INFLUENCE OF METHANE, BENZENE, AND CH_3, CH_2, AND CH RADICALS ON THE FORMATION OF SOOT PARTICLES DURING PYROLYSIS OF HIGHLY DILUTED MIXTURES OF ACETYLENE WITH ARGON

P. A. Vlasov[1,2], V. N. Smirnov[1], A. R. Akhunyanov[1], G. L. Agafonov[1], and E. Busillo[3]

[1]N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation
[2]National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation
[3]I. M. Gubkin Russian State University of Oil and Gas, 65 Leninsky Prosp., Moscow 119991, Russian Federation

Abstract: The paper considers the effect of additives of methane, benzene, and CH_3, CH_2, and CH radicals on the formation of soot particles during pyrolysis of highly diluted mixtures of acetylene with argon. Direct comparison of the results of detailed kinetic simulations on soot particle formation during pyrolysis of the mixtures of acetylene, benzene, and methane with argon has been performed using the unified kinetic model of soot formation with the results of the authors' own experiments in a shock tube behind reflected shock waves. The obtained good agreement between the results of kinetic simulations and experimental results was the basis for conducting numerical experiments for highly diluted mixtures at elevated pressures which made it possible both to maintain the concentration of carbon atoms in the mixtures and to minimize the temperature change during pyrolysis and soot particle formation.

Keywords: hydrocarbon pyrolysis; soot formation; shock tube; detailed kinetic modeling; promotional additives

DOI: 10.30826/CE22150102

Figure Captions

Figure 1 Temperature dependences of the soot yield during pyrolysis of a mixture of acetylene with argon ($0.05\,C_2H_2 + 0.95\,Ar$), $p_5 = 4.5$ bar: *1* — results of the present authors' experiments in reflected shock waves; and *2* — results of the present authors' kinetic calculations using the unified kinetic model of soot formation

Figure 2 Temperature dependences of the soot yield during pyrolysis of a mixture of benzene with argon ($0.0105C_6H_6 + 0.9895\,Ar$), $p_5 = 3.0$ bar: *1* — results of the present authors' experiments in reflected shock waves; and *2* — results of the present authors' kinetic calculations using the unified kinetic model of soot formation

Figure 3 Temperature dependences of soot yield during pyrolysis of mixtures of methane with argon (triangles — $0.05\,CH_4 + 0.95\,Ar$; and squares — $0.1\,CH_4 + 0.9\,Ar$), $p_5 = 4.5$–6.7 bar: *1* — results of the present authors' experiments in reflected shock waves; and *2* — results of the present authors' kinetic calculations using the unified kinetic model of soot formation

Figure 4 Temperature dependences of the soot yield during pyrolysis of a mixture of acetylene with argon (*1* — $0.03\,C_2H_2 + 0.97\,Ar$), acetylene–methane with argon (*2* — $0.02\,C_2H_2 + 0.02\,CH_4 + 0.96\,Ar$) and acetylene–methyl radicals with argon (*3* — $0.02\,C_2H_2 + 0.02\,CH_3 + 0.96\,Ar$), $p_5 = 3$ bar

Figure 5 Temperature dependences of the soot yield during pyrolysis of a mixture of acetylene with argon (*1* — $0.003\,C_2H_2 + 0.997\,Ar$), acetylene–methane with argon (*2* — $0.002\,C_2H_2 + 0.002\,CH_4 + 0.996\,Ar$), and acetylene–methyl radicals with argon (*3* — $0.002\,C_2H_2 + 0.002\,CH_3 + 0.996\,Ar$), $p_5 = 30$ bar

Figure 6 Temperature dependences of the soot yield during pyrolysis of a mixture of acetylene with argon (*1* — $0.0003\,C_2H_2 + 0.9997\,Ar$), acetylene–methane with argon (*2* — $0.0002\,C_2H_2 + 0.0002\,CH_4 + 0.9996\,Ar$), and acetylene–methyl radicals with argon (*3* — $0.0002\,C_2H_2 + 0.0002\,CH_3 + 0.9996\,Ar$), $p_5 = 300$ bar

Figure 7 Temperature dependences of the soot yield during pyrolysis of a mixture of acetylene with argon (*1* — $0.0003\,C_2H_2 + 0.9997\,Ar$), acetylene–CH with argon (*2* — $0.0002\,C_2H_2 + 0.0002\,CH + 0.9996\,Ar$), and acetylene–benzene with argon (*3* — $0.0002\,C_2H_2 + 0.00003334\,C_6H_6 + 0.99976666\,Ar$), $p_5 = 300$ bar

Acknowledgments

This work was performed within the framework of the Program of Fundamental Research of the Russian Academy of Sciences on the research issue of N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences 0082-2019-0014 (State registration number AAAA-A20-120020590084-9).

