OXYCRACKING AND MATRIX CONVERSION OF COMPONENTS OF REFINERY GAS TO ETHYLENE, HYDROGEN, AND CARBON MONOXIDE

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Abstract: The technological scheme of oxidative cracking of components of refinery gases with production of olefins (mainly, ethylene), CO, and hydrogen is suggested. Since oxycracking of components of refinery gases does not allow obtaining the necessary amount of hydrogen and CO for catalytic hydrogenation and hydroformylation of the total volume of ethylene produced in the process, it is suggested to use the matrix conversion of the exhaust from the stage of hydroformylation gases as their additional source. It is shown that with the help of oxidative cracking and matrix conversion of components of refinery gases, it is possible to obtain mixtures of ethylene, CO, and hydrogen in the ratios suitable for their further hydroformylation and hydrogenation to C_{3+} alcohols, which can be used as high-octane additives to fuels.

Keywords: refinery gases; oxidative cracking; matrix conversion; ethylene; carbon monoxide; hydrogen

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References

1. Korjubaev, A. G., L. V. Eder, and V. Yu. Nemov. 2011. Neftepererabatyvayushchaya promyshlennost' Rossii: tendentsii, ugrozy, perspektivy [Oil-refining industry of Russia: Trends, dangers, and prospects]. *Problemy ekonomiki i upravleniya heftegazovym kompleksom* [J. Problems Economics Management Oil Gas Complex] 11:31–38.
2. Churilin, A. S., and N. I. Zelentsova. 2013. Metody ochistki i vydeleniya etilena iz sukhikh gazov kataliticheskogo krekinga [Methods for treatment and ethylene recovery from fluidized catalytic cracking off-gases]. *Exspozitsiya Neft' Gaz* [Exposition Oil Gas] 1:49–53.
3. Bondareva, V. M., E. V. Lazareva., and V. I. Sobolev. 2018. Processing of oil refinery gases: Oxidative dehydrogenation of the ethane–ethylene fraction. *Russ. J. Appl. Chem.* 91(6):977–980. doi: 10.1134/S1070427218060150.
4. 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.
5. Gorbunov, D. N., M. V. Terenina, Yu. S. Kardasheva, A. L. Maksimov, and E. A. Karakhanov. 2017. Oxo-processes involving ethylene (a review). *Petrol. Chem.* 57(12):1137–1140. doi: 10.1134/S0965544117060159.
6. Gorbunov, D. N., Yu. S. Kardasheva, and E. A. Karahanov. 2018. Novye rodiysoderzhashchie geterogennye katalizatory gidroformilirovaniya etilena [New rhodium-containing heterogeneous catalysts for ethylene hydrofomylation process]. *12th Symposium (International) of Young Scientists on Petroleum Chemistry*. Zvenigorod. 308–310.
7. Arutyunov, V. S., V. I. Savchenko, I. V. Sedov, V. M. Shmelev, A. V. Nikitin, I. G. Fokin, S. A. Eksanov, O. V. Shapovalova, and K. A. Timofeev. 2016. Experimental studies of natural gas to synthesis gas converters based on permeable cavity matrices. *Russ. J. Appl. Chem.* 89(11):1816–1824. doi: 10.1134/S1070427216110124.
8. Nikitin, A. V., A. V. Ozerskii, K. A. Timofeev, I. K. Komarov, Ya. S. Zimin, I. V. Sedov, V. M. Shmelev, and V. S. Arutyunov. 2018. Vliyanie dobavok vodyanogo para na protsess matrichnoy konversii metana v sintez-gaz [Effect of steam addition on the process of matrix conversion of methane to syngas]. *Goren. Vzryv (Mosk.) — Combustion*

and Explosion 11(2):18–23. doi: 10.30826/CE18110203.

9. Nikitin, A. V., V. I. Savchenko, I. V. Sedov, K. A. Timofeev, V. M. Shmelev, and V. S. Arutyunov. 2017. Matrichnaya konversiya metana v sintez-gaz s nizkim soderzhaniem azota [Matrix conversion of methane into syngas with low content of nitrogen]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 10(1):28–33.
10. Nikitin, A. V., A. S. Dmitruk, and V. S. Arutyunov. 2016. Effect of pressure on the oxidative cracking of C_2–C_4 alkanes. *Russ. Chem. Bull.* 65(10):2405–2410. doi: 10.1007/s11172-016-1597-3.
11. CWB 4.0.9150. Available at: http://www.kintechlab.com/products/chemical workbench/ (accessed September 24, 2019).
12. Healy, D., D. M. Kalitan, C. J. Aul, E. L. Petersen, G. Bourque, and H. Curran. 2010. Oxidation of C_1–C_5 alkane quinternary natural gas mixtures at high pressures. *J. Energ. Fuel.* 24(3):1521–1528. doi: 10.1021/ef9011005.
13. Combustion Chemistry Center at NUI Galway: Database Mechanism of Natural gas (including C_5) Oxidation http://c3.nuigalway.ie/media/researchcentres/combustionchemistrycentre/files/mechanismdownloads/nc5_49_mech.dat (accessed September 24, 2019).
14. Belyaev, A. A., A. V. Nikitin, P. D. Toktaliev, P. A. Vlasov, A. V. Ozerskii, A. S. Dmitryk, A. V. Arutyunov, and V. S. Arutyunov. 2018. Analiz literaturnukh modeley okisleniya metana v oblasti umerennykh temperatur [Analysis of literature models of oxidation of methane at moderate temperatures]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 11(1):19–26. doi: 10.30826/ce1811010.

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