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From coal towards renewables: Catalytic/synergistic effects during steam co-gasification of switchgrass and coal in a pilot-scale bubbling fluidized bed

Mohammad S. Masnadi [a, *], John R. Grace [a], Xiaotao T. Bi [a], C. Jim Lim [a], Naoko Ellis [a], Yong Hua Li [b], A. Paul Watkinson [a, b]

[a] Clean Energy Research Centre, Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver V6T 1Z3, Canada
[b] Highbury Energy Inc., Suite 1820 Cathedral Place, 925 West Georgia Street, Vancouver V6C 3L2, Canada

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ABSTRACT

Recent environmental sharp curbs on fossil fuel energy systems such as coal power plants due to their greenhouse gas emissions have compelled industries to include renewable fuels. Biomass/coal co-gasification could provide a transition from energy production based on fossil fuels to renewables. A low-ash coal and switchgrass rich in potassium were selected on the basis of previous thermogravimetric studies to steam co-gasify 50:50 wt% coal:switchgrass mixtures in a pilot scale bubbling fluidized bed reactor with silica sand as the bed material at ~800 and 860 °C and 1 atm. With the switchgrass added to coal, the hydrogen and cold gas efficiencies, gas yield and HHV of the product gas were enhanced remarkably relative to single-fuel gasification. The product gas tar yield also decreased considerably due to decomposition of tar catalyzed by switchgrass alkali and alkaline earth metals. Switchgrass ash therefore can act as inexpensive natural catalysts for steam gasification and assist in operating at lower temperatures without being penalized by an increase in product tar yield. An equilibrium model over-predicted hydrogen and under-predicted methane concentrations. However, an empirically kinetically-modified model was able to predict the product gas compositions accurately.

1. Introduction

The recent UN IPCC fifth assessment reports on “the physical science basis” [1], “impacts, adaptation, and vulnerability” [2], and “mitigation” [3] of climate change, once again underlining that anthropogenic warming of the atmosphere and ocean system is unequivocal. It is extremely likely that human impact has been the overriding cause of observed warming since 1950, with the level of confidence having increased since the fourth IPCC report [4].

Environmental legislative actions like the recent US government regulation on coal power plants [5] are imposing incentives to integrate alternative sources of fuels. The quest for substitutes to fossil fuels, the need to mitigate the negative environmental effects of fossil fuels utilization and the necessity to safely and economically dispose of wastes have encouraged the development of alternative sources of energy and utilization of low-quality fuels. Thermochemical co-conversion of coal and biomass for energy purposes and chemicals are among these alternatives [6].

Some synergistic benefits that might be realized by biomass/coal co-feeding are summarized in Table 1. Whether these can be realized in practice depends on operating and fuel conditions such as feedstock type, direct particle contact, temperature, pressure, reactor type, etc. [7]. As highlighted in Table 1 and presented elsewhere [8–11], alkali and alkaline earth metals (AAEM), induce catalytic activity. Wood et al. [12] found that, under identical conditions, the rate of steam gasification of char and carbon was about twice the rate of CO_2 gasification. Addition of K_2CO_3 enhanced the rate significantly. The same mechanisms were found to apply for both CO_2 and steam gasification. McKee and Chatterji [13] and McKee [14] proposed an oxidation-reduction sequence of elementary reactions parallel to those for CO_2 gasification to explain the catalytic effects of potassium, sodium and caesium carbonates in steam involving intermediate formation of hydroxide (see Fig. 1):

* Corresponding author. Chemical & Biological Engineering Building, 2360 East Mall, Vancouver, V6T 1Z3, Canada.
E-mail address: s.masnadi@gmail.com (M.S. Masnadi).

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Table 1
Summary of advantages of utilizing coal and biomass in co-gasification process.

Coal	Biomass
• High carbon content and energy density	• Carbon neutral if produced sustainably
• Economically viable and well-developed technology	• Higher hydrogen content than coal
• Relatively low transportation cost	• Higher reactivity and lower char yield than coal
• No seasonal limitation	• Catalytic carbonaceous materials gasification via biomass ash minerals (e.g. AAEM[a])
• Overcoming biomass feeding issues by co-feeding	• Catalytic tar reforming via biomass ash minerals (e.g. AAEM)
• Typically less tar release than for biomass	• Capturing chlorine and sulfur via AAEM
• Little or no need for pre-drying	• Less SO_x/COS/H_2S/NO_x/NH_3/HCN than for coal gasification
• Not fibrous	• Less heavy metals than coal
• Better fluidization properties	• Reduction of biomass landfill methane emissions
	• Improved energy source diversity and security

[a] Alkali and alkaline earth metals.

$$M_2CO_3(s,l) + 2C(s) \leftrightarrow 2M(g) + 3CO(g) \quad (1)$$

$$2M(g) + 2H_2O(g) \leftrightarrow 2MOH(s,l) + H_2(g) \quad (2)$$

$$2MOH(s,l) + CO(g) \leftrightarrow M_2CO_3(s,l) + H_2(g) \quad (3)$$

where M denotes an alkali metal. The sum of the above reactions is the steam-carbon reaction ($C(s) + H_2O \leftrightarrow H_2 + CO$ −131.2 kJ/mol). Since reaction (1) is inhibited by increasing amounts of CO, reaction (1) is likely to be rate-determining [15]. Other similar approaches have been reported in the literature for alkali metals [14,16–18,57]. Also mechanisms comparable to those of the alkali metals have been proposed for a cyclic sequence of redox reactions for alkaline earth elements [19,20].

