# THE REACTIVITY BEHAVIOR OF $^{13}$C-LABELLED PHENOL-FORMALDEHYDE RESIN CHAR

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## Introduction

A number of studies have examined the dependence of the morphology of phenol-formaldehyde resin chars (PRC) on pyrolysis conditions [1-5]. The objective of the current work is to examine the manner in which gasification occurs in these materials as a function of pyrolysis regimen and char burn-off. To this end, a phenol formaldehyde resin was synthesized using $^{13}$C-labelled formaldehyde. Since the labelled carbons are concentrated in the methylene bridges in the polymer, and there is evidence that these decompose first during pyrolysis, it is hypothesized that a larger proportion of the labelled carbon would reside in the amorphous carbon material than in the aromatic rings which are primarily formed from the unlabelled phenol. The evolution of labelled and unlabelled carbon as CO and $CO_2$ was monitored during gasification and post-gasification desorption experiments in order to investigate this hypothesis.

## Experimental

The synthesis procedure for the resin is described elsewhere [6]. The chars were prepared at 850 and 1000°C for 1.5 (Sample 1] and 3 (Sample 2) hours, respectively, in a helium atmosphere. The particles were 30-100 Tyler mesh. The samples were heated in a TGA system to 850°C and 1000°C, respectively, to desorb surface oxygen until gas evolution ceased, as indicated by the mass spectrometer (MS). Gasification was performed in the same TGA at 400°C in one atmosphere of pure $O_2$. Post-gasification temperature programmed desorption (TPD) was performed on the samples in the same apparatus in flowing helium at 50K/min to 1100°C. This entire procedure was repeated a number of times to obtain data at several burn-offs. For Sample 1, the entire procedure, including pyrolysis, was performed in the TGA. Sample 2 was pyrolyzed in a tube furnace and subsequently placed in the TGA.

## Results and Discussion

The initial $^{13}$C/$^{12}$C ratios for Samples 1 and 2 were determined by burning them completely in oxygen and integrating the corresponding CO and $CO_2$ signals, as measured with the MS. (The labelled oxides are designated with an asterisk.) The resultant value of $^{13}$C/$^{12}$C was about 0.12 for both samples. (The corresponding ratio for the natural abundance is 0.011.)

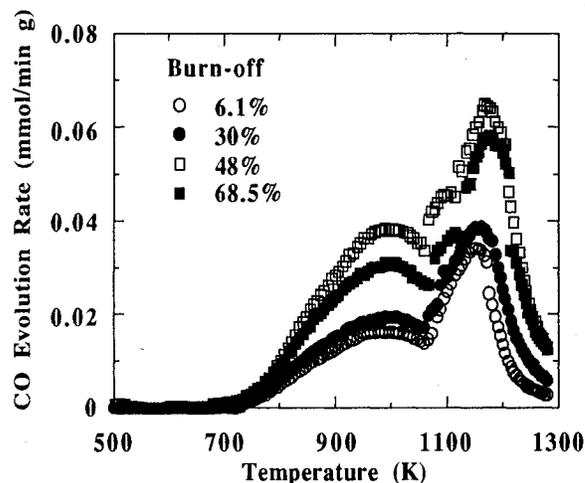Figure 1 presents CO TPD spectra from Sample 1 as a function of burn-off.



**Figure 1.** CO evolution rate from Sample 1 as a function of burn-off.

These results are somewhat different than others found in the literature [4], insofar as multiple desorption peaks were observed instead of the single broad peak obtained in the latter work. The TPD spectra in Figure 1 were deconvoluted to estimate the total integrated amount of surface complexes involved in each peak, as well as the peak temperatures. These results are presented in Table I as a function of burn-off for Sample 1. As shown, at low burn-offs, the spectra exhibit two peaks, which subsequently become three at higher burn-offs. For Sample 2, three peaks were observed at all burn-offs. Companion experiments with an unlabelled resin char, prepared in the same fashion as Sample 2, revealed just two peaks at all burn-offs, similar to the results for Sample 1 at low burn-offs, and also to the results of Zhang with the same resin char [7]. It appears that the two peaks observed for the unlabelled resin char and Sample 1 at early stages of burn-off are the same, and that the third peak observed for Sample 2 and during the later stages of gasification of Sample 1 occurs between the two original peaks. This third peak could be caused by a change in structure of the char due to heat treatment, since by the time the third peak appears for Sample 1, the char sample had been heated to 1400K twice during TPD. This is also consistent with the fact that the third peak is present from the outset for Sample 2, which had been prepared at the higher temperature of 1300K.

