DOE/PC/91044--T6

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Final Report • July 1994

MITIGATING CROSSLINKING REACTIONS THROUGH PRECONVERSION STRATEGIES

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SRI Project 2869
Contract No. DE-AC22-91PC91044
MP 94-114

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INTRODUCTION

BACKGROUND

Under a contract with the Pittsburgh Energy Technology Center (PETC) of the Department of Energy (Contract No. DE-AC2291PC91044), SRI has conducted research on potential pretreatments to minimize the impact of crosslinking reactions during coal liquefaction. Liquefaction is generally achieved by heating coals with a donor solvent and, preferably, with a catalyst and hydrogen pressure at temperatures around 425°C. Although temperature is the factor with the strongest influence on conversion rates, there is a limit to which it can be usefully implemented. Beyond a point, attempts to achieve higher conversion by simply using higher temperatures often lead to coking and lower liquid yields; increased conversion rates are simply overwhelmed by greater increases in retrograde reactions.

Oxygen functions in general, and specifically carboxylic acids and phenols, have been implicated as important in the retrograde reactions of coals.¹⁻⁴ Phenols severely hamper the processability of coals both during liquefaction and during subsequent catalytic upgrading.⁵⁻⁶ Deoxygenation of phenols is chemically the most difficult heteroatom removal to achieve.⁷ Furthermore, some phenolic structures that deoxygenate readily also couple very readily during heat-up, often before temperatures at which coals become fluid (and easily contactable by heterogeneous catalysts) and before those at which thermal hydrogen-transfer reactions lead to bond cleavage.^{3,8} Carboxyl groups have also been associated with crosslinking. Solomon and coworkers have shown that decarboxylation, particularly in the low temperature regime of 200° to 250°C, correlates with crosslinking.⁴ Thus, pretreatments that can effectively deoxygenate phenols or decarboxylate without the attendant crosslinking constitute a technical challenge whose resolution would greatly facilitate utilization of coal through direct liquefaction. Consideration of the mechanisms by which phenols can be deoxygenated suggested that reducing systems which operate by ionic (i.e., hydridic reductions) or electron-transfer (e^- followed by $H^\bullet$) pathways would be particularly effective,⁸⁻¹¹ and these pretreatments became the principal focus of this study.

OBJECTIVES

The primary objective of our project was to determine the effect of reductive pretreatments of low-rank coals through the use of electron-transfer agents. This potential was explored in laboratory studies through determination of the impact on the evolution of oxygen functions,

crosslinking, and conversion. The pretreatments explored include treatment with CO/water/base and hydroquinones or other electron-transfer agents in various combinations. The effects of these pretreatments on functional group distribution, macromolecular structure, and liquefaction were compared with those of pretreatments that have in the past shown promise for improved conversions, such as simple hydrothermal pretreatment, mild hydrogenation with dispersed catalysts, and demineralization.

Additional objectives were to improve test procedures for assessing the effect of the pretreatment on subsequent liquefaction and to achieve some understanding of the chemical origins of the effects observed. These tests are: (1) proton magnetic resonance thermal analysis^{12,13} (PMRTA) for determining the effect of pretreatment on fluidity as liquefaction conditions (temperature, pressure) are approached and (2) a thermogravimetric assay (TGA)-based simulated distillation for convenient measurement of product volatility following small-scale batch[†] liquefaction experiments. The purpose of the PMRTA test is to gain additional insight into whether beneficial pretreatments primarily affect pre-existing crosslinks in the coals or primarily limit additional crosslinking during liquefaction. The TGA-based simulated distillation test is being developed so that we can obtain conversion data and also assess the nature of the product (distillation profile) instead of only a single-point measure of conversion such as wt% conversion to THF-solubles or the yield of 975°F- distillates.

HIGHLIGHTS OF THE FINDINGS

Three major efforts undertaken during this project were (1) determining the effect of various reductive pretreatments on liquefaction of Wyodak and Zap coals, (2) determine the effect of pretreatments on the development of mobility in the coal structure, using proton magnetic resonance to and (3) developing a TGA-based simulated distillation apparatus for evaluating products of coal liquefaction. Although the major emphasis in the program was understanding and mitigating crosslinking reactions due to oxygen functions, we also examined the possible role of hydrocarbon structures in crosslinking and coking reactions. This study comprised reexamination of recent literature results in light of our mechanistic model developed under a previous PETC-supported contract (DE-FG22-86PC90908). The results of these studies are described in detail in several manuscripts, which are included in the appendices. In this section, we limit the discussion to an overview of the findings and their significance.

PRETREATMENT OF WYODAK AND ZAP COALS

Batch liquefaction tests of Wyodak and Zap coals were performed after the coals were treated with CO/H₂O, generally for 1 h at 350°C. We also explored the effect of promoters that could aid deoxygenation of phenols by reductive electron transfer during hydrothermal pretreatment. Pretreatment and liquefaction tests of promoters for CO/H₂O pretreatment of low-rank coals show that hydrothermal pretreatment of low-rank coals, which is already known to be beneficial to subsequent donor-solvent liquefaction when pure liquid water is the pretreatment medium, can be made more beneficial through the presence of moderate CO pressure and the addition of specific agents. A very low level (0.1 wt%) of sodium carbonate in the added water increased the improvement in liquefaction of hexane-solubles by 2 wt% dry ash-free basis, (daf basis) over that provided by water itself. This beneficial impact is probably due to the increased steady-state concentration of formate anions.

The addition of the electron-transfer agents *p*-hydroquinone and tetrakis(dimethylamino)ethylene ("TAME") to the pretreatment led to increase of 0 and 2%, respectively, in yields of hexane-solubles for Zap lignite beyond that already achieved with water/Na₂CO₃. These increases are smaller than we had hoped for. However, the addition of 2.5 wt% (raw-coal basis) of CS₂ to the carbonate-containing water increased the benefit to an improvement of 8 wt% (daf coal basis) over the yields achieved with pretreatment in pure water. Interestingly, the impact of carbon disulfide was negligible in the absence of Na₂CO₃ (less surprisingly, CS₂ was also "activated" by the presence of FeSO₄). While the inability to remove all of the pretreatment agents

with the water layer means that some of the observed benefits derive from the presence of these agents during the subsequent liquefaction, and an actual process-benefit remains to be demonstrated, this study provides further evidence that chemistry occurring during contact with liquid water under near-critical conditions can significantly increase subsequent liquefaction yields, and that beneficial chemistry can be enhanced via inexpensive additives. A manuscript describing the pretreatment-liquefaction study has been prepared for submission to *Energy & Fuels* and is included here as Appendix A.

PMRTA MEASUREMENTS OF PRETREATED COALS

Proton magnetic resonance thermal analysis was performed on selected samples of pretreated Wyodak and Zap coals. These analyses were conducted by Drs. Lynch and Sakurovs at CSIRO, Australia. Their report is included as Appendix B. We examined the PMRTA findings in light of the liquefaction data. For Wyodak, a very good correlation was observed between the temperature-dependent molecular mobility and the convertibility of the pretreated coals to hexane-soluble material under subsequent donor solvent liquefaction. For Zap lignite, the degree of molecular mobility developed during heating of the pretreated coals was much lower and there was poor correlation with the liquefaction tests. The increased molecular mobility shown by the Wyodak pretreated coals began appearing at about 200°C, well below temperatures at which significant thermal cleavage of covalent bonds is significant, and also before the temperatures at which early crosslinking in low-rank coals has been observed. We therefore conclude that the benefits of pretreatment result primarily from the cleavage or disruption of pre-existing crosslinks, either covalent or hydrogen-bonded. This interpretation is further elaborated in the paper dealing with the pretreatment-liquefaction study (Appendix A).

DEVELOPMENT OF A TGA-BASED SIMULATED DISTILLATION TECHNIQUE

The characteristic of coal-derived liquids that is most relevant to refining operations is distillability, and ASTM (American Society for Testing and Materials) methods such as D1160 are designed to determine that property. Unfortunately, when such test are applied to small scale samples, such as those produced by batch microautoclave liquefaction, problems with coking in the distillation vessel due to differences between the vessel temperature and reflux-head temperature are markedly aggravated. Therefore, most laboratory-scale coal liquefaction studies use solubility-based techniques for characterizing the products. However, the relevance of the solubility data to processing is questionable, and furthermore, this characterization provides only limited points for comparison (oil, asphaltene, preasphaltene content) and no information about the nature (distillability) of the materials within each class. Small-scale TGA techniques can be used to

obtain detailed process-relevant characterizations. The chief difficulty with this technique lies in obtaining representative samples from laboratory-scale batch liquefaction experiments.

Because of the difficulties in representative sampling, we have assembled a TGA apparatus large enough to distill a large fraction, or perhaps even an entire batch, liquefaction reactor product. The TGA apparatus that we have designed and assembled uses a large-capacity (200-g) Mettler force-cell balance, a temperature-controlled oven, and a computer for data acquisition. We have shown that this technique is suitable for application to heterogeneous samples up to at least 1.5 g and have established conditions that give weight-loss vs. temperature curves which agree within about $\pm 3\%$ (across the entire boiling range) with true ASTM correlations for heavy distillate material (635°-975°F) and are relatable to ASTM distillation for heavier materials. Details of this apparatus and the test results are given in Appendix C.

RING GROWTH AND CROSSLINKING REACTIONS IN HYDROCARBONS

As mentioned above, crosslinking reactions due to oxygen functions were the primary focus of our program. However, while awaiting NEPA approval, without which we could not begin any laboratory work, we reexamined the literature dealing with crosslinking reactions in hydrocarbons and conducted some mechanistic numerical modeling of thermal reactions. These reactions constitute a background against which we must assess the impact of oxygen functions.

In a previous PETC-funded program (DE-FG22-86PC90908), we had developed a mechanistic numerical model that described detailed chemical reactions encompassing bond cleavage, bond formation, and hydrogen transfer reactions for a limited range of structures. Simple recombination of resonance-stabilized radicals leads to the formation of weak bonds and does not constitute true retrogression. However, addition of resonance-stabilized radicals to arenes could lead to strong bonds if the hydrogen from the intermediate cyclohexadienyl radical can be removed. Under most conditions, the reversal of the radical addition is favored by a large factor over the removal of hydrogen. With the help of the numerical model, we considered, qualitatively and quantitatively, the conditions necessary for hydrogen removal from retrograde intermediates (i.e., radical adducts) to be sufficiently rapid to prevent thermal splitting of the weakly bound intermediates. We found that bimolecular removal of hydrogen from the intermediate is substantially increased by high concentrations of polycyclic aromatic hydrocarbons (PAH) or by disproportionation with other radicals. A paper discussing the role hydrogen transfer plays in forming the strong bonds that constitute retrograde reactions during coal liquefaction and pyrolysis was presented at the American Chemical Society meeting in April 1992. A copy of the preprint is included as Appendix D.

Growth of arene ring systems by addition of aliphatic chains constitutes another important retrogressive pathway; this pathway is also made possible by hydrogen-transfer reactions. Our mechanistic model has not included these ring-growth reactions, and we addressed them in a small experimental study on the pyrolysis of alkylpyrene structures. We found that analogues of phenalenyl structures are a key in the ring-growth process. Formation of these structures is not predicated on having the alkyl chain originally attached to the arene unit; they were also observed in experiments wherein pyrene was heated with alkanes. Interestingly, such phenalenyl structures are seen in resids from petroleum hydrotreating as well as in those from coal liquefaction. A manuscript dealing with the ring-growth products in model systems is included as Appendix E.

Finally, we also wrote a paper discussing how the liquefaction picture that includes cleavage of strong bonds is relevant to coal liquefaction technology. This paper, which was presented at the joint DOE-NEDO meeting in San Francisco in 1992, was subsequently published in *Energy & Fuels* and is included as Appendix F.

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Appendix A

EFFECT OF REDUCTIVE PRETREATMENTS ON COAL CONVERSION

EFFECT OF REDUCTIVE PRETREATMENTS ON COAL CONVERSION

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INTRODUCTION

Liquefaction is generally achieved by heating coals with a donor solvent and, preferably, with a catalyst and hydrogen pressure at temperatures around 425°C. Attempts to achieve higher conversion by simply using higher temperatures often lead to coking and lower liquid yields. Furthermore, retrograde reactions can lead to crosslink formation (particularly in the case of low-rank coals) even before nominal liquefaction conditions are reached.¹ Thus, besides the bond cleavage reactions that lead to disintegration of the coal matrix, there are also retrogressive reactions that lead to the formation of new refractory linkages. In many instances, conversion appears to be limited by these retrogressive reactions more than by any inherent lack of reactivity of the coal.²

Oxygen functions in general, and specifically carboxylic acids and phenols, have been implicated as important in the retrograde reactions of coals.¹⁻⁴ Furthermore, phenols severely hamper the processability of coals both during liquefaction and during subsequent catalytic upgrading.⁵⁻⁶ Thus, substantial benefits might be realized if coals were even partially deoxygenated before liquefaction. Ideally, this deoxygenation would be achieved in a preconversion step, before widespread retrogression occurs.

Deoxygenation of phenols is chemically the most difficult heteroatom removal to achieve,⁷ particularly for heterogenous systems, where access of a solid catalyst (even if very finely divided) to the depth of an organic matrix is quite limited. Furthermore, some phenolic structures that deoxygenate readily also couple very readily during heat-up, often before temperatures at which coals become fluid (and easily contactable by heterogeneous catalysts) and before those at which thermal hydrogen-transfer reactions lead to bond cleavage.^{3,8} Carboxyl groups have also been associated with crosslinking. Solomon and coworkers have shown that decarboxylation, particularly in the low-temperature regime of 200° to 250°C, correlates with crosslinking.⁴ Thus, pretreatments that can effectively deoxygenate phenols or decarboxylate without the attendant crosslinking constitute a technical challenge whose resolution would greatly facilitate utilization of coal through direct liquefaction.

The combination of CO and water is well recognized as a thermodynamically powerful but kinetically limited reducing system. It has been extensively explored as a liquefaction system for low-rank coals by Appell⁹ and by researchers in North Dakota,¹⁰ following much earlier (1920s) work¹¹ in Germany. The utility of the system has been severely hampered by the requirement for high partial pressures of water, so effective promoters must be found if it is to be useful under pretreatment conditions for removal of phenolic OH and for crosslink cleavage in low-rank coals. Since CO/water easily deoxygenates polycyclic phenols such as anthrone, and since the overall thermodynamic driving force for deoxygenation of monocyclic phenols is essentially identical to that for polycyclic phenols, the potential exists for greatly accelerating the reaction with promoters.

We report here on a study to explore the effect of pretreatments that hold promise for effecting deoxygenation (or other reduction)—for example, treatment with CO/water/base and hydroquinones or other electron-transfer agents in various combinations. These studies were conducted with Argonne Wyodak and Zap lignite coals. In addition to determining the effects of these pretreatments on coal conversion under a standard set of conditions, we determined their effect on the development of mobility in the coal during heating. This determination was made by using proton magnetic resonance thermal analysis (PMRTA).^{12,13} The purpose of the PMRTA test was to gain additional insight into whether the pretreatments primarily affect pre-existing crosslinks in the coals or primarily limit additional crosslinking during liquefaction.

EXPERIMENTAL PROCEDURES

Pretreatment. The pretreatment experiments were performed in an unstirred, 90-mL, 304 stainless steel reactor fitted with a quartz insert and heated in a fluidized sand bath. The basic pretreatment condition involved heating in liquid water at 350°C for 30 min., under a CO partial pressure of 500 psi (cold). Each pretreatment test used 10 g (2 ampules) of -100 mesh Argonne Premium Coal Sample Bank Wyodak or Zap Lignite, to which 15 had been added mL of a 2 vol % solution of methanol (to facilitate wetting of coal) in deionized, deoxygenated water. The reactor heat-up time was ~20 min., and the total reaction time was 50 min. After the reaction was cooled in a cold sand bath, the excess water was removed with three stages of centrifuging and pipetting of the supernatant liquid. One-third of the wet coal was stored under argon in a freezer for future analysis, and the remainder was subjected to liquefaction on the same day that the pretreatment was run.

