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**MITIGATING CROSSLINKING REACTIONS
THROUGH PRECONVERSION STRATEGIES**

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INTRODUCTION AND OBJECTIVES

The ultimate goal of this research is to develop preconversion techniques that will mitigate crosslinking reactions and thereby substantially increase liquid yields during subsequent liquefaction. The immediate objective is to explore the effect of several pretreatments on the evolution of oxygen functions, crosslinking, and conversion in laboratory studies. The pretreatments to be explored include several that hold promise for effecting deoxygenation or other reduction, for example, treatment with CO/water/base and hydroquinones, either alone or in conjunction. The effects of these pretreatments on functional group distribution, macromolecular structure, and liquefaction will be compared with those that have shown promise in the past for improved conversions, such as simple hydrothermal pretreatment, mild hydrogenation with dispersed catalysts, and demineralization. A second objective is to develop suitable test procedures for assessing the effect of the pretreatment on subsequent liquefaction and achieve also an understanding the chemical origin of the effect. These test procedures will include the use of proton magnetic resonance thermal analysis (PMRTA) for determining the effect of pretreatment on fluidity as liquefaction conditions (temperature, pressure) are approached. They will also involve the use of simpler and more pertinent laboratory measures of volatile product yields following the batch liquefactions that will be run to test the susceptibility of pretreated coals to subsequent liquefaction.

During the first quarter no experimental work was performed. Project planning was carried out, the NEPA report was prepared, the Project Management Plan was developed and submitted, and the new specialized equipment needed for the project was requested (SRI capital equipment funds). Preparation of the management plan included a review of the literature relevant to one of the objectives of this project, namely to use hydroquinones or other electron-transfer agents to promote the deoxygenation of single ring phenols by CO/H₂O systems under preconversion conditions. It also involved assessment of (1) the advantages/disadvantages of using a thermogravimetric analysis (TGA) to provide a rapid and measurement of volatiles yields from liquefaction, and (2) various approaches to coupling a high-capacity recording analytical balance to a temperature-programmed, heated, evacuated chamber so that we have the equivalent of an automated vacuum distillation operable with sample sizes much larger than any commercially available TGA apparatus. In this report we discuss some aspects of the deoxygenation chemistry and the TGA approach to measuring volatilities as well.

Thermochemistry of Phenol Deoxygenation

The rate of phenol deoxygenation is of course controlled by thermochemical and kinetic properties of the phenols, the respective deoxygenated aromatics, and the intervening intermediates and transition states. The general thermochemistry of phenol deoxygenation is represented by the benzene (phenol) and naphthalene (naphthol) systems, values for which are shown in Figure 1, reproduced from the technical discussion section of Management Plan. We have drawn this figure assuming that the deoxygenation of the phenols proceeds through tautomerization to the respective keto forms (Step 1), reduction of these keto forms to the "dihydro-hydroxy" intermediates (Step 2), which in the condensed phase will eliminate water (Step 3) extremely rapidly at liquefaction, or even preconversion, temperatures.

Figure 1. Potential energy diagram for the deoxygenation of phenol and naphthol via reduction of their respective keto forms.

The enthalpy values shown in Figure 2 are all relative to each of the starting phenols, which are set at 0. All of the minima represent either measured values from the literature or estimated by group additivity, which should be quite adequate for these two systems. The maxima or transition state values in the figure are all "artist's conceptions" for which no measured values are available, but which are drawn so as do no violence to expectations based on a Hammond's Postulate view of free energy (or enthalpy) relationships.

The reaction coordinate diagrams illustrate the fact that the overall deoxygenation enthalpy is the same for both systems, but that the probable first and second steps become progressively more difficult as one moves from the polycyclic systems towards the monocyclic systems. In other words, in going from the bicyclic naphthalene system to the monocyclic benzene system, the tautomerization to the keto form and its reduction to a hydroxyl dihydro intermediate become more endothermic, but this increase in endothermicity is compensated for by an increase in the exothermicity of dehydration of the dihydroaromatic intermediate. The result is that the overall heat of deoxygenation is essentially unchanged. Unfortunately, the increasing deoxygenation difficulty encountered in practice is an indication that relatively little (perhaps none) of this increasing exothermicity of the third step (i.e., dehydration) is available to help "pull" the difficult hydrogenation step along. This means in essence that (hydrogenation) is not reversible: the dehydration of the dihydro intermediate is much faster than its dehydrogenation, and everything that gets hydrogenated already gets dehydrated. This in turn means the only practical expedient for increasing reaction rate is to use thermodynamically and/or kinetically more powerful systems for reducing the keto form of the phenol.

Reduction of the keto-form of the phenol (Step 2 in Figure 1) is itself a step that consists of two or three fundamental reactions. Literature data suggest¹⁻⁴ that different quinone-hydroquinone redox systems under different conditions undergo different sequences of reactions, all of which can achieve the same net result (transfer of two hydrogen atoms from a reducing agent to an oxidizing agent). These sequences can either be a strict hydride-transfer/proton-transfer, or the sequence of electron-transfer—H-atom-transfer—proton-transfer that has the same net result, or even the reverse of the latter, proton-transfer—H-atom-transfer—electron-transfer. For this reason it is difficult to make an *a-priori* prediction how various H-atom sources and electron transfer agents will interact; we have indicated in the Management Plan that we will test a number of combinations.

