EFFECT OF REACTOR VOLUME ON AUTOTHERMAL NATURAL GAS CONVERSION AND ALLOTHERMAL GASIFICATION OF ORGANIC WASTE BY ULTRASUPERHEATED STEAM*

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Abstract: The pulsed detonation gun (PDG) technology was applied for autothermal high-temperature conversion of natural gas and allothermal oxygen-free gasification of liquid/solid organic wastes with ultrasuperheated steam (USS) at atmospheric pressure using two flow reactors of significantly different volumes: 100 and 40 l. The PDG operated at a frequency f of 1 Hz on a mixture of natural gas and oxygen. Waste machine oil and sawdust with a moisture content of 10 to 30 %(wt.) were used as liquid and solid organic wastes. It was expected that a decrease in the volume of the flow reactor from 100 to 40 l, on the one hand, should not affect the natural gas conversion and, on the other hand, could lead to an increase in the gasification temperature in the flow reactor and, accordingly, to an increase in the quality of the product syngas (H_2 + CO). As expected, complete conversion of natural gas to syngas was achieved in the PDG with H_2/CO and CO_2/CO ratios of 1.25 and 0.25 which were independent of the reactor volume. Liquid and solid wastes were converted in the flow reactors into gas containing H_2, CO, CO_2, and CH_4. The steady-state values of the H_2/CO and CO_2/CO ratios in the syngas obtained from waste machine oil were 0.8 and 0.5 in the 100-liter reactor and 0.9 and 0.2 in the 40-liter reactor, respectively, which indicates an expected increase in the syngas quality. At the same time, the maximum mass flow rate of feedstock in the 40-liter reactor increased by a factor of more than 4 compared to the 100-liter reactor. The steady-state values of the H_2/CO and CO_2/CO ratios in the syngas obtained from a batch of sawdust of a fixed mass (2 kg) were 0.5 and 0.8 for both reactors and the gasification time in both reactors was about 5–7 min. It has been shown that the measured volume fractions of H_2, CO, and CO_2 in the syngas produced both by autothermal high-temperature conversion of natural gas and by allothermal oxygen-free gasification of liquid/solid organic wastes in the USS medium at atmospheric pressure and $f = 1$ Hz are almost independent of the feedstock and reactor volume which is associated with high values of the local instantaneous gasification temperature.

Keywords: natural gas conversion; gasification of liquid/solid wastes; ultrasuperheated steam; pulsed detonation gun technology

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Figure Captions

Figure 1 Schematics of two waste converters with a pulsed detonation gun and (*a*) 100-liter spherical reactor and (*b*) 40-liter cylindrical reactor

Figure 2 Time histories of the syngas temperature measured by a thermocouple in the outlet tube of 100- and 40-liter reactors with a PDG operating at $0.95 \le \Phi \le 1.8$ and $f = 1$ Hz; $P \approx 0.1$ MPa

Figure 3 Comparison of the measured (symbols) and calculated (curves) volume fractions of dry cooled detonation products of natural gas – oxygen mixture in a 100-liter reactor (circles) and a 40-liter reactor (squares) at $f = 1$ Hz and $P \approx 0.1$ MPa. The calculation was made for a composition-freezing temperature of 2200 K. Measurement errors are shown only for values of Φ close to the limiting values

Figure 4 Time histories of the syngas temperature measured by a thermocouple in the outlet tube of 100- and 40-liter reactors with a PDG operating at $f = 1$ Hz. Time point 0 corresponds to the beginning of the supply of waste machine oil to the reactor with $G = 2$ g/s (100-liter reactor) and 4 g/s (40-liter reactor); $P \approx 0.1$ MPa

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Figure 5 Measured compositions of dry cooled syngas obtained by allothermal gasification of waste machine oil as a function of the liquid mass flow rate ($f = 1$ Hz, $P \approx 0.1$MPa) in 100-liter (dark symbols) and 40-liter (light symbols) reactors. Measurement errors are shown only for the limiting values of G