Liquefaction. The liquefaction tests of the pretreated coals were run in 40-mL, horizontally held, vertically shaken (~500 cps, 5/8-in stroke) 316 stainless steel microautoclaves. The liquefaction tests were all run on about 6 g of coal (as-received basis) at 430°C for 50 min. in

tetralin (solvent:coal 2:1, on an as-received basis), under 1000 psi (cold) hydrogen. After the reactor was cooled in sand and dry-ice baths, its contents were transferred to a beaker with 200 mL hexane, sonicated for 10 min., and filtered through a 0.45- μ m polytetrafluoroethylene (PTFE) membrane filter. The filter residue was dried at 76°C overnight in a vacuum oven at ~0.2 torr. The weight of the dried residue was determined and used to calculate the wt% conversion to hexane-soluble material.

We have relied on the residue-based method of determining conversion to hexane-solubles as a rough measure (albeit generally an overestimate) of conversion to distillate material. The baseline pretreatment and liquefaction conditions seem to be appropriate for this conversion criterion: pretreatment in water at 350°C for 30 min., followed by liquefaction in tetralin at 420°C for 1 h, yields about 40% conversion dry ash-free, (daf) to hexane-solubles. We judged that this was a high enough conversion to secondary liquefaction products to have some relevance to high-severity two-stage liquefaction, but low enough to leave latitude for observing the benefits of improved pretreatment on the initial coal conversion reactions.

PMRTA Analyses of Pretreated Coals. Selected pretreated coals were analyzed by the PMRTA technique.^{12,13} This programmed temperature method measures NMR relaxation parameters to obtain a measure of molecular mobility, or fluidity, as the coal is heated through the liquefaction temperature region. In the present case, the pretreated coals were dried under nitrogen at 105°C for 18 h. The PMRTA test conditions involved heating at 4°C/min to 600°C, as described by Lynch et al.¹²

RESULTS AND DISCUSSION

Pretreatment and Liquefaction of Wyodak and Zap Lignite Coals

On the basis of recent studies at SRI and other laboratories, we used hydrothermal pretreatment under CO pressure at 350°C as a baseline for both Wyodak and Zap coals. These conditions provide modest improvement in yields in subsequent liquefaction or coprocessing experiments. We compared the liquefaction yields obtained from baseline-pretreated coals with those obtained when base, electron-transfer agent, carbon disulfide, or ferrous sulfate are added to the pretreatment in various combinations. In brief, these experiments confirmed the moderate improvements in liquefaction yield resulting from pretreatment, and showed a further improvement when base, carbon disulfide, and electron-transfer agent are added to the aqueous pretreatment medium. These results are summarized in Tables A-1 (for Wyodak and Zap coal). As described under Experimental Procedures, the conversion diagnostic was the (daf) of hexane-insolubles obtained after the pretreatment and subsequent liquefaction.

The results in Table A-1 reflect a precision of 2-3 wt% hexane-insolubles and a maximum total improvement (i.e., decrease) of about 5 wt% daf in hexane-insolubles with pretreatment agents, *beyond* the benefit provided by 350°C hydrothermal pretreatment. Hydroquinone appears to add little if any benefit once a very low level of base and/or CS₂ is present. The greatest limit to precision appears to be the steep dependence of conversion on temperature. In fact, later experiments show that the high yield (low hexane-insolubles) observed in Run JC-14 (Na₂CO₃/HQ) is primarily due to the higher temperature, rather than to the combination of promoters and the 48-h "hold" time to which the pretreated coal was subjected in this run before the liquefaction test could be performed. Although the temperature of the fluidized sand bath is controlled to within ±2°C, the rate of reactor heat-up is dependent on the degree of fluidization and the location of the reactor in the sand bed. Notwithstanding these fluctuations in net reaction severity, the results in Table A-1 give little indication that hydroquinone provides any added benefit over base and/or CS₂ under the pretreatment conditions employed here.

Carbon disulfide was tested (as a source of H₂S) as one of the promoters because these low-rank coals, being low in sulfur, are known to benefit, sometimes very substantially,¹⁴ from addition of CS₂ or other sources of sulfur. We did not wish any benefits observed for hydroquinones or other added electron transfer agents to be misleadingly high because of the low sulfur content of these coals.

The results obtained for the Zap coal, shown in Table A-2, indicate the following:

- The addition of 0.1 wt% Na₂CO₃ (on the added water) yields a small (~2 wt%) improvement in the amount of hexane-insolubles.
- By itself, the addition of 6.3 wt% CS₂ (on the raw coal) does not lead to any improvement in the hexane-insolubles.
- The addition of 2.5 wt% CS₂ (on the raw coal) together with base leads to a substantial (~9 wt%) improvement in the hexane-insolubles.
- The addition of 2.5 wt% *p*-hydroquinone (*p*-HQ, on the raw coal) to a pretreatment system containing either base alone or a base/CS₂ mixture does *not* lead to improvement in the hexane-insolubles compared to the same system without added *p*-HQ.
- The addition of a mixture of 4.8 wt% of the powerful electron donor tetrakisdimethylaminoethylene TAME (on the raw coal) and 0.1 wt% base leads to a small (1.5 wt%) improvement in the hexane-insolubles when compared to the base-only case. TAME is thus slightly more effective than *p*-HQ but still less effective than the base/CS₂ mixture.
- The addition of 2.5 wt% FeSO₄ together with 6.3 wt% CS₂ yields a substantial (~9 wt%) improvement in the hexane-insolubles.

- If the above $\text{FeSO}_4/\text{CS}_2$ system is washed with base prior to liquefaction (after the pretreatment), there is no further improvement (or degradation) in the amount of hexane-insolubles compared with the unwashed system.

As detailed above, the two most promising systems involve pretreatment with a mixture of either base/ CS_2 or $\text{FeSO}_4/\text{CS}_2$. Both of these treatments yield an improvement of about 9 wt% in the amount of hexane-insolubles. In part, these results are at least qualitatively expected: The addition of iron and sulfur compounds, particularly to low-rank coals poor in these two elements, is well known to be beneficial.

The electron-transfer agents *p*-HQ and TAME did not yield the same degree of improvement as FeSO_4 or CS_2 . HQ addition did not help at all when either base or base/ CS_2 were already present. TAME was somewhat more effective but did not help as much as the already-known-to-be-useful additives CS_2 and FeSO_4 . Thus, these electron-transfer agents do not appear to offer great promise, *at least as pretreatment agents*. We are somewhat surprised to see essentially no additional benefit from hydroquinone, given that it and related hydroquinones have been shown¹⁵ to be of significant benefit under liquefaction conditions, and that hydroquinone derivatives are used, in their oxidized forms, as hydrogen-transfer agents in synthetic procedures to promote low-temperature dehydrogenation. Two possible reasons for the observed lack of benefit are (1) the added hydroquinone was largely removed when the excess water was removed after the pretreatment step and therefore was not present during liquefaction, where it is known to be beneficial; and/or (2) the low-rank coals, which have indigenous sources of catechol and other hydroquinone species, simply do not benefit very much from the additional small amount of hydroquinone.

The removal of hydroquinone after the pretreatment step was intentional, since the purpose was to explore the benefits of these promoters under *pretreatment* conditions. But in fact, the removal of excess water after pretreatment could also remove some of the indigenous hydroquinones that are generated from the coal at about 300°C, and could thereby actually be detrimental to the subsequent liquefaction. In contrast with the probable removal of much of the added and indigenously generated hydroquinones, the added FeSO_4 and/or added CS_2 , by virtue of conversion to iron sulfide, will be at least partially retained when the excess pretreatment water is removed. Therefore these latter additives having been favorably activated during the pretreatment, may be positively impacting the liquefaction.

Evolution of Oxygen Functional Groups

Although the deoxygenation of single-ring phenols under mild liquefaction conditions in general, or under CO/water conditions in particular, is not facile, it is thermodynamically just as favorable as the kinetically facile deoxygenation of polycyclic phenols. There was good reason to

hope that the right combination of electron-transfer agents would substantially promote it. The monocyclic phenols have a more endothermic first step (reduction of keto-form) and a much more exothermic second step (water elimination), so they have a net deoxygenation thermochemistry essentially identical to that for the easily reduced polycyclic phenols. Successful promotion requires that the chemical potential of the reducing system be increased in order to accomplish the first step. This may require not only a catalyst but also an effective reservoir of reducing agent to keep the chemical potential high even after some reduction has taken place. However, direct oxygen analysis (as well as determination of oxygen by difference) of pretreated coals shows that all of the pretreatments tested here, including baseline conditions, reduce the O-content of Zap lignite from 20 wt% to about 15.5 wt% and that of the Wyodak coal from 18 wt% to about 14 wt%. Similarly, very little difference with respect to hydrogen content was observed between the different pretreatments. The relative invariability of oxygen loss under various short-term pretreatment conditions observed here is consistent with the results reported by Loo and Ross.¹⁶ It is interesting that the pretreatment conditions employed did not accomplish the additional deoxygenation that was desired but nevertheless did result in modest improvements in liquefaction yields.

The modest CO pressure used here (500 psi, cold) evidently did not provide sufficient reduction potential to drive the deoxygenation. Since the reducing potential of the system is defined not merely by the CO partial pressure but also by the $[CO]/[CO_2]$ ratio, the potential may also be increased by chemical or physical removal of CO_2 . We had hoped that the high solubility of CO_2 in the near-critical aqueous pretreatment medium would provide for effective removal of the CO_2 from the vicinity of the reaction site. However, it was clearly not enough to bring about the desired reaction.

Possible modifications of the pretreatment could involve addition to the pretreatment of some condensed-phase reservoir (e.g., a hydroaromatic), or perhaps the use of hydroquinones and other electron-transfer agents under nominally nonaqueous (no added water) conditions. Such conditions are, after all, more representative of current liquefaction practice and would avoid some of the experimental problems known to be associated with excessive water in liquefaction systems. We also believe that it would be helpful to the goal of enhanced oxygen removal during pretreatment (as well as of fundamental interest) to make actual deoxygenation rate measurements using surrogates for the coal phenols (e.g., cresol and/or xylene mixtures).

It should be noted that early deoxygenation of the coals has, in addition to the beneficial impacts that constituted the rationale for this effort, potential detrimental impacts. Hydroxyl groups not only activate aromatic systems toward retrograde reactions but also activate coupled aromatic systems toward cleavage.^{17,18} The net impact of removal of such oxygen functional

groups will depend on the balance of progressive and regressive reactions they promote under a particular set of conversion conditions. We had speculated, and still do anticipate, that since some 20 to 50% of the oxygen in the low-rank coals of interest is in the form of ether linkages that are fairly readily cleaved, the removal of new phenolic oxygen relatively soon after it is generated by cleavage of ether linkages would provide a net benefit. We were simply not able, under conditions that projected practicality of a pretreatment step, to substantially enhance deoxygenation.

Lim et al.¹⁹ have reported results from a similar effort to improve liquefaction yields by means of a CO/H₂O pretreatment. They chose to operate at slightly lower temperature and higher CO pressure, apparently projecting that more is to be gained by doubling CO pressure (e.g., from 400 to 800 psi, cold) than is to be lost by decreasing the temperature 20° to 30°C and thereby lowering the vapor pressure of water by ~600 psi. In general terms, their results appear to be similar to those described here: modest improvement in subsequent liquefaction yields, but no increase in pretreatment oxygen loss.

At this point, we can summarize our general conclusion for enhanced oxygen removal pretreatment using CO/H₂O. Without substantial improvement in the pretreatment benefits of added electron-transfer agents, we believe the prognosis for these agents being a practical pre-additive in an aqueous pretreatment scheme is not good. The improvements resulting from the pretreatment conditions we have tested thus far are significant, amounting to a 9 wt % (maf) increase in hexane-soluble material (~20% improvement on a base-case hexane-solubles yield of 46%). However, the 20% improvement noted above was obtained not with the hydroquinone or TAME but with promoters already known to be effective under liquefaction conditions (donor solvent) themselves and already exploited in that context. Furthermore, their effectiveness may in substantial part have resulted from their action (or that of their descendents) during the liquefaction process itself. Finally, even if the CO/H₂O/electron-transfer agent system had given this 9 wt% improvement in hexane solubles (and a corresponding increase in distillate yield), it would remain to be seen whether this could provide any real process advantage, given that the pretreatment conditions are now not greatly lower in temperature/pressure severity than the liquefaction itself. We were well aware at the beginning of this project that the pressure and temperature requirements for straight CO-water systems severely limit their utility as liquefaction approaches per se and that significant catalysis would be necessary to overcome these limitations for a CO-water pretreatment. We had hoped to overcome these limitations.

PMRTA Analyses of Pretreated Coals

To learn more about how any pretreatment benefits are related to the development of fluidity in pretreated coals, we analyzed pretreated coals by using proton magnetic resonance

thermal analysis (PMRTA). For PMRTA, we selected a set of pretreated coals for which the subsequent liquefaction yields varied most widely. The objectives were to (1) determine the temperature-dependent molecular mobility of the pretreated coals to learn how this factor may correlate with their susceptibility to liquefaction and (2) obtain information relevant to the question of whether the benefits observed are due to breakage of pre-existing crosslinks by the pretreatment or to inhibition of crosslinking that takes place during liquefaction itself.

Figures A-1 and A-2 show the results of PMRTA analysis of variously pretreated Wyodak coal and Zap lignite. The figures show the variation of the M_{2T16} parameter with temperature. M_{2T16} is an NHR relaxation parameter (the second moment, truncated at 16 kHz, of the Fourier transform of the transverse relaxation signal) that provides a measure of molecular mobility, or fluidity. Dry coals at room temperature, or essentially rejected organic solids, exhibit M_{2T16} values above 50, whereas a fully fused pitch would have a value close to zero. For the Wyodak coal, the minimum impact (ΔM_{2T16}) was provided by baseline pretreatment at 350°C for 53 min. in CO/H₂O only, and the maximum impact was obtained from CO/H₂O with added sodium carbonate or ferrous sulfate and carbon disulfide. A larger number of samples of the pretreated Zap lignite were analyzed because control of the liquefaction conditions was more precise in that series of runs. In fact, included with the pretreated Wyodak coals were a pair of samples where the pretreatments were nominally identical but the hexane-insoluble yields of the subsequent liquefactions were substantially different. The purpose here was to use this pair as an additional test of how closely the liquefaction yields would be paralleled by the PMRTA mobility measurements. The pretreatment conditions, liquefaction yields, and PMRTA values are shown in Table A-3.

The data in Table A-3 show that the range of mobility is much larger for the Wyodak coal than for the zap lignite, a finding consistent with the general trend of greater softening with increasing rank. (All of the $M_{2T16min}$ values for the Wyodak are lower than all of the $M_{2T16min}$ values for the Zap.) Furthermore, although the range of samples is limited, there is an excellent correlation between the liquefaction yields and both sets of minimum M_{2T} values for the Wyodak, as shown in Figures 3 and 4. The correlation was just as good with M_{2T40} as it was with M_{2T16} , even though the interpretation of the M_{2T40} results in terms of gross molecular mobility is less straightforward. Wyodak samples JC16 and JC18, are the pair for which the pretreatment conditions are nominally identical but the liquefaction yields are quite different. Figures A-3 and A-4 show that the difference in liquefaction yields is exactly paralleled by the difference in M_{2T} values; this finding indicates (at least in this small set of samples) that both the batch liquefaction and the PMRTA measurements are more reliable as indicators of the impact of pretreatment than the presumed reproducibility of the pretreatment itself. This was somewhat surprising: we had projected that the differences in liquefaction yields between Samples JC-16 and JC-18 was most likely the result of differences in *liquefaction* reactor heating rate and therefore in

net severity of liquefaction, but it seems that it was the *pretreatment* that was more variable. The factors determining the effectiveness of the pretreatment are evidently more ephemeral in nature. We also note that the minimum M_{2T16} value for the pretreatment blank (CO/H₂O, no other added reagents) is actually *higher* than that for the untreated Argonne Wyodak, even though we have previously found that even this basic pretreatment condition improves subsequent liquefaction (albeit in a poorer liquefaction solvent, Maya atmospheric bottoms).

