

IGNITION OF MODEL BIOGAS MIXTURES IN AN ADIABATIC COMPRESSION REACTOR

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Abstract: The partial oxidation of two model biogas mixtures (vol./vol.) is investigated under adiabatic compression conditions: $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60/40/0$ and $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60/20/20$. Oxygen is used as oxidant, the oxidant-to-air equivalence ratio for both mixtures is $\alpha = 0.4$. Major (H_2 , CO , and H_2O) and minor reaction products are determined, including ethylene and olefins $\text{C}_3\text{--C}_5$, acetylene and its homologues, dienes $\text{C}_3\text{--C}_5$, benzene, and toluene. The ranges of degrees of transformation of mixtures by the sum of all products are 0.8%–65% for mixture 1 and 1.7%–72% for mixture 2. It is found that at ignition in a narrow range of compression ratios there is a sharp increase in the degree of transformation of O_2 and CH_4 . Three modes are found for CO_2 as a function of temperature: an increase in its content in the product mixture as compared to the initial mixture under conditions of partial oxidation without ignition, an increase in its content at ignition, and a decrease in its content at ignition.

Keywords: biogas; methane; CO_2 ; ignition; oxidation; adiabatic compression; synthesis gas; hydrogen

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Figure Captions

Figure 1 Pressure histories at adiabatic compression of mixtures No. 1 (a) and No. 2 (b)

Figure 2 The residual content of O_2 (1), CH_4 (2), CO_2 (3), and C_2H_6 (6) and yields of methane partial oxidation products as functions of maximum compression ratio ε_{\max} for mixture No. 2: 4 — CO ; 5 — H_2O (on balance); 7 — C_2H_4 ; 8 — C_2H_2 ; 9 — H_2 ; 10 — C_3H_8 ; 11 — C_3H_6 ; 12 — benzene; 13 — methylacetylene; 14 — allene; 15 — vinylacetylene; 16 — diacetylene; 17 — *n*-butane; 18 — but-1-ene; 19 — cyclopentadiene; 20 — isobutane; 21 — 1,3-butadiene; 22 — toluene; 23 — isobutene; 24 — *n*-pentane; 25 — pentene sum; 26 — sum of unidentified $\text{C}_5\text{--C}_7$ hydrocarbons; 27 — *trans*-but-2-ene; 28 — isopentane; 29 — but-1-yne; 30 — *cis*-but-2-ene; 31 — isoprene; 32 — but-2-yne; and 33 — *n*-hexane

Figure 3 The conversion degrees of O_2 (1) and CH_4 (2) and conversion degree by total product (3) as a function of maximum compression ratio ε_{\max} for mixtures No. 1 (a) and No. 2 (b)

Figure 4 The conversion degrees of CO_2 as a function of maximum compression ratio ε_{\max} for mixtures No. 1 (1) and No. 2 (2)

Figure 5 Selectivities of partial oxidation products of model biogas mixture No. 2: 3–33 the same as for Fig. 2; 34 — 2-methylbut-1-ene; 35 — 2-methylbut-2-ene; 36 — 3-methylbut-1-ene; 37 — *trans*-pent-2-ene; 38 — pent-1-ene; and 39 — *cis*-pent-2-ene

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References

- Hosseini, S. E., and M. A. Wahid. 2014. Development of biogas combustion in combined heat and power generation. *Renew. Sust. Energ. Rev.* 40:868–875. doi: 10.1016/j.rser.2014.07.204.
- Gao, Y., J. Jiang, Y. Meng, F. Yan, and A. Aihemaiti. 2018. A review of recent developments in hydrogen production via biogas dry reforming. *Energ. Convers. Manage.* 171:133–155. doi: 10.1016/j.enconman.2018.05.083.
- Zhao, X., B. Joseph, J. Kuhn, and S. Ozcan. 2020. Biogas reforming to syngas: A review. *iScience* 5(22):101082. doi: 10.1016/j.isci.2020.101082.
- Kumar, R., A. Kumar, and A. Pal. 2022. Overview of hydrogen production from biogas reforming: Technological advancement. *Int. J. Hydrogen Energ.* 47(9):34831–34855. doi: 10.1016/j.ijhydene.2022.08.059.
- Jung, S., J. Lee, D. H. Moon, K.-H. Kim, and E. E. Kwon. 2021. Upgrading biogas into syngas through dry reforming. *Renew. Sust. Energ. Rev.* 143:110949. doi: 10.1016/j.rser.2021.110949.
- Borisov, A. A., G. G. Polytenkova, K. Ya. Troshin, and I. O. Shamshin. 2009. Partsial'noe okislenie biogaza v nekataliticheskikh rezhimakh goreniya [Partial oxidation of biogas in noncatalytic regime of combustion]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 2:3–6.
- Yang, Y. C., M. S. Lim, and Y. N. Chun. 2009. The syngas production by partial oxidation using a homogeneous charge compression ignition engine. *Fuel Process. Technol.* 90:553–557. doi: 10.1016/j.fuproc.2009.01.002.
- Shmelev, V. M., and V. M. Nikolaev. 2011. Nekataliticheskaya konversiya smesey biogaza s vozdukhom v khimicheskem reaktore sverkhadiabaticeskogo szha-