Figure 6 Time histories of the syngas temperature measured by a thermocouple in the outlet tube of 100- and 40-liter reactors with a PDG operating at $f = 1$ Hz. Time point 0 corresponds to the beginning of the experiment in a cold reactor loaded with a 2-kilogram batch of sawdust

Figure 7 Time histories of the composition of dry cooled syngas obtained by allothermal gasification of a 2-kilogram batch of sawdust in a 40-liter reactor with a PDG operating at $f = 1$ Hz; $P \approx 0.1$ MPa

Figure 8 Measured steady-state compositions of dry cooled syngas obtained by allothermal gasification of sawdust in 100- and 40-liter reactors with a PDG operating at $f = 1$ Hz; $P \approx 0.1$ MPa

Figure 9 Comparison of syngas compositions in all experiments with autothermal natural gas conversion (squares) and allothermal gasification of liquid (circles) and solid (triangles) wastes with a PDG operating at $f = 1$ Hz. Large empty symbols correspond to a 100-liter reactor, small empty symbols correspond to a 40-liter reactor, large filled symbols correspond to plasma reactors [19, 22], diamonds correspond to RDF gasification [19]; $P \approx 0.1$ MPa

Table Captions

Table 1 Natural gas composition

Table 2 Proximate analysis of liquid and solid wastes

Table 3 Ultimate analysis of liquid and solid wastes

References

1. Hu, J., and D. Shekhawat. 2022. *Direct natural gas conversion to value-added chemicals*. Boca Raton, FL: CRC Press. 454 p.
2. Base, P. 2010. *Biomass gasification and pyrolysis. Practical design*. Burlington, ON: Academic Press. 376 p.
3. Bain, R. L., and K. Broer. 2011. Gasification. *Thermochemical processing of biomass: Conversion into fuels, chemicals and power*. Ed. R. C. Brown. 1st ed. John Wiley & Sons. 47–77.
4. Frolov, S. M. 2021. Organic waste gasification: A selective review. *Fuels* 2:556–651. doi: 10.3390/fuels2040033.
5. Frolov, S. M. 2021. Gazifikatsiya organicheskikh otkhodov ul'traperegretym vodyanym parom i dioksidom ugleroda [Gasification of organic wastes by ultra-superheated steam and carbon dioxide]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 14(3):74–97. doi: 10.30826/CE21140308.
6. Portofino, S., A. Donatelli, P. Iovane, C. Innella, R. Civita, M. Martino, D. A. Matera, A. Russo, G. Cornacchia, and S. Galvagno. 2013. Steam gasification of waste tyre: Influence of process temperature on yield and product composition. *Waste Manage.*33:672–678.
7. Wilk, V., and H. Hofbauer. 2013. Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier. *Fuel* 107:787–799.
8. Pilon, G., and J.-M. Lavoie. 2013. Pyrolysis of switchgrass (Panicum virgatum L.) at low temperatures within N_2 and CO_2 environments: Product yield study. *ACS Sustain. Chem. Eng.* 1:198–204.
9. Sadhwani, N., S. Adhikari, and M. R. Eden. 2016. Biomass gasification using carbon dioxide: Effect of temperature, CO_2/C ratio, and the study of reactions influencing the process. *Ind. Eng. Chem. Res.* 55:2883–2891.
10. Galvagno, S., G. Casciaro, S. Casu, M. Martino, C. Mingazzini, A. Russo, and S. Portofino. Steam gasification of tire waste, poplar, and refuse-derived fuel: A comparative analysis. *Waste Manage.* 29:678–689.
11. Soni, C. G., A. K. Dalai, T. Pugsley, and T. Fonstad. 2011. Steam gasification of meat and bone meal in a two-stage fixed-bed reactor system. *Asia-Pac. J. Chem. Eng.* 6:71–77.
12. Eshun, J., L. Wang, E. Ansah, A. Shahbazi, K. Schimmel, V. Kabadi, and S. Aravamudhan. 2017. Characterization of the physicochemical and structural evolution of biomass particles during combined pyrolysis and CO_2 gasification. *J. Energy Inst.* 92:32–93.
13. Minkova, V., S. P. Marinov, R. Zanzi, E. Bjornbom, T. Budinova, M. Stefanova, and L. Lakov. 2000. Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide. *Fuel Process. Technol.* 61:45–52.
14. Galvagno, S., S. Casu, G. Casciaro, M. Martino, A. Russo, and S. Portofino. 2006. Steam gasification of refuse-derived fuel (RDF): Influence of process temperature on yield and product composition. *Energ. Fuel.* 20:2284–2288.
15. Umeki, K., K. Yamamoto, T. Namioka, and K. Yoshikawa. 2010. High temperature steam-only gasification of woody biomass. *Appl. Energ.* 87:791–798.
16. Guizani, C., F. J. Escudero Sanz, and S. Salvador. 2014. Effects of CO_2 on biomass fast pyrolysis: Reaction rate, gas yields and char reactive properties. *Fuel* 116:310–320.
17. Hlina, M., M. Hrabovsky, T. Kavka, and M. Konrad. 2014. Production of high quality syngas from argon/water plasma gasification of biomass and waste. *Waste Manage.* 34:63–66.