For the pretreated Zap samples, the degree of mobility was much less, and the correlation between liquefaction yields and M_{2T} values was very poor. Figure A-5 shows the essential absence of any correlation with M_{2T16} values (although elimination of the point at 43.7 and 48.5 provides a correlation coefficient of 0.7). Figure A-6 shows what appears to be a modest correlation between hexane-soluble liquefaction yield and M_{2T40} (correlation coefficient 0.7) but actually depicts a trend opposite to that observed for the pretreated Wyodak samples; that is, the liquefaction yield increases with *increasing* M_{2T} values. We suspect that this latter correlation is simply spurious and results from the very small extent of fluidity development exhibited by either the raw or the pretreated lignite. It is *possible* that, since liquefaction of this lignite normally takes place without benefit of very much thermal relaxation (i.e., melting or other phase change), whatever small amount of relaxation does occur is not large enough to dominate and other factors produce a valid negative correlation. However, we believe that the apparent inverse correlation between molecular mobility and liquefaction yield shown in Figure A-6 for pretreated lignite is merely accidental.

The temperature dependence of increased molecular mobility allows us to determine, at least provisionally, whether pretreatments are beneficial to liquefaction primarily because they decrease crosslinking in the starting coal, or primarily because they inhibit crosslinking during liquefaction. The PMRTA data in Figure A-3 for the Wyodak coal reveal that the mobility of all of the pretreated samples is similar at room temperature, but by the time 200°C is reached, the sample that exhibits the best liquefaction yield is already showing substantially higher mobility. In contrast, by ~400°C, when the mobility is rapidly decreasing, there is little differentiation among the samples. Differentiation that is already seen at 200°C, when little hydrogenolysis (or homolysis) of coal linkages is thought to take place, suggests that the pretreatment has removed some of the original crosslinks, either covalent or hydrogen-bonded, in the coal. Similarly, confluence of the curves at about 400°C suggests that pretreatment has little impact on the high-temperature crosslinking that dominates in the absence of a good liquefaction solvent.

SUMMARY

Pretreatment and liquefaction tests of promoters for CO/H₂O pretreatment of low-rank coals provided the following results:

- The addition of 0.1 wt% Na₂CO₃ (on the added water) yields a small (~2 wt%) improvement in the amount of hexane-insolubles.
- By itself, the addition of 6.3 wt% CS₂ (on the raw coal) does not lead to any improvement in the hexane-insolubles; however, the addition of CS₂ together with base leads to a substantial (~9 wt%) improvement in the hexane-insolubles.
- The addition of 2.5 wt% *p*-hydroquinone (*p*-HQ, on the raw coal) to a pretreatment system containing either base alone or a base/CS₂ mixture does *not* lead to improvement in the hexane-insolubles compared to the same system without added *p*-HQ.
- The addition of a mixture of 4.8 wt% TAME (on the raw coal) and 0.1 wt% base leads to a small (1.5 wt%) improvement in the hexane-insolubles compared to the base-only case. TAME is thus slightly more effective than *p*-HQ but still less effective than the base/CS₂ mixture.
- All pretreatments tested remove about 25% of organic oxygen.
- We conclude that the benefits of near-critical hydrothermal pretreatment can be augmented by additives such as base, CS₂, and FeSO₄, but the specific benefits of hydroquinones are not significant under the conditions tested here. The benefits of CO/H₂O pretreatment can presumably be enhanced further by increasing CO pressure, but the total CO and H₂O pressure, even if the temperature is reduced to 320°C, is still uncomfortably close to that necessary for liquefaction itself.
- PMRTA of pretreated Wyodak coals showed a very good correlation between the temperature-dependent molecular mobility and the convertibility of the pretreated coals to hexane-soluble material under subsequent donor solvent liquefaction; however, a poor correlation was observed for Zap lignite.
- The increased molecular mobility shown by pretreated Wyodak coals began appearing at about 200°C, well below temperatures at which significant thermal cleavage of covalent bonds is significant, and also before the temperatures at which the early crosslinking in low-rank coals has been observed. We therefore conclude that the benefits of pretreatment result primarily from the cleavage or disruption of pre-existing crosslinks, either covalent or hydrogen-bonded.

ACKNOWLEDGMENT

We gratefully acknowledge financial support for this work from the Pittsburgh Energy Technology Center, U.S. Department of Energy, under Contract No. DE-AC22-91PC91044.

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Table A-1

**EFFECT OF PRETREATMENT ON CONVERSION OF WYODAK COAL
IN THERMAL BATCH LIQUEFACTION**

Expt. No.	Pretreatment ^a			Gas	Liquefaction Temp. (°C) ^f	Hexane- Insolubles ^g
	Additives ^b					
	0.1 wt% Na ₂ CO ₃ ^b	5 wt% p-HQ ^{c,d}	2.5 wt% CS ₂ ^{c,e}			
JC2				Ar	420	55.0
JC2A				Ar	430	50.2
JC3				CO	430	52.5
JC12		X		CO	430	53.8
JC14	X	X		CO	440 ^h	41.3
JC14B	X	X		CO	430	48.0
JC14C	X	X		CO	430	47.8
JC14D	X	X		CO	430 ^h	49.9
JC16	X	X	X	CO	430	44.8
JC17			X	CO	430	44.1
JC18	X	X	X	CO	430	50.5

a. 10.0 g coal; 15 ml H₂O, mixed but unstirred; 53 min at 350°C.

f. 1 hr; 1000 psi H₂ (cold).

g. Defined as %daf coal that was insoluble in 200 mL hexane.

b. As wt% of the added H₂O.

c. As wt% of raw coal.

d. p-HQ = p-hydroquinone

e. Calculated to produce H₂S at 13% of the level of H₂ pressure.

h. Pretreated coal allowed to sit for 48 hr (at room temperature, under CO pressure) after 350°C pretreatment.

Table A-2
EFFECT OF PRETREATMENT ON CONVERSION OF ZAP LIGNITE
IN THERMAL BATCH LIQUEFACTION

	Pretreatment ^a						Liquefaction Temp. (°C) ^g	% Hexane- insolubles ^h
	Additives (wt%)					Gas		
Expt No..	Na ₂ CO ₃ ^b	p-HQ ^{c,d}	CS ₂ ^c	FeSO ₄ ^e	TAME ^{c,f}	500 psi (cold)		
JC18A						CO	430	53.4
JC19	0.1	5				CO	= 410 ⁱ	59.1
JC20	0.1					CO	430	51.5
JC22	0.1	5				CO	430	51.5
JC28	0.1	5				CO	430	51.1
JC24	0.1	5	2.5 ^j			CO	430	44.5
JC26	0.1	5	2.5 ^j			CO	430	45.1
JC25	0.1		2.5 ^j			CO	430	47.5
JC27	0.1		2.5 ^j			CO	430 ^k	44.8
JC34	0.1		2.5 ^j			CO	430	44.3
JC30	0.1				4.8	CO	430	49.7
JC29			6.3	2.5 ^l		CO	430	43.6
JC32			6.3	2.5 ^l		CO	430	45.2
JC33	m		6.3	2.5 ^l		CO	430	44.2
JC31			6.3			CO	430	53.8

- a. 10.0 g coal; 15 mL H₂O, mixed but unstirred; 53 min at 350°C.
g. Unless noted, reaction times are 1 h under 1000 psi H₂ (cold)
h. Defined as the percent of the organic portion of the coal that was insoluble in 200 mL hexane.
b. As wt% of the added H₂O.
c. As wt% of raw coal.
d. p-HQ = p-hydroquinone
e. As FeSO₄·7H₂O; weight percentages are on raw coal and refer to the nominal amount of unhydrated material.
f. TAME = tetrakis(dimethylamino)ethylene
i. Fluidized sand bath temperature set at 430 °C, but temperature did not recover after insertion of reactor, apparently because of excessive air flow through bath.
j. Calculated to produce H₂S at ~13% the level of H₂ ostensibly available from the water-gas shift reaction.
k. Fluidized sand bath temperature set at 430°C, but temperature dropped to 381°C and recovered to 400°C only after 15 min. Total reaction time 75 min.
l. Washed with several aliquots of H₂O after pretreatment; calculated to remove >99% of material freely soluble in pretreatment water. Initial ratio CS₂/FeSO₄ (mol/mol) = 5.
m. Final H₂O wash after pretreatment (note l) contained 0.1 wt% Na₂CO₃.

Table A-3
COMPARISON OF WYODAK AND PRETREATMENT CONDITIONS, LIQUEFACTION
YIELDS, AND MINIMUM PMRTA VALUES

Sample No.	Pretreatment Conditions ^a	(100 - Hex Insol) ^b	Minimum M _{2T} Values	
Wyodak			M _{2T} 16(min) ^c	M _{2T} 40(380°C) ^d
	Untreated ^a	—	39.9	100.2
JC3 (blank)	CO/H ₂ O only.	47.5	40.9	107.1
JC16	Na ₂ CO ₃ /HQ/CS ₂	55.2	32.4	90.1
JC18	Na ₂ CO ₃ /HQ/CS ₂	49.5	38.2	103.0

Zap Lignite			M _{2T} 16 (Min) ^c	M _{2T} 40 (300°C)
	Untreated	—	42.5	114.6
JC18A (blank)	CO/H ₂ O only.	46.6	45.0	124.8
JC20	Na ₂ CO ₃	48.5	44.4	121.3
JC22	Na ₂ CO ₃ /HQ	48.5	43.7	117.9
JC27	Na ₂ CO ₃ /CS ₂	55.2	44.1	128.0
JC29	CS ₂ /FeSO ₄	56.4	— ^f	— ^f
JC30	Na ₂ CO ₃ /TAME	50.3	44.7	124.8

- a. "Untreated" coal was tested as received from the Argonne Premium Coal Sample Bank. The blank samples were pretreated at 350°C for 53 minutes in water with 500 psi (cold) CO pressure without any *additional* reagents. The other additional reagents used were sodium carbonate (Na₂CO₃, 0.1 wt% of raw coal), carbon disulfide (CS₂, 2.5 wt% or 6.3 wt% of raw coal), ferrous sulfate (FeSO₄, 2.5 wt% of raw coal), hydroquinone (HQ, 5.0 wt% of raw coal), and tetrakis(dimethylamino)ethylene (TAME, 4.8 wt% of raw coal). No liquefaction tests were performed on the untreated coal: previous work had shown that pretreatment in water alone at 350°C has a beneficial impact on the subsequent coprocessing (i.e., liquefaction in a poor solvent) of the Argonne Wyodak and Zap coals.
- b. 100 minus the wt fraction (maf) insoluble in a fixed volume of hexane was taken as the measure of liquefaction effectiveness, and as a rough indicator of the distillate yield.
- c. M_{2T}16 and M_{2T}40 are relaxation parameters from broad-band solid state nmr signals. These parameters are indicators of molecular mobility in the coal structure that provide a measure of the degree of softening as the coal is heated in the spectrometer. M_{2T}16 values range from near 50 for a normal organic solid (or coal at room temperature) to near zero for a fully fused pitch.
- d. The values of M_{2T}40 shown in this column are only local minima for the value of this parameter, achieved at about 380°C in the case of the pretreated Wyodak samples.
- e. The Zap samples did not show even a consistent local minimum in the 300 to 400°C range, so the values at 300°C, where the most differentiation among the various pretreated samples was seen, have been included in this table.
- f. Sample JC29, which was pretreated with carbon disulfide and ferrous sulfate, appeared to have ferromagnetic materials that completely blocked the ability to use the M_{2T} values as measures of molecular mobility.

Figure A-1. PMRTA analysis of variously pretreated Wyodak coals.
Pretreatment conditions shown in Table A-3.

Figure A-2. PMRTA analysis of variously pretreated Zap lignites.
Pretreatment conditions shown in Table A-3.

Figure A-3. Correlation of conversion of Wyodak coal minimum M_{2T16} values.

Figure A-4. Correlation of conversion of Wyodak coal minimum M_{2T40} values.

Figure A-5. Correlation of conversion of Zap lignite with minimum M₂T₁₆ values.

Figure A-6. Correlation of conversion of Zap lignite with minimum M₂T₄₀ values.

Appendix B

ANALYSIS OF TREATED LOW-RANK COALS

INVESTIGATION REPORT CET/IR149

**ANALYSIS OF TREATED
LOW-RANK COALS**

Report to SRI International

by

Richard Sakurovs and Leo J. Lynch

June, 1993

Analysis of treated low-rank coals

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Summary

1. Relevant PMRTA data have been obtained for all treated Wyodak and Zap coal samples supplied except for the Zap sample JC29, which gave anomalous results probably because of contamination by magnetic material.
2. The data for two of the Wyodak specimens - JC18 and JC16 - are consistent with major breakdowns in crosslinking and/or molecular weight in these specimens.
3. The other treated samples are not significantly more fusible than the untreated coals.

PMRTA characterisation of brown coals

PMRTA studies (Lynch et al., 1987, Lynch and Sakurovs, 1991, Sakurovs et al., 1991) have shown that, as the temperature of dry, low rank coals is increased, their molecular mobility increases, reaching a maximum between 300 and 375°C, before decreasing as the mobilised structures either

- i) evaporate,
- ii) decompose to form low molecular weight volatile material, or
- iii) condense to an immobile or rigid residue. (There is evidence that some crosslinking reactions occur that inhibit molecular mobility at temperatures as low as 300°C (Lynch and Sakurovs, 1991).)

The molecular mobility activated during heating of brown coals is almost entirely associated with an aliphatic-rich component petrographically identified as liptinite (Sakurovs et al., 1991). The molecular mobility of the other, aromatic-rich material, which is the low rank analog of vitrinite, is not significantly enhanced at any stage during heating to 600°C. The infusible nature of this material can be attributed to its extensive covalent crosslinking.

Experimental

Samples

Table 1 lists the additives applied to the coal samples before their treatment at 430°C for 1hr in the presence of carbon monoxide and hydrogen. This treatment, performed at SRI, is termed here the hydrogenation step. The JC3 and JC28A samples, which had been treated at elevated temperatures and pressures in the absence of additives, provide blanks against which the effect of additives can be ascertained. The 'hexane insolubles' is the percentage of the material that is insoluble in hexane after the hydrogenation step. A reduced 'hexane insolubles' value indicates an increased conversion to hexane-soluble oils and gases.

Table 1
Additives used by SRI in the preparation of the supplied samples.

Coal	Sample ID	Additives (wt%)					Hexane insolubles (%)
		Na ₂ CO ₃	p-hydro-quinone	CS ₂	FeSO ₄	TAME	
Wyodak	JC3						52.5
Wyodak	JC16	0.1	5.0	2.5			44.8
Wyodak	JC18	0.1	5.0	2.5			50.5
ND Zap	JC20	0.1					51.5
ND Zap	JC22	0.1	5.0				51.5
ND Zap	JC27	0.1		2.5			44.8
ND Zap	JC28A ¹						53.4
ND Zap	JC29			6.3	2.5		43.6
ND Zap	JC30	0.1				4.8	49.7

¹ This sample is called sample JC18A in the fax from SRI that supplied these experimental details.

Each of these hydrogenated samples has been characterised by PMRTA. Results obtained earlier for untreated Argonne Premium samples of Wyodak and Zap coals are included for comparison. It is assumed that the untreated coals examined earlier are representative of the coals used to prepare the hydrogenated coal samples.

Procedure

The hydrogenated samples were dried under nitrogen at 105°C overnight prior to analysis. PMRTA test conditions were: heating at four degrees per minute, under nitrogen, to 600°C (Sakurovs et al, 1991). Transient NMR signals were recorded at one minute intervals from which the values of the analytical parameters M_{2T16} and M_{2T40} were calculated. Only single PMRTA tests were performed due to the limited amounts of each sample provided.

Parameters

M_{2T16}

The M_{2T16} parameter characterises the extent to which the specimen acquires and loses molecular mobility as a consequence of thermally activated transformations that occur during the test. Dry coals at room temperature exhibit M_{2T16} values of about 50, indicating that, other than for a degree of segmental mobility of aliphatic structures, they are rigid organic solids. A fully fused organic material such as a pitch above its softening temperature would have an M_{2T16} value of close to zero. Thus variations in M_{2T16} with temperature are in response to changes in the molecular dynamics and hence reveal information about the nature of the material under test and are useful for characterisation of the material. For example, the minimum M_{2T16} value on heating to 600°C (M_{min}) is a measure of the maximum extent of molecular mobility attained on heating to pyrolysis temperatures - the 'fusibility'. M_{min} values have a repeatability of about 1 unit.

