OXIDATIVE PYROLYSIS OF ETHANE UNDER PULSED ADIABATIC COMPRESSION

I. V. Bilera

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

Abstract: The oxidative pyrolysis of ethane has been studied in a rapid compression machine with a free flied piston over a range of temperatures 1100–1450 K. In the initial mixtures with a constant ethane content of 2 %(vol.), the oxygen content varied from 0 to 1.05 %(vol.). The ranges of conversion degrees of ethane were 6%–86% and of oxygen 8%–97%. The main (ethylene, hydrogen, methane, and CO) and secondary reaction products were determined. The composition of the mixture of products qualitatively corresponds to the products of ethane pyrolysis previously studied in the adiabatic compression reactor. It is found that an increase in the O_2/C_2H_6 ratio in the studied range leads to a monotonic decrease in the residual ethane content, an increase in the residual oxygen content, and an increase in the degree of conversion of both initial components. As the O_2/C_2H_6 ratio increases, the yields of H_2, CO, CH_4, acetylene, 1,3-butadiene, and some other hydrocarbons increase. The value of ethylene yield passes through a maximum approximately at $\alpha = 0.05$.

Keywords: ethane; oxidative pyrolysis; rapid compression machine (RCM); ethylene

DOI: 10.30826/CE23160303 **EDN:** CNWMHL

Figure Captions

Figure 1 Dependence of conversion degree of O_2 (*1*), C_2H_6 (*2*) and total conversion (*3*), residual content of O_2 (*4*) and C_2H_6 (*5*), and oxipyrolysis product yields on the maximum compression ratio $\varepsilon_{\max}$: *6* — C_2H_4; *7* — CO; *8* — CH_4; *9* — H_2; *10* — C_2H_2; *11* — C_3H_6; *12* — 1,3-butadiene; *13* — C_3H_8; *14* — n-butane; *15* — but-1-ene; *16* — vinylacetylene; *17* — methylacetylene; *18* — allene; *19* — pent-1-ene; *20* — $trans$-but-2-ene; *21* — cis-but-2-ene; *22* — the sum of $trans$-pent-2-ene and cis-pent-2-ene; *23* — the sum of isopentenes; *24* — C_6H_6; *25* — cyclopentadiene; *26* — the sum of C_{6+} hydrocarbons (except C_6H_6); and *27* — isoprene. Initial mixture 3 ($\alpha = 0.075$)

Figure 2 Selectivity of ethane oxypyrolysis products, initial mixture 3 ($\alpha = 0.075$): *6*–*25* as for Fig. 1; and *28* — the sum of butenes

Figure 3 Effect of oxygen admixtures on the yields of ethane oxypyrolysis products and C_2H_6 and O_2 residual content: *1* — mixture 1 ($\alpha = 0$); *2* — mixture 2 ($\alpha = 0.05$); *3* — mixture 3 ($\alpha = 0.075$); *4* — mixture 4 ($\alpha = 0.10$); and *5* — mixture 5 ($\alpha = 0.15$)

Table Captions

Table 1 The compositions of the studied gas mixtures

Table 2 The parameters of the studied gas mixtures at compression

Acknowledgments

The work was carried out within the framework of the State Order of the Institute of Petrochemical Synthesis of the Russian Academy of Sciences. Students L. V. Salnikov and A. E. Semochkin took part in the experimental part of the work.

References

1. Lapidus, A. S. 1972. Sovremennoe sostoyanie promyshlennykh sposobov proizvodstva atsetilena. *Khimiya atsetilena. Tr. III Vsesoyuzn. konf.* [The chemistry of acetylene. Proceedings of the 3rd All-Union Conference]. Ed. A. A. Petrov. Moscow: Nauka. 5–16.
2. Pässler, P., W. Hefner, K. Buckl, H. Meinass, A. Meiswinkel, H.-J. Wernicke, G. Ebersberg, R. Müller, J. Bässler, H. Behringer, and D. Mayer. 2012. Acetylene. *Ullmann's encyclopedia of industrial chemistry*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA. 1: 277–326. doi: 10.1002/14356007.a01_097.pub3.
3. Dubrovay, K. K., and A. B. Sheynman. 1936. *Okislitel'nyy kreking* [Oxidative cracking]. Moscow–Leningrad: ONTI NKTP SSSR. 393 p.
4. Tmenov, D. N., and S. P. Gorislavets. 1978. *Intensifikatsiya protsessov piroliza* [Intensification of pyrolysis processes]. Kiev: Tekhnika. 192 p.