In any case, since the net reduction capacity in this pretreatment study is to be provided by the CO/H₂O system, it may be important to remove the oxidation product, CO₂, as much as possible from contact with the reduced product, the deoxygenated or cleaved coal. Thus, the

presence of base, which is known to promote CO/H₂O reductions, may be helpful both because it promotes the formation of formate ion and because it sequesters the waste oxidation product, CO₂, as bicarbonate.

In the case of a reducing system that provides a net hydride transfer via an electron transfer -- H-atom transfer sequence, the occurrence of rate-controlling electron-transfer would mean that it could be helpful to add another electron-transfer agent, which could provide help in electron transfer, while still relying on the hydroquinone for the H-atom transfer component. One candidate for this role that we have proposed to test is the very powerful electron donor tetrakis(dimethylamino)ethylene (TAME).

If CO/H₂O and the electron transfer agent do indeed act in a cooperative fashion, then the utility of using progressively stronger ET agents will depend among other things on whether the reduced form of the ET agent attacks the coal directly or whether it serves to maintain a higher steady state concentration of some formate species which in turn attacks the coal structure. As we noted in the technical discussion section of the Management Plan, since the CO/H₂O system provides the ultimate reducing power, the redox potential of the electron transfer catalyst *itself* may not matter, *if* the ET catalyst couple and the CO/H₂O system are maintained in thermodynamic equilibrium. However, this equilibrium will not necessarily be maintained; moreover, the kinetics of the hydroquinone or other ET agent may make a difference, and these may well vary with the standard oxidation potential of the agent itself. It is also important to remember that we are not seeking merely to achieve electron transfer (or even hydride transfer): we are hoping for useful combination of electron transfer and the utilization of thermal energy to effect cleavage or other desired reactions of the intermediates. Thus it may be best to have the electron transfer take place in a particular temperature region, with reactions of the same intermediates at either higher or lower temperatures being less favorable. Thus the point here is that the number of potentially significant variables is rather substantial, and it will be important to test them in a reasonably systematic fashion.

The Use of TGA Techniques for Assessment of Distillate Yields in Liquefaction.

In considering an alternative to the solvent-solubility methods that have been traditionally used for assessing yields in small scale batch liquefaction studies, we of course considered gas chromatographic simulated distillation approaches. However, here we were interested not only in the lighter fractions that are easily chromatographable, but also in heavier materials, all the way up to the vacuum resid. Furthermore, we were interested in minimizing the problems associated with transfer losses for small samples, and with sample heterogeneity. We therefore looked to a technique that would measure the yields by subjecting the entire liquefaction product to a volatility-

based separation, preferably under conditions in which we could distill directly from a liquefaction micro-reactor. Thermogravimetric approaches that measure weight loss as a function of temperature seemed attractive, but commercial TGA systems are limited to small sample size (on the order of 100 mg). In order to utilize weight of container plus sample in the 10 or even hundred gram range, we have purchased, using SRI funds, a specially equipped recording analytical balance from Mettler, Inc. that can handle sample weights up to 200 grams (with 0.1 mg accuracy) and that can have the weighing cell isolated in vacuum. While we await delivery of the balance, we are reviewing the literature for other such attempts and planning the assembly of the system.

Vacuum thermogravimetric analysis has been previously used as a simulated distillation technique for coal-derived liquids, though most often using commercially available micro-scale TGA systems.^{5,6} For example, Southern et al. report⁵ that heating rates below 10°C/min and the use of a thin sample layer helped to minimize their most severe problem—that of the sample spattering out of the pan as the internal pressure builds within an increasingly viscous residue. Furthermore, they show relatively little time-dependent effect of sample size on percent weight loss (% overhead) as a function of time, and essentially no effect of sample size on volatiles distilled after the 20 minute isothermal period they recommend at the end of the temperature ramp. We anticipate that in our case the ability to use much larger sample sizes and to distill directly from a micro reactor having a length to diameter ratio of at least 3:1 will substantially minimize losses from spattering, while only slightly retarding entrainment of the vapors in the inert gas purge stream.

Mondragon and Ouchi⁶ show data indicating that at 7°C/min heating rate they increased the percent of a VGO distilled at 240°C from 14 to 28% (as compared to an ASTM distillation at 50%) by decreasing the length/diameter ratio of the TGA sample holder from 133/1 to 33/1. By then going all the way to an open pan sample holder (with an l/d of ca. 0.5), the percent distilled at this same temperature increased to 65%, that is, the percent distilled at 240°C now *exceeded* that of the ASTM distillation by 15 percentage points. At that heating rate, they evidently needed some l/d intermediate between 33/1 and that of the open pan. However, rather than construct a new series of sample holders, the authors simply changed the heating rate. In order to match the ASTM distillation with an the open pan sample holder, they increased the heating rate from 7°C/min to 20°C/min. In this work we plan to use a slower heating rate and also increase the l/d to about 10/1, so as to minimize the sample spattering referred to above, and to allow distillation directly from the micro-reactor in which the liquefaction test was performed. In any case, we will calibrate the system using liquefaction products that have already been characterized by an ASTM distillation procedure.

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