

Direct Plasma Chemical Conversion of Methane to Methanol (a review)*V. A. Panov¹, A. G. Abramov² and A. V. Ugryumov²*¹JIHT RAS

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Interest in the one-stage conversion of methane, which makes up the majority of natural gas, has been maintained for many years and decades. One of the actively developing areas is the plasma-chemical conversion of methane to methanol. During this time, various laboratory designs of reactors were invented, mainly of a barrier discharge type, the influence of temperature, pressure, flow rates, energy input and other parameters in the reactor on the process efficiency, expressed in the degree of methane conversion, methanol selectivity, methanol yield and specific energy input per unit, was studied. useful product. This review presents the main results obtained by authors around the world over the past 30 years in both experimental and numerical studies of the process of obtaining methanol from methane in one-stage processes.

Keywords: methane conversion, methanol, plasma-chemical conversion, chemical kinetics, modeling, barrier discharge, electron beam.

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REFERENCES

1. Arutyunov V. S. and Strekova L. N., *Neftegazohimiya*, № 1, 17 (2020).
2. Srivastava R. K., Sarangi P. K., Bhatia L., Singh A. K. and Shadangi K. P. / *Biomass Conversion and Biorefinery* **12** (5), 1851 (2021).
3. Шарафутдинов Р. Г., Константинов В. О., Федосеев В. И., Шукин В. Г. / *Прикладная физика*. 2017. № 2. С. 13.; Sharafutdinov R. G., Konstantinov V. O., Fedoseeva V. I. and Shchukin V. G., *Plasma Physics Reports* **44** (9), 886 (2018).
4. Bhatnagar R. and Mallinson R. G. *Methane Conversion in AC Electric Discharges at Ambient Conditions / Methane and Alkane Conversion Chemistry*. – Springer New York, NY, 1995.
5. RICK MOODAY B. / Submitted to the Graduate Faculty of Texas Tech University in Partial Fulfillment. 1998.
6. Matsumoto H., Tanabe S., Okitsu K., Hayashi Y. and Suib S. L. / *The Journal of Physical Chemistry A*. **105** (21), 5304 (2001).
7. Okumoto M. and Mizuno A. / *Catalysis Today* **71** (1–2), 211 (2001).
8. Okumoto M., Kim H. H., Takashima K., Katsura S. and Mizuno A. / *IEEE Transactions on Industry Applications* **37** (6), 1618 (2001).
9. Zou J.-J., Zhang Y.-p., Liu C.-J., Li Y. and Eliasson B. / *Plasma Chemistry and Plasma Processing* **23** (1), 69 (2003).
10. Goujard V., Nozaki T., Yuzawa S., Ağiral A. and Okazaki K. / *Journal of Physics D: Applied Physics* **44** (27), 274011 (2011).
11. Nozaki T., Goujard V., Yuzawa S., Moriyama S., Ağiral A. and Okazaki K. / *Journal of Physics D: Applied Physics* **44** (27), 274010 (2011).
12. Krawczyk K., Młotek M., Ulejczyk B., Pryciak K. and Schmidt-Szalowski K. / *The European Physical Journal Applied Physics* **61** (2), 24307 (2013).
13. Indarto A. / *Plasma Sources Science and Technology* **25** (2), 025002 (2016).
14. Shepelev S. S., Gesser H. D. and Hunter N. R. / *Plasma Chemistry and Plasma Processing* **13** (3), 479 (1993).
15. Okumoto M., Tsunoda K., Katsura S. and Mizuno A. / *Journal of Electrostatics* **42** (1–2), 167 (1997).

