

# THE EFFECTS OF THE "QUENCH PROCESS" ON MEASUREMENTS OF OXYGEN SURFACE COMPLEX POPULATIONS

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## Introduction

The effects of the "quench process" following steam gasification on measurements of oxygen surface complex populations were investigated as a function of reaction temperature for phenol-formaldehyde resin char samples. The results clearly show that the less stable oxygen surface complexes can be considerably affected by the time-temperature history of the quench process, in comparison to the more stable complexes. Implications of these results on char reactivity are discussed.

## Experimental

Chars were prepared from synthesized resin at 1000°C for 2h in ultrapure flowing helium. A TGA system was adapted to perform the gasification experiments in 9 - 67% steam-helium mixtures. Post-gasification temperature programmed desorption (TPD) was performed in a different apparatus in flowing helium at 25 torr at a heating rate of 50K/min to 1100°C.

## Results and Discussion

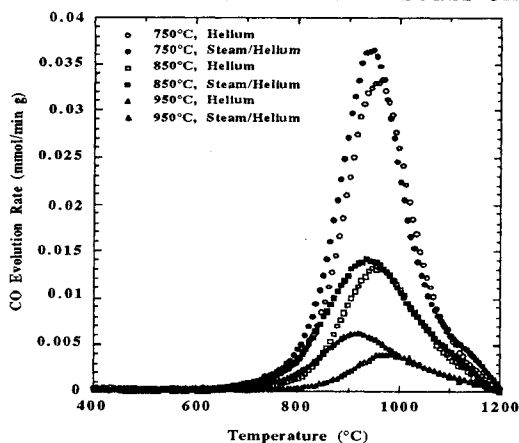


Figure 1. CO TPD spectra following gasification in 50% steam-helium mixtures and different quench atmospheres.

Figure 1 presents CO TPD spectra from resin char samples gasified to 10% burn-off at different reaction temperatures, following quenching in two different atmospheres: 50% steam-helium mixtures, and pure helium. The quench rate was about 300K/min in all cases. As shown, the primary difference between the two spectra at each temperature is that some of the oxygen surface complexes that desorb at the lowest temperatures are "lost" when the samples are quenched in pure helium. Apparently, cooling in steam keeps many of these sites populated

during the quench process. It is noted that the population of oxygen surface complexes that desorb at high temperatures, however, is not as dependent on the quench atmosphere. Moreover, this effect becomes more severe with increasing reaction temperature. This result supports the view that the low temperature surface complexes are less stable than the high temperature complexes; i.e., that the oxygen surface complex population is distributed with respect to desorption activation energy.

Assuming a distribution of desorption activation energies and a linear cooling curve, the following expression for the evolution rate of CO can be derived:

$$\frac{d[\text{CO}]}{dt} = \frac{d[\text{CO}]}{dt} \Big|_0 \exp \left[ -\frac{\nu_0 RT^2}{\alpha E^*} \exp(-E^*/RT_r) \right] \quad [1]$$

where  $d[\text{CO}]/dt$  represents the actual desorption rate,  $\{d[\text{CO}]/dt\}_0$  represents the rate without "loss,"  $T_r$  is the gasification temperature,  $\alpha$  is the cooling rate,  $\nu_0$  is the pre-exponential factor of the desorption rate constant, and  $E^*$  is the local desorption activation energy. The distribution of desorption activation energies was determined from the following expression [1]:

$$[\text{C}-\text{O}]_0 S(E^*) = \frac{d[\text{CO}]}{dt} \frac{T}{\beta E^*} \quad [2]$$

where,  $\beta$  is the heating rate and  $[\text{C}-\text{O}]_0 S(E^*)$  is the distribution of desorption activation energies.

Figure 2 presents predicted desorption rates compared to data from samples cooled in steam-helium atmospheres.

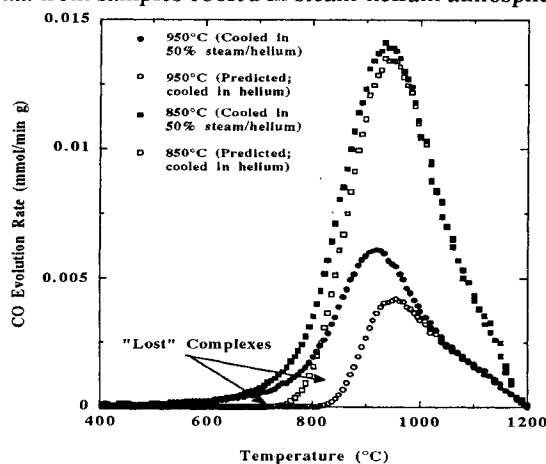
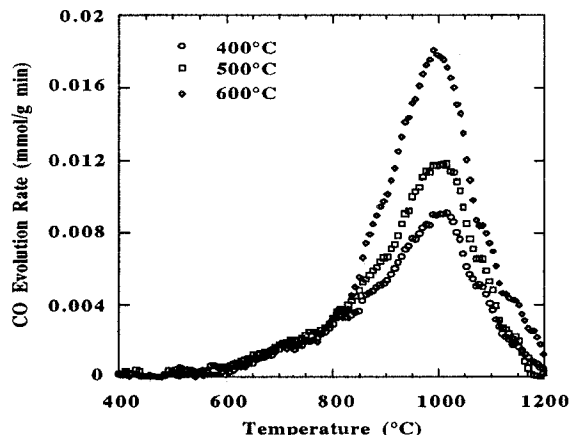


Figure 2. Measured (cooled in steam-helium) and predicted (cooled in helium) CO TPD spectra following gasification at 850°C and 950°C.

