

# GREEN AND SUSTAINABLE CATALYSIS USING A PALLADIUM DOPED BIOCHAR UNDER MILD CONDITIONS

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## Abstract

With ever increasing scrutiny of how industrial chemistry is conducted, biochar offers a route to the preparation of green heterogeneous catalysts. Biochar is simply prepared by the pyrolysis of pretreated lignocellulosic biomass in an inert atmosphere. Biochar supported Pd nanoparticles showed great potential in the liquid phase selective hydrogenation of phenylacetylene under mild conditions, without sacrificing activity, as validated by the LECO GCxGC 7890B. It was found that varying the pyrolysis temperature altered the activity of the Pd/Char catalyst resulting in an activation energy as low as 10 kJ mol<sup>-1</sup>.

## Introduction

To lower energy requirements and provide greener, more sustainable options for the production of fine chemicals and fuels, the use of catalysts derived from waste materials has gained attention. Specifically, the use of carbonised lignocellulosic biomass as a support material.<sup>1</sup> The biochar support is produced via the slow pyrolysis of biomass in an inert atmosphere and can then be doped with a metal generating a functionalised biochar derived catalyst. These have seen significant interest as compared to other commercial catalysts like metal oxides as biomass is cheap, requiring no ore extraction/refinement with readily available renewable stocks.<sup>2</sup> The lignocellulosic waste used in this work is barley straw, a highly abundant feedstock. Before use, these waste streams must undergo pre-treatments (milling, leaching) to remove the presence of any additional metal such as alkali and alkali earth metals (AAEM). AAEM are known to degrade the char during the pyrolysis process, thereby reducing the biochar yield. Whilst the presence of AAEM complicates biochar production it is negligible compared to the shortcomings of current industrial methods.

Styrene is a key industrial compound used in the synthesis of polymers vital for the modern world, such as ABS, EPS and PS. The global demand for styrene has increased by 500% since 1983. Industrially styrene is produced through the energy intense dehydrogenation of ethylbenzene using potassium iron (III) oxide as a catalyst at 600-650 °C, accounting for 99% of global ethylbenzene demand in 2020 so far. Due to this energy intensive process the production of styrene has a massive environmental strain. As such new methods look to produce styrene from the selective hydrogenation of phenylacetylene under very mild conditions with high selectivity.<sup>3</sup>

Our goal is to expand on this process using, biochar supported catalysts to sustainably produce styrene from phenylacetylene under mild conditions, achieving high selectivity and high conversion of the phenylacetylene in the liquid phase. This would be tested using palladium supported on biochars pyrolyzed at a range of temperatures to determine if there are physical or chemical alterations to the support that can promote the phenylacetylene hydrogenation.

## Biochar preparation

Barley straw, a highly abundant herbaceous and low-quality feedstock was milled (10,000RPM) using a Retsch GM200 Knife Mill for 1 min, followed by separating via a Retsch AM200 sieve stack to reclaim <250µm particles. These fractions were then pretreated via leaching in deionized water, with a feedstock ratio of 10 g L, for 24 h at 25 °C. The slurry was separated and dried under vacuo before drying in a Fisherbrand Gravity Convection Oven at 105 °C for 24 h, according to ASTM standards.<sup>4</sup> The leached feedstock was pyrolysed in a tube furnace at 500 °C, 600 °C or 700 °C (5 °C/min heating rate, holding for 1 h) under N<sub>2</sub> flow. This was left to cool to room temperature under a N<sub>2</sub> flow to prevent the char combusting. Biochar was then washed with 20 mL deionised water, ethanol and acetone before subsequently dried at 105 °C for 24 h.

## References

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## Catalyst preparation

A series of biochar supported Pd catalysts were prepared via incipient wetness impregnation (IWI).<sup>5</sup> The nominal metal loading of all catalysts synthesised was kept constant at 5 wt. %. Three types of monometallic catalysts Pd/C<sub>500</sub>, Pd/C<sub>600</sub> and Pd/C<sub>700</sub> were prepared. In a typical synthesis of Pd/Biochar, biochar was impregnated with the appropriate amount of Pd(ac)<sub>2</sub> (Sigma Aldrich). Before adding the saturated solutions of corresponding metal salts to the bare support, the solutions were sonicated in a water bath for 0.5 h to ensure complete metal salt dissolution. After sonication, the solutions were dispersed onto the support under continuous stirring at room temperature for 2 h before heating to 80 °C and aging overnight. Subsequently, the catalyst slurries were collected, annealed and reduced under flowing 10% H<sub>2</sub>/N<sub>2</sub> at 450 °C for 2 h at 5 °C/min.

## Biochar and Catalyst Characterisation

Scanning Electron Microscopy (SEM) images were acquired via a Zeiss EVO 60 instrument at a pressure of 10<sup>-2</sup> Pa and an electron acceleration potential of 20 kV (Figure 2). Energy Dispersed X-ray spectroscopy (EDX) was carried out on bare biochars using an Oxford Instruments Inca System 350 (Table 1). Fourier Transform Infrared (FTIR) spectra were obtained using a Thermo Scientific Nicolet iS5 instrument fitted with a PIKE MIRacle single reflection horizontal ATR accessory (Figure 3). Powder X-Ray Diffraction (PXRD) patterns were acquired using a Malvern Panalytical Empyrean diffractometer (Figure 4).