M_{2T40}

The related M_{2T40} parameter, computed to include sensitivity to lower frequency molecular motions than the M_{2T16} parameter, is also more sensitive to the hydrogen density of the sample and the density of unpaired electrons in the sample. The greater these densities the greater is the magnitude of M_{2T40} , other factors being equal. M_{2T40} values have a repeatability of about 3 units.

Results

Comparison of untreated Wyodak and Zap coals

The M_{2T16} pyrograms of Wyodak and Zap coals differ from that of a typical Victorian brown coal in that their minima occur near 400°C, whereas for the brown coal the minimum is broad and occurs near 350°C (Figure 1). This is consistent with the higher rank of the two US coals than brown coal, and thus the correspondingly greater thermal stability of their liptinite.

The greater fusibility of the Wyodak coal indicates that it is richer in liptinite than Zap coal. The fusibilities of the Wyodak and Morwell coals are similar indicating that the liptinite contents of these coals are similar, even though the temperatures at which the minimum M_{2T16} values occur are different. The molecular weight and/or crosslink density of Zap and Wyodak liptinite is probably greater than for the brown coal.

Figure 1 M_{2T16} pyrograms of untreated Wyodak and Zap coals and that of a Victorian (Morwell) brown coal.

Wyodak samples

Table 2 lists the M_{min} values and the M_{2T40} value before and after heat treatment for these samples. Figures 2 and 3 compare the M_{2T16} and M_{2T40} pyrograms of the untreated Wyodak coal and the blank Wyodak sample. Figures 4 and 5 show the effect of additives prior to the hydrogenation step on the M_{2T16} and M_{2T40} pyrograms of the Wyodak coal samples.

Table 2
Some PMRTA values of the Wyodak specimens

Wyodak sample	M _{min}	M _{2T40} (before test)	M _{2T40} (after test)
untreated	40	172	123
JC3	41	178	138
JC16	32	186	146
JC18	38	198	142

Figure 2 Comparison of the M_{2T16} pyrograms of the untreated and heat-treated Wyodak coals.

Figure 3 Comparison of the M_{2T40} pyrograms of the untreated and heat-treated Wyodak coals.

Figures 2 and 3 show that the heat and pressure treatment applied to Wyodak coal has significantly reduced its M_{2T16} value at temperatures below 300°C, i.e. the treatment has reduced the thermal stability of the fusible part of the coal (the liptinite). The JC3 sample has a similar M_{min} value (fusibility) to the untreated sample, and both the M_{2T40} and M_{2T16} values for the JC3 sample are below those of the untreated coal below 300°C and above them between 300 and 400°C. These facts suggest that the nature of the infusible portion of the JC3 sample is similar to that of the untreated coal, and thus that its properties have not been strongly modified by this treatment.

Figure 4. M_{2T16} pyrograms of the treated Wyodak coals.

Figure 5 M_{2T40} pyrograms of the treated Wyodak coals.

The fusibilities of both the JC16 and JC18 samples are much greater than that of the blank (Figure 4). If the liptinite in the blank is mobilised completely at elevated temperatures, the lower M_{2T16} values of the JC16 and JC18 samples at these temperatures imply that a normally infusible - possibly aromatic-rich - component of the coal has become partially fusible.

The lower room temperature M_{2T16} values, and hence greater molecular mobility, of each of the hydrogenated Wyodak specimens compared to the blank, are consistent with a greater aliphatic nature and/or lower crosslink density of these materials. In the case of the JC16 sample, the facts that it is substantially more fusible than the other Wyodak specimens, and its room temperature M_{2T40} is greater than that of the blank, yet between 100°C and 450°C, its M_{2T40} values are much lower than those of the blank, indicate that the JC16 specimen is more rich in hydrogen compared to the other Wyodak specimens, i.e. it has been significantly hydrogenated by the treatment.

The JC18 sample has somewhat different characteristics from the JC16 sample. It is significantly less fusible (Table 1). The differences in the M_{2T40} pyrograms of these two specimens are also significant in that the M_{2T40} values of the JC18 sample decrease rapidly between 350 and 400°C and thus it is possible that this behaviour and its high room temperature M_{2T40} value are due to the same magnetic anomaly that occurs in sample JC29 (see below), albeit to a much smaller extent.

The treatments applied to the JC16 and JC18 samples are nominally the same (Table 1). However, the fact that PMRTA behaviours of these two specimens are very different is consistent with their very different hexane insolubles yield, and indicates that these materials are different.

Zap samples

Figures 6 and 7 compare the M_{2T16} and M_{2T40} pyrograms of the untreated Zap coal and the heat-treated Zap coal. Figures 8 and 9 compare the M_{2T16} and M_{2T40} pyrograms of the treated coals. Table 2 lists the M_{min} values and the M_{2T40} value before and after heat treatment for these samples.

The fusibility of the JC28A sample is substantially less than the untreated coal (Fig. 6). The combination of heat and pressure has therefore either resulted in the fusible material being lost or caused some of it to condense or crosslink. However, the M_{2T40} values of the JC28A sample are consistently greater than that of the untreated coal (Fig. 7), which suggests that the infusible component of the Zap coal has been modified by the treatment.

Figure 6 Comparison of the M_{2T16} pyrograms of the untreated and heat-treated Zap coals.

Figure 7 Comparison of the M_{2T40} pyrograms of the untreated and heat-treated Zap coals.

Figure 8 M_{2T16} pyrograms of the treated Zap coals.

Figure 9 M_{2T40} pyrograms of the treated Zap coals.

Table 3
Some PMRTA values of the Zap specimens

Zap sample	M _{min}	M _{2T40} (before test)	M _{2T40} (after test)
untreated	43 ^{42.5}	170	121
JC20	44 ^{44.4}	177	133
JC22	44 ^{42.7}	177	133
JC27	44 ^{44.1}	186	131
JC28A	45 ^{45.0}	178	134
JC29	-	250	148
JC30	45 ^{44.7}	177	133

The ¹H nmr transient signals of the JC29 sample recorded below 400°C are highly distorted in that they have abnormally rapid decay rates. The signal distortion increases the M_{2T40} values and decreases the M_{2T16} value of this sample (Figures 8 and 9). It is speculated that the distortion arises from a secular magnetic interaction of the protons with a high density of unpaired electrons in the specimen, associated with inorganic species that are superparamagnetic or ferromagnetic in nature (Lynch et al., 1986). It is noted that this sample had FeSO₄ added prior to the treatment. However, the M_{2T40} value of the residue of the JC29 sample on cooling after pyrolysis is only slightly greater than those of the other samples (Table 3). This indicates that the secular interaction and hence the inorganic compound involved is destroyed on heating above 400°C.

The M_{2T16} pyrograms in Figure 8 show that the treated Zap specimens are slightly more fusible than the JC28A (blank) sample, though less so than the untreated coal (Table 3). The JC20 sample, which had been treated with sodium carbonate, was only slightly more fusible than the blank. Addition of mixtures of sodium carbonate with either p-hydroquinone, carbon disulfide or TAME, prior to the hydrogenation step, did not significantly change the fusibility of the treated Zap coal (Samples JC22, JC27 and JC30, respectively) from that of the JC20 sample, which had been treated with sodium carbonate only.

The additive applied to the Wyodak coal prior to the hydrogenation that gave the product a substantially increased fusibility was a mixture of sodium carbonate, p-hydroquinone and carbon disulfide. This suggests that p-hydroquinone and carbon disulfide may have synergistic effects on the fusibility of the treated coals (i.e. they have little effect when mixed independently with sodium carbonate and the coal, but when mixed together have a strong effect on the fusibility of the product). In order to verify this, study of a Zap coal that has been treated with the mixture of sodium carbonate, p-hydroquinone and carbon disulfide is warranted.

The M_{2T40} values of the JC27 sample are significantly greater than those of the other samples below 350°C, even though their M_{2T16} values are similar. This suggests that the nature of the infusible component of the JC27 coal has been altered by treatment with carbon disulfide.

The fusibility of the treated coals does not appear to correlate to the hexane insolubles yield. The two Zap specimens with the least hexane insolubles yields were JC27 and JC29, both of which had been treated with carbon disulfide. Although PMRTA results were affected by the presence of magnetic contamination in the JC29 sample, the JC27 sample, which shows no evidence of such contamination, is not noticeably more fusible than the other Zap specimens.

Excluding the JC29 sample, the room temperature M_{2T40} value is significantly greater for treated coals that had reduced hexane insolubles yield (Samples JC16, JC18 and JC27). An increase in the room temperature M_{2T40} value, if not due to magnetic contamination, can indicate an increased hydrogen density in the material, (due, for example to an increased aliphaticity or hydroaromaticity), which could mean an increased extractability by hexane.

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Appendix C

DEVELOPMENT OF LARGE-SCALE TGA APPARATUS FOR CHARACTERIZING COAL LIQUIDS

DEVELOPMENT OF A LARGE-SCALE TGA APPARATUS FOR CHARACTERIZING COAL LIQUIDS

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INTRODUCTION

The chief impetus for direct coal liquefaction comes from the possible use of coal liquids as feedstocks in a refinery. The characterization most sought by the refiners is the distillability of the feedstock, and ASTM (American Society for Testing and Materials) methods such as D1160 are designed to determine that property.¹ Unfortunately, ASTM distillation techniques are not well suited for characterizing products that tend to contain high concentrations of very heavy (e.g., preasphaltene) material, mineral matter, and unconverted (i.e., insoluble) carbon. Particularly for small samples, such as those produced by batch microautoclave liquefaction, problems with coking in the distillation vessel are markedly aggravated by differences between the vessel temperature and reflux-head temperature.

Alternative techniques have been developed for characterizing coal liquids. Prominent among them are solubility classifications,² liquid chromatography,³ gas chromatography (GC)-simulated distillations,⁴ and small-scale thermogravimetric analysis⁵ (TGA). As discussed below, these techniques either pose serious difficulties in representative sampling or provide data whose relevance to processing is questionable. We have devised a large-scale TGA apparatus for improved characterization of coal liquids.

Classification of liquefaction products by their solubility (e.g., oils, asphaltenes, preasphaltenes, and unconverted coal), while simple in principle, is painstaking to perform, is highly procedure-dependent, and can be only grossly related to distillability. Hexane- or heptane-insolubles are often taken as a rough measure of nondistillable material, but the actual ratio of distillate to hexane-solubles can vary substantially.⁶ That is, two hexane-insoluble fractions will often contain substantially different proportions of distillable material. Furthermore, the solubility classification is not detailed enough to describe the nature of products within any class. For example, two samples with the same "oils" yield (hexane-solubles) can contain widely differing amounts of naphtha and light gas oils.

Liquid chromatography techniques (which on an analytical scale can be readily automated) have been developed to deal with the operator-intensive nature and the limited discrimination

capability of solubility fractionation. Notable among these efforts is the pioneering work of Whitehurst and coworkers fifteen years ago.³ However, these approaches still do not address the problem of relationship to distillability, and because in an analytical mode they are applied to only a small portion of the sample, they are not readily suited to solving the problem of representative sampling of products that are markedly heterogeneous, multiphase mixtures.

The availability of bonded-phase fused-silica capillary chromatography columns with upper temperature limits of 400°C makes capillary GC-based simulated distillation *nominally* practical up to about C₁₀₀ alkanes atmospheric equivalent boiling point ((AEBP) ~1300°F).⁷ Although this technique may be very useful for assessing petroleum, it is not so promising for assessing the volatility of whole coal products. First, for the alkyl-aromatic and polar structures that tend to dominate single-stage coal liquefaction products, the AEBP that is accessible without excessive tailing will be significantly lower than the AEBP for simple alkanes. Second, if the material to be analyzed is not simply dominated by a series of straight-chain alkanes but contains (as do coal liquids) an incredible variety of cycloaliphatic, aromatic, polar structures, the definition of baseline and peak integration can be very problematic.

What most limits GC-based simulated distillation for raw, unfiltered liquefaction products is the problem of representative sampling. Somewhat less of a problem, but still a concern, is that the fraction of the injected sample that is nondistillable (i.e., does not elute from the column) is not directly determinable without a reliable independent measure of detector sensitivity for the eluted fraction. For all these reasons, we believe that capillary GC-based simulated distillation techniques are not the most promising approach to a convenient and more process-related diagnostic for small-scale batch liquefaction products.

The process-relevant information most desired is the weight fraction distillable at various temperatures. Therefore, the most natural choice seems to be some version of thermogravimetric analysis (TGA), where weight loss is continuously recorded as a function of temperature during programmed heating of the sample. TGA is not a distillation process per se but evaporation in a 1-atm or reduced-pressure carrier stream, where carbonization in the "distillation vessel" is substantially reduced because most of the heat needed to maintain a column of refluxing vapor is not needed and the temperature gradient required to drive the relatively minimal heat flow is very small.

TGA data will mimic those for distillation as long as two requirements are met. First, the rate of evaporation must have the same temperature dependence as the equilibrium vapor pressure; this requirement is met *except* when heavy molecules are carried, or entrained, into the gas phase by lighter molecules. Second, the rate of temperature rise must be roughly "tuned" to the sample

size and surface area, so that the temperature rise does not outrun the rate at which components can diffuse through the layer or film of condensed material to the surface where they will vaporize. In practice, this requirement means that the samples must be fairly small so that the rate of weight loss per unit surface area can be relatively low.

In 1984 Ouchi and coworkers,⁵ in conjunction with personnel at the Pittsburgh Energy Technology Center, performed extensive tests at the 10-mg scale, using samples from light distillate up through high-vacuum gas oil, and found that by varying several TGA parameters, they could closely match the ASTM distillation data. For the lighter materials and operation at atmospheric pressure, the sample had to be contained in a small vessel with a capillary exit about 1 cm long and 0.5 cm diameter. For both vacuum gas oils (AEBP 514° to 1050°F), and high-vacuum gas oils (581° to 1119°F), they found that a simple open vessel, operation at reduced pressure (1 Torr), and a 20°C/min heating rate gave the best match to actual ASTM distillation curves. Thus, although a match to a true ASTM distillation curve could not be obtained with a single experimental procedure for a full boiling range material, a very good match could be obtained for a wide range of heavy material, extending from an atmospheric boiling point of about 500°F to materials even beyond the common 1050°F end point of process distillations.

Thus, the TGA approach appears to be most suited for routine assessment of small-scale batch reactor liquefaction products. The major question about the routine application of TGA is that of representative sampling. In operation, a sample of only 10 to 30 mg is transferred from the microautoclave to the TGA. If the original charge to the autoclave includes, say, 3 g of coal containing 10% mineral matter, there will be about 300 mg of insoluble inorganic material, probably concentrated near the bottom or on the walls of the reactor. Clearly the probability is high that, in transferring a 10-mg sample, 1 mg (or more) too much or too little mineral matter will be included, and the result would be a distillate yield value that is 10 percentage points too high or too low.

If the insoluble material is finely divided and readily dispersible, one can imagine adding a solvent such as toluene or tetrahydrofuran (THF), slurrying the entire product, and quickly withdrawing a "representative" sample. We have taken this approach when performing tests with a Wilsonville Black Thunder heavy recycle material that was a solid at room temperature and only partially soluble in tetralin.⁸ We were successful in obtaining representative samples, but these samples were much larger—about 2 g—and the insoluble material appeared to be quite fine. Procedures currently in use at Hydrocarbon Research, Inc. (HRI) and at CONSOL, Inc., for TGA measurements of continuous unit products, particularly filtered liquid samples, are apparently sufficient to ensure representative sampling of these materials.⁹ Of course, for continuous-unit

products, the need for representative sampling does not constitute a new requirement: it is only a question of the scale at which such sampling can be achieved.

Kottenstette¹⁰ at Sandia National Laboratories described successful 20-mg-scale sampling of the THF-soluble fraction of batch liquefaction products. However, he also reported that representative sampling could not be achieved with simple batch liquefaction products or other products containing ashy material. Recent experience at University of Kentucky has also led them to move away from a TGA-based assessment and to use instead a vacuum distillation approach.¹¹

Thus, a small-scale TGA approach is unlikely to provide a reliable representative sampling of about 10 mg out of a 2 to 10-g product mixture from different coals when the coals have different mineral matter distributions and the products have a solution phase, a mineral matter phase, a solid carbonaceous phase, and perhaps a semiliquid tarry phase. Therefore, notwithstanding the simplicity of a milligram-scale TGA approach using one of the common commercial instruments, we conclude that simulated distillation measurements on a much larger fraction of the batch reactor product are desirable.