5. Arutyunov, V. S. 2011. *Okislitel'naya konversiya prirodnogo gaza* [Oxidative reforming of natural gas]. Moscow: KRASAND. 640 p.
6. Arutyunov, V. S., and R. N. Magomedov. 2012. Gas-phase oxypyrolysis of light alkanes. *Russ. Chem. Rev.* 81(9):790–822. doi: 10.1070/RC2012v081n09ABEH004267.
7. Arutyunov, V. S., V. I. Savchenko, I. V. Sedov, A. V. Nikitin, R. N. Magomedov, and A. Yu. Proshina. 2017. Kinetic features and industrial prospects of the selective oxidative cracking of light alkanes. *Russ. Chem. Rev.* 86(1):47–74. doi: 10.1070/RCR4648.
8. Cavani, F., N. Ballarini, and A. Cericola. 2007. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal. Today* 127:113–131. doi: 10.1016/j.cattod.2007.05.009.
9. Najari, S., S. Saeidi, P. Concepcion, D. D. Dionysiou, S. K. Bhargava, A. F. Lee, and K. Wilson. 2021. Oxidative dehydrogenation of ethane: Catalytic and mechanistic aspects and future trends. *Chem. Soc. Rev.* 50(7):4564–4605. doi: 10.1039/D0CS01518K.
10. Sampson, R. J. 1963. The reaction between ethane and oxygen at 600–630°. *J. Chem. Soc.* 5095–5106. doi: 10.1039/JR9630005095.
11. Jones, J. H., T. E. Daubert, and M. R. Fenske. 1969. Oxidation and oxidative dehydrogenation of ethane and propane. *Ind. Eng. Chem. Proc. DD.* 8(1):17–25. doi: 10.1021/i260029a004.
12. Taylor, J. E., and D. M. Kulich. 1973. Homogeneous gas-phase with a wall-less reactor. oxygen-ethane reaction. Pyrolyses. III. The a double reversal in oxygen and surface effects. *Int. J. Chem. Kinet.* 5(3):455–468. doi: 10.1002/kin.550050314.
13. Sheverdenkin, E. V., V. M. Rudakov, V. I. Savchenko, V. S. Arutyunov, and O. V. Sokolov. 2004. Kinetics of partial oxidation of alkanes at high pressures: Oxidation of ethane and methane–ethane mixtures. *Theor. Found. Chem. Eng.* 38(3):311–315. doi: 10.1023/B:TFCE.0000032194.61049.0e.
14. Magomedov, R. N., A. Y. Proshina, and V. S. Arutyunov. 2013. Gas-phase oxidative cracking of ethane in a nitrogen atmosphere. *Kinet. Catal.* 54(4):383–393. doi: 10.1134/S0023158413040113.
15. Burch, R., and E. M. Crabb. 1993. Homogeneous and heterogeneous contributions to the catalytic oxidative dehydrogenation of ethane. *Appl. Catal. A — Gen.* 97(1):49–65. doi: 10.1016/0926-860X(93)80066-Y.
16. Choudhary V. R., and S. R. Mulla. 1997. Coupling of thermal cracking with noncatalytic oxidative conversion of ethane to ethylene. *AIChE J.* 43(6):1545–1550. doi: 10.1002/aic.690430516.
17. Chen, Q., E. J. A. Schweitzer, P. F. Van Den Oosterkamp, R. J. Berger, C. R. H. De Smet, and G. B. Marin. 1997. Oxidative pyrolysis of ethane. *Ind. Eng. Chem. Res.* 36(8):3248–3251. doi: 10.1021/ie960585z.
18. Kolbanovskiy, Yu. A., V. S. Shchipachev, 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.
19. Kolbanovskiy, Yu. A. 1989. Adiabatic compression in studies on the kinetics and mechanism of reactions involving fluorine-containing carbenes. *Russ. Chem. Rev.* 58(11):1024–1032. doi: 10.1070/RC1989v058n11ABEH003494.
20. Buravtsev, N. N., and Yu. A. Kolbanovsky. 1999. Intermediates of thermal transformations of perfluoroorganic compounds. New spectral data and reactions. *J. Fluorine Chem.* 96(1):35–42. doi: 10.1016/S0022-1139(98)00325-X.
21. Sal'nikova, L. V., A. E. Semochkina, and I. V. Bilera. 2010. Degidrirovanie etana pri impul'snom pirolize i oksipirolize [Dehydrogenation of ethane during pulsed pyrolysis and oxypyrolysis]. *Tezisy VIII Vseross. nauch.-tekhn. konf. "Aktual'nye problemy razvitiya neftegazovogo kompleksa Rossii"* [8th All-Russian Scientific and Technical Conference "Actual Problems of Development of the Russian Oil and Gas Complex" Abstracts]. Moscow: RGUNG im. I. M. Gubkina. 1:281–282.
22. Bilera, I. V. 2017. Vysokotemperaturnyy gomogennyy piroliz etana v reaktore adiabaticheskogo szhatiya [The high-temperature homogeneous pyrolysis of ethane in the adiabatic compression reactor]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 10(2):12–17.
23. 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.
24. Buravtsev, N. N., L. S. German, A. S. Grigor'ev, Yu. A. Kolbanovskii, A. A. Ovsyannikov, and A. Yu. Volkonskii. 1993. Trifluoromethylfluorocarbene formation and reactions under $C_2F_5SiF_3$ pulsed adiabatic compression pyrolysis. *Mendeleev Commun.* 3(4):133– 134. doi: 10.1070/MC1993v003n04ABEH000254.
25. ScanView — an application and chromatogram database. Available at: https://community.agilent.com (accessed October 16, 2018).
26. Heracleous, E., and A. A. Lemonidou. 2004. Homogeneous and heterogeneous pathways of ethane oxidative and non-oxidative dehydrogenation studied by temperature-programmed reaction. *Appl. Catal. A — Gen.* 269:123–135. doi: 10.1016/j.apcata.2004.04.007.

Received January 10, 2023

Contributor

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