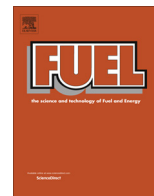




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Influence of char composition and inorganics on catalytic activity of char from biomass gasification

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ABSTRACT

This research investigates the catalytic properties of char which was recovered directly from a biomass gasifier. Poplar wood was gasified in steam and CO₂ environments in a fluidized bed reactor at temperatures ranging from 550 to 920 °C. Char was composed of 85% carbon with concentrations of N, H, and S between 0.3% and 3%, depending on gasification conditions. The inorganics (Ca, K, Na, P, Si, Mg) were quantified, revealing that Ca was present in the highest concentration (0.5–1%), followed by K, ranging from 0.1% to 0.8%. The char had catalytic activity for decomposition of methane, which was used as a model molecule. The quantity of inorganics in the char was modified by acid washing in 16% aqueous HCl, which removed >95% of Ca, K, P, and Mg from the char. This resulted in an 18% decrease in the quantity of methane reacted compared to the original char sample, demonstrating that inorganics, which only make up approximately 2% of the char, play a significant role in its catalytic activity for methane cracking reactions. In addition, carbon was found to play an important role in the catalytic activity of the char, both as a catalyst and a support on which the inorganics were dispersed. The activity of carbon free ash was approximately 90% lower than that of char, and deactivated to have no measurable activity after 45 min on stream, demonstrating the importance of carbon and dispersed inorganics for catalytic activity. When char was heated to 1000 °C in N₂, inorganics and oxygen migrated to the surface of the char, covering the carbon surface in a metal oxide layer. This decreased the catalytic activity by approximately 40%. Acidic (e.g. carboxylic, lactones) and basic (e.g. carbonyl, pyrone) oxygen functional groups were identified on the char surface. However, acidic oxygen groups desorbed at reaction temperatures, so these groups likely do not participate in cracking reactions.

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1. Introduction

In recent years, there has been growing interest in gasification as a method for energy recovery from solid fuels such as biomass, waste, sludge, or coal. The primary product of gasification is synthesis gas, which is a gas mixture that is rich in CO and H₂. Synthesis gas can be used for production of fuels or chemicals (ex. diesel, methanol, ethanol), for steam generation via combustion boilers, or for electricity production in a gas turbine or fuel cell. One of the main issues with commercialization of gasification processes is the production of by-products such as tar and char. Tar is a mixture of hydrocarbons that condense at standard conditions, and must be either removed or reformed because it can cause problems in downstream equipment such as clogging or deposition

on surfaces. One way to address this is to catalytically reform tar, which increases the gaseous product yield. However, when using heterogeneous feed stocks such as agriculture or forestry residues, or municipal solid waste, catalysts are prone to deactivation. For example, sulfur or chlorine species which are present in the feed-stock may poison catalytic sites or tars may crack and form coke on the catalyst. In this research, we are investigating utilization of char as a catalyst for tar reforming. This would be beneficial since the char is produced on-site, making it a cheap and available resource. In this research, the surface reactivity of char that was recovered directly from a biomass gasifier (with no modification) is studied. The contribution of inorganics, carbon, and oxygen groups to the catalytic activity of char is reported.

1.1. Catalytic activity of char

Char has been considered for a variety of applications such as energy recovery (via combustion), soil amendment, or as daily

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cover for landfills. This research investigates utilization of char in high value applications, such as catalysis. In recent years, char, or similar materials such as activated carbon (AC), have been reported to have catalytic activity for reforming or cracking of hydrocarbons [1–7]. When placed downstream of gasifiers, these materials have been shown to reduce tar production and increase syngas yield [2,3,7]. In addition, char has been used as a support for different metals (Ni, Fe) and these catalysts have been used for reforming of biomass tars and tar surrogate compounds [6,8].

Char properties vary with gasification conditions, so it is important to understand how these properties influence the catalytic activity of char. This enables one to identify which gasification processes produce char which is appropriate for use in catalytic applications. While char has similar properties to materials such as activated carbon (AC) and carbon molecular sieves (CMS), which have been studied extensively, there are some important differences. Since char is a by-product of gasification, its properties are dictated by the gasification conditions and the starting feedstock. The primary objective of a gasification process is to produce a high yield of syngas with a CO/H₂ ratio that is appropriate for a targeted end use. Therefore, the process conditions in which the char is produced are adjusted so the syngas yield is maximized. In contrast, in processes where the primary product is AC, the material is often chemically activated with potassium hydroxide, phosphoric acid, or steam which can affect both surface area and surface oxygen groups. In addition, AC is often de-ashed via acid washing whereas char is not. With growing interest in co-gasification of biomass with coal or municipal solid waste, which contain higher concentrations of ash species, it is important to consider the role of ash species in the catalytic activity of the char. Furthermore the oxygen functional groups may affect the catalytic activity and are also studied here.

