

From fossil fuels towards renewables: Inhibitory and catalytic effects on carbon thermochemical conversion during co-gasification of biomass with fossil fuels



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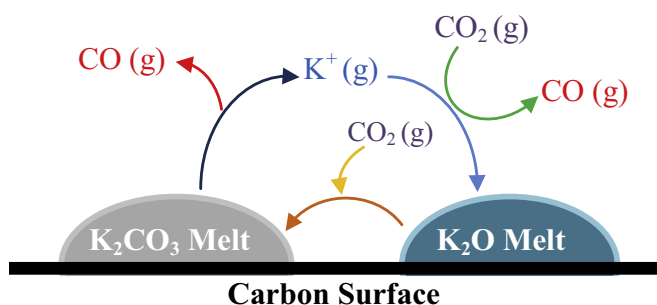
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HIGHLIGHTS

- Ash minerals have two-fold effects on biomass/fossil fuels co-gasification kinetic.
- For low potassium contents, inhibitory effect was observed during co-gasification.
- For $K/Al > 1$ M ratios, biomass enhanced coal gasification significantly.
- Biomass rich in minerals and fossil fuels poor in aluminosilicates are recommended.

GRAPHICAL ABSTRACT

Oxidation–reduction reaction pathways at the carbon/catalyst junction during CO_2 co-gasification.



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ABSTRACT

Recent environmental regulatory sharp curbs on fossil fuel power plants have obliged industries to incorporate alternative sources of fuels for energy production. Cost and recovery of synthetic catalysts are major challenges in carbonaceous materials catalytic gasification. Biomass rich in alkali metals can be added as fuel and also to provide inexpensive natural catalysts to boost fossil fuel gasification. Biomass/fossil fuel co-gasification could provide bridging energy production based on renewable and fossil fuels. In this work, CO_2 co-gasification of switchgrass and sawdust with coal and fluid coke was conducted in a thermogravimetric analyzer. Gasification kinetics were inhibited or enhanced, depending on the potassium concentration in the mixture. For low K/Al and K/Si molar ratios, the coal ash sequestered the biomass potassium needed for $KAlSiO_4$ formation, and thus, no catalytic effect was observed until the biomass-to-coal mass ratio reached 3:1, where the switchgrass ash supplied enough potassium to more than satisfy the minerals in the coal ash. For high K/Al and K/Si molar ratios, unreacted residual potassium acted as catalyst, enhancing coal gasification. Fluid coke contained much lower Al and Si than for the coal. Hence, the gasification kinetics of fluid coke were significantly augmented by blending the coke with switchgrass due to the abundance of potassium in the biomass.

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1. Introduction

Every day we use energy and ask for more. With global population set to rise from ~7 to ~9 billion by 2050 [1], world energy consumption is expected to increase by ~56% over the next 30 years

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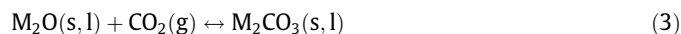
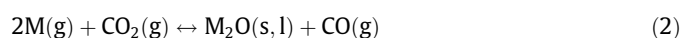
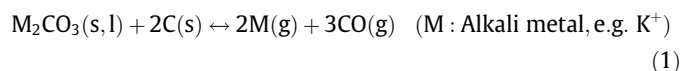
[2]. The world is far from achieving a sustainable energy future. Instead, we are intensely addicted to fossil fuels as the source of energy. Growth in global CO₂ emissions from energy use accelerated in 2013 [3]. Alarming statistics about the dramatic rise in atmospheric greenhouse gas (GHG) emissions [4] and consequent rise in the global surface temperature in recent decades oblige us to move towards sustainable technologies.

Among fossil fuels, coal continues to be a major global energy source throughout the 21st century. Coal consumption grew by 3% in 2013, well below the 10-year average of 3.9%, but it is still the fastest-growing fossil fuel. Coal's share of global primary energy consumption reached 30.1%, the highest since 1970 [3]. However, coal has a major drawback: it accounts for 44% of the share of global CO₂ emissions [5]. Legislative actions like the recent US Environmental Protection Agency (EPA) sharp curbs on coal power plants [6] have pushed industries to incorporate alternative sources of fuels.

Coal has low cost and high carbon content relative to biomass. Thus, the thermochemical conversion of coal via gasification to produce synthesis gas (syngas) is a feasible well-developed technology. Gasification has several advantages over direct combustion, including higher potential overall energy efficiencies, cleaner processing, relatively lower volumetric flow of flue gas for treatment, ability to transport in pipelines, ease of control and continuous operation. Alternatively, the produced syngas can be converted to a variety of downstream products such as dimethyl ether (DME), methanol, ethanol, transportation fuel, and acetic acid, as nicely depicted by Spath and Dayton [7].

Biomass is considered a carbon-neutral form of energy as the CO₂ released during its utilization is equal to the CO₂ absorbed from the atmosphere during its growth through photosynthesis. It also has lower sulfur, nitrogen and heavy metals than coal. However, biomass gasification technologies are typically not viable economically [8] due to the low energy density of biomass and its high transportation costs.