16. Fathollahi P., Farahani M., Rad R. H., Khani M. R., Asadi A., Shafiei M. and Shokri B. / Journal of Electrostatics **112**, 103594 (2021).
17. Okumoto M., Su Z., Katsura S. and Mizuno A. / Journal of Electrostatics **42**, 167 (1997).
18. Okumoto M., Su Z., Katsura S. and Mizuno A. / IEEE Transactions on Industry Applications **35** (5), 1205 (1999).
19. Yao S. L., Takemoto T., Ouyang F., Nakayama A., Suzuki E., Mizuno A. and Okumoto M. / Energy & Fuels **14** (2), 459 (2000).
20. Aghamir F. M., Matin N. S., Jalili A. H., Esfarayeni M. H., Khodagholi M. A. and Ahmadi R. / Plasma Sources Science and Technology **13** (4), 707 (2004).
21. Nozaki T., Abe S., Moriyama S., Kameshima S., Okazaki K., Goujard V. and Ağıral A. / Japanese Journal of Applied Physics **54** (1S), 01AG01 (2014).
22. Chawdhury P., Ray D. and Subrahmanyam C. / Fuel Processing Technology **179**, 32 (2018).
23. Snoeckx R., Wang W., Zhang X., Cha M. S. and Bogaerts A. / Scientific Reports **8** (1), 15929 (2018).
24. Chawdhury P., Ray D., Vinodkumar T. and Subrahmanyam C. / Chemical Engineering Journal **337**, 117 (2019).
25. Okumoto M., Kim H.-H., Takashima K., Katsura S. and Mizuno A. / Conference Record of the 2000 IEEE Industry Applications Conference. Thirty-Fifth IAS Annual Meeting and World Conference on Industrial Applications of Electrical Energy (Cat. No.00CH37129) **1**, 636 (2000).
26. Nozaki T. and Okazaki K. / Catalysis Today **211**, 29 (2013).
27. Okazaki K., Hirai S., Nozaki T., Ogawa K. and Hijikata K. / Energy **22** (2–3), 369 (1997).
28. Ağıral A., Nozaki T., Nakase M., Yuzawa S., Okazaki K. and Gardeniers J. H. / Chemical Engineering Journal **167** (2–3), 560 (2011).
29. Zhang Y.-P., Li Y., Wang Y., Liu C.-J. and Eliasson B. / Fuel Processing Technology **83** (1–3), 101 (2003).
30. Okazaki K., Kishida T., Ogawa K. and Nozaki T. / Energy Conversion and Management **43** (9–12), 1459 (2002).
31. Mahammadunnisa S., Reddy P. M. K. and Subrahmanyam C. / RSC Adv. **4** (8), 4034 (2014).
32. Indarto A., Choi J.-W., Lee H. and Song H. K. / Chinese Science Bulletin September 2008 **53** (18), 2783 (2008).
33. Larkin D. W., Caldwell T. A., Lobban L. L. and Mallinson R. G. / Energy & Fuels **12** (4), 740 (1998).
34. Hyeock C. B., Yeong L. G. and Won L. D. Method for the conversion to methanol from methane: pat. KR 20000039170 A South Korea application KR19980054418A, 1998-12-11, published 2000-07-05.
35. Larkin D. W., Zhou L., Lobban L. L. and Mallinson R. G. / Industrial & Engineering Chemistry Research **40** (23), 5496 (2001).
36. Larkin D. W., Lobban L. L. and Mallinson R. G. / Industrial & Engineering Chemistry Research **40** (7), 1594 (2001).
37. Conversion of greenhouse gases into fuel or chemical intermediates: pat. DE 19605547 A1 Deutschland application DE19605547A Baden B. A., Baldur E., Birmenstorf, Wettingen K. E., Ulrich K., Hausen, 1996-02-15, published 1997-08-21
38. Nozaki T., Kado S., Hattori A., Ken Okazaki and Muto N. / Studies in Surface Science and Catalysis **147**, 505 (2004).
39. Nozaki T., Hattori A. and Okazaki K. / Catalysis Today **98** (4), 607 (2004).
40. Par Erick Osvaldo MARTINEZ RUIZ / Université Pierre et Marie CurieEcole Doctorale 391 – Sciences Mécaniques, Acoustique, Electronique etRobotiqueEquipe 2PM / IRCP UMR8247 (CNRS-Chimie ParisTech). 2017.
41. Bugaev S. P., Kozyrev A. V., Kuvshinov V. A., Sochugov N. S. and Khryapov P. A. / Plasma Chemistry and Plasma Processing **18** (2), 247 (1998).
42. Rajanikanth B., Shimizu K., Okumoto M., Katsura S. and Mizuno A. / IAS '95. Conference Record of the 1995 IEEE Industry Applications Conference Thirtieth IAS Annual Meeting. **2**, 1459 (1995).
43. Kozlov K. V., Michel P. and Wagner H.-E. / Plasmas and Polymers **5** (3/4), 129 (2001).
44. Lee H. and Kim D. H. / Scientific Reports **8**, 9956 (2018).
45. Jurković D. L., Puliyalil H., Pohar A. and Likožar B. / International Journal of Energy Research **43** (14), 8085 (2019).
46. Plasma microjet arrays for selective oxidation of methane to methanol: pat. US6924401B2 USA, application US64506203A, Giapis K. P., Sankaran R. M., McHugh S., 2003-08-21, published 2005-08-02.
47. Tsuchiya T. and Izuka S. / Journal of Environmental Engineering and Technology **2** (3), 35 (2013).
48. Huang J., Badani M. V., Suib S. L., Harrison J. B. and Kablauoi M. / The Journal of Physical Chemistry **98** (1), 206 (1994).
49. Wang Y.-F., Tsai C.-H., Shih M., Hsieh L.-T. and Chang W. / Aerosol and Air Quality Research **5** (2), 204 (2005).
50. Wang Y.-F., Tsai C.-H., Shih M., Hsieh L.-T. and Chang W. / Aerosol and Air Quality Research **5** (2), 211 (2005).
51. Zhou L. M., Xue B., Kogelschatz U. and Eliasson B. / Plasma Chemistry and Plasma Processing **18** (3), 375 (1998).
52. Nozaki T., Ağıral A., Yuzawa S., Gardeniers J. H. and Okazaki K. / Chemical Engineering Journal **166** (1), 288 (2011).
53. Nozaki T. and Okazaki K. / Green Processing and Synthesis **1** (6), 517 (2012).
54. Qian M., Li G., Kang J., Liu S., Yuan D., Ren C., Zhang J. and Wang D. / AIP Advances **8** (12), 125224 (2018).
55. Rajanikanth B., Okumoto M., Katsura S. and Mizuno A. / Department of Ecological Engineering, Toyohashi University of Technology **1**, 1813 (1996).
56. Hoeben W. F. L. M., Boekhoven W., Beckers F. J. C. M., van Heesch E. J. M. and Pemen A. J. M. / Journal of Physics D: Applied Physics **47** (35), 355202 (2014).
57. Chen L., Zhang X.-W., Huang L. and Lei L.-C. / Chemical Engineering and Processing: Process Intensification **48** (8), 1333 (2009).
58. Bie C. D., Verheyde B., Martens T., van Dijk J., Paulussen S. and Bogaerts A. / Plasma Processes and Polymers **8** (11), 1033 (2011).