In addition to surface chemistry, catalytic activity is affected by char morphology. In a previous publication, we reported the influence of char surface area and porosity on its catalytic activity [11]. Higher gasification temperatures (up to 920 °C) produced char with higher surface area. For example, increasing the gasification temperature from 750 to 920 °C in a CO₂/N₂ environment resulted in an increase in surface area from 435 to 687 m² g⁻¹. For all surface area measurements, the correlation coefficient was greater than 0.999. Preliminary data showed that char with higher surface area had higher catalytic activity. The goal of the research presented in this paper is to further understand the contributions of inorganics, carbon, and oxygen groups to the catalytic activity of char that was recovered directly from a biomass gasification process.

1.2. Inorganics in biomass char

Biomass is primarily composed of carbon, oxygen, and hydrogen in molar ratios of approximately 6/4/10. Importantly, it also contains inorganics which have been demonstrated in the literature to impact various reactions. The inorganic fraction of biomass is typically composed primarily of alkali and alkaline earth metallic species (AAEM), such as Ca, Na, K, Mg, but also contains Si and P, and transition metals such as Fe, Al, and Mn. While the concentrations of these elements vary depending on the species of biomass or its growing conditions, they are found in many types of biomass. Dupont et al. characterized the inorganic elements in 21 different types of wood, including spruce, poplar, oak, pine, and beech, and found significant differences in concentrations, yet commonality of species [12]. For example, ash content varied from 0.5% to 4.3%, calcium varied from 0.086% to 1.6% by mass (based on dry biomass), and potassium concentration varied from 0.011 to 0.18% by mass (based on dry biomass). Yip et al. determined that the ash of mallee biomass contained >85% alkali and alkaline earth metallic species (AAEM) [13], and that 80–90% of these inorganics

remained in the solid residue following steam gasification at 750 °C. Others have observed volatilization of some of the inorganic species during gasification [14,15]. However, in general at least some fraction of the inorganics remain in the solid residue after gasification. Therefore, char from biomass gasification has an inorganic fraction which will remain despite the starting feedstock and operating conditions that will influence its catalytic activity.

1.3. Catalytic activity of inorganic elements in gasification reactions

Gasification involves many complex reactions and significant efforts have been made to understand reaction mechanisms. It has been shown that inorganics participate in catalyzing gasification reactions. For example, Yip et al. gasified mallee biomass and observed lower reactivity when the feedstock had been acid washed prior to gasification [13]. Marquez-Montesinos et al. studied the role of inorganics on gasification of grapefruit skin char and found that the presence of inorganics improves the reaction kinetics [16]. Dupont et al. correlated the rate of gasification to the ratio of potassium to silicon in the biomass, and concluded that potassium has a catalytic effect and silicon an inhibitory effect [12]. Habibi et al. also observed inhibitory effects of silicon during co-gasification of potassium rich switchgrass with high ash sub-bituminous coal. They found that the potassium can be rendered inactive when potassium aluminosilicate is formed [17]. Since inorganics have been correlated to gasification kinetics it is important to more quantitatively understand how they impact the catalytic activity of char, specifically for hydrocarbon decomposition reactions. Tar reforming with steam showed Ni-char catalysts performing better than Fe-char. The authors chose to further study the Fe-char and obtained an interesting finding. The syngas produced during the reforming maintained Fe in the reduced state comparable to pre-reduction which gave the catalyst its activity [18]. Fe-char catalyst from coal showed stable activity for up to 50 min time on stream for the steam reforming of mallee biomass tar. It was also found that the activity was affected by the char structure and the properties of the Fe speciation [19].

1.4. Role of oxygen groups in catalytic activity of carbon materials

It is well known that acid groups play a role in many types of catalytic reactions, such as cracking, isomerization, and polymerization [20]. Acidic or basic sites are formed on a char surface when oxygen reacts with defect sites on the surface, forming functional groups. Some examples of the functional groups detected are carboxylic acids, lactones, or phenols (acidic) and pyrones or chromenes (basic). Acidic surface groups have been studied more extensively than basic sites, and it is understood which types of surface functionalities give rise to surface acidity [21,22]. In general, acidic sites are formed when a surface is heated in an oxidizing environment and basic groups are formed when an oxidized surface is reduced by heating in an inert environment [22].

The surface functional groups influence the adsorption of molecules to the char surface. For example, oxygen sites enhance the adsorption of polar molecules, such as water which is present in many systems. Lee et al. studied the adsorption of water vapor on chemically activated carbons derived from coal and wood and found that in cases where the relative pressure of water was low ($P/P_0 < 0.4$), the density of oxygen groups on the carbon surface was the most important factor that influenced water adsorption [23]. When char is used as a catalyst, reactants must adsorb to the surface, react, and products must desorb. However, it is not desirable for molecules that do not participate in the catalytic reaction to adsorb to the surface as this can hinder access to catalytic sites. Therefore, surface properties and the adsorption of reactant

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