Catalyst can be added as an additional solid component to coal gasifiers to augment carbon thermochemical conversion. The presence of catalytic action in the char bed can also aid operation, decreasing the gas tar yield. The oxidation–reduction catalytic mechanism (see reactions (1)–(3)) of synthetic alkali and alkaline earth metals (AAEM) on carbonaceous materials gasification has been extensively studied [9–26]. Key steps are



The relative activities of alkali metal carbonates have been shown [11,27] to be Li₂CO₃ > Cs₂CO₃ > Rb₂CO₃ > K₂CO₃ > Na₂CO₃ for pure graphite (a pure and well-ordered carbon) H₂O or CO₂ gasification on a weight % basis. However for coal char gasification, the order of catalytic activity of alkali metal carbonates for gasification with H₂O and CO₂ has been reported to be: Cs₂CO₃ > K₂CO₃ > Na₂CO₃ > Li₂O₃ [12]. Potassium is one of the most effective catalysts for carbon gasification. Walker et al. [28] compared the catalytic activity of a lignite char for steam gasification in the presence of a number of inorganic cation species, demineralized chars and raw coal chars. The order of activity was found to be K > Ca > Na > - Fe > raw coal > Mg > demineralized coal. For steam gasification of a highly caking coal, Tomita et al. [14] found that the catalytic order was K > Ba > Ni > Fe > coal ash, for an ash containing iron, calcium and magnesium. Veraa and Bell [29] also found potassium to be the most effective cation in a study of a series of alkali salts for

steam gasification of a sub-bituminous coal char. Potassium compounds are mobile and more easily dispersed than calcium compounds. Unlike calcium, potassium appears to be able to diffuse through the char to form active gasification sites [9].

The activity of potassium salts depends also on the anion. For a series of potassium salts in graphite–CO₂ reaction, McKee [10] showed the carbonate, sulfate and nitrate to be more effective as catalysts than silicates and halides. K₂SO₄ was significantly less active than K₂CO₃ [12]. Alkali metal hydroxides were of similar effectiveness to carbonates in promoting CO₂ and H₂O gasification [29]. It seems likely that an oxygen-containing anion, or an anion which is converted to an oxygen-containing species, is necessary for effective catalysis [13]. The chlorides (i.e. LiCl, NaCl, KCl, RbCl and CsCl) appeared to behave in a similar manner, acting as inhibitors during the early stages of steam gasification, although accelerating the rate later [29].

Gasification proceeds by loss of carbon atoms from faces of basal planes, steps and crystal edges. If catalysts promote gasification by the former method, the formation of pits, which become progressively deeper and more circular, is observed. Catalysts acting on crystal edges produce a channeling effect [15,17]. Marsha et al. [16] reported that while isotropic components are more susceptible to gasification, anisotropic components (e.g. carbon prismatic edges) are more susceptible to attack by alkali, and therefore to catalyzed gasification.

Although adding synthetic catalysts can be very effective in enhancing gasification, cost and recovery of the catalysts are major issues. One possibility to address this is to co-gasify biomass with the coal, incorporating the ash minerals of the biomass, particularly its alkali constituents (e.g. K⁺, Na⁺ and Ca²⁺), as inexpensive natural catalysts to enhance co-gasification. Co-gasification reduces transportation costs for a facility of given size and greenhouse gas emissions. Biomass/coal co-gasification could therefore be a bridge between energy production based on fossil fuels and energy production based on renewable fuels [30]. Whether such positive synergetic effects can be realized depends on the gasification operating and fuel conditions, such as feedstock type, direct particle contact, temperature and pressure, and reactor type [31].

Studies on synergistic effects during biomass/fossil fuel thermochemical co-conversion are scarce and have led to different conclusions. Some authors [31–35] observed catalytic interactions during biomass/fossil fuel co-conversion, while others [36–38] did not. For instance, Brown et al. [32] performed a study on catalytic gasification of coal char using potassium salts, with CO₂ as the medium in a TGA. The results showed an almost eightfold increase in coal char gasification rate at 896 °C in a 10:90 by weight mixture of coal char and biomass ash. On the other hand, although the results of Hernandez et al. [39] in an entrained flow gasifier showed improvements in product gas quality and cold gas efficiency with increasing biomass content in the fuel blend, their thermogravimetric analyses did not provide enough information about possible interaction between biomass and coal–coke. A comprehensive literature review on co-gasification in different reactor types is provided elsewhere [40].

In our own previous study [41], co-pyrolysis kinetics of different pairings of two types of biomass with two types of fossil fuels were investigated. The rate data indicated that biomass and fossil fuel reacted independently in the blend samples, and adding biomass had no significant effect on fossil fuel pyrolysis weight loss patterns. The roles of both biomass and fossil fuel ash components during co-gasification have not been investigated systematically. In this work therefore, based on a systematic approach, we shed new light on kinetic interactions between biomass and fossil fuel chars during co-gasification, with the aid of a thermogravimetric analyzer (TGA).

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