## Catalyst testing

Catalytic testing of 5 wt% palladium supported on waste derived biochars was carried out using a parallel batch reactor set up using a Radleys Carousel Reaction Station. Mixtures of phenylacetylene (0.25 M), ethanol (25 mL) and toluene (0.2 M) as an internal standard were charged to the reactor along with 50 mg Pd/Char. Hydrogen gas (99.99%) was bubbled through the stirred reaction mixture and mixed at 600 rpm across various temperatures. Aliquots of the reaction solutions were removed periodically, filtered, diluted and analysed offline on a LECO GCxGC 7890B (Figure 1 and Figure 5).

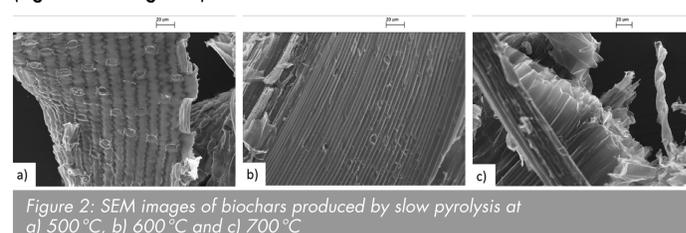


Figure 2: SEM images of biochars produced by slow pyrolysis at a) 500 °C, b) 600 °C and c) 700 °C

## Results

### Catalyst Characterisation

Figure 2a-c shows SEM images for slow pyrolyzed biochars prepared at 500 °C, 600 °C and 700 °C, respectively. All images show the effect of pyrolysis temperature on the resultant biochar morphology and structure. The surface morphology of the char materials show increasing disruption to the biomass surface with increasing pyrolysis temperature. Figure 2a, clearly shows the stomata remaining undisturbed by the pyrolysis process, showing the limited impact the process has on the physical structure in the resultant biochar. Yet, when the temperature is increased to 600 °C (Figure 2b), the stomata structures show disruption from their original morphology, in addition to the early signs of delamination of the structure resulting in fraying of the particle edges. At 700 °C (Figure 2c) the resultant biochar structure has been greatly disrupted with no stomata visible and clear delamination of the lignocellulosic structure.

EDX analysis of the biochar materials showed successful pyrolysis of the biomass, with the predominant element within all samples being carbon (>83 wt%). These results are summarised in Table 1. Of interest was the decrease in oxygen content between biochars prepared at 500 °C and those

prepared at higher temperatures, with an approximately 6 wt% difference in oxygen content between these samples. This discrepancy in oxygen content was determined to be due to the release of aromatic alcohols from within the lignin structure at higher pyrolysis temperatures. Trace amounts of other elements were expected to be present in the biochar materials, with these elements being non-water soluble, their removal from the waste material is problematic. However, none are expected to show catalytic properties, nor will they promote hydrogen based catalytic transformations.

Element	wt%		
	500 °C	600 °C	700 °C
C	83.43	89.32	85.76
O	13.46	7.67	7.34
F	0	1.61	1.19
Mg	0	0	0.25
Si	0.92	0.27	0.44
K	0.84	0	0.85
Ca	1.35	1.13	4.16

Table 1: Summary of EDX analysis of biochars pyrolysed at different temperatures

FTIR was carried out on all biochars before impregnation (Figures 3a, 3c and 3e) and after with Pd (Figures 3b, 3d and 3f). The impregnation followed by annealing and reduction was determined not to influence the chemical nature of the biochar. This is shown by the lack of additional visible peaks, corresponding to acetate in the Pd impregnated samples.

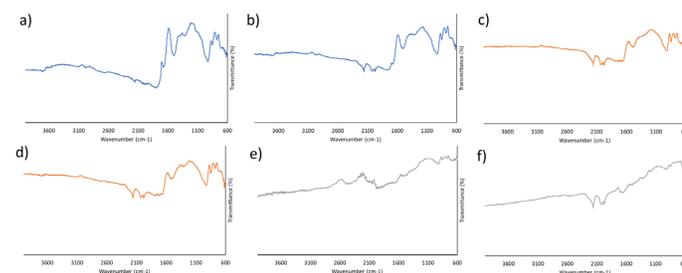


Figure 3: FTIR of bare biochars and Pd impregnated chars, a) 500 °C, b) 5% Pd/500 °C, c) 600 °C, d) 5% Pd/600 °C, e) 700 °C and f) 5% Pd/700 °C

PXRD was carried out on the biochars before and after Pd impregnation to determine the presence of any crystalline phases within the biochar and to determine the presence of Pd within the impregnated biochars. For the bare biochars, there was no distinct crystalline graphite phase at any temperature indicating that the carbon present was amorphous in nature (Figure 4a), where the blue line is the carbon at 500 °C, yellow is 600 °C and grey is 700 °C. Once impregnated with Pd, annealed and reduced, clear peaks attributed to cubic Pd (Fm3m) can be identified (Figure 4b) showing the presence of Pd(0) in the sample. The absence of peaks attributable to palladium oxide or palladium acetate, shows the successful decomposition of the Pd precursor and reduction of Pd(II) to Pd(0).

