INFLUENCE OF CO AND CO_2 ADDITIVES ON SYNGAS FORMATION DURING STEAM CONVERSION OF METHANE FROM BIOMASS GASIFICATION PRODUCTS

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Abstract: A detailed kinetic modeling of the process of syngas production during steam reforming of various oxygen-free mixtures of methane with additives of H_2, CO, and CO_2 highly diluted with argon has been carried out taking into account the formation of microheterogeneous soot particles in the gas phase under conditions of variable temperature. In such mixtures typical for biomass gasification products, additives of H_2O, CO, and CO_2 acted as oxidizers. A direct comparison of the authors' kinetic calculations with the results of experiments in a heated flow reactor, in which the concentrations of initial, intermediate, and final products of methane conversion in mixtures with additives of H_2, H_2O, CO, and CO_2 were quantified, was performed. Experiments and calculations were carried out in the temperature range 1100–1800 K at atmospheric pressure for reaction time $t = 0.68$ s. Detailed calculations of the soot formation process were performed for all studied mixtures and experimental conditions. Comparison of the results of the authors' kinetic calculations with the results of experiments and calculations performed in a heated flow reactor made it possible to assess the effect of soot formation on the process of steam conversion of methane in mixtures with additives of H_2, CO, and CO_2. Two ways of consumption of carbon atoms from the reacting system have been analyzed: the first way is the heterogeneous deposition of acetylene molecules from the gas phase on the surface of the reactor followed by the formation of solid carbon, and the second way is the homogeneous formation of soot particles from nuclei in the gas phase.

Keywords: gasification of biomass and natural gas; methane; steam reforming; syngas; H_2, CO, and CO_2 additives; microheterogeneous soot particles; heterogeneous formation of solid carbon; kinetic modeling

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Figure Captions

Figure 1 Direct comparison of the experimental results [34] (*1*) and kinetic simulations [34] (*2*) with authors' kinetic simulations (*3*) of temperature dependences of the mole fraction of methane (CH_4) (*a*) and hydrogen (H_2) (*b*) molecules during the thermal decomposition of mixtures $0.0126CH_4 + 0.05CO + 0.05H_2 + 0.05H_2O$ (left column) and $0.0126CH_4 + 0.05CO_2 + 0.05H_2 + 0.05H_2O$ (right column) for total reaction time $t = 0.68$ s

Figure 2 Direct comparison of experimental results [34] (filled signs) and kinetic simulations [34] (curves) with authors' kinetic simulations (empty signs) of the temperature dependences of the mole fraction of CO (*1*) and CO_2 (*2*) molecules during the thermal decomposition of mixtures $0.0126CH_4 + 0.05CO + 0.05H_2 + 0.05H_2O$ (*a*) and (*b*) and $0.0126CH_4 + 0.05CO_2 + 0.05H_2 + 0.05H_2O$ (*c*) for total reaction time $t = 0.68$ s

Figure 3 Direct comparison of experimental results [34] (*1*) and kinetic simulations [34] (*2*) with authors' kinetic simulations (*3*) of the temperature dependences of the mole fraction of ethylene (C_2H_4) (*a*) and acetylene (C_2H_2) (*b*) molecules during the thermal decomposition of mixtures $0.0126CH_4 + 0.05CO + 0.05H_2 + 0.05H_2O$ (left column) and $0.0126CH_4 + 0.05CO_2 + 0.05H_2 + 0.05H_2O$ (right column) for total reaction time $t = 0.68$ s

Figure 4 Temperature dependences of soot yield for mixtures of methane with hydrogen, water, CO, and CO_2 with argon: *1* — $0.0126CH_4 + 0.05CO + 0.05H_2 + 0.05H_2O$; and *2* — $0.0126CH_4 + 0.05CO_2 + 0.05H_2 + 0.05H_2O$. Reaction time was 0.68 s

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