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Co-processing methane in high temperature steam gasification of biomass

Aaron W. Palumbo*, Erica L. Jorgensen, Jeni C. Sorli, Alan W. Weimer*

Department of Chemical & Biological Engineering, University of Colorado at Boulder, Boulder, CO 80303, USA

HIGHLIGHTS

- ▶ CH₄ and biomass were reacted simultaneously in an entrained flow steam-gasifier.
- ▶ Equilibrium accurately predicts the syngas composition at 1500 °C; not at 1200 °C.
- ► ANOVA reveals temperature dominates syngas composition and conversion.
- ▶ Product syngas composition can be tuned for downstream processing.

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1. Introduction

High temperature, steam-only thermochemical processing of biomass initially involves rapid pyrolysis into char, permanent gases, and condensable vapors. Condensable vapors continue to undergo secondary homogeneous reactions such as cracking and reforming to form more permanent gases. The resulting char particles undergo conventional heterogeneous gasification per Eqs. (1)-(3). The reverse water-gas shift reaction, Eq. (4), is also a significant gas phase reaction whose products are thermodynamically favored above approximately 850 °C. If the gasifier temperature is higher than about 1100 °C, little to no condensable species are present in the synthesis gas (syngas) product (Milne et al., 1998).

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (0.5x + 1 - y)H_2 \quad \Delta H_R > 0$$
 (1)

$$C_{(s)} + H_2 O \leftrightarrow CO + H_2 \quad \Delta H_{298K} = 131 \text{ kJ/mol}$$
(2)

ABSTRACT

High temperature steam gasification/reforming of biomass-methane mixtures was carried out in an indirectly heated entrained flow reactor to analyze the feasibility of controlling the output composition of the major synthesis gas products: H₂, CO, CO₂, CH₄. A 2³ factorial experimental design was carried out and compared to thermodynamic equilibrium predictions. Experiments demonstrated the product gas composition is mostly dependent on temperature and that excess steam contributes to CO₂ formation. Results showed that with two carbon-containing reactants it is possible to control the gas composition of the major products. At 1500 °C, the equilibrium results accurately predicted the syngas composition and can be used to guide optimization of the syngas for downstream liquid fuel synthesis technologies.

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$$C_{(s)} + CO_2 \leftrightarrow 2CO \quad \Delta H_{298K} = 160 \text{ kJ/mol}$$
(3)

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
 $\Delta H_{298K} = 41 \text{ kJ/mol}$ (4)

Several researchers (Adams and Barton, 2011; Dufour et al., 2009; Fiaschi and Carta, 2007; Perkins et al., 2010; Rodrigues et al., 2003; Song and Guo, 2007; Steinberg, 1997; Sudiro and Bertucco, 2007, 2009; Valin et al., 2009) have considered using methane, or natural gas, as an additive in thermochemical processes to increase the calorific value of the syngas or to improve combustion characteristics. Methane can be co-processed simultaneously with a carbonaceous solid (Adams and Barton, 2011; Perkins et al., 2010; Song and Guo, 2007; Sudiro and Bertucco, 2007, 2009), reacted in a parallel step to gasification (Adams and Barton, 2011; Borgwardt, 1997; Steinberg, 1997; Sudiro and Bertucco, 2009), added to the products of gasification and reacted further in a serial step (Adams and Barton, 2011; Dufour et al., 2009; Valin et al., 2009), or simply added to the products of gasification without further modification (Fiaschi and Carta, 2007; Rodrigues et al., 2003). The primary reactions methane undergoes in steam-only processing are outlined in Eqs. (5)-(7).

$$CH_4 \leftrightarrow C_{(s)} + 2H_2 \quad \Delta H_{298K} = 41 \text{ kJ/mol}$$
 (5)



^{*} Corresponding authors. Address: 3415 Colorado Ave., 596 UCB, Boulder, CO 80303, USA.

E-mail addresses: aaron.palumbo@colorado.edu (A.W. Palumbo), alan.weimer@ colorado.edu (A.W. Weimer).

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