As shown, the results from Eq. [1] are consistent with the data presented in Figure 1. In addition, Eq. [1] predicts that

the fraction of surface complexes lost during the quench process increases with reaction temperature. These empty sites may be populated during gasification, but cannot be observed following quenching in pure helium.

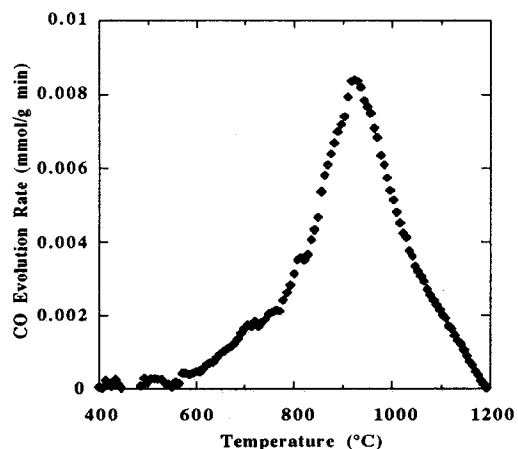


**Figure 3.** TPD spectra following steam chemisorption in 50% steam-helium mixtures after exposure for 30 min.

Under certain conditions, the reactivity of carbons and chars can be correlated/predicted from desorption rate data [1]. Using the current data, such calculations produce reasonable agreement with measured reactivities at low temperatures (i.e., 700°C and 750°C), but consistently underpredict the measurements at higher temperatures by about an order of magnitude. This observation is consistent with the loss of a significant fraction of the lowest energy complexes (which exhibit the highest desorption rates, and, consequently, have the most effect on reactivity) due to the quench process at higher temperatures. In order to estimate the potential effect of these "lost" complexes on reactivity, the following approach was taken.

Following steam chemisorption (i.e., for net mass increase), Figure 3 shows a constant population of low temperature oxygen surface complexes up to about 800°C, independent of temperature. These complexes do not appear in the CO TPD spectra following steam gasification at higher temperatures. However, the populations of the high temperature oxygen surface complexes following chemisorption are quite similar to those following gasification. Therefore, it is suspected that the low temperature complexes observed after chemisorption may be related to the surface complexes "lost" during the quench process following steam gasification.

Consequently, it was assumed that during gasification the population of low temperature surface complexes was the same as measured for the steam-chemisorbed char, up to a desorption temperature of 900°C. The population of high temperature oxygen surface complexes at temperatures greater than 900°C was taken as that determined from the TPD spectrum of resin char gasified at 950°C and quenched in a 50% steam-helium mixture. The 900°C point was selected because the CO desorption rates are very close for the two spectra at this point. Figure 4 presents the resultant "reconstructed" CO TPD spectrum following gasification at 950°C.



**Figure 4.** "Reconstructed" CO TPD spectrum following gasification at 950°C, as discussed in the text.

The desorption rate-controlled reactivity predicted from this spectrum, is 0.017 g/g min at 950°C, in comparison to a measured value of 0.035 g/g min. This considerably improved agreement (in comparison to the original order of magnitude discrepancy) suggests that the low temperature oxygen surface complexes that are "lost" during the quench process could account for a significant portion of the char reactivity observed at higher temperatures.

The issue of whether or not the population of low temperature complexes ceases to be desorption rate-controlled at some point is an important one. In which case, these sites would be depopulated during gasification such that their contribution to the overall reactivity would gradually become their rate of formation. However, in order for the formation rate to be controlling, it must be considerably less than the desorption rate. And, if the desorption rate is already insufficient to account for the reactivity when these sites are completely filled (under desorption rate-control) at higher temperatures, then it stands to reason that formation rate-control would certainly provide an even worse correlation.

## Conclusions

It has been demonstrated that the quench process can be quite important in measurements of the populations of oxygen surface complexes following gasification. Proper interpretation of experimental desorption rate data must take this factor into account.

## Acknowledgments

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## References

1. Calo, J.M. and Hall, P.J., in *Fundamental Issues in the Control of Carbon Gasification Reactivity*, Lahaye and Ehrburger, eds., NATO ASI Series, Vol. 192, Kluwer Academic Publishers, Dordrecht, 1991. p. 329.