



# Catalytic decomposition of tar using iron supported biochar



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## ABSTRACT

Iron supported biochar catalysts were used to decompose toluene, a model tar compound, over a temperature range of 600–900 °C. Toluene conversion and decomposition rates increased linearly with increasing temperature and catalyst loading from 600 to 700 °C. Relative to biochar alone, the iron supported catalysts lowered the activation energy by 47% and decreased the formation of benzene, an intermediate in toluene decomposition. At 800 °C for the 13 and 18.7 wt.% iron loaded catalyst, toluene conversion approached 100% and benzene selectivity ( $S_B$ ) was zero, compared to an  $S_B$  of 0.025% and 0.35% for 10% iron and the biochar, respectively. Time on stream studies with the 13 wt.% iron biochar catalyst, over the course of four days, resulted in a mean toluene conversion of 91% and benzene selectivity of 0.02%. These results indicate that inexpensive iron impregnated biochar catalysts could potentially be used to catalytically decompose tar molecules in syngas generated via biomass gasification.

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## 1. Introduction

Gasification and pyrolysis are two technologies that can be used to generate renewable  $H_2$ , synthesis gas ( $CO_2$ ,  $CO$ ,  $H_2$ ), or bio-oils from biomass. The synthesis gas can be catalytically reformed into liquid fuels (e.g., methanol, hydrocarbons), or  $H_2$  and used directly in fuel cells [7,17]. Bio-oils can, in theory, be converted to fuels and chemicals [24]. One of the major drawbacks limiting the use of biomass in both processes is the generation of tar, which can coke downstream reforming, upgrading, Fischer–Tropsch, and fuel cell catalysts, foul other unit operations, and is an environmental hazard (toxic and carcinogenic – [19]). Tar is typically composed of toluene (24%), one ringed aromatics other than toluene (22%), naphthalene (15%), 2 ringed PAH's other than naphthalene (13%), 3–4 ringed PAH's (7%), phenolics (7%), and heterocyclics (10%) [18]. Catalytic removal or transformation of tar to synthesis gas components is the most practical method of solving this problem compared to physical separation or thermal treatment of the tar [18].

A wide range of catalysts have been studied for tar removal including, Ni supported catalysts, dolomite, olivine, zeolites, and carbon supported catalysts [18]. Olivine (a mineral containing magnesium, iron, and silicon) has low surface area ( $<0.5 \text{ m}^2/\text{g}$ ), typically requires calcination at high temperature (e.g., 900 °C in air for 10 h) and has low activity, which results in lower tar decomposition rates relative to other catalysts [4,18,3] and deactivates rapidly due to coke formation and low surface area [18]. Iron is theorized to be the catalytically active

metal in olivine and significant efforts have been explored to increase the surface area and active site density of this metal in olivine [18]. Dolomite ( $CaMg(CO_3)_2$ ), although an effective tar removal catalyst, easily sinters and rapidly deactivates, again leading to a significant reduction in tar removal (Dayton et al., 2002). Zeolites and Ni supported catalysts are more expensive than olivine and dolomite, and coke easily [18,3] leading to a significant reduction in tar removal. Key attributes of an effective catalyst for tar removal are low cost, high activity, resistant to coking and poisoning, and ease of regeneration [3]. Only recently have carbon catalysts been studied for tar removal/transformation and may hold advantages over the other catalysts, including high surface area and resistance to coking [18].

Biochar produced by slow or fast biomass pyrolysis is an attractive carbon catalyst or support since it is inexpensive, produced from biomass (i.e., lignocellulosics) and not mined, can have high surface area, and contains catalytically active alkali metals which migrate to the surface upon pyrolysis. Recent research indicates that biochar catalytically removes tar components partly due to the presence surface alkali metals such as Na, Ca, K and potentially Fe ([1,12]).