18. Billaud, J., S. Valin, M. Peyrot, and S. Salvador. 2016. Influence of H_2O, CO_2 and O_2 addition on biomass gasification in entrained flow reactor conditions: Experiments and modelling. *Fuel* 166:166–178.
19. Agon, N., M. Hrabovsky, O. Chumak, *et al.* 2016. Plasma gasification or refuse derived fuel in a single-stage system using different gasifying agents. *Waste Manage.* 47:246–255.
20. Hrabovsky, M., M. Hlina, V. Kopecky, A. Maslani, O. Zivny, P. Krenek, and O. Hurba. 2017. Steam plasma treatment of organic substances for hydrogen and syngas production. *Plasma Chem. Plasma P.* 37:739–762.
21. Wang, M., M. Mao, M. Zhang, G. Wen, Q. Yang, B. Su, and Q. Ren. 2019. Highly efficient treatment of textile dyeing sludge by CO_2 thermal plasma gasification. *Waste Manage.* 90:29–36.
22. Shie, J. L., F. J. Tsou, K. L. Lin, and C. Y. Chang. 2010. Bioenergy and products from thermal pyrolysis of rice straw using plasma torch. *Bioresource Technol.* 101:761–768.
23. Hrabovsky, M. 2011. Plasma aided gasification of biomass, organic waste and plastics. *30th Conference (International) on Phenomena in Ionized Gas Proceedings*. Belfast, Northern Ireland. 4 p.
24. Vecten, S., M. Wilkinson, N. Bimbo, R. Dawson, and B. M. J. Herbert. 2021. Hydrogen-rich syngas production from biomass in a steam microwave-induced plasma gasification reactor. *Bioresource Technol.* 337:125324.
25. Bebelin, I. N., A. G. Volkov, A. N. Gryaznov, and S. P. Malyshenko. 1997. Development and research of an experimental hydrogen–oxygen steam generator with a capacity of 10 MW(t). *Therm. Eng.* 8:48–52.
26. Lewis, F. M. 2007. Generation of an ultra-superheated steam composition and gasification therewith. U.S. Patent US20030233788A1.
27. Sariev, V. N., V. A. Veretennikov, and V. V. Troyachenko. 28.03.2018. Sistema kompleksnoy bezotkhodnoy pererabotki tverdykh bytovykh i promyshlennykh otkhodov [System of complex recycling of solid domestic and industrial waste]. Patent of Russian Federation No. 2648737. Priority 28.03.2016.
28. Pierce, T. H., E. M. Afify, and R. T. Zickefoose. 1979. Detonation-induced coal gasification. Raleigh, NC: Department of Mechanical and Aerospace Engineering, North Carolina State University. Final Report No. DOE/ET/10451-T1.
29. Pierce, T. H. 1987. Detonation-induced coal gasification. *Int. J. Energ. Res.* 11(2):203–231.
30. Hunter, L. G. 30.09.1997. Pulse detonation device for coal gasification. U.S. Patent 5,672,184.
31. Frolov, S. M., V. A. Smetanyuk, I. A. Sadykov, A. S. Silantiev, I. O. Shamshin, V. S. Aksenov, K. A. Avdeev, and F. S. Frolov. 2002. Natural gas conversion and liquid/solid organic waste gasification by ultra-superheated steam. *Energies* 15:3616. doi: 10.3390/en15103616.