SRI'S 200-G CAPACITY TGA

Because of the difficulties in representative sampling, we have developed a TGA large enough to distill a large fraction, or perhaps even an entire batch, of liquefaction reactor product.¹² Our goal is to eliminate the operator time and the inaccuracies involved in obtaining complete transfer of the contents of a batch liquefaction reactor by using a TGA large enough that the entire liquefaction reactor, after removal of the cap and umbilical cord, can simply be suspended in the TGA tube and serve as the distillation vessel. In this report we describe the design of our apparatus and its calibration, and give preliminary results which indicate that this TGA apparatus meets the need for a convenient, process-related, broadly discriminating diagnostic for small batch liquefaction tests.

Physical Configuration

The components of the TGA apparatus we have assembled are a Mettler force-cell balance (200-g capacity and 0.1-mg sensitivity, Model AE-200-SE, "separate electronics" version), a 14-in. vacuum bell jar to house the balance in a reduced-pressure atmosphere, a Unistrut frame to support the assembly, Watlow 2-in.-dia $\times$ 6-in.-long furnace elements, a Eurotherm 808 temperature controller, a vacuum pump equipped with a manostat, a pressure gauge, two Tylan mass flow controllers, and a Macintosh MacPlus computer. The general construction of the TGA apparatus is shown in Figures C-1 and C-2, which are roughly to scale. The bell jar housing the

Mettler is supported by a 6-foot Unistrut frame, which rests on the laboratory floor and is bolted to the wall by shock-absorbing connections. The temperature controller and computer and balance control are located on a separate bench. Gas flow is controlled by Tylan mass flow controllers. The furnace is raised and lowered by a counterweighted, tracked shelf assembled out of standard Unistrut parts. At the standard 10°C/min heating rate, about 2 h per run is required, but the apparatus does not need to be attended during this time; actual loading of a sample and pumpdown require only about 10 min.

Temperature Measurement

During an actual run, the thermocouple for measuring the temperature and providing the feedback for the temperature controller is placed outside the distillation vessel, about 3 mm away from its outside wall (Figure C-2). Although the heated section of the tube is well heat-shielded, a significant temperature differential is expected between the temperature registered by the control thermocouple and that inside the vessel. The size of this temperature differential depends on the size and mass of the distillation vessel, the thermal conductivity of the sweep gas, the heating rate, and the temperature. Thus, the system was calibrated in runs in which a second thermocouple was placed inside the vessel. This placement necessarily precluded any mass measurements, so we did not record any weight changes during the calibration runs.

The location of the control thermocouple is a compromise between easing control by being close to the heat source and minimizing the temperature differential by being closer to the vaporizing liquid. Use of separate control and measurement thermocouples is a possible future modification that would allow us to effectively eliminate this temperature differential. However, at present we have chosen to impose linear temperature ramps on a single control thermocouple and to determine, in "blank" experiments in which no weight-loss measurements are made, the temperature lag between the control thermocouple and an extra thermocouple inside the distillation vessel (in the liquid layer and touching the inner wall of the vessel). As expected, experiments show a variable lag, large at first, when heating is begun, and smaller and fairly constant as a temperature of about 150°C is passed. This variable temperature lag is then used to adjust the control thermocouple readings during the actual run to reflect the actual temperature within the liquid inside the distillation vessel. Thus, the establishment of conditions that suitably mimic the ASTM distillation can be a painstaking procedure, requiring the recording of a "blank" for every temperature program that is tested. However, once a suitable heating regimen is established, all this adjustment can be automated and the thermocouple data translated into atmospheric equivalent temperature (AET).

Matching ASTM Distillation Curves

We have performed extensive tests on the TGA apparatus to define operating parameters that would allow us to satisfactorily mimic an ASTM vacuum distillation of a heavy-oil/resid mixture as a test for providing process-relevant distillation data for microautoclave products. These tests were conducted with a short vessel (aspect ratio 0.7). Since this vessel is wider than our liquefaction reactor, the liquid layer in it is thinner. Distillation from the short vessel therefore minimizes the transport requirements for materials in both the liquid and the gas phase. However, the short vessel increases splattering problems, which we were able suppress by including a wire mesh cover on the distillation vessel.

Figure C-3 shows the weight-loss curve for a 2:1 mixture of tetralin and heavy oil (1.3, 0.65 g), simulating a whole-product mixture of a liquefaction experiment. At this heating rate and pressure [heat rapidly to 80°C, hold for 30 min, ramp to 500°C (1336°F AET at 2.5 Torr of He) at 10°C/min] and with the having gas oil (HGO) having an initial boiling point (IBP) of 635°F, a distinct plateau separates the tetralin loss from the heavy oil distillation. The lower portion of this curve matches very closely with the CANMET ASTM correlation curve, as shown in Figure C-3.

We also tested a very heavy Wilsonville recycle vehicle (Black Thunder, Run 263, 63% nonvolatile at 1050°F AEBP) to determine whether the same set of parameters that worked for a heavy but fully distillable liquid also allow us to match ASTM data *and* distill deeply into the 1050°F+ fraction for a material containing a substantial amount of nondistillables. Figure C-4 shows that, at a TGA temperature corresponding to an AEBP of 1050°F, namely, 353°C, we observed about 65% weight loss. We were puzzled by the almost 30 wt% discrepancy with the Wilsonville data. However, conversation with Charles Cantrell of Southern Company Services revealed that, in fact, the 0.1 torr distillation regimen used at Wilsonville involved cutting the heat to the distillation vessel shortly after the vessel reached 600°F (316°C) because of concern that the weight loss after that point would have an excessive contribution from pyrolysis, although substantial weight loss would be observed at their end point if that temperature were simply held for a longer time.

We also performed a standard 1-atm TGA (Perkin-Elmer Series 7) on a 17-mg sample of the Black Thunder recycle vehicle. We observed a 68% weight loss at the point where the TGA curve really began to level off [about 480°C (896°F) actual temperature], which is very similar to our 65% weight loss at an atmospheric equivalent of 1050°F (but an actual TGA furnace temperature of only 353°C). The similar weight losses observed at significantly different actual temperatures suggest that in neither case was there substantial production of volatiles through pyrolysis. To address this question further, we also analyzed this sample by field ionization mass

spectrometry (FIMS). The mass spectra were recorded as the sample was gradually heated to above 400°C under vacuum. We observed no small fragments in the spectra recorded above 400°C, which proves that there is very little, if any, decomposition during TGA simulated distillation up to about 350°C (AEBF ~1050°F).

SUMMARY AND CONCLUSIONS

The above tests demonstrate the validity of a large-scale TGA system for automated simulated distillation of heavy fossil fuel products at the scale of 1-2 g. The unit has a total capacity of 200 g and a weighing precision of better than ± 0.5 mg, so that weight loss for a 1-g sample can be determined to $\pm 0.05\%$. When used with a distillation vessel having an aspect ratio of 0.7, it produced a weight-loss curve for a HGO-tetralin mixture that matched within 2-3% those obtained by automated D1160 distillation. However, the present system is not without its shortcomings. The system can be further improved by (1) modifying procedures to allow distillation directly from the liquefaction reactor and (2) adding provisions for collecting samples. We believe the limit to sample size that can be distilled while still matching ASTM data is set primarily by the sample viscosity and layer thickness in the distillation vessel.

The data in Figure C-3, which show close correspondence with the ASTM data, were obtained in a short distillation vessel with enough capacity that the entire product from a batch liquefaction run can be placed in it. However, to eliminate the physical transfer of the product and any attendant errors in the transferring the sample, we would like to be able to distill the product directly from the liquefaction reactor.

The liquefaction reactors designed to fit in our TGA apparatus are about 9.5 cm. high $\times$ 1.9 cm (0.75 in) outside diameter. In a few tests with these reactors, we observed that the weight-loss curve lagged behind the ASTM curve by as much as 50°C (or about 5 min). In comparison to the vessels used to obtain the distillation curves shown in Figures C-3 and C-4, the reactors have a smaller diameter and a much larger aspect ratio. The smaller diameter means that the liquid layer will be thicker in the reactor, and the larger aspect ratio means that the vapors will need to traverse a longer distance to escape from the reactor. Hence, the use of reactors places greater requirements for mass transport in the liquid and vapor phases.

Simple estimation of the characteristic diffusion times suggests that transport through the liquid, rather than the vapor phase, is rate controlling, but it does not provide a really definitive answer. This information is necessary to further optimize the operating conditions and needs to be experimentally determined by decreasing the height of the gas column without changing the diameter of the vessel (and therefore the liquid layer thickness). By doing this, we will be able to

determine directly if diffusion in the gas column is the limiting factor. Likewise, by changing the amount of the liquid in the reactor, we can change the thickness of the liquid layer without significantly affecting the gas column.

We anticipate that we can adopt simple expedients to circumvent either of the above transport limitations. If diffusion through the gas column is the limiting factor, we can make provision for some flow of He directly into the reactors. If transport through the liquid film turns out to be the important factor, we will use 1-in.-diameter reactors and/or reduce the amount of coal/solvent in a given test. We wish to emphasize that, while matching the ASTM curves is a desirable objective, it is not essential to meeting our primary goal of discriminating between coal liquids produced under different conditions.

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Figure C-1. Large-capacity vacuum TGA apparatus.

Figure C-2. Heated portion of vacuum TGA apparatus.

Figure C-3. TGA of CANMET HGO 313 at 10°C/min with ASTM correlation.

CAM-330581-248

Figure C-4. High temperature portions of two TGA simulated distillation runs of mixture of tetralin and Wilsonville Run 263 recycle vehicle containing 63 wt% of nominal 1050°F + AEBP material.

Appendix D

HYDROGEN-TRANSFER IN RETROGRADE REACTION— THE HERO AND THE VILLAIN

HYDROGEN-TRANSFER IN RETROGRADE REACTION -- THE HERO AND THE VILLAIN

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Keywords: Liquefaction Mechanism, Hydrogen-Transfer, Bond-Cleavage, Retrograde Reaction.

INTRODUCTION

Much attention has been focused over the years on the nature of the bond cleavage that takes place during coal liquefaction, pyrolysis, and combustion. Owing to the essential impossibility of determining the "critical" linkages between clusters in the organic structure of coals, much of what we now "know" has only been inferred from comparisons between coal behavior and that of model compounds or probe molecules. Nevertheless, it is now generally recognized that a picture of this bond cleavage that involves only the spontaneous thermal scission of weak bonds is, at best, incomplete and that the cleavage of strong bonds as a *result* of hydrogen-transfer should be included in our picture of coal conversion chemistry (1).

Scheme 1. Cleavage of strong bonds engendered by H-transfer to ipso position.

Recognition of the fact that hydrogen-transfer is a *prerequisite* to strong bond cleavage (rather than merely a subsequent step necessary to limit recombination) leads, via consideration of microscopic reversibility, to the conclusion that hydrogen-transfer is also a prerequisite to the *formation* of strong bonds, or retrograde reaction. Tracing Scheme 1 backwards, for instance, the link between Coal and Coal' is not "locked" into place until some agent removes the ipso H-atom in what amounts to the reverse of the first step. Thus, the task of increasing coal liquefaction yields may in some cases involve the dilemma that introduction of a particular H-transfer agent will increase bond *formation* as well as bond cleavage. It follows then that the relative utility of various H-transfer agents in liquefaction cannot be truly understood unless we know their proclivity for promoting both bond-cleavage and bond-formation. This paper is an attempt to assess the various categories of coupling reactions that may constitute the retrograde processes limiting coal conversion yields and their sensitivity to changing reaction conditions.

Although the importance of retrogressive reactions has become more obvious through careful studies of liquefaction kinetics and products, the fundamental chemical reactions and their kinetics have remained obscure. For instance, researchers such as Neavel recognized some time ago that soluble products could be generated *and consumed* very rapidly under coal liquefaction conditions (2). Similar observations have been made for pyridine solubles under pyrolysis conditions, where there is no added solvent (3). In a sense the whole technology of heavy oil conversion is bound up with retrograde reactions, in that thermal treatment of petroleum asphaltenes under a variety of conditions can produce similar amounts of distillate, but the amount of retrograde product (coke) generated in conjunction with these volatiles is critically dependent on conditions of catalyst, medium, and hydrogen pressure (4-5). Thus the impact of retrograde processes can be quite obvious, but the detailed nature of the responsible bond forming reactions is unclear.

In order to provide a background for better addressing retrograde reactions, we have examined the literature for evidence of retrograde reactions not only in actual coal conversions, but in studies of model compounds, probe molecules, and grafted-probes, and have tried to extend our understanding of the bond-forming chemistry in some of these circumstances by mechanistic numerical modeling. This model was chemically detailed, but structurally limited -- not intended in any way to actually model the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances.

This modeling incorporates the most basic of the bond cleavage types now thought to be important in coal liquefaction, and its validity is dependent of course on the appropriateness of the reactions considered. In this paper we summarize some of the results of this literature scrutiny and modeling effort.

RESULTS AND DISCUSSION

Pyrolysis of Grafted Coals. Zabransky and Stock have covalently grafted various groups to an Illinois No. 6 coal through various C-O and C-C linkages and pyrolyzed these coals using a resistively heated wire grid reactor (6-12). Through isotopic labeling of various carbons and hydrogens in the grafted groups, followed by mass spectrometric analysis of the gaseous products, identifiable portions of the grafted structures were tracked with a degree of certainty that is not achievable with unmodified coals. These studies have allowed the authors to reach a number of interesting conclusions regarding the nature of bond cleavages in structures typified by the grafted groups. Here we wish to focus instead on what limits this cleavage, specifically on how retrograde reactions compete with the bond scission processes.

Some indication of the severity of retrogression can be seen from the products reported by Zabransky and Stock (6-12) for pyrolysis of deuterium- and ^{13}C -labeled- O-n-propyl, O-nC₁₈H₃₇, O-CH₂CH₂Ph, and O-CH₂Ph Illinois No. 6 coals. Selected results are shown in Table 1, derived from their data.

The authors have discussed the extent to which the results reveal that the cleavage of strong bonds by β -scission, following either H-abstraction from an alkyl group or H-transfer to an aromatic group, are important routes for fragmentation of the grafted structures. They conclude, for instance, that the abstraction route for the aliphatic portion of alkylaromatic structures tends to be more facile than the ipso-addition route; at least when the aromatic is a single phenyl ring. These pathways account for cleavage of 2 to 40% of the grafted groups (6,9). Just as important as determination of the modes of cleavage, however, is comparison of the yields of cleaved products with the inferred yields of uncleaved, or retrograde, products. Table 1 shows the percents of the grafted portions that are converted to various cleavage products, as determined by isotopic labeling. Though the heavier products were not fully analyzed, and high precision was difficult to achieve on the scale of the experiments, the general trend is clear: substantially less than half of the grafted groups were evolved, via either weak bond thermolysis or induced scission of strong bonds, during pyrolysis to final temperatures generally in the 750 to 850°C range. This observation becomes still more striking when the rate of thermolysis of the O-C linkages in the various graftings are considered.

Table 2 shows estimated rates of cleavage for various final pyrolysis temperatures, and also the fractions of the linkage expected to be still intact by the time a particular temperature is reached (at the 1000°C/s heating rate used in the pyrolysis experiments). To take into account cage recombination, the last three columns in Table 2 are estimated by assuming that 99% of the radicals produced by thermolysis recombine before they can escape the cage, in effect extending the life of the weakly bonded species by a factor of 100 [SSD85].

The slowest homolysis is of course expected for the O-alkyl grafts, in which the O-C bonds are about 10 kcal/mol stronger than any of the O-arylmethyl cases (14). Even for this most strongly bound group, pyrolysis to a final temperature of 750°C (with zero hold-time), would leave an unconverted fraction of less than 1%, were there no recombination. However, if 99% recombination occurred in the cage, the fraction unconverted by 750°C would increase to 97%. Thus, for the O-alkyl grafted coals, the expected homolytic conversion of the graft to volatiles would critically depend on the extent of cage recombination. In contrast, the O-benzyl-type graftings have estimated homolysis rates that are higher by at least two orders of magnitude, and the fractions unconverted by 750°C would be no more than 4%, even assuming 99% cage recombination. Given this difference, it is striking that, in spite of having the slowest homolysis rates, the O-alkyl graftings are seen in Table 3-1 to have the highest fractional conversions to the corresponding alkane and its degradation products (~40%). For comparison, row 4 in Table 1 shows that only 8% of the weakly bound benzyl group of O-benzyl coal was detected as toluene. Clearly, the ease of conversion to volatile products in the case of alkyl structures is not dependent primarily on the ease of homolysis.