- tiya [Noncatalytic conversion of the biogas mixtures with air in a chemical reactor of super adiabatic compression]. *Gazokhimiya* [Gas Chemistry] 4:54–60.
9. Shapovalova O. V., Y. N. Chun, M. S. Lim, V. M. Shmelev, and V. S. Arutyunov. 2012. Syngas and hydrogen production from biogas in volumetric (3D) matrix reformers. *Int. J. Hydrogen Energ.* 37(82):14040–14046. doi: 10.1016/j.ijhydene.2012.07.002.
 10. Nikolaev, V. M., and V. M. Shmelev. 2012. O vosplamenenii smesey biogaza s vozdukhom pri szhatii [Towards compression-induced ignition of biogas–air mixtures]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 5: 66–70.
 11. Kolbanovskii, Y.A., N. N. Buravtsev, I. V. Bilera, I. V. Rossikhin, and Yu. A. Borisov. 2015. Konversiya biogaza v sintez-gaz v reaktore s vysokoy teplonapravzhennost'yu [Conversion of biogas to syngas in reactor with a high heat density]. *Oil Gas Chemistry* 1:28–32.
 12. Zeng, H., Y. Wang, Y. Shi, M. Ni, and N. Cai. 2017. Syngas production from CO₂/CH₄ rich combustion in a porous media burner: Experimental characterization and elementary reaction model. *Fuel* 199:413–419. doi: 10.1016/j.fuel.2017.03.003.
 13. Nikitin, A., A. Ozersky, V. Savchenko, I. Sedov, V. Shmelev, and V. Arutyunov. 2019. Matrix conversion of natural gas to syngas: The main parameters of the process and possible applications. *Chem. Eng. J.* 377:120883. doi: 10.1016/j.cej.2019.01.162.
 14. Gosser, H., S. Drost, S. Porras, R. Schießl, U. Mass, and O. Deutschmann. 2019. The internal combustion engine as a CO₂ reformer. *Combust. Flame* 207:186–195. doi: 10.1016/j.combustflame.2019.05.031.
 15. Guerrero, F., L. Espinoza, N. Ripoll, P. Lisbona, I. Arauzo, and M. Toledo. 2020. Syngas production from the reforming of typical biogas compositions in an inert porous media reactor. *Front. Chem.* 8:145. doi: 10.3389/fchem.2020.00145.
 16. Chen, D., and Li-H. Gan. 2022. Non-catalytic direct conversion of CH₄ and CO₂ into high-quality syngas. *Chem. Eng. J.* 439:135732. doi: 10.1016/j.cej.2022.135732.
 17. Drost, S., W. Xie, R. Schießl, U. Maas. 2023. CO₂/CH₄ Conversion to synthesis gas (CO/H₂) in an internal combustion engine. *P. Combust. Inst.* 39(4):4519–4527. doi: 10.1016/j.proci.2022.07.033.
 18. Mishra, P., H. Gossler, and O. Deutschmann. 2023. Optimization of operating conditions of an internal combustion engine used as chemical reactor for methane reforming using ozone as an additive. *Applications Energy Combustion Science* 13:100109. doi: 10.1016/j.jaecs.2022.100109.
 19. Banke, K., and S. A. Kaiser. 2023. Syngas production from biogas in a polygeneration process: Simultaneous partial oxidation and dry reforming in a piston engine. *P. Combust. Inst.* 39(4):5011–5020. doi: 10.1016/j.proci.2022.08.132.
 20. Kolbanovskiy, Yu. A., V. S. Shechipachev, N. Ya. Chernyak, et al. 1982. *Impul'snoe szhatie gazov v khimii i tekhnologii* [Impulsive compression of gases in chemistry and technology]. Moscow: Nauka. 240 p.
 21. Bilera, I. V. 2023. The formation of small amounts of cyclopropane during pulsed pyrolysis of C₄–C₅ acyclic alkanes in the adiabatic compression reactor. *Reactions* 4(3):381–397. doi: 10.3390/reactions4030023.
 22. Rudolph C., and B. Atakan. 2023. Dry methane reforming in a piston engine for chemical energy storage and carbon dioxide utilization: Kinetic modeling and thermodynamic evaluation. *Energy Technol. — Ger.* 11(10):2201252. doi: 10.1002/ente.202201252.
 23. Bilera, I. V. 2023. Okislitel'nyy piroliz etana v usloviyakh adiabaticheskogo szhatiya [Oxidative pyrolysis of ethane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 16(3):21–29. doi: 10.30826/CE23160303.
 24. Bilera, I. V., V. A. Bogdanov, A. A. Borisov, Yu. A. Kolbanovskii, G. G. Politenkova, K. Ya. Troshin, and S. M. Frolov. 2007. Physicochemical peculiarities of partial oxidation of methane in the self-ignition regime. *Nonequilibrium processes. Plasma, combustion and atmospheric phenomena*. Eds. G. D. Roy, S. M. Frolov, and A. M. Starik. Moscow: TORUS PRESS. 37–38.
 25. Arutyunov, V. S. 2011. *Okislitel'naya konversiya prirodno-gaza* [Oxidative conversion of natural gas]. Moscow: KRASAND. 640 p.
 26. Grigoriev, A. S., Y. A. Kolbanovsky, and V. S. Shechipachev. 1977. Oxidation of methane at adiabatic compression of its mixture with oxygen. *Petrol. Chem.* 17(1):64–75. doi: 10.1016/0031-6458(77)90023-5.
 27. Kaczmarek, D., B. Atakan, and T. Kasper. 2019. Plug-flow reactor study of the partial oxidation of methane and natural gas at ultra-rich conditions. *Combust. Sci. Technol.* 191(9):1571–1584. doi: 10.1080/00102202.2019.1577829
 28. Bilera, I. V. 2014. Gomogenenny piroliz n-butana v usloviyakh adiabaticheskogo szhatiya [Homogeneous pyrolysis of n-butane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 7:35–41.
 29. Bilera, I. V. 2020. Sopiroliz dimetilovogo efira i etana v usloviyakh adiabaticheskogo szhatiya [Copyrolysis of dimethyl ether and ethane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 13(4):20–28. doi: 10.30826/CE20130403.

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