59. *Khoshtinat M., N. A. S. Amin and Noshadi I.* / World Academy of Science, Engineering and Technology International Journal of Chemical and Molecular Engineering **2** (4), 181 (2010).
60. *Indarto A.* / IEEE Transactions on Dielectrics and Electrical Insulation **15** (4), 1038 (2008).
61. *Indarto A., Choi J.-W., Lee H., Song H. K. and Palgunadi J.* / Journal of Rare Earths **24**, 513 (2006).
62. *Li D., Rohani V., Fabry F., Ramaswamy A. P., Sennour M. and Fulcheri L.* / Applied Catalysis B: Environmental **261**, 118228 (2019).
63. *Whitehead J. C.* / Journal of Physics D: Applied Physics **49** (24), 243001 (2016).
64. *Li S., Ahmed R., Yi Y. and Bogaerts A.* / Catalysts **11** (5), 590 (2021).
65. *Chen L., Zhang X., Huang L. and Lei L.* / Chemical Engineering & Technology **33** (12), 2073 (2010).
66. *Chawdhury P., Bhargavi K. V. S. S. and Subrahmanyam C.* / Sustainable Energy & Fuels **5**, 3351 (2021).
67. *Chen L., Zhang X., Huang L. and Lei L.* / Journal of Natural Gas Chemistry **19** (6), 628 (2010).
68. *Indarto A.* / Ionics **20** (3), 445 (2014).
69. *Chawdhury P., Bhargavi K. V. S. S., Selvaraj M. and Subrahmanyam C.* / Catalysis Science & Technology **10** (16), 5566 (2020).
70. *Chawdhury P., Bhargavi K. and Subrahmanyam C.* / Catalysis Communications **147**, 106139 (2020).
71. *Starokon E. V., Parfenov M. V., Arzumanov S. S., Pirutko L. V., Stepanov A. G. and Panov G. I.* / Journal of Catalysis **300**, 47 (2013).
72. *Bols M. L., Hallaert S. D., Snyder B. E. R., Devos J., Plessers D., Rhoda H. M., Dusselier M., Schoonheydt R. A., Pierloot K., Solomon E. I. and Sels B. F.* / Journal of the American Chemical Society **140** (38), 12021 (2018).
73. *Kim Y., Kim T. Y., Lee H. and Yi J.* / Chemical Communications **53** (29), 4116 (2017).
74. *Ab Rahim M. H., Forde M. M., Jenkins R. L., Hammond C., He Q., Dimitratos N., Lopez-Sanchez J. A., Carley A. F., Taylor S. H., Willock D. J., Murphy D. M., Kiely C. J. and Hutchings G. J.* / Angewandte Chemie International Edition **52** (4), 1280 (2013).
75. *Agarwal N., Freakley S. J., McVicker R. U., Athahban S. M., Dimitratos N., He Q., Morgan D. J., Jenkins R. L., Willock D. J., Taylor S. H., Kiely C. J. and Hutchings G. J.* / Science **358** (6360), 223 (2017).
76. *Jin Z., Wang L., Zuidema E., Mondal K., Zhang M., Zhang J., Wang C., Meng X., Yang H., Mesters C. and Xiao F.-S.* / Science **367** (6474), 193 (2020).
77. *Cui X., Li H., Wang Y., Hu Y., Hua L., Li H., Han X., Liu Q., Yang F., He L., Chen X., Li Q., Xiao J., Deng D. and Bao X.* / Chem **4** (8), 1902 (2018).
78. *Kwon Y., Kim T. Y., Kwon G., Yi J. and Lee H.* / Journal of the American Chemical Society **139** (48), 17694 (2017).
79. *Hammond C., Forde M. M., Ab Rahim M. H., Thetford A., He Q., Jenkins R. L., Dimitratos N., Lopez-Sanchez J. A., Dummer N. F., Murphy D. M., Carley A. F., Taylor S. H., Willock D. J., Stangland E. E., Kang J., Hagen H., Kiely C. J. and Hutchings G. J.* / Angewandte Chemie International Edition **51** (21), 5129 (2012).