If the primary determinant of the extent of conversion of these weakly bound grafts is not the homolysis rate, then it must be either the rate of retrogression of these structures (including the fate of initially formed radicals), or the rate of the induced bond scission. For the case of O-nPr coal, Zabransky and Stock have shown (by examination of alkane/alkene ratios) that facile volatiles production with the O-nPr coal is not due to bond-scission induced by H-abstraction, but does indeed arise from homolysis (11,12). Thus, the conversion of O-propyl coal to aliphatic fragments is more complete than the conversion of O-benzyl coal to toluene, *in spite* of the fact that the former conversion occurs via a much slower homolysis. The successful homolysis of aliphatic linkages that are significantly stronger than the weak bond in the O-benzyl coal thus fixes the cause for the low yields of toluene on the proclivity of aromatic structures for undergoing retrograde reactions.

Pyrolysis of Polymeric Coal Models. More detail about the structural factors that facilitate retrograde reaction (other than the simple presence of aromatic groups) can be obtained from polymeric coal model studies. Several years ago, Solomon and Squire studied 27 polymers containing aromatic, hydroaromatic, and heteroaromatic groups linked together by ethylene, methylene, propylene, oxymethylene, ether, aryl-aryl, sulfide, and ester bridges (15,16), using the same heated-grid technique for the pyrolysis of the polymer models as was used by Zabransky and Stock used for their grafted coals. Because of limitations of space, we will merely summarize some of the conclusions that can be drawn from this study.

The primary focus of Solomon was on two-atom, i.e., weak linkages, for the reason that the traditional picture of thermal coal conversion chemistry then held that coal conversion resulted from spontaneous thermal cleavage (i.e., homolysis) of such weak linkages. However, precisely because most of the polymers consisted of low molecular weight clusters linked in linear chains by weak bonds, we find that the results offer a clearer view of the impact of retrograde reactions than they would with models containing some strongly linked clusters. These results reiterate some of the conclusions drawn from the grafted coal studies of Zabransky and Stock (6-12) and allow new ones to be drawn regarding the factors that limit the conversion of the polymers to volatiles. Among the most important of these conclusions are the following.

- Retrograde reactions profoundly limit volatile (or liquid) yields, which are controlled more by these coupling reactions than by the weakness of connecting bridges.
- Polymers or coal grafts containing aromatic components undergo retrograde reaction much more readily than aliphatic components.
- Increasing size of the aromatic clusters increases char yield, even under conditions where oligomer volatility limitations are unlikely to play a large role.
- As expected, the presence of hydroaromatic structure within the polymeric network decreases the retrograde reaction.
- Retrograde reactions tend to be worse for oxymethylene bridged polymers (particularly if in quinonoidal structures), notwithstanding an ~ 10 kcal/mol lowering of bond strength;
- Strengthening of weak ethylene bridges by removal of aliphatic hydrogen when there is no better source available contributes to char formation, but perhaps more importantly induces other crosslinking reactions to take place.

Nature of the Retrograde Reactions. From the studies highlighted above, together with related studies of coals and polymeric models and the work of Stein on the coupling of aromatics (17-21), we arrive at the following conclusions about the potential classes of retrograde reaction involving uncharged species in coal structures.

1. Radical Recombination

- Resonance stabilized radicals -- Two resonance stabilized radicals can result only in the formation of weak bonds, providing only temporary retrograde products, *except* in the case of ring recombination of phenoxy radicals. The latter case can result in successful retrograde reaction because the highly unstable initial adduct is able to rapidly rearrange through facile inter-molecular *proton* transfer reactions that are known (22) to be accessible to phenolic structures at coal liquefaction temperatures *even* in hydrocarbon solvents.

Scheme 2. Formation of strong retrograde linkages by ring recombination of aryloxy radicals.

- Aryl radicals -- Recombination of two aryl radicals would produce a biaryl linkage, at ca. 115 kcal/mol the strongest C-C single bond possible in hydrocarbons; however, the reactivity of aryl radicals necessarily means their concentrations will normally be far too low to participate in cross-recombination reactions, let alone self-recombination reactions.

2. Radical Addition to Unsaturated Systems

- Aryl radicals -- Aryl radicals, if formed, are known to add readily to any other aromatic system. The strength of the new bond formed means that hydrogen is readily displaced, even in the gas phase (18,21), where the primary loss process available is direct unimolecular loss of H-atoms. In the condensed phase, where H-atom loss by radical disproportionation and radical hydrogen-transfer will be relatively much more favored, we would expect aryl radical addition to be essentially irreversible. That is, during coal liquefaction effective H-atom removal would be no problem and the principal factor limiting aryl radical addition will be the rate of aryl radical generation.
- Resonance stabilized radicals -- The addition of resonance stabilized radicals to aromatic systems constitutes the opposite extreme: the carbon-carbon bond formed will be at least 20 kcal/mol weaker than the C-H bond that needs to be displaced (13,14), i.e., direct addition-elimination or displacement of H atoms by resonance-stabilized radicals are much less favored. Such coupling requires "special" circumstance that are nonetheless present during much of the liquefaction process. These circumstances are either high concentrations of displacing radicals, the presence good leaving groups on these aromatic systems, extremely effective H-atom acceptors in the reaction mixture, or multiple opportunities for radical addition. In other words, coupling reactions of this type will be highly dependent on the nature of the H-atom removal agents.
- Molecular coupling -- Stein found it necessary to invoke direct bimolecular coupling of closed-shell aromatics to form biradicals in order to account for the coupling of anthracene (20). This reaction can be thought of as the addition of a highly unstable biradical; no bimolecular H-transfer process is fast enough to compete with the β -scission of the resulting biradical adduct to re-generate the two closed-shell aromatics. Adducts formed by such additions can evidently be stabilized only when geometrical factors favor very rapid *intra*-molecular H-atom transfer reactions.

ASSESSMENT OF RETROGRADE REACTION BY MECHANISTIC MODELING.

In this section we summarize some results from use of a numerical reaction model (23) employing a surrogate coal structure to help address the factors controlling competing bond scission and retrograde reaction pathways during the initial stages of coal liquefaction. The addition of stabilized radicals was chosen as the retrograde reaction type, not because we believe it to necessarily be always the most important class of retrograde reaction, but because it is the class of bond-making reaction whose outcome is most likely to be sensitive to changing hydrogen-transfer conditions. The addition of resonance-stabilized radicals is highly reversible, such that if it results in successful formation of strong bonds between aromatic clusters, it will be because a very small fraction of a large number of original additions ultimately go on to stable products. For simplicity, we have limited the model to a pure hydrocarbon system, though the same general considerations will also apply to systems containing phenolics, where the presence of the -OH groups will in all likelihood further promote radical addition.

The model we have used is very detailed; it incorporates all relevant fundamental chemical reactions (non-ionic) of essentially all species, both closed shell and free radical, in the reaction system. Because of this detail, the model, of necessity, includes only a very limited set of starting structures. The model is homogeneous; it consists of relatively low molecular weight species assumed to be miscible in all proportions. We have made the simplifying assumptions that the system is free of concentration gradients and requires no mass- or heat-transport. The activity of H₂ in solution is taken to equal that provided by presumed equilibrium with the gas-phase H₂ pressure. This model was not intended in any way to actually simulate the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances. There has been absolutely no attempt to force the model results to correspond to the phenomenology of coal liquefaction or pyrolysis.

Space prevents a full description of the model and results here; these details will be presented elsewhere (24). Given below is a brief summary of the results of the modeling as they apply to the prevention of retrograde

reaction. In some cases these results are a quantitative illustration of what could be qualitatively anticipated from thermochemical considerations. In other cases the results were qualitatively surprising.

- All scavengers that operate via a radical capping process have a dual role—they also act as initiators.
- "Scavengers" typically found to best aid coal conversion to volatiles or liquids appear to perform better because they are superior in some aspect other than scavenging.
- At short reaction times, where there is a large generation of fragment radicals from homolysis of the weakly bonded coal surrogate, modeling indicates that dihydroanthracene, as the better scavenger, indeed maximizes the yield of capped fragment radicals, and minimizes the yield of recombination products and radical displacement retrograde products.
- However, at long reaction times, the "better" scavenger actually *enhances* the yield of retrograde product. This is because, at longer reaction times when the burst of radicals from the decomposing coal has largely died away, the principal source of fragment radicals is abstraction of hydrogen atoms from the previously capped fragment species by the pool of scavenger radicals generated by the scavenger itself. Thus, the model elaborates a trend which has been noted previously (25), namely that coal conversion tends to be better in the presence of hydroaromatics that are not the best scavengers, and is evidently better because these latter scavengers tend to be better hydrogenolysis reagents, while being poorer radical initiators.
- Higher temperatures provide more reaction, but if there is not something to mitigate retrograde reactions, higher temperatures tend to cause the retrograde reactions to increase as fast or faster than the bond-cleavage reactions. This modeling result appears to be completely in accord with the common observation that increasing liquefaction temperature beyond about 440°C tends to lower coal conversion, and similarly in pyrolysis, that higher heating rates tend to decrease char yields, *primarily* when the higher heating rates are associated with more rapid removal of volatile products, (26).
- Under the conditions modeled, displacement of carbon-centered radicals from aromatic rings accounted for roughly four times as many retrograde products as did displacement of H-atoms
- The presence of H₂ does not inhibit retrograde product formation as much as it hydrogenolyzes retrograde products faster after they are formed. In fact, modeling indicates that H₂ can, at certain reactions times, *increase* the yield of retrograde products.
- The impact of added H₂ on hydrogenolysis (at least in the short term) does *not* come primarily through its maintenance of a useful hydroaromatic content, as has often been postulated in coal liquefaction, but through a higher steady state concentration of H• that is established long before the hydroaromatic content can be substantially affected.

Summary and Conclusions

Our examination of literature data, together with thermochemical considerations and the associated numerical modeling of simplified reaction systems leads us to the following summary picture of retrograde reaction during coal conversion.

Recombination with Phenoxy Radicals. The major case where where radical recombination can lead to a true retrograde product is ring-recombination of a phenoxy radical with resonance-stabilized carbon-centered radicals. Studies with the model compound benzyl phenyl ether have shown that the presence of scavengers can decrease but cannot easily eliminate the formation of diarylmethane linkages though this route. We suggest that facile intramolecular proton-transfer efficiently converts the initially formed and unstable keto-form to the strongly bonded phenolic form. No such isomerization pathway is available for ring-recombination of two benzylic radicals.

Dual Function of Radical Scavengers. Modeling has illustrated the apparent paradox that the best scavengers may do the worst job of preventing radical addition. Hydroaromatic structures such as 9,10-dihydroanthracene that have very weak benzylic C-H bonds will also tend to have high steady state concentrations

of the $\text{ArH}\cdot$ radicals generated in the scavenging act. Thus, the "better" scavengers may result in a lower steady state concentrations of candidate retrograde radicals *only* when the principal source of such radicals is something other than these abstractions, such as a rapid homolysis or β -scission. Accordingly, the concentration of resonance-stabilized radicals like benzyl and phenoxy can sometimes be decreased by scavengers, but they cannot be lowered below a minimum corresponding to the level that is generated by the hydroaromatic scavenger system functioning as an initiator.

Modeling also reveals that in many instances, the donor solvent content or H_2 pressure do not serve so much to decrease the rate of retrograde product formation as to cleave such products after they have been formed. In fact, the presence of these reagents may actually *increase* the rate of retrograde product formation at certain times. thus, the major impact of H_2 lies not in its scavenging ability, which is very modest, but in the fact that whatever scavenging does take place produces free H-atoms, which are highly active hydrogenolysis agents. This "direct" hydrogenolysis activity of free H-atoms is seen to be a much more important effect of H_2 , at least at short reaction times, than the indirect effect of maintenance of donor level.

Aryl Radical Addition. Since aryl-aryl bonds are so strong, displacement of H-atoms by addition of aryl radicals is prevented primarily by minimizing formation of these radicals in the first place. Literature results suggest the somewhat counterintuitive observation that aryl radicals are generated principally by the much larger pool of (individually much less reactive) resonance stabilized radicals.

Resonance Stabilized Radical Addition. The displacement of C-H bonds by resonance stabilized radicals (whether acyclic and therefore leading to diarylmethane linkages, or cyclic and leading ultimately to biaryl linkages) will usually be dependent not only on the concentration of potential displacing radicals, but also on the facility with which the reaction system stabilizes the intermediate adduct by removing the hydrogen atom that is being substituted. For example, modeling indicates that retrograde products from homolytically generated benzylic radicals are lower when dihydroanthracene (rather than dihydrophenanthrene) is the hydroaromatic scavenger. However, at long reaction times, when the main source of benzylic attacking radicals is the radical soup itself, the higher radical concentration provided by the "better" scavenger acts to *generate* more attacking radicals and also to more readily stabilize the adducts through radical disproportionation. In addition, the very good H-atom accepting capability of anthracene itself also increases the fraction of the initial adducts that are successfully stabilized as retrograde products.

ACKNOWLEDGEMENT

The authors wish to acknowledge the Support of the U.S. Department of Energy in various projects whose goals have included an improved understanding of the chemistry responsible for coal liquefaction.

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TABLE 1
FATE OF STRUCTURES GRAFTED TO COAL VIA PHENOLIC OXYGEN:
PYROLYSIS IN A HEATED WIRE GRID^a

Grafted Structure	% of Graft Converted to			
	C ₁ - C ₃	PhH	PhCH ₃	Unaccounted ^b
—nC ₃ H ₇	1.7 C ₁ 9.1 C ₂ 28 C ₃	NA	NA	61
—nC ₁₈ H ₃₇	7.2	NA	NA	-
—CH ₂ CH ₂ Ph	4.5 C ₁ ≤ 10 C ₂	≤ 1	≤ 2	≥ 83
—CH ₂ Ph	-	1.2	8.0	91
—CH ₂ PhCH ₂ CH ₃	5.3 C ₂	NR	NR	-

^aHeating rate approximately 1000°C/s to a maximum temperature of about 800°C

^bUnaccounted for and presumably adducted to the coal. Where the analysis of major fragment pieces was not reported ("NR"), this column was left blank.

TABLE 2
ESTIMATED RATES OF HOMOLYSIS AND ANTICIPATED FRACTIONAL REACTION FOR GRAFTED LINKAGES

Coal Structure	Grafted Structure	BDE ^a	k _{Homolysis} (s ⁻¹) ^b			Unconverted Fraction Remaining at T ^c			Unconverted Fraction Remaining at T ^d with 99% Recombination		
			650	700	750	700	750	800	700	750	800
CoalO-	-nC ₃ H ₇	61	8.4	4.9x10 ³	2.3x10 ²	0.65	0.09	9.9x10 ⁻⁶ 1 x 10 ⁻⁵	.996	.97	.89
CoalO-	-CH ₂ Ph	52	1.5x10 ³	6.6x10 ³	2.5x10 ⁴	0	0	0	0.5	0.04	5 x 10 ⁻⁶
CoalO-		47	2.3 x 10 ⁴	8.7 x 10 ⁴	2.9 x 10 ⁵	0	0	0	1 x 10 ⁻⁵	1 x 10 ⁻¹⁹	0

^aEstimated from values given in References 13 and 14. The assumption is made that coal structure bearing the oxygen atom is a single, unsubstituted phenyl ring. Inasmuch as this phenyl ring must have at least one other "substituent" to be a part of a polymeric coal matrix, this assumption provides an upper limit to the strength of the grafted linkage.

^bBased on an $E_a = \text{BDE} + RT$; $A = 10^{15.5} \text{ s}^{-1}$.

^cUnreacted Fraction $\sim e^{-(k_{T-50})(0.05s)}$, where 0.05s is the time for the sample to heat from (T-50)°C to T_{final} at 1000°C/s, the heating rate used by Zabransky and Stock. Because k_{T-50} is a lower limit to the rate constant during the last 50°C, the calculated value over-estimates the unreacted fraction.