Figure 2 presents the corresponding evolution rate data of CO* from Sample 1. As would be expected, a similar number of peaks is observed, but they are shifted to slightly higher peak temperatures. For Sample 1, both

CO* and CO exhibit their first peak maxima at 1000K and 993K, respectively. This is in agreement with the values obtained by Zhang (7), who also observed two peaks at about the same temperatures for unlabelled resin char.

Even more importantly, however, while the amount of evolved CO increases monotonically with burn-off until about 40% burn-off, and decreases thereafter (as was also observed by Zhang [7] for unlabelled resin char), the trend is quite different for CO*. As presented in Table I, the largest amount of total evolved CO* occurs following the first burn-off. From this table, the corresponding CO*/CO ratio is 0.15 for 6.1% burn-off, and it gradually decreases monotonically to 0.04 for 68.5% burn-off. This is consistent with the hypothesis that the $^{13}$CO methylene bridge carbons in the original phenol-formaldehyde resin, which arise from the labelled formaldehyde, are preferentially enriched in the amorphous carbon material which burns off first before the more crystalline regions. The latter regions, on the other hand, arise primarily from the unlabelled aromatic phenol rings.
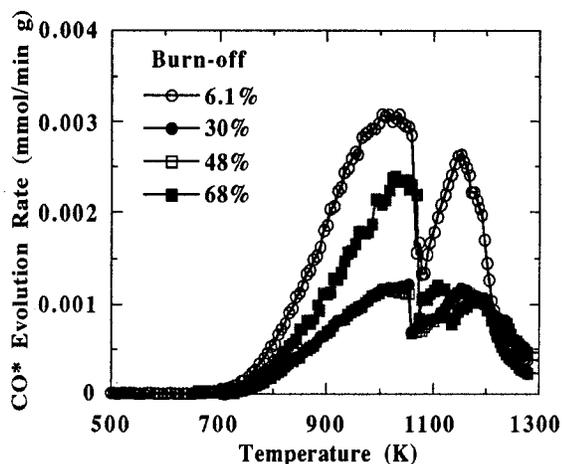


**Figure 2.** CO* evolution rate from Sample 1 as a function of burn-off.

These char samples were observed to undergo large mass losses following TPD, which tended to decrease somewhat with progressive burn-off. In order to explore this behavior further, surface areas were determined by single point nitrogen BET at a relative pressure of 0.3. The freshly pyrolyzed resin char exhibited a surface area of 372 m$^2$/g. Following 8% burn-off, the surface area increased to 444 m$^2$/g. However, following TPD of this same sample, the surface area increased markedly to 1233 m$^2$/g. The corresponding mass loss following TPD was 24%. Both

the surface area and mass loss are unusually large in comparison to those that have been more typically found for phenol-formaldehyde resin chars of this type in our laboratory [6,7]. These results are consistent with a very high degree of microporosity which is blocked by oxygen surface complexes during gasification such that nitrogen at 77K cannot penetrate. This microporosity then becomes accessible to nitrogen when these complexes are subsequently evolved during TPD. It is speculated that the larger than typical microporosity of these samples arose due to significantly greater crosslinking of the resin structure during curing.

## Conclusions

The process of gasification of a carbonaceous material has been investigated using a $^{13}$C-labelled phenol-formaldehyde resin as a model compound. The evolution patterns of CO upon post-reaction TPD are consistent with the early burn-off of amorphous carbon regions where $^{13}$C originating from methylene bridges in the resin had concentrated, followed by attack of more crystalline aromatic regions. The unusually large amount of mass loss upon post-reaction TPD from these chars has been attributed to a well developed microporosity arising from a highly crosslinked resin.

## Acknowledgments

## References

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**Table I.** Peak temperatures (Tp) and total integrated amounts of CO and CO* desorbed (Ap) in each peak for Sample 1.

| Burn-off (%) | CO | CO* | CO | CO* | CO | CO* | CO | CO* | CO | CO* | CO | CO* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tp (Peak #1) (K) | | Ap (Peak #1) (μmol/g) | | Tp (Peak #2) (K) | | Ap (Peak #2) (μmol/g) | | Tp (Peak #3) (K) | | Ap (Peak #3) (μmol/g) | |
| 6.1 | 993 | 1000 | 93.5 | 16.8 | 1152 | 1170 | 53.0 | 5.0 | - | - | - | - |
| 30 | 993 | 1000 | 112.4 | 6.9 | 1155 | 1180 | 63.8 | 2.9 | - | - | - | - |
| 48 | 993 | 1000 | 235.4 | 11.6 | 1105 | 1100 | 25.9 | 5.5 | 1180 | 1205 | 106.3 | 5.8 |
| 68.5 | 993 | 1000 | 183.4 | 9.9 | 1115 | 1108 | 22.1 | 1.1 | 1185 | 1210 | 92.7 | 3.5 |