

# KINETIC ANALYSIS OF OXIDATIVE DRY REFORMING OF METHANE INTO SYNGAS AND ASSESSMENT OF THE POSSIBILITY OF METHANOL PRODUCTION

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**Abstract:** Noncatalytic oxidative dry reforming of methane in matrix converters was investigated by kinetic modeling. Main reaction pathways were identified. The study demonstrates the potential of oxidative dry reforming of methane as an effective process of methanol production with high carbon dioxide utilization and low carbon-footprint. Acetylene (the main product of thermal methane pyrolysis) reforming, was shown to be determined by CO<sub>2</sub> conversion under conditions of thermal dry reforming of methane. When oxygen was added to the mixture, it decreased the contribution of CO<sub>2</sub> to acetylene conversion. However, due to generation of additional OH<sup>•</sup> radicals, the rate of methane conversion and subsequent transformation of acetylene to CO was significantly increased while the rate of CO<sub>2</sub> consumption was reduced.

**Keywords:** natural gas; carbon dioxide; matrix dry conversion of methane; syngas; methanol

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## Figure Captions

**Figure 1** Dependence of reagent concentrations (*1* – CH<sub>4</sub>; *2* – CO<sub>2</sub>; and *3* – O<sub>2</sub>) on the reaction time during dry (grey curves) and oxidative dry (black curves) reforming of methane under isothermal conditions (*T* = 1600 K) at volumetric ratios of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75 and CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub> = 1 : 1 : 0.75

**Figure 2** Dependence of H<sub>2</sub> (*1*), H<sub>2</sub>O (*2*), and CO (*3*) concentrations on the reaction time during dry (grey curves) and oxidative dry (black curves) reforming of methane under isothermal conditions (*T* = 1600 K) at initial volumetric ratios of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75 and CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub> = 1 : 1 : 0.75

**Figure 3** Dependence of C<sub>2</sub>H<sub>4</sub> (*1*) and C<sub>2</sub>H<sub>2</sub> (*2*) concentrations on the reaction time during dry (grey curves) and oxidative dry (black curves) reforming of methane under isothermal conditions (*T* = 1600 K) at volumetric ratios of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75 and CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub> = 1 : 1 : 0.75

**Figure 4** Sensitivity analysis of CO<sub>2</sub> concentration at *T* = 1600 K: (*a*) dry reforming of CH<sub>4</sub> at lg(*t*, *s*) = –0.8 and a volumetric ratio of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75; and (*b*) oxidative dry reforming of CH<sub>4</sub> at lg(*t*, *s*) = –1 and a volumetric ratio of CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub> = 1 : 1 : 0.75

**Figure 5** Dependence of CH<sub>2</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> concentrations on the reaction time during oxidative dry reforming of methane under isothermal conditions (*T* = 1600 K) at different initial CO<sub>2</sub> levels (*1* – CH<sub>4</sub>/CO<sub>2</sub> = 1 : 1; *2* – 1 : 0.8; *3* – 1 : 0.6; and *4* – CH<sub>4</sub>/CO<sub>2</sub> = 1 : 0.4) and initial volumetric ratio of CH<sub>4</sub>/O<sub>2</sub> = 1 : 0.75

**Figure 6** Dependence of H<sub>2</sub> (*a*) and CO (*b*) concentrations on the reaction time during oxidative dry reforming of methane under isothermal conditions (*T* = 1600 K) at different initial CO<sub>2</sub> levels (*1* – CH<sub>4</sub>/CO<sub>2</sub> = 1 : 1; *2* – 1 : 0.8; *3* – 1 : 0.6; and *4* – CH<sub>4</sub>/CO<sub>2</sub> = 1 : 0.4) and initial volumetric ratio of CH<sub>4</sub>/O<sub>2</sub> = 1 : 0.75

**Figure 7** Dependence of CH<sub>4</sub> and CO<sub>2</sub> concentrations on the reaction time during oxidative dry reforming of methane at temperatures of 1200 (*1*), 1400 (*2*), 1600 (*3*), and 1800 K (*4*). Initial volumetric ratios: CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub> = 1 : 1 : 0.75

**Figure 8** Main routes of product formation during dry and oxidative dry reforming of methane at different stages of the process at temperatures 1200–1800 K: (*a*) –3 < lg(*t*, *s*) < –1.5; (*b*) –1.5 < lg(*t*, *s*) < –0.5; and (*c*) lg(*t*, *s*) > –0.5

**Figure 9** Sensitivity analysis of C<sub>2</sub>H<sub>2</sub> concentration at *T* = 1600 K at different time points during dry reforming of methane: *1* – lg(*t*, *s*) = –0.3; *2* – –1.2; and *3* – lg(*t*, *s*) = –1.8. Initial volumetric ratio CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75

**Figure 10** Sensitivity analysis of C<sub>2</sub>H<sub>2</sub> concentration at *T* = 1600 K at different time points during oxidative dry reforming of methane: *1* – lg(*t*, *s*) = –0.3; *2* – –1.2; and *3* – lg(*t*, *s*) = –2.8. Initial volumetric ratio CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1 : 1 : 0.75

**Figure 11** Routes of  $C_2H_2$  conversion into methane during dry reforming of methane at  $\lg(t, s) = -0.8$  and  $T = 1600$  K. Initial volumetric ratio  $CH_4/CO_2/N_2 = 1 : 1 : 0.75$

**Figure 12** Schematic of methanol production process from  $CH_4$  and  $CO_2$ . Streams: Ia — natural gas (methane) with  $CO_2$ ; Ib — natural gas (methane); II — air; III — syngas after matrix conversion; IV — raw water; Va, Vb, Vc, and Vd — syngas with steam; VI — water; VIIa and VIIb — dried syngas; VIIIa, VIIIb, and VIIIc — nitrogen-containing gas with methanol; IX — methanol; X — syngas for recycling; and XI — nitrogen-containing gas

## Table Captions

**Table 1** Initial data for calculating the process of methanol production from methane and  $CO_2$

**Table 2** Material balance of the combined process of producing methanol and hydrogen-containing gas (see Fig. 12)

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