ON THE STRUCTURAL AND REACTIVITY DIFFERENCES BETWEEN BIOMASS- AND COAL-DERIVED CHARS

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Introduction

There is now a very abundant literature on both the structure and reactivity of coal-derived chars. Over the many years of research and development, a very good qualitative understanding has emerged of the structure-reactivity relationships for coal-derived carbons; progress in achieving good quantitative understanding has been much slower, but recent contributions from computational quantum chemistry are quite promising in this regard [1].

As the use of coal – e.g., in gasification and combustion processes – becomes increasingly limited in the 21st century due to concerns over global warming, the usefulness of the renewable and presumably CO_2-neutral biomass resources is growing quite rapidly. In fact, their popularity is such that the associated R&D efforts are not benefiting enough from the vast knowledge regarding the behavior of coal in essentially very similar (*e.g.* gasification and combustion) processes. Thus, for example, chars obtained after pyrolysis from both materials exhibit similar structural characteristics and behavior during its gasification.

The objective of this report is to illustrate and rationalize, experimentally and via computational chemistry, the similarities and differences in reactivity of chars derived from coal and biomass under comparable heat treatment conditions.

Experimental

The raw materials used for preparing the carbons were low-rank Pecket coal (C), *Pinus Radiata* sawdust (A) and tannins extracted from *Pinus Radiata* bark (T). All samples were demineralized by an acid treatment and will be named Dem-X-HTT where X is the raw material abbreviation and HTT is the heat treatment temperature in °C.

The heat treatment was done in a horizontal tube furnace with a high purity nitrogen (O_2 < 10 ppm) flow. The maximum temperature (550, 700, 850, 1000 or 1150 °C, and recently obtained 1300 and 1450 °C) was kept during 1 h.

XRD measurements were performed in a Rigaku Geigerflex D max C with CuKα radiation using a scanning speed of 2 °/min. All the heat-treated samples were also subjected to elemental analyses: C, H, N (Leco CHN 2000) measured directly, while O was calculated by balance.

Finally, the reactivity of the samples towards oxygen was measured in a TG-DTA system (Netzsch Luxx). The analyses were done with a ramp of 10 °C/min in air and the temperature of maximum heat generation (maximum DTA signal) is reported.

Computational chemistry energies for transition states were calculated using Gaussian® with geometry optimization at the B3LYP/6-31G(d) level of approximation. Carbons derived from coal included oxygen as semiquinones and biomass derived as ether both at the edges of the graphene molecular model and the activation energy was calculated in the range 300 – 2000 K.

Results and Discussion

Regarding the preparation of carbons, expected results obtained are the efficient demineralization of raw materials which resulted in samples almost ash-free (ash <0.8%) and the pyrolysis yields which are consistent (50% for Dem-C, 25% for Dem-A and 42% for Dem-T) with literature values [2, 3] for similar materials.

The most important aspect of the scrutiny of correlations between structure and surface chemistry of carbons, especially those derived from oxygen-rich biomass, is a comparison between trends in H/C and O/C ratio, on one hand, and carbon reactivity, on the other. It has long been known that the concentration of active sites increases as H/C increases, but whether this is a causal relationship is not clear; it is unlikely, for example, that H-terminated edge sites in graphene are the reactive sites responsible for carbon gasification [4].
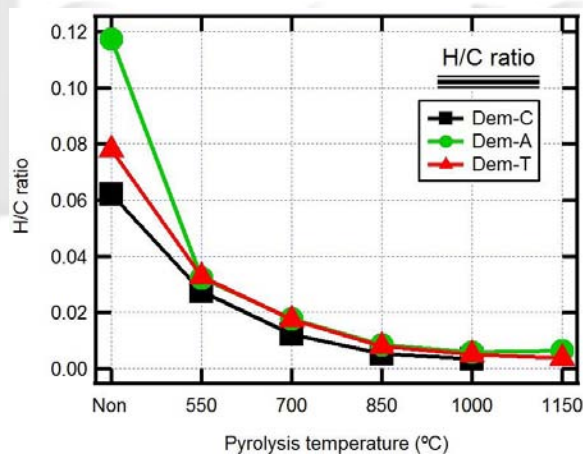

Fig. 1 H/C ratio for all prepared carbons

On the other hand, it has also been reported that carbon reactivity increases with increasing oxygen surface coverage and thus, presumably, with increasing O/C; the reason for this correlation is also not entirely clear, beyond the well documented induced heterogeneity effect, in the sense that the presence of surface oxygen (*e.g.*, as quinone groups at graphene edges) weakens the adjacent C–C bonds and thus facilitates CO and CO_2 desorption.