^dUnreacted fraction assuming 99% recombination is given by $e^{-(k_{T-50})(0.05s)(0.01)}$, again an over-estimate of the unreacted fraction.

Appendix E

HYDROGEN TRANSFER IN HYDROCARBON PROCESSING

HYDROGEN TRANSFER IN HYDROCARBON PROCESSING

August 21-26, 1994, Washington, D.C.

HYDROGEN TRANSFER PROMOTED RING GROWTH DURING CATALYTIC RESID HYDROPROCESSING.

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Keywords: Hydrogen transfer, coke formation, resid upgrading, PAH

INTRODUCTION

Hydrogen-Transfer and Bond Cleavage. In recent years the role of H-transfer in promoting strong-bond cleavage during coal liquefaction even under noncatalytic conditions has received substantial recognition.(1-9) We have also proposed that direct transfer of an H-atom from a radical species to a π -system in a closed shell molecule (radical hydrogen-transfer, or RHT) is an additional H-transfer process that contributes to the induced bond cleavage.(1,6,8) However, because other competing transfer processes (H-abstraction by radicals, radical disproportionation, the reverse of radical disproportionation (RRD), and addition of free H atoms) complicate the issue, the experimental evidence for RHT has been inconclusive. Very recently, *ab initio* (UHF mp2/6-31g**) and semi-empirical (AM1) calculations (9) and kinetic analyses (10,11) have raised questions about the generality of RHT. However, the broader claim (3) that H-transfer due to some agent other than free H atoms is responsible for aryl-alkyl strong-bond cleavage remains undisputed.

Hydrogen Transfer and Bond Formation during Resid Upgrading. Cracking of resids to form distillate is well known to be primarily driven by thermal reactions and that the most pronounced effect of H₂ and catalyst is to prevent the associated coke formation.(12-14) If the cracking reactions that convert resid to distillate are primarily thermal, then it follows that the coking that is associated with this cracking will probably also be thermal and remote from the catalyst. Thus, while improved catalysts certainly improve resid hydroprocessing by limiting coke formation, they must do so *indirectly*. By communicating the hydrogenation capability of the catalyst, the bulk reaction medium is what directly mitigates coke formation.

In this paper, we further consider the connection between H-transfer and strong-bond formation. Just as strong bonds cannot be broken without prior hydrogen transfer, neither can strong bonds be formed without hydrogen transfer, and the same hydrogen transfer can presumably accomplish both. We have used field ionization mass spectrometry (FIMS) and GC-MS to identify and quantify some of the coke precursors generated during catalytic upgrading of coal-derived resids and the pyrolysis of long-chain alkylpyrenes.

EXPERIMENTAL SECTION

Pyrolysis experiments were conducted in evacuated fused-silica ampoules, protected in stainless steel pressure jackets, and heated in a molten salt bath as previously described.(15) Conditions used were similar to those used by Savage and coworkers. (7,8) The product mixtures were analyzed by GC-MS and field ionization mass spectrometry (FIMS). Qualitative and quantitative analysis was provided by mass-selective and flame-ionization detectors. Molar

response factors were determined for compounds for which we had authentic samples and estimated by comparison with similar species when a particular authentic sample was unavailable. For most species the reproducibility was within $\pm 2\%$ and we estimate the overall analytical accuracy to be within $\pm 5\%$. FIMS analyses were performed in order to assess coke precursors such as polyaryls and ring growth products whose analysis by GC is difficult or impossible because of low volatilities and multiple isomers.

RESULTS AND DISCUSSION

Results from batch pyrolysis experiments with n-hexadecylpyrene, 1-tridecylbenzene, 1-methylpyrene, biphenyl, and water are summarized in Table 1. FI mass spectra of the products of moderate and high conversions are shown in Figures 1 and 2. Alkyl PAH, even in the absence of added H-donors, tend to undergo moderate-to-rapid cleavage of the strong aryl-alkyl bonds, in striking preference to cleavage of the ca. 30 kcal/mol weaker bonds between the α - and β -carbons. Furthermore, the alkyl fragments are largely saturated alkanes and not olefins (Eqs. 1 and 2). These findings are in concert with those of Savage et al.(7,8) and also of Freund et al.(16)

The pseudo first-order rate constant for dealkylation is more than an order of magnitude higher at ~80% conversion than it is at ~10% conversion. A consequence of this highly autocatalytic behavior is that the source of hydrogen is *neither* one of the original reactants, *nor* an intermediate whose steady-state concentration is determined *only* by the original reactants. Therefore, the H-transfer agent is *not* the α -hydrogen on the starting material itself, acting in an RRD reaction, as Franz and co-workers have suggested,(11) and probably is not limited to the collection of three different non-ipso hydro-pyrenyl radicals, acting via RHT reactions, as suggested by Savage and coworkers.(7,8) If the transfer agents are these hydro-pyrenyl radicals, their concentration is clearly driven up by the production of some other intermediates that accumulate as reaction proceeds.

The spectrum of the moderate-conversion product, Figure 1, shows not only a larger peak for remaining starting material at m/z 426, but also a large group of peaks surrounding the starting material. This group has similar intensities for the even *and* odd masses from $M-1$ to $M+3$, and substantially lower, but still significant, intensities for every mass from more than 100 Da below 426 to over 100 Da above 426. Peaks at intervals of two Da above and below the molecular ion for the starting material corresponding to hydro- and dehydro-alkylpyrenes are expected. A range of satellite peaks representing loss or addition of one or more methylene units is also expected. However, the relative abundance of odd-mass peaks in this spectrum, which has been corrected for ^{13}C content, is not expected and it points to a propensity for the products to fragment.

Because the dealkylation products are alkane-rich, some species must give up the hydrogen required to form the alkanes (i.e., must get oxidized). Examination of the FI mass spectra of the conversion products helps identify the nature of the oxidized species. Figure 2 shows small

peaks at m/z 242 and 276 most likely represent the phenalene analog 1,10-trimethylenepyrene and benzo[ghi]perylene, both of which have been identified previously as major products in the upgrading of petroleum resids(17) and coal-derived vacuum resids.(18) In both cases, the appearance of significant amounts of these products has been correlated with declining process performance. These peaks representing ring-growth products appear small in Figure 2, but it should be remembered that generation of each benzoperylene molecule results in freeing enough hydrogen for five reductive cleavages. If we make the reasonable assumption that the sensitivity factors for various pyrene derivatives are the same, these small peaks together account for about 80% of the sum of all reductive cleavage products.

It is clear from the FIMS analysis that a whole range of hydrogenated and de-hydrogenated intermediates springs up and later disappears as most of the alkyl pyrenes either dealkylate or are oxidized to ring-growth and biaryl products. We suggest that initially reactions are dominated by the H-abstraction, β -scission Rice-Herzfeld sequence that is known (19) to dominate long-chain alkylbenzene pyrolysis. This sequence results in the generation of alkyl fragments and terminal olefins, either connected to or free from the pyrene. Those fragments still connected to the original pyrene become the sequence of satellites on the low-mass side of the original starting material at m/z 426. The radical fragments, whether freed from or still connected to the original pyrene, can also add to another pyrene, producing a hydrodialkylpyrenyl radical. This addition can either reverse or the radical can obtain a hydrogen atom (most likely by disproportionation with another radical) to form a dihydrodialkylpyrene derivative. Sequences such as this would generate the group of satellite peaks at mass higher than 426.

It is interesting that the more important coke precursors in these product mixtures are the ring-growth products, whereas in the product mixture from 1-ethylpyrene pyrolysis discussed previously,(15) ring coupling products (bi-aryls) are more important. This is not unreasonable: when there are only a limited number of short alkyl chains ring coupling is relatively faster, but when there is an abundance of alkyl chains, the ring growth via attachment and closure of alkyl fragments leads to the most abundant oxidation products. Furthermore, experiments in which n-hexadecylpyrene was replaced with a mixture of 1-methylpyrene and n-tridecylbenzene produced roughly similar amounts of the first ring-growth products, m/z 242 and 276. Evidently, prior attachment of the radical chain is not critical to the ring growth. This seems consistent with the view that many of these addition reactions are highly reversible,(20) and that the stability of the ring-growth products provides the driving force for the system towards alkanes and coke.

As previously described,(15) we have also briefly explored the impact of added water on the reactions of alkyl pyrenes. We were surprised to find no utilization of hydrogen from water to generate reduced products as observed in hydrous pyrolyses.(21) We have extended that study to reactions in the presence of supercritical water at progressively increasing densities, up to 0.4 g/cc. Data in Table 1 clearly show that increasing water density results in (i) a *decrease* in reductive dealkylation, (ii) a dramatic decrease in the alkane/olefin ratio, and (iii) a smaller decrease in the formation of coke precursors. These observations appear to be a consequence of simple dilution that results from the increased solubility of the organic reaction mixture in the supercritical water phase as the fluid density is increased toward those of normal liquids. The absence of any identifiable chemical effect of water under these conditions reflects the thermochemical reality that at 400°C the 118 kcal/mol H-OH bond in water is too high for H-abstraction by carbon-centered radicals to constitute a kinetically accessible pathway, particularly in the absence of electron-transfer agents or catalysts that could connect the free-radical reaction manifold to the ionic reaction manifold.

Interestingly, supercritical water inhibits the formation of coke precursors along with reductive dealkylation, but does *not* inhibit conversion of alkylpyrene by the non-reductive H-abstraction, β -scission pathway. Since both of these processes proceed by radical chain pathways, it appears that one such pathway has a dilution-dependent branching, and the other doesn't. Perhaps the radicals that abstract alkyl hydrogen and induce cleavage of alkyl chains have basically nothing

else to do, but the species that induce hydro-dealkylation can be shunted elsewhere. This could be the case if the latter species were mainly hydroaryl radicals that have H-elimination alternatives that become relatively more favorable with increasing extents of dilution.

SUMMARY AND CONCLUSIONS

GC-MS and FIMS analyses on the products of alkylpyrene pyrolysis allow us to arrive at the following conclusions about the cleavage of strong bonds by hydrodealkylation.

- Hydrodealkylation is not a result of H transfer from alkylpyrene itself, but from various hydrogenated intermediates.
- The hydrogen necessary for the reductive dealkylation can be largely accounted for by the formation of ring-growth products, principally 1,10-trimethylene-pyrene (m/z 242) and benzo[ghi]perylene (m/z 276) and their respective alkylated derivatives.
- Since there is little dependence of coke-precursor formation on prior attachment of the alkyl chain to the pyrene nucleus, the ring-growth process evidently involves the facile and reversible addition of alkyl fragments.

ACKNOWLEDGMENTS

The authors wish to acknowledge the Support of the U.S. Department of Energy under Contract No. DE-AC22-91PC91044.

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**Table 1. Conversion of n-hexadecylpyrene at 400°C
in the absence and presence of water**

	<u>J51A</u>	<u>J60</u>	<u>J53</u>	<u>J52</u>	<u>J54</u>	<u>J61</u>
Reaction Conditions						
C ₁₆ -Pyrene (mol%)	28.3	25.3	28.0	25.9	25.8	25.7
H ₂ O density (g/cc)	0	0	0	0.12	0.40	0.41
Time (min)	90	250	513	90	90	250
Products^a						
C ₁₆ -Pyrene	89.2	15.0	≤ 3	^b	96.7	55.2
Pyrene (%)	1.9	37.8	51.4	1.4	0.26	3.0
Σ (C ₀ - C ₁₅ -Pyrenes)	11.9	74.9	78.5	12.4	14.1	32.0
Σ (C ₈ - C ₁₆ -Aliphatics)	11.0	63.9	88.4	13.0	9.8	22.6
Alkane/alkene	1.5	61.9	>128	0.79	0.26	0.79
k₁ (Total reaction)^c / ×10⁵s⁻¹	2.2	6.8	7.0	2.6	5.1	1.7
k₁ (Hydrodealkylation)^d / ×10⁵s⁻¹	0.38	4.0	4.1	0.28	0.05	0.23

^aMol percent of starting C₁₆-pyrene in biphenyl.

^bChromatogram did not give an integratable peak for the starting material.

^cDefined 1st order rate constant where Σ (C₈ - C₁₆-Aliphatics) is taken as the most reliable (lower limit) measure of converted C₁₆-pyrene.

^dDefined 1st order rate constant for the total reaction multiplied by the fractional yield of pyrene.

Figure 1. FI mass spectrum of n-hexadecylpyrene pyrolysis products obtained under moderate-conversion conditions.

Figure 2. FI mass spectrum of n-hexadecylpyrene pyrolysis products obtained under high-conversion conditions.

Appendix F

RELEVANCE OF CLEAVAGE OF STRONG BONDS IN COAL LIQUEFACTION

Relevance of Cleavage of Strong Bonds in Coal Liquefaction

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Received September 28, 1992. Revised Manuscript Received December 22, 1992

Almost ten years ago we proposed that cleavage of bonds too strong to undergo simple thermolysis but which are cleaved by the mediation of solvent or solvent-derived radicals may be an important contributor to the liquefaction of coals. In this paper we discuss the process implications of this revised view. We show how this picture continues to help rationalize many otherwise inexplicable observations in fossil fuel conversion technology. These observations include the breaking of nonhomolyzable bonds in grafted and doped coals, the ineffectiveness (in liquefaction) of nonhydroaromatic radical scavengers, the effectiveness of nondonor polycyclic aromatic hydrocarbons (PAH), the "activation" of cyclic aliphatics by PAH, increasing hydrogen utilization efficiency observed with added PAH, and the decrease in gas formation observed at lower temperatures or with added PAH. We also discuss examples that show the importance of the solvent medium in transferring and transporting hydrogen in catalytic systems. Finally, we discuss how the solvent or solvent-derived radicals may also promote retrogressive reactions under certain conditions.

Introduction

Conversion of coals to liquids or gases necessarily involves breaking of chemical bonds. Hence, much attention has been focused on the nature of the bond cleavage that takes place during coal liquefaction, pyrolysis, and combustion. Owing to the essential impossibility of determining the "critical" linkages between clusters in the organic structure of coals, most of the information about bond cleavage has been inferred from comparisons between coal behavior and that of model compounds or probe molecules. Poutsma has recently published two outstanding and very detailed reviews of the thermolysis of coal model compounds.¹ Our purpose in this review is to examine coal conversion phenomenology in light of data such as those discussed by Poutsma.

Traditionally, coal structure has been thought to come apart by the thermolysis of inherently weak bonds upon application of heat. Thermolysis would lead to a pair of radicals that are then scavenged by the donor solvents. According to this model, the efficacy of donor solvents should correlate with the weakness of their C-H bonds. However, some years ago we noticed that literature data on liquefaction yields in different solvents does not correlate with their ability to scavenge radicals.² For example, among the common donor solvents, dihydroanthracene is the most efficient radical scavenger, and yet it is recognized to be a poorer liquefaction solvent than a number of other hydroaromatics. Also, solvents such as indane and ethylbenzene, which have C-H bonds that are as weak as tetralin and are hence equally effective radical scavengers, are much less effective than tetralin as liquefaction solvents.

Scheme I. Solvent-Mediated Hydrogenolysis of a Strong Linkage in Coal

Furthermore, in studies with model structures, we observed that even strong linkages, like $C_{aryl}-C_{alkyl}$ bonds, undergo cleavage under liquefaction conditions (e.g., donor solvents, 400 °C, 1 h).³ Simple thermolysis of this bond type will proceed with a half-life of no less than 10^6 years and should be wholly unobservable under the experimental conditions. On the other hand, these bonds would be expected to cleave if a hydrogen atom were to be first transferred to the ipso position. This ipso displacement can be very facile for certain categories of PAH structures and has been shown to be promoted under both thermal and catalytic coal liquefaction conditions.³⁻⁵

The lack of correlation between liquefaction effectiveness and scavenging ability of different donor solvents, together with the observed cleavage of relatively strong bonds under liquefaction conditions, prompted us to propose a revised model for coal liquefaction.^{2,5} The key element of this model is that the solvents or solvent-derived radicals mediate the cleavage of the bonds, and hence the name solvent-mediated hydrogenolysis or SMH (Scheme I).