References

1. Agafonov, G. L., I. V. Bilera, P. A. Vlasov, I. V. Zhil'tsova, Yu. A. Kolbanovskii, V. N. Smirnov, and A. M. Tereza. 2016. Unified kinetic model of soot formation in the pyrolysis and oxidation of aliphatic and aromatic hydrocarbons in shock waves. *Kinet. Catal.* 57(5):557–572.
2. Agafonov, G. L., D. I. Mikhailov, V. N. Smirnov, A. M. Tereza, P. A. Vlasov, and I. V. Zhiltsova. 2016. Shock tube and modeling study of chemical ionization in the oxidation of acetylene and methane mixtures. *Combust. Sci. Technol,* 188(11-12):1815–1830. doi: 10.1080/00102202.2016.1211861.
3. Vlasov, P. A., I. V. Zhiltsova, V. N. Smirnov, A. M. Tereza, G. L. Agafonov, and D. I. Mikhailov. 2018. Chemical ionization of n-hexane, acetylene, and methane behind reflected shock waves. *Combust. Sci. Technol.* 190(1):57–81. doi: 10.1080/00102202.2017.1374954.
4. Eremin, A., E. Mikheyeva, and I. Selyakov. 2018. Influence of methane addition on soot formation in pyrolysis of acetylene. *Combust. Flame* 193:83–91.
5. Drakon, A., A. Eremin, E. Mikheyeva, Bo Shu, M. Fikri, and C. Schulz. 2018. Soot formation in shock-wave-induced pyrolysis of acetylene and benzene with H_2, O_2, and CH_4 addition. *Combust. Flame* 198:158–168.
6. Eremin, A., and E. Mikheyeva. 2019. The role of methyl radical in soot formation. *Combust. Sci. Technol.* 191(12):2226–2242. doi: 10.1080/00102202.2018.1551892.
7. Li, Z., H. M. F. Amin, P. Liu, Yu Wang, S. H. Chung, and W. L. Roberts. 2018. Effect of dimethyl ether (DME) addition on sooting limits in counterflow diffusion flames of ethylene at elevated pressures. *Combust. Flame* 197:463–470.
8. Li, Z., P. Liu, P. Zhang, Yu Wang, H. He, S. H. Chung, and W. L. Roberts. 2020. Role of dimethyl ether in incipient soot formation in premixed ethylene flames. *Combust. Flame* 216:271–279.
9. Drakon, A., A. Eremin, M. Korshunova, and E. Mikheyeva. 2021. PAH formation in the pyrolysis of benzene and dimethyl ether mixtures behind shock waves. *Combust. Flame* 232:111548. doi: 10.1016/j.combustflame.2021.111548.
10. Agafonov, G. L., P. A. Vlasov, and V. N. Smirnov. 2011. Soot formation in the pyrolysis of benzene, methylbenzene, and ethylbenzene in shock waves. *Kinet. Catal.* 52(3):358–370.
11. Stupochenko, E. V., S. A. Losev, and A. I. Osipov. 1965. *Relaksatsionnye protsessy v udarnykh volnakh* [Relaxation processes in shock waves]. Moscow: Nauka. 328 p.
12. Haynes, B. S., and H. G. Wagner. 1981. Soot formation. *Prog. Energ. Combust.* 7(4):229–273.
13. Agafonov, G. L., I. V. Bilera, P. A. Vlasov, Yu. A. Kolbanovskii, V. N. Smirnov, and A. M. Tereza. 2015. Soot formation during the pyrolysis and oxidation of acetylene and ethylene in shock waves. *Kinet. Catal.* 56(1):12–30.
14. Wang, H., X. You, A. V. Joshi, S. G. Davis, A. Laskin, F. Egolfopoulos, and C. K. Law. 2007. USC Mech Version II. High temperature combustion reaction model of H_2/CO/C_1–C_4 compounds. Available at: http://ignis.usc.edu/USC-Mech_II.htm (accessed May 2007).
15. Skjøth-Rasmussen, M. S., P. Glarborg, M. Østberg, J. T. Johannessen, H. Livbjerg, A. D. Jensen, and T. S. Christensen. 2004. Formation of polycyclic aromatic hydrocarbons and soot in fuel-rich oxidation of methane in a laminar flow reactor. *Combust. Flame* 136:91–128.
16. Richter, H., S. Granata, W. H. Green, and J. B. Howard. 2005. Detailed modeling of PAH and soot formation in a laminar premixed benzene/oxygen/argon low-pressure flame. *P. Combust. Inst.* 30:1397–1405.
17. Frenklach, M., and J. Warnatz. 1987. Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame. *Combust. Sci. Technol.* 51:265–283.
18. Wang, H., E. Dames, B. Sirjean, D. A. Sheen, R. Tangko, and A. Violi. 2010. A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures. JetSurF version 2.0. Available at: http://web.stanford.edu/group/haiwanglab/JetSurF/JetSurF2.0/index.html (accessed February 21, 2022).
19. Correa, C., H. Niemann, B. Schramm, and J. Warnatz. 2000. Reaction mechanism reduction for higher hydrocarbons by the ILDM method. *P. Combust. Inst.* 28:1607–1614.
20. Hansen, N., S. J. Klippenstein, P. R. Westmoreland, T. Kasper, K. Kohse-Höinghaus, J. Wang, and T. A. Cool. 2008. A combined *ab initio* and photoionization mass spectrometric study of polyynes in fuel-rich flames. *Phys. Chem. Chem. Phys.* 10:366–374.

Received December 30, 2021

Contributors

Vlasov Pavel A. (b. 1955) — Doctor of Science in physics and mathematics, leading research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; assistant professor, National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation; iz@chph.ras.ru

Smirnov Vladimir N. (b. 1950) — Doctor of Science in physics and mathematics, chief research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str.,Moscow 119991, Russian Federation; vns1951@yandex.ru

Akhunyanov Artur R. (b. 1994) — research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str.,Moscow 119991, Russian Federation; jkratos69@yandex.ru

Agafonov Gennadii L. (b. 1954) — senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str.,Moscow 119991, Russian Federation; agafonov@chph.ras.ru

Busillo Emmanuel (b. 1996) — magister, I. M. Gubkin Russian State University of Oil and Gas, 65 Leninsky Prosp., Moscow 119991, Russian Federation; emmanuel.busillo@gmail.com