Table 2 Characteristics of gas generator at pyrolysis of granular polyethylene (1 g) in a closed reactor

Table 3 Composition of pyrogas (%(vol.)) at polyethylene pyrolysis in a closed reactor with $T_p = 650$ and 850°C and $m_0 = 1\text{ g}$

Table 4 Characteristics of gas generator at pyrolysis of polyethylene sample with $m_0 = 15\text{ g}$ in an open reactor

Table 5 Composition of pyrogas (%(vol.)) at pyrolysis of polyethylene in an open reactor ($m_0 = 15\text{ g}$)

Table 6 Operation cyclogram of the standard pulsed detonation tube

Acknowledgments

This work was supported by the subsidy given to the N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences to implement the state assignment on the topic No. 0082-2016-0011 (Registration No. AAAA-A17-117040610346-5) and to the Scientific Research Institute for System Analysis to implement the state assignment on the topic No. 0065-2019-0005 (Registration No. AAAA-A19-119011590092-6), and was also funded by RFBR (grant No. 18-08-00076a).

References

1. Frolov, S. M., V. I. Zvegintsev, V. S. Aksenov, I. V. Bilera, V. V. Kazachenko, I. O. Shamshin, P. A. Gusev, M. S. Belotserkovskaya, and E. V. Koverzanova. 2018. Detonatsionnaya sposobnost' vozdushnykh smesey produktov piroliza polipropilena [Detonability of air mixtures of the polypropylene pyrolysis products]. *Goren. Vzryv (Mosk.) – Combustion and Explosion* 11(4):44–60. doi: 10.30826/CE18110406.
2. Zvegintsev, V. I., A. V. Fedorychev, D. V. Zhesterev, I. R. Mishkin, and S. M. Frolov. 2019. Gazifikatsiya legkoplavkikh uglevodorodnykh materialov v vysokotemperaturnom gazovom potoke [Gasification of low-melting hydrocarbon materials in high-temperature gas flow]. 2019. *Goren. Vzryv (Mosk.) – Combustion and Explosion* 12(3):108–116. doi: 10.30826/CE19120312.
3. Shipliyuk, A. N., V. I. Zvegintsev, S. M. Frolov, D. A. Vnuchkov, S. V. Lukashevich, and D. G. Nalivaychenko. 2019. Experimental study of the low-melting hydrocarbons regression rate in the air flow. *J. Phys. Conf. Ser.* 1404:012066. doi: 10.1088/1742-6596/1404/1/012066.
4. Shipliyuk, A. N., V. I. Zvegintsev, S. M. Frolov, D. A. Vnuchkov, S. V. Lukashevich, and D. G. Nalivaychenko. Experimental study of the low-melting hydrocarbons regression rate in the inert gas flow. *J. Phys. Conf. Ser.* 1404:012068. doi: 10.1088/1742-6596/1404/1/012068.
5. Frolov, S. M., V. I. Zvegintsev, V. S. Aksenov, I. V. Bilera, V. M. Kazachenko, I. O. Shamshin, P. A. Gusev, and M. S. Belotserkovskaya. 2019. Deflagration-to-detonation transition in air mixtures of polypropylene pyrolysis products. *Dokl. Phys. Chem.* 488(1):129–133. doi: 10.1134/S0012501619090045.
6. Shipliyuk, A. N., V. I. Zvegintsev, S. M. Frolov, D. A. Vnuchkov, T. A. Kiseleva, V. A. Kislovsky, S. V. Lukashevich, A. Yu. Melnikov, and D. G. Nalivaychenko. 2020. Gasification of low-melting hydrocarbon material in the airflow heated by hydrogen combustion. *Int. J. Hydrogen Energ.* 45:9098–9112. doi: 10.1016/j.ijhydene.2020.01.099.

7. Frolov, S. M., I. O. Shamshin, V. S. Aksenov, M. B. Kazachenko, and P. A. Gusev. 2019. Ranzhirovanie gazovykh toplivno-vozdushnykh smesey po ikh detonatsionnoy sposobnosti s pomoshch'yu etalonnogo impul'sno-detonatsionnoy trubyy [Ranking of gaseous fuel-air mixtures according to their detonability using a standard pulsed detonation tube]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 12(3):78–90. doi: 10.30826/CE19120309.
8. Frolov, S. M. 2006. Initiation of strong reactive shocks and detonation by traveling ignition pulses. *J. Loss Prevent. Proc.* 19(2-3):238–244.
9. Viktorov, S. B., and S. A. Gubin. 1999. Primenenie sistemy termodinamicheskikh raschetov TDS dlya modelirovaniya fiziko-khimicheskikh protsessov [Application of the TDS system of thermodynamic calculations for modeling of physical and chemical processes]. Scientific Session “MEPhI-99:” Collection of research works. Moscow: MEPhI Publ. 8:73–74.
10. Lee, J. H. S. 2008. *The detonation phenomenon*. Cambridge, Cambridge University Press. 400 p. doi: 10.1017/CBO9780511754708.
11. Oppenheim, A. K. 1972. *Introduction to gasdynamics of explosions*. Wien – New York: Springer. 220 p.

Received May 15, 2020

Contributors

Frolov Sergey M. (b. 1959) — Doctor of Science in physics and mathematics, head of department, head of laboratory, N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; professor, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe Sh., Moscow 115409, Russian Federation; senior research scientist, Scientific Research Institute for System Analysis, Russian Academy of Sciences, 36-1 Nakhimovskii Prosp., Moscow 117218, Russian Federation; smfrol@chph.ras.ru

Zvegintsev Valery I. (b. 1944) — Doctor of Science in technology, chief research scientist, S. A. Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences, 4/1 Institutskaya Str., Novosibirsk 630090, Russian Federation; zvegin@itam.nsc.ru

Shamshin Igor O. (b. 1975) — Candidate of Science in physics and mathematics, senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; research scientist, Scientific Research Institute for System Analysis, Russian Academy of Sciences, 36-1 Nakhimovskii Prosp., Moscow 117218, Russian Federation; igor_shamshin@mail.ru

Kazachenko Maxim V. (b. 1997) — junior research scientist, N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; student, Department of Power Engineering, N. E. Bauman Moscow State Technical University, 5-1 Baumanskaya 2nd Str., Moscow 105005, Russian Federation; maksx71997@gmail.com

Aksenov Victor S. (b. 1952) — Candidate of Science in physics and mathematics, senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; associate professor, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe Sh., Moscow 115409, Russian Federation; v.aksenov@mail.ru

Bilera Igor V. (b. 1968) — Candidate of Science in chemistry, leading research scientist, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prosp., Moscow 119991, Russian Federation; bilera@ips.ac.ru

Semenov Ilia V. (b. 1979) — Candidate of Science in physics and mathematics, leading research scientist, Scientific Research Institute for System Analysis, Russian Academy of Sciences, 36-1 Nakhimovskii Prosp., Moscow 117218, Russian Federation; semenov@icad.org