However, tar removal rates using biochar are lower than metal supported catalysts, such as Ni/olivine and Ni/dolomite [23]. Attaching an active metal to the biochar surface may improve biochar catalytic performance. Nickel supported catalysts have been studied extensively and shown to have high tar removal rates, yet rapidly deactivate due to coke deposition and  $H_2S$  poisoning, and pose an environmental risk upon disposal [23]. Alternatively, iron, an earth abundant, non-toxic metal, can potentially be used for tar removal. Previous research indicates that iron and iron oxides (hematite,  $Fe_2O_3$ , reduced to magnetite,

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Fe<sub>3</sub>O<sub>4</sub>) can act to catalytically oxidize tar and ammonia as well [16], potentially by promoting steam reforming and the water gas shift reaction. Most research using iron oxide or iron as a tar removal catalyst has been studied using aluminum, olivine, or coal char as a support [2,16,22]. Given the limited information on the kinetics of tar removal and longevity of iron loaded catalysts synthesized from biochar, our objectives were to determine the reaction kinetics for catalytic cracking of toluene using iron supported biochar and evaluate the longevity of the catalyst for tar cracking applications.

## 2. Materials and methods

### 2.1. Catalyst preparation

Char was prepared by pyrolyzing pine bark (Southern Pine bark, Waycross, GA) at 950 °C for 2 h as described in [12]. Iron loaded biochars were prepared by dissolving 16 g of ferric nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O; Sigma Aldrich, 98<sup>+</sup>%] in 20 mL of acetone, and subsequently mixing 20 and 15 g of char respectively (~9 and 13 wt.% Fe). An additional type of catalyst was prepared by dissolving 24 g of ferric nitrate in 30 mL of acetone and adding 12 g of char (18.7 wt.% Fe). The biochars were contacted with the iron nitrate solution for 30 min, until there was no excess liquid, and subsequently dried at 105 °C (air) for 8 h. The dried samples were calcined at 300 °C for 1 h in a furnace with air flow of 10 L/min.

### 2.2. Catalyst characterization

The physical and chemical characteristics of biochar and iron loaded biochar were determined and included surface area, pore size distribution (BET and BJH methods, using a Quantachrome Autosorb 1C, Quantachrome, Boynton Beach, FL), and elemental composition as described in Mani et al. [12].

X-ray diffraction (XRD) analyses were performed with a Scintag XDS 2000 diffractometer equipped with a cobalt X-ray tube. Powdered samples were mounted on quartz plates and stepped scanned over the angular range 15–50° 2θ. The step size for the analysis was 0.01° 2θ with a count time of 10 s/step. All crystalline phases were identified based on comparison of the observed data with a reference database of crystalline materials produced by the International Center for Diffraction Data (ICDD). In this study a scanning electron microscope (SEM-EDS, FEI Inspect F FEG-SEM equipped with EDAX-EDS, EDAX is energy dispersive analysis of X-rays) was used to image the biochars. Prior to scanning, the powdered samples were coated with gold and spread out on a scanning plate and EDAX-EDS used to determine the elemental composition and mapping of the surface. Quantitation was achieved by comparing the X-ray yields from the sample with yields obtained from standards and ZAF (Z = element number, A = absorption, F = secondary fluorescence) correction was applied for bulk sample analysis using the following equation,  $C_{\text{spec}}/C_{\text{std}} = k Z A F c$ . Where,  $C_{\text{spec}}$  is the element concentration in the catalyst sample or specimen,  $C_{\text{std}}$  is the concentration of the element in the standard, Z is the atomic correction factor, A is the absorption correction factor, F and c are secondary fluorescence corrections for bremsstrahlung and continuum radiation respectively, and k is ratio of X-ray intensity (I) for the specimen to standard;  $k = I_{\text{spec}} / I_{\text{std}}$  [13,14].

### 2.3. Catalyst testing

The catalytic conversion of toluene was studied in a previously described continuous flow packed bed reactor system at different temperatures (400–900 °C) and atmospheric pressure. Nitrogen was used as the carrier gas (700 mL/min) and streams of toluene and water were added to the main flow by two syringe pumps. Toluene was injected using a stainless steel syringe (Cole-Parmer-74900 series, 60 mL) and water was added using a syringe (Becton Dickinson

Plastipak 60 mL, Luer lok tip). The nitrogen, toluene and water mixture was then passed through a static mixer (stainless steel, length — 0.53 m, o.d. 0.006 m) and then transported down the reactor (stainless steel, length 0.6 cm, i.d. 0.025 m), enclosed in a furnace (Lindberg Blue M), containing a 0.45 m preheating zone, followed by 0.03 m of catalyst supported by a steel wire mesh (0.025 m i.d.) and quartz wool (Leco fine quartz wool; 3.8 g catalyst or biochar). Previous details concerning the reactor set-up and conditions implemented during catalytic testing have been published [12].

