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Fuel characterization and co-pyrolysis kinetics of biomass and fossil fuels

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HIGHLIGHTS

- ▶ The char yields of biomass and fossil fuels were almost independent of char ultimate temperature.
- ► Alkali and alkaline earth metals of biomass ash began to evaporate as the temperature rose.
- ▶ Biomass and fossil fuel pyrolyzed almost independently in blended mixtures.
- ▶ Pyrolysis of biomass and fossil fuels occurred in three stages.
- ▶ The reaction mechanism of each pyrolysis stage was inferred from the Coats-Redfern method.

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ABSTRACT

It is not well understood how co-feeding of coal and biomass influences the reaction kinetics of gasification and pyrolysis. Co-pyrolysis of biomass and fossil fuels is investigated in this paper. After fuel characterization, the influences of temperature on the physical and chemical properties of char produced from biomass and non-biomass fuels were investigated, and the kinetics of atmospheric-pressure pyrolysis in a nitrogen environment were determined. The results show that product physical properties, such as surface area, depend on the pyrolysis temperature. For individual fuels, pine sawdust char prepared at 750 °C had the highest CO₂ and N₂ uptake, while switchgrass had very low N₂ uptake, but high CO₂ uptake. The surface area of the fluid coke decreased with increasing temperature, but was almost constant for coal. Co-pyrolysis in a thermogravimetric analyzer exhibited three stages. Devolatilization of the biomass and coal portions of blended samples occurred independently, i.e. without significant synergy. The Coats–Redfern method was used to analyze the kinetics of solid fuel pyrolysis, indicating that it can be described by multi-step reactions. The model was able to identify likely reaction mechanisms and activation energies of each pyrolysis stage, giving predictions consistent with the experimental results.

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1. Introduction

The world is off course for a sustainable energy future. There are persistent concerns about the long-term balance of supply and demand, and CO_2 emissions have increased dramatically over the last decade. If the future aligns with present trends, GHG emissions of CO_2 , CH_4 and N_2O , and oil demand will continue to grow rapidly over the next 25 years [1,2]. Among alternative energy sources, biomass is promising, since it is widespread and cheaply available in many countries. Canada enjoys the third largest share (6%) of the world's forest resource [3] and is a leader in biomass utilization [4]. Biomass constitutes more than 10% of the global primary energy demand [5]. Among bioenergy technologies, gasification is one of the most promising and diversified clean energy options. The major challenge to achieve commercialization of biomass gasifiers is the high cost of harvesting and transporting the fuel supply. This leads to heavy dependence on the proximity of the gasifier to the bio-feedstock source, while coal can be transported more easily and economically due to its higher density and concentration at source.

As a fossil fuel, coal can be burned to produce heat, coupled with gas turbines or fuel cells to produce electricity or converted into synthesis gas (syngas) to produce liquid fuels and other chemicals. Catalysts, such as alkali salts, can also be added to the feed solids of coal gasifiers [6]. However cost and recovery of the catalysts are major issues in catalytic gasification.

Adding biomass is an attractive way of reducing CO_2 emissions from coal, as the carbon in biomass is neutral since it has been





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Nomenclature			
$A \\ E \\ f(\alpha) \\ F \\ g(\alpha) \\ k \\ m_i \\ m_0 \\ m_f \\ m_{0,dry}$	pre-exponential factor (s ⁻¹) activation energy (J mol ⁻¹) reaction mechanism function (-) mass fraction of fuel (-) function defined by Eq. (5) (-) reaction rate constant (s ⁻¹) mass of fuel at time t (g) mass of fuel at $t = 0$ (g) final mass of fuel (g) dry mass of fuel at $T = 200 ^{\circ}\text{C}$ (g)	m _{calc} m'i q R t T T _{peak} α	expected mass of fuel based on calculation (g) ash free mass of fuel at time t (g) heating rate constant (K s ⁻¹) universal gas constant (J mol ⁻¹ K ⁻¹) time (s) temperature (K) temperature at the highest rate of devolatilization of fuel (K) chemical conversion (-)

produced from atmospheric CO₂ through photosynthesis over times short relative to fossil fuel time scale. Thermochemical conversion of biomass for power generation could result in negative CO₂ emissions if coupled with carbon capture and storage (CCS) technologies. However adding biomass to coal during thermal conversion may have synergistic interactions, positive or negative affecting the thermal reactivity or chemical or physical properties of the solid, liquid and gaseous products [7]. For instance, the interparticle mobility of potassium may allow transfer of catalyst species from a biomass feedstock to a second less reactive feedstock. Hence, ash from some types of biomass could provide inexpensive catalysis for fossil fuel gasification.