80. *Groothaert M. H., Smeets P. J., Sels B. F., Jacobs P. A. and Schoonheydt R. A.* / Journal of the American Chemical Society **127** (5), 1394 (2005).
81. *Pappas D. K., Martini A., Dyballa M., Kvande K., Teketel S., Lomachenko K. A., Baran R., Glatzel P., Arstad B., Berlier G., Lamberti C., Bordiga S., Olsbye U., Svelle S., Beato P. and Borfecchia E.* / Journal of the American Chemical Society **140** (45), 15270 (2018).
82. *Pappas D. K., Borfecchia E., Dyballa M., Pankin I. A., Lomachenko K. A., Martini A., Signorile M., Teketel S., Arstad B., Berlier G., Lamberti C., Bordiga S., Olsbye U., Lillerud K. P., Svelle S. and Beato P.* / Journal of the American Chemical Society **139** (42), 14961 (2017).
83. *Knorpp A. J., Pinar A. B., Newton M. A., Sushkevich V. L. and van Bokhoven J. A.* / ChemCatChem **10** (24), 5593 (2018).
84. *Beznis N. V., Weckhuysen B. M. and Bitter J. H.* / Catalysis Letters **136** (1–2), 52 (2010).
85. *Shan J., Huang W., Nguyen L., Yu Y., Zhang S., Li Y. and Frenkel A. I.* / Langmuir **30** (28), 8558 (2014).
86. *Liu Z., Huang E., Orozco I., Liao W., Palomino R. M., Rui N., Duchon T., Nemsak S., Grinter D. C., Mahapatra M., Liu P., Rodriguez J. A. and Senanayake S. D.* / Science **368** (6490), 513 (2020).
87. *Lustemberg P. G., Palomino R. M., Gutierrez R. A., Grinter D. C., Vorokhta M., Liu Z., Ramirez P. J., Matolin V., Ganduglia-Pirovano M. V., Senanayake S. D. and Rodriguez J. A.* / Journal of the American Chemical Society **140** (24), 7681 (2018).
88. *Shan J., Li M., Allard L. F., Lee S. and Flytzani-Stephanopoulos M.* / Nature **551** (7682), 605 (2017).
89. *Bai S., Yao Q., Xu Y., Cao K. and Huang X.* / Nano Energy **71**, 104566 (2020).
90. *Liu R.-S., Iwamoto M. and Lunsford J. H.* / Journal of the Chemical Society, Chemical Communications, № 1, 78 (1982).
91. GRIMech. URL: combustion.berkeley.edu/gri-mech/
92. USCmech. URL: ignis.usc.edu/Mechanisms/USC-Mech%20II/USC_Mech%20II.htm
93. DRM. URL: combustion.berkeley.edu/drm/
94. SDmech. URL: web.eng.ucsd.edu/mae/groups/combustion/mechanism.html
95. NUIGmech. URL: c3.universityofgalway.ie/combustionchemistrycentre/mechanismdownloads/
96. *Konnov A. A.* / Combustion and Flame **162** (10), 3755 (2015).
97. *Vasil'ev V. M., Vol'pert A. I. and Hudyaev S. I.* / Zhurnal vychislitel'noj matematiki i matematicheskoy fiziki **13** (3), 3755 (1973).
98. *Levanov A. V., Analiz predelov vosplamneniya smesi H₂-O₂ obobshchennym metodom kvazistacionarnyh koncentracij* (MGU, Moscow, 2017).
99. *Арутюнов В. С., Басевич В. Я., Веденеев В. И.* / Успехи химии. 1996. Т. 65. № 3. С. 211; Arutyunov V. S., Basevich V. Ya. and Vedeneev V. I., Russian Chemical Reviews **65** (3), 197 (1996).
100. *Tsang W. and Hampson R. F.* / Journal of Physical and Chemical Reference Data **15** (3), 1087 (1986).
101. *Oumghar A., Legrand J. C., Diamy A. M. and Turillon N.* / Plasma Chemistry and Plasma Processing **15** (1), 87 (1995).
102. *de Bie C., van Dijk J. and Bogaerts A.* / The Journal of Physical Chemistry C **119** (39), 22331 (2015).