### 2.4. Mass transfer effect calculations

Given the small particle size range of the catalysts (0.2–0.4 mm), medium range surface area (180–350 vs. 1000–1500 m<sup>2</sup>/g for activated carbon) and pore volume (Table 1), we did not expect that external or internal mass transfer would limit toluene decomposition and falsify our kinetic analysis. Additional evidence is presented to indicate that external and internal mass transfers were not rate limiting and thus criterion for external diffusion (Eq. (1)) and internal diffusion (Eq. (3)) were calculated [6].

#### 2.4.1. External effects

According to the Mear's criterion (Eq. (1)) if the calculated value is less than 0.15, external mass transfer effects can be neglected.

$$\frac{r_{\text{Toluene}} \rho_b R n}{k_c C_{\text{Toluene}}} < 0.15 \quad (1)$$

where,  $r_{\text{Toluene}}$  is the measured reaction rate (mol g<sup>-1</sup> s<sup>-1</sup>),  $\rho_b$  is the packing density of the catalyst bed (g m<sup>-3</sup>), R is the catalyst particle radius (in m; in this case we used a particle diameter,  $d_p = 1000 \mu\text{m}$  or  $R = 5 \times 10^{-4}$  m),  $n$  the reaction order,  $k_c$  (m s<sup>-1</sup>) the mass-transfer coefficient shown in Eq. (2),  $D_{AB}$  the effective diffusivity of toluene in N<sub>2</sub> ( $4.24 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>, 823 K); estimated using the Wilke–Lee equation [21],  $Re$  the Reynolds number based on the particle size,  $Sc$  the Schmidt number, and  $C_{\text{Toluene}}$  the bulk gas phase concentration (mol m<sup>-3</sup>).

$$k_c = 0.6 \left( \frac{D_{AB}}{d_p} \right) Re^{1/2} Sc^{1/3} \quad (2)$$

The Mear's criterion for the highest reaction rate data (4500 ppmv toluene, 550 °C, 19 wt.% Fe-biochar) ranged between 0 and 0.007, significantly less than 0.15 (for  $k_c = 0.02$ – $0.5$  m s<sup>-1</sup>,  $n$  or reaction order = 1–1.5, and  $d_p$  0–1 mm), indicating that external mass transfer limitations did not occur.

#### 2.4.2. Internal effects

SEM and BET analyses of the biochar and iron supported char clearly indicated a surface area and pore structure in the material used in our experiments (Fig. 1 and Table 1), suggesting possible internal mass transfer resistance [12]. Thus, the Wiesz–Prater criterion ( $C_{WP}$ ), Eq. (3), was used to estimate the effect of internal mass transfer in the reactions with the iron supported catalysts [6], where a  $C_{WP} \ll 1$  indicates that internal mass transfer resistance can be ignored.

$$C_{WP} = \frac{-r_{\text{Toluene}} \rho_p R^2}{D_e C_{\text{Toluene,s}}} \quad (3)$$

The Wiesz–Prater criterion ( $C_{WP}$ ) was estimated to be 0.0–0.2 (much smaller than 1) for biochar and the iron supported catalysts ( $d_p = 0$ –1 mm;  $R = d_p / 2$ ), utilizing measured reaction rate data, the measured catalyst packing density ( $\rho_p$ ), the concentration of toluene at the surface ( $C_{\text{Toluene,s}}$ ) and an estimated effective diffusivity,  $D_e$  ( $\sim 1$ – $2 \times 10^{-8}$  m<sup>2</sup> s<sup>-1</sup>). The effective diffusivity was estimated from the toluene–N<sub>2</sub> diffusion coefficient ( $D_{\text{eff, Toluene}}$ ) and Knudsen diffusion

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