32. Frolov, S. M., V. A. Smetanyuk, K. A. Avdeev, and S. A. Nabatnikov. 24.04.2019. Sposob polucheniya sil'no peregretogo para i ustroystvo detonatsionnogo parogeneratora (varianty) [Method for obtaining highly overheated steam and detonation steam generator device (options)]. Patent of Russian Federation No. 2686138. Priority 26.02.2018.
33. Frolov, S. M., V. A. Smetanyuk, and S. A. Nabatnikov. 01.04.2019. Sposob gazifikatsii uglya v sil'no peregretom vodyanom pare i ustroystvo dlya ego osushchestvleniya [Method of gasification of coal in a highly overheated water vapor and device for its implementation]. Patent of Russian Federation No. 2683751. (WO2019/226074 A1 dated 28.11.2019.)
34. Frolov, S. M., S. A. Nabatnikov, K. V. Diesperov, and E. R. Achildiev. 22.12.2020. Sposob obezzarazhivaniya letuchey zoly, obrazuyushcheysya pri szhiganii otkhodov, i ustroystvo dlya ego osushchestvleniya [Method for decontamination of a fly ash formed during burning of wastes and a device for its implementation]. Patent of Russian Federation No. 2739241. Priority 11.06.2020.
35. Frolov, S. M., V. A. Smetanyuk, I. O. Shamshin, A. S. Koval', F. S. Frolov, and S. A. Nabatnikov. 2019. Poluchenie sil'no peregretogo vodyanogo para s pomoshch'yu tsiklicheskoy detonatsii troynoy gazovoy smesi "propan – kislorod – vodyanoy par" [Generation of highly superheated steam by pulsed detonation of the ternary gas "propane – oxygen – steam" mixture]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 12(4):95–103. doi: 10.30826/CE19120410.
36. Frolov, S. M., V. A. Smetanyuk, and S. S. Sergeev. 2020. Reactor for waste gasification with highly superheated steam. *Dokl. Phys. Chem.* 495(2):191–195. doi: 10.1134/S0012501620120039.
37. Frolov, S. M., V. A. Smetanyuk, I. O. Shamshin, I. A. Sadykov, A. S. Koval', and F. S. Frolov. 2021. Production of highly superheated steam by cyclic detonations of propane and methane–steam mixtures with oxygen for waste gasification. *Appl. Therm. Eng.* 183(1):116195. doi: 10.1016/j.applthermaleng.2020.116195.
38. Frolov, S. M., V. A. Smetanyuk, I. A. Sadykov, A. S. Silantiev, V. S. Aksenov, I. O. Shamshin, K. A. Avdeev, and F. S. Frolov. 2022. Avtotermicheskaya konversiya prirodnogo gaza i allotermicheskaya gazifikatsiya zhidkikh i tverdykh organicheskikh otkhodov ul'traperegretym vodyanym parom [Autothermal natural gas conversion and allothermal gasification of liquid and solid organic wastes by ultrasuperheated steam]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 15(2):75–87. doi: 10.30826/CE22150207.
39. Frolov, S. M., V. Ya. Basevich, V. S. Aksenov, and S. A. Polikhov. 2005. Optimization study of spray detonation initiation by electric discharge. *Shock Waves* 14(3):175–186. doi: 10.1007/s00193-005-0263-8.
40. Ferreira, S., E. Monteiro, P. Brito, and C. 2019. A holistic review on biomass gasification modified equilibrium models. *Energies* 12:160.

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