Synergistic interactions during co-pyrolysis of coal and biomass have been widely investigated [8-10]. The observed synergistic effects might be due to "gas-coal" or "char-coal" interactions. It has been shown [9,10] that coal pyrolysis may be influenced by product gases (CO, CO₂, H₂, CH₄, H₂O) which rapidly evolve from biomass at high temperatures, resulting in variations in reaction kinetics, conversion and product distributions. Biomass contains a much higher proportion of oxygen-containing species than coal, which may be major contributors to such "gas-coal" interactions. Thermochemical conversion of coal may also be influenced by "char-coal" interactions due to the presence of alkali and alkaline earth metal species, which are present in greater abundance in biomass than in coal. These effects on co-pyrolysis kinetics are less well studied. Although some previous studies showed catalytic effect of alkali and alkaline earth metals on the reactivity and volatile product distribution during pyrolysis [11,12], it is unclear whether alkali and alkaline earth metals from biomass catalyze high temperature pyrolysis of coal. There is still debate in the literature over whether there are kinetic and product distribution effects when biomass is added to coal [13].

Full understanding of co-feed gasification stage is not possible without studying the change in the feedstock physical and chemical properties during pyrolysis [14,15]. The focus of this paper is therefore on physical and chemical fuel characterization and pyrolysis kinetics of blended biomass and fossil fuels, as a foundation for enhancing understanding of the kinetic effects of biomass on fossil fuel gasification and the interaction between biomass and fossil fuel minerals [16]. Physical and chemical properties of two fossil fuels (sub-bituminous coal and fluid coke) and two types of biomass (switchgrass and sawdust) were first investigated at different pyrolysis temperatures. The surface area of each fuel was analyzed using Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich-Kaganer (DRK), and scanning electron microscope (SEM) methods. Next, the pyrolysis kinetics of fresh and blended samples were studied in a thermogravimetric analyzer (TGA). Finally, a kinetic model was developed to predict the fuel conversion, and to determine the pyrolysis activation energy of single-fuel and mixture reactions.

2. Experimental

2.1. Feedstock

Two types of Canadian biomass with widely differing ash compositions, Manitoba switchgrass (SG) and beetle-killed BC pine sawdust (SD) from British Columbia, were chosen. Panicum virgatum, commonly known as switchgrass, is a perennial warm-season bunchgrass native to North America, where it occurs naturally from Canada southwards into the United States and Mexico. Switchgrass has also been identified as having potential as an energy crop for Eastern Canada [17] and for the US, where it was selected as a model herbaceous crop for Oak Ridge National Laboratory's Biofuel Feedstock Development Program [18].

The fossil fuels were an Alberta Genesee coal, classified as subbituminous and suitable for IGCC systems for electricity generation [19], and fluid coke (FC) from Syncrude Canada Ltd. in Fort McMurray, Alberta, a low-ash fuel. The fluid coke is a byproduct in the conversion of oil sands bitumen to synthetic crude oil. Large quantities of this coke are being stockpiled in northern Alberta [20]. Containing over 85 wt.% carbon, the oil sands fluid coke represents a significant energy resource.

2.2. Sample characterization

All samples were crushed and sieved to a particle size of 300-355 µm (US mesh #45-50) before the analysis and pyrolysis experiments. ASTM D346 and D346M-11 were used for feedstock sampling. All fresh samples were characterized according to ASTM D3176/D5373 for carbon, hydrogen, nitrogen and sulfur (CHNS) content (based on Elementar vario MACRO); ASTM D4239 for total sulfur content (using Leco S632); ASTM D3174 for ash content (using Carbolite AF1100 ashing furnace); ASTM D3302/D3173 for moisture content (via Carbolite MFS/1); ASTM D3175 for volatile matter (using Leco S632) and ASTM D5865 for heating value (using Leco AC600). The "blend samples" were well-mixed mechanically prior to being added to the reactor basket. Elemental carbon, hydrogen, nitrogen and sulfur was performed on dried MoP precursors, calcined MoP precursors and reduced/passivated MoP, using a Perkin-Elmer 2400 Series II CHNS/O analyzer operated in the CHNS mode [21].

BET tests (nitrogen adsorption) were performed for fresh samples, as well as for chars derived from these samples, to determine their surface areas using a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to the adsorption measurements, the samples were degassed at 105 °C and 0.15 mbar_{abs} for 24 h. N₂ surface areas were calculated using the Brunauer–Emmett–Teller equation [22], whereas the Dubinin–Radushkevich–Kaganer equation [23] was used to determine CO₂ surface areas, as it is more

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