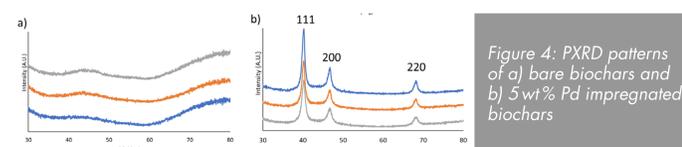


Figure 4: PXRD patterns of a) bare biochars and b) 5 wt% Pd impregnated biochars

## Catalytic Testing

Selective hydrogenation of phenylacetylene (PA, blue line) to styrene (Styr, grey line), avoiding over conversion to ethylene benzene (EB, orange line), was carried out to probe the differences in catalytic activity of 5 wt% Pd/biochars pyrolyzed at different temperatures. The hydrogenation reactions were carried out at 25 °C,

40 °C and 70 °C, for all three catalysts (Figure 5). In all cases studied the greatest rate of PA conversion was seen with 5% Pd/700 °C catalyst. However, it was noted that 5% Pd/700 °C maintained selectivity of the Styr for longer than the other catalysts, only losing Styr selectivity once all PA had been consumed. The reactions carried out at using 500 °C biochar supported Pd, were dramatically slower than those carried out using the other two biochar supported catalysts. This may have been due to the higher oxygen content of the 500 °C biochar interfering with substrate binding. The 600 °C catalyst showed similar activity to that of the 700 °C catalyst, however, the Styr selectivity was lost more readily indicating a higher affinity of this catalyst for the reduction of Styr, inciting a greater overall activity not selectivity.

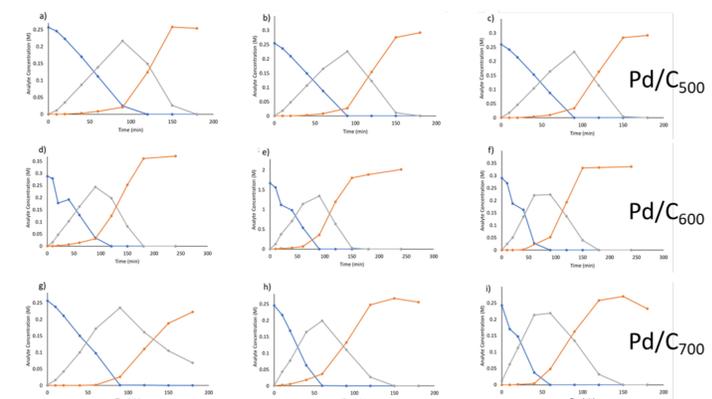


Figure 5: Reaction profiles for a) 5% Pd/500 °C at 25 °C, b) 5% Pd/500 °C at 40 °C, c) 5% Pd/500 °C at 70 °C, d) 5% Pd/600 °C at 25 °C, e) 5% Pd/600 °C at 40 °C, f) 5% Pd/600 °C at 70 °C, g) 5% Pd/700 °C at 25 °C, h) 5% Pd/700 °C at 40 °C and i) 5% Pd/700 °C at 70 °C

Activation energy of PA hydrogenation was calculated using Arrhenius modelling and the initial rate of PA consumption. The activation energy for the reaction was ~10 kJ mol<sup>-1</sup>, this low activation energy can be attributed to the high loading of Pd(0) and high loading of the catalyst within the reactor (~50 mg).

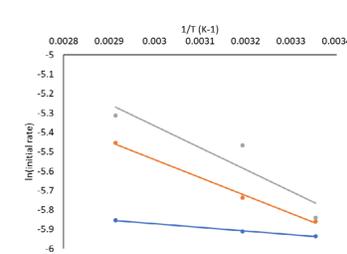


Figure 6: Arrhenius plot for the activation energy of PA hydrogenation for 5% Pd/500 °C (blue), 5% Pd/600 °C (orange), 5% Pd/700 °C (grey)

phenylacetylene. In general it was observed that the higher the pyrolysis temperature of the support the more active the end catalyst proved to be, where by subtly altering the pyrolysis temperature the selectivity of the chemical reaction can be optimized.

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## Conclusions

In the drive for more sustainable chemical processes a locally sourced biomass feedstock provides an avenue to provide a novel support option for the selective hydrogenation of phenylacetylene. By using scalable pre-treating and pyrolysis methods, biochars with different physical and chemical structures can be produced. These biochars can be impregnated with palladium via an easily scalable incipient wetness impregnation method. The resulting catalysts can be applied to the selective hydrogenation of phenylacetylene.