Studies on synergistic effects during biomass/fossil fuel thermochemical co-conversion are scarce, confusing and have led to different conclusions [6]. Our lab-scale thermogravimetric investigation [9] showed that, depending on the biomass and fossil fuel minerals concentrations in the blend, two-fold inhibition and synergistic effects can be observed; Providing enough biomass alkali and alkaline earth metals (AAEM) to satisfy the fossil fuel ash aluminum and silicon contents, unreacted AAEM can catalyze fossil fuel gasification, consistent with results reported by Brown et al. [21].

As reference data, our pilot-scale parametric study on steam gasification separately of coal and switchgrass is presented elsewhere [22]. In this paper, steam co-gasification of the same biomass and fossil fuels in an atmospheric bubbling fluidized bed (BFB) reactor was investigated and the co-gasification is compared with the earlier single-fuel results. Minimizing the reactions Gibbs free energy, a computer simulation is also presented to predict the co-gasification product gas composition. This paper is one of the first works on catalytic effects of switchgrass on coal gasification in a pilot scale reactor.

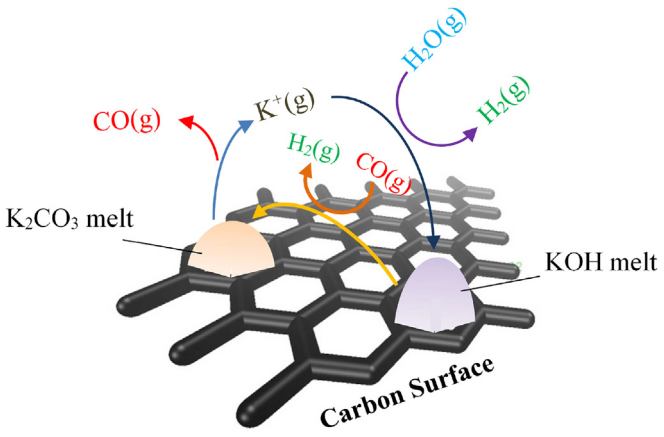

Fig. 1. Oxidation-reduction catalytic mechanism of potassium carbonate on carbonaceous material steam gasification.

2. Materials and methods

2.1. Feedstocks

Fossil fuel ash constituents, in particular aluminum and silicon, can be major obstacles to catalytic effects of biomass ash constituents on fossil fuel gasification. Previous results [9,10] led us to select a biomass whose ash is rich in potassium, and a thermal coal with low ash content, poor in aluminum and silicon, as fuels for pilot-scale co-gasification experiments. Thus, Ontario spring and fall harvest switchgrass (called SP-SG and F-SG, respectively) and Vancouver Island thermal coal were tested in this study. Table 2 presents the ultimate, proximate and elemental ash analyses of the parent fuels. The Quinsam mine coal contained much less ash and moisture (12.9 and 4.25 wt%, respectively) than the Alberta sub-bituminous coal tested in our co-gasification kinetics study [9] (30.5 wt% and 17.5 wt%, see Table 2), appropriate for this research; The silicon content of the Quinsam mine coal (16.9 wt%) was also less than for the sub-bituminous coal (26.9 wt%). Switchgrass ash samples were rich in potassium, 10.8 wt% for spring harvest switchgrass (SP-SG) and 21.8 wt% for fall harvest switchgrass (F-SG). The fall harvest switchgrass was therefore expected to have the highest catalytic effect on coal gasification, as it contained the highest proportion of potassium in its ash. Further details on the fuels characterization are provided elsewhere [8–11,22].

2.2. Experimental apparatus and operation

Steam co-gasification was performed in the Highbury Energy Inc. (HEI) pilot-scale bubbling fluidized bed (BFB) reactor using silica sand as the bed material. A simple schematic is shown in Fig. 2. See the Appendix (Fig. A1) for a more detailed flow diagram. The gasifier consisted of a 102 mm ID, 1219 mm long, stainless steel (800H/HT, S40, SMLS) pipe as an inner reactor, with a perforated gas distributor installed above the steam entrance. The sand was sieved to a particle size of 300–355 μm (US mesh #45–50) (resulting in Geldart group B particles). The static bed height for all experiments was ~0.30 m. This height was thought to be optimal for temperature distribution in the column based on previous HEI experiments. Key particle properties are listed in Table 3, with super-heated steam (at 525 °C and 1 atm) as fluid and the bubbling bed operated at an inlet superficial gas velocity of ~0.37 m/s. For