The stability of the different raw materials to the heat treatment can be studied from the corresponding X-ray diffraction patterns which show that the stacking of carbon

layers occurs over 700 °C for biomass materials (tannins and sawdust) and below 550 °C for coal, this higher structural sensitivity of Dem-C compared to biomass samples should be reflected also in a higher reactivity of these carbons if this would be the only feature which has an effect on reactivity. By comparing all the parameters which can be roughly quantified for the broad peaks of these still amorphous carbons (*i.e.* L_c, L_a and d_{002}), the crystallinity order is coal (C) >> sawdust (A) > tannins (T) considering similar HTTs.
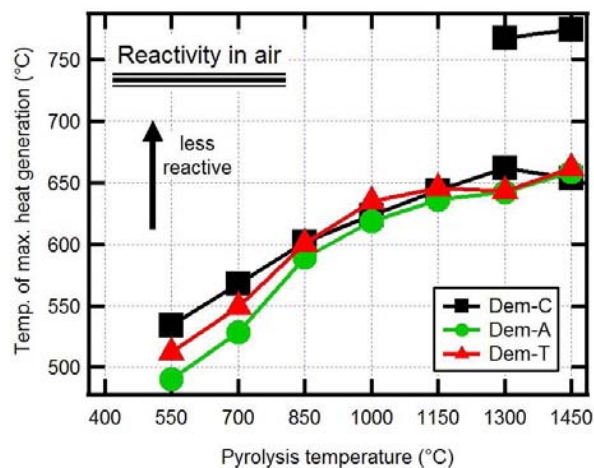
Fig 2. Reactivity of all heat treated carbons

As expected, the reactivity of all carbons (see Fig. 2) decrease with an increase in the size of the graphene layers (XRD data, not shown) and the oxygen and hydrogen content in the carbon structure (Fig. 1) decrease with increasing heat treatment temperature. The coal-derived carbons are, considering a low HTT, less reactive than the biomass corresponding ones, but when the HTT increased (*i.e.* T > 850 °C), the reactivities are quite similar: this seems to indicate that the biomass heteroatoms are readily desorbed after the HT.

It is interesting (and intriguing!) to notice that the reactivities are very well correlated with the H/C ratio except in the case that tannins- are less reactive than sawdust-carbons which could indicate (a) a higher reactivity per active site or (b) a higher number of active sites (but the crystal size is bigger!).

Table 1. Activation energies (kcal/mol) calculated for $2C + O_2 \rightarrow CO_{(g)} + C(O)$

	Dissociation	1st CO desorption
Coal-derived char	8.6	72.7
Biomass-derived char	8.2	53.7
CO desorption from semiquinone [5]	theoretical: 83.6	
CO desorption [6, 7]	experimental: 70.5 - 85	

Results obtained from computational chemistry (Table 1) indicate that biomass-like molecules are more reactive in O_2 gasification; this is experimentally demonstrated for low-HTT chars. For higher-HTT chars, containing less residual and/or surface oxygen, the reactivity differences are much smaller, this is (tentatively) attributed to similar presence of C−O complexes in both type of samples.

Conclusions

Experimentally, coal-derived chars prepared at low heat treatment temperature (HTT) are less reactive than their biomass-derived analogous which agree well with the results predicted by computational chemistry.

For similar HTTs, the structure of carbons derived from coal tends to order more easily than biomass-derived.

At HTT over 850 °C, the reactivities of coal-derived and biomass-derived carbons are much more similar, this is (tentatively) attributed to a higher loss of C—O surface groups in biomass chars of similar HTT.

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