By proposing this model, we did not mean to suggest that the cleavage of weak linkages does not occur. To the extent that there are weak bonds in the coal, they will undergo thermolysis, and this will be one of the initiating reactions. However, we asserted that the factor that

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Table I. Beneficial Effects Not Attributable to Improved Scavenging

factor	observation	source
PAH concentration	improved oil yields with partial replacement of donors with nondonor PAH increased efficiency of hydrogen utilization by partial replacement of donors with nondonor PAH activation of perhydroaromatics by addition of PAH	Derbyshire et al., ¹² Cassidy et al., ¹³ Mochida et al., ¹⁴
PAH type	greater efficiency with pyrene as opposed to smaller aromatics	Derbyshire et al., ¹²
temperature	incremental conversion of coals from pyrolysis under H ₂ pressure results in selective formation of oils when the temperature is maintained below a certain threshold	Gorbaty and Maa ¹⁶

Scheme II. Cleavage of Strong Bonds Engendered by H Transfer to Ipso Position

discriminates between effective and less effective solvents is their ability to facilitate transfer of hydrogen atoms to the ipso positions. This view of liquefaction constitutes a fundamental shift in the *perceived* role of the liquefaction solvent, from one of a passive component involved in merely stabilizing the radicals formed as a result of bond cleavage to one of an active reagent that engenders bond scission.

The H atoms can be transferred to the ipso position by several pathways. We have studied these pathways experimentally and through the use of a detailed mechanistic numerical model based on the thermochemistry of the various elementary steps.^{2,5} These studies also brought to light a previously unrecognized pathway for hydrogen transfer involving a direct bimolecular transfer of a hydrogen atom from a radical to a closed-shell species. We have termed this pathway radical hydrogen transfer or RHT. The fundamental aspects of this type of H transfer are still under experimental and theoretical scrutiny by several groups.⁶⁻⁸ Scheme II illustrates this pathway for the cleavage of a coal linkage by the 9-hydrophenanthryl radical. Other modes of transferring H atoms include reverse radical disproportionation (RRD)⁹ and addition of the free H atoms. The free H atoms could themselves be produced by β -elimination from various radicals or, as proposed by Vernon,¹⁰ by the reaction of resonance-stabilized (benzylic) radicals with molecular hydrogen. In this paper we focus on the implications for coal processing of those bond cleavages that are mediated by the solvent. These implications hold for solvent-mediated hydrogenolysis, regardless of the exact details of the RHT reaction.

Implications of Solvent-Mediated Hydrogenolysis for Coal Liquefaction

Interactive Effects of Solvent Components. Interactive effects between solvent components are not readily

rationalized in terms of the traditional model of coal liquefaction. However, they are a natural consequence of the SMH model. The species responsible for transferring the H atoms are generated by the interaction of different solvent components. The relative importance of various H-transfer pathways changes with changing conditions (such as temperature and solvent composition) and results in differing rates and efficiencies of hydrogen utilization.^{3,5} We have modeled the competition between these different modes of H transfer and have shown that thermochemical considerations allow us to rationalize many puzzling observations such as increased conversions or efficiencies of hydrogen utilization upon addition of nondonor polycyclic aromatic hydrocarbons (PAH) and reduction in temperature.^{5,11} Some of these observations are summarized in Table I.

We have discussed these observations and their rationalization in terms of the SMH model elsewhere.^{3,5,11} Briefly, the beneficial effect of PAH addition stems from the fact that they are good H acceptors. The PAH react with hydroaromatic donors to give cyclohexadienyl radicals, which are capable of engendering hydrogenolysis, thereby increasing the overall rates. In the case of perhydroaromatics, PAH can accept H from the tertiary aliphatic radicals to give cyclic olefins, which can further donate hydrogen and produce hydroaromatic structures.¹¹ The PAH also help minimize wasteful transfer of hydrogen that leads to reduced but uncleaved products, and hence improve the overall efficiency of H utilization. In some of these instances, changes in the solvency power of the medium could contribute to the observed phenomena;¹⁷ however, in some cases there are specific chemical changes that occur upon addition of PAH that make it highly unlikely that purely physical factors are responsible for all of these observations.^{11,15}

We have extended this concept of interactive effects in hydrogen transfer to rationalize the synergy that has been reported for coprocessing of coal and oil.¹¹ We made semiquantitative estimates of the fate of aliphatic radicals in the presence and absence of PAH components. These estimates show that in the absence of PAH species the aliphatic radicals undergo the expected β -scission reaction to give olefins and other aliphatic radicals, both of which

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Table II. Effect of C₆₀ Cleavage Rate and Selectivity of 1,2'-Dinaphthylmethane^a

system	cleavage rate ($\times 10^6$ s ⁻¹)		selectivity	
	control	with C ₆₀	control	with C ₆₀
anthracene/AnH ₂	4.4	10.8	4.8	5.4
pyrene/PyH ₂	8.6	11.3	4.0	4.4
phenanthrene/PhenH ₂	4.2	6.5	2.9	4.6

^a Substrate/arene/dihydroarene/catalyst (weight ratio): 1/5/5/1. Temperature 400 °C. Time 1 h.

Scheme III. Cleavage of 1,2'-Dinaphthylmethane in Aromatic/Hydroaromatic Solvents Leads to Naphthalene and Either 2- or 1-Methylnaphthalene Depending on Whether H Was Transferred to the 1- or the 2-Position

place demand on hydrogen supply and neither of which is good at cleaving bonds. In the presence of PAH components, the chain is diverted to give an olefin and a cyclohexadienyl radical. The latter can induce bond scission by RHT. Analysis of the solvent components by Clarke et al.¹⁵ in their coal liquefaction study with perhydroaromatics, provides further evidence for the chemistry we suggest. Thus, we have proposed that the reported synergy in coprocessing may have, in part, a chemical origin and result from the PAH species provided by the coals. By accepting hydrogen from resid-derived aliphatic radicals and forming cyclohexadienyl radicals, the PAH species channel the available, but ineffective, hydrogen in the system to useful bond cleavage reactions.

From the above discussion it is clear that effective solvents must contain a balance of good hydrogen donors and hydrogen acceptors. Hydrogen acceptors in general will have extended π -systems, and PAH as a class are good hydrogen acceptors. We would also expect graphitic carbon to act in this manner. Recent work by Farcasiu and Smith¹⁸ shows that "Black Pearls", a form of graphitic carbon black, catalyzes the cleavage of strong C_{aryl}-C_{alkyl} bond in model structures. We have studied the catalytic effect of another form of carbon, C₆₀ or buckminsterfullerene, which also has an extended π -system and hence can act as a hydrogen acceptor, on the cleavage of strong bonds. The results are shown in Table II. We found that addition of C₆₀ increased the cleavage rate of 1,2'-dinaphthylmethane in each of the three hydroaromatic/aromatic solvent systems we studied.¹⁹ The selectivity of cleavage at the 1-position (which leads to the formation of 2-methylnaphthalene) was also increased in each case. Higher reactivity in the face of higher selectivity indicates that the increase in number of H carriers more than compensates for the increased selectivity of those generated from C₆₀. Moreover, since the background reaction (i.e., without C₆₀) contributed to about half of the net cleavage, the selectivity of the C₆₀-catalyzed path is even greater than that observed for the total reaction.

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Scheme IV. Possible Role of Medium in Shuttling Hydrogen in Catalytic Systems

Role of Reaction Medium in Catalytic Conversion.

The benefits noted in Table I from improved solvent composition are not limited to purely "thermal" conversion processes, but also have implications for catalytic systems. In discussions of coal liquefaction processes, one often perceives a tendency to think that thermal and "catalytic" coal liquefaction proceed by two entirely different sets of reactions. Scheme III is intended to suggest that, in multiphase systems such as those found in coal liquefaction, the reaction medium may play a very important role in moving the H-atom activity generated at the catalyst surface to the coal-structure site where it is needed for hydrogenolysis. This is to say that reaction promoted by a heterogeneous catalyst, if it is to be "catalytic" in the strict sense of the word, must occur at the surface of the catalyst. If the enhanced reaction occurs even a few angstroms from the catalyst surface, it is a *thermal* reaction, described by a potential energy surface that is no different than it would be if the reaction occurred a thousand molecular diameters from the catalyst surface. In multiphase reaction systems like coal liquefaction with heterogeneous catalysts (particularly with nonsoftening coals), the opportunity for every reacting solid-phase molecule to contact the catalyst directly may be very limited. Thus much of the reaction will necessarily be thermal in the strict sense of the word. However, many of these thermal reactions may be substantially augmented by the catalyst through changes it has brought about in the reaction medium.

One long-accepted mode of hydrogen transport is the generation of closed-shell di- and tetrahydro species, which can then carry their hydrogen as they migrate throughout the reaction system. Solvent hydrogen transport may also be effected via cyclohexadienyl carrier radicals, such as that shown in Scheme IV. These radicals will be generated thermally from the reaction between donor species and PAH acceptors. However, we suggest they may also be formed directly at the surface of the catalyst by single H-atom transfer and then act as the species that carry the hydrogen to the vicinity of the coal/preasphaltene structure to be converted. In the context of coal liquefaction, we are mostly concerned with activated molybdenum catalysts supported on alumina or dispersed molybdenum catalysts which inadvertently get supported on carbonaceous char. Scheme IV depicts the former case; in the latter case, the primary reaction would be a spillover of hydrogen from Mo to the char. In either case, the primary reaction of concern is the transfer of H from Mo to C. The thermochemistry will be different for different systems, and more detailed studies are needed to determine the extent and limitations of this pathway.

Desorption of radicals from catalyst surfaces was until recently considered to be an unlikely event. However, work by Lunsford²⁰ and others²¹ has shown that radicals can be desorbed even directly into the gas phase at high temperatures. There is no reason in principle why desorption of radicals into solution could not occur at the lower temperatures of coal liquefaction. A related type of radical migration, by "hydrogen hopping" on a surface-immobilized organic substrate, has recently been demonstrated by Buchanan and Britt.²² The similarity of cyclohexadienyl radical departing from the catalyst and the hydrogen hopping lies in the fact that both processes involve migration of "reactivity" without the actual movement of the reactive molecular species. In the hydrogen hopping case, it is migration of a radical site resulting from hydrogen abstraction which results in a reactive site at a new location. In the case of the catalyst/solvent, it is transfer of the hydrogen on the catalyst surface to the arene in the solvent that results in transfer of the activity from catalyst surface to the solvent. In any case, regardless of whether such new modes of reactive species transport are important in coal liquefaction, it is clear that much of the augmented conversion that occurs in the presence of heterogeneous catalysts is the result of certain categories of thermal reaction that are enhanced through changes in the reaction medium including increased local concentration of radicals. The distances over which such radicals might migrate before disproportionation and other reactions return their concentration to that in the bulk may be very short in macroscopic terms, say 100 nm. This distance, however, is roughly several hundred molecular diameters and may be very critical, since it is probably a lower limit to the space between adjacent particles of even a very finely dispersed catalyst. In the effort to optimize these catalytic liquefaction processes, it is useful to better understand the thermal or solvent-mediated reactions.

In the following paragraphs, we consider some of the phenomenology from recent liquefaction development efforts that shows the possible role of SMH in catalytic coal conversion. Most of these examples happen to involve coprocessing, partly because much recent effort has been spent on coprocessing, but primarily because petroleum residu typically make up greater than 50% of the fresh feed, with the result that the "liquid" portion of the feed is dominated by structural types that are known to be poor liquefaction solvents, namely long-chain alkanes and alkyl substituents. As a result, coprocessing studies provide an interesting baseline to compare the impact of solvent additives.

Microautoclave Studies. In a recent study on the interactions of catalysts, solvent, and coal in the context of coprocessing, Curtis and Cassel²³ pointed out the variable importance of the medium under catalyzed processing conditions. Their results showed that, for the "homogeneous" catalyst molybdenum naphthenate, the nature of the solvent had relatively little impact, but for supported catalysts, the character of the solvent was quite important: that is, the yields benefited much more from the addition of supported catalyst if the medium in which the coal was dispersed contained even a modestly effective PAH in addition to straight-chain alkanes. These results

illustrate a general trend that the nature of the medium becomes less important as the catalyst becomes more finely divided and suggest that the finely dispersed catalyst can indeed access a larger portion of the coal and/or preasphaltenes structures directly.

Another indication that communication between catalyst and substrate is facilitated by the medium is provided by recent results of Bockrath and co-workers.²⁴ They conducted liquefaction runs with ammonium thiomolybdate catalyst impregnated into an Illinois No. 6 coal. They emphasize the need for appropriate activation of the catalyst for high conversions. However, once the catalyst was activated, the need for dispersal was greatly diminished because, as they showed, the insoluble fraction (IOM, ash, and catalyst) from one run was similarly effective even when simply mixed with fresh coal in a subsequent run. Thus, it appears that not only is the liquid medium important, but also the solids including the catalyst support can help transmit the benefits the active metal. In fact, the benefits observed here may be related to those observed with Black Pearls or C₆₀ (see above).

The benefits reviewed above for microautoclave studies are also seen in larger scale studies with both dispersed and supported catalysts. In the two examples from process development studies discussed below, benefits were noted as a result of changes in certain operating conditions. Whether intentional or not, in both cases an increase in the PAH content of the medium accompanied the changes, and we have to consider if PAH may have been directly responsible for the observed beneficial impact.

Inclusion of a Recycle Loop. Studies at Universal Oil Products, Inc. (UOP), using a proprietary dispersed molybdenum catalyst, have shown dramatic improvement in the temperature limits of operability (i.e., decreased coking) as a result of recycling the heavy ends of the reactor.²⁵ This recycle loop was added with no change in the rate of the fresh feed, so there was no change in the average residence time, and therefore the improved yields must be due to improved chemical reactivity, physical solvency, and/or hydrodynamic factors. These results are very interesting, since most of coprocessing development efforts thus far have relied on a once-through approach. The once-through approach has been based in part on the rationale that heavy use of catalysts (particularly dispersed catalysts) will obviate concerns about solvent quality. In addition, it had been argued that because solvent quality is known to bear most directly on conversion of coal to preasphaltenes, rather than on upgrading of preasphaltenes or asphaltenes, the issue of nondistillables conversion in coprocessing is best addressed by focusing on optimization of the catalyst.^{26,27}

Increasing Coal Content of Feed. Additional insight into the nature of the recycle benefits is obtained from coprocessing development work at Hydrocarbon Research, Inc. (HRI).²⁸ This effort has focused on the use of reactors

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that are "once-through" but well-mixed. Researchers there have specifically made the point²⁹ that, although there is generally no recycle in their system, the back-mixed reactor inherently provides an "internal recycle" such that the incoming feed encounters a partially reacted medium which contains coal-derived PAH as well as the highly aliphatic resid.³⁰ The HRI researchers have also observed that increasing the coal concentration in a continuous-run development unit from 20 to 40% caused a substantial increase in the conversion of both coal and nondistillables, which more than compensated for the decline in catalyst activity as the run proceeded.²⁸ This change was performed with no change in total feed rate (i.e., space velocity), so the improvement they observed cannot be attributed to improved hydrodynamic factors and the benefits must have accrued from the changes in the solvent quality.

On the basis of these continuous unit results from HRI, and of various batch autoclave studies that have shown improved yields in coprocessing from the addition of PAH or PAH-rich mixtures, under both thermal³¹ and catalytic³² conditions, we speculate that hydrodynamic factors played no more than a minor role in the improvements described above when a recycle loop was added in the UOP system, and therefore the benefits achieved by UOP are also most likely due to improvements in chemical reactivity and/or physical solvency of the reaction medium. In either case, a better understanding of just how thermal hydrogen transfer is affected by the catalyst and the reaction medium is not only of fundamental interest but also of probable technological importance in catalytic hydroprocessing of coal and petroleum.

Hydrogen Transfer and Retrogressive Reactions. Although the importance of retrogressive reactions has become more obvious through careful studies of liquefaction kinetics and products, the fundamental chemical reactions and their kinetics have remained obscure. For instance, researchers such as Neavel³³ recognized some time ago that soluble products could be generated and consumed very rapidly under coal liquefaction conditions. Similar observations have been made for pyridine solubles under pyrolysis conditions, where there is no added solvent.³⁴ In a sense the whole technology of heavy oil conversion is bound up with retrograde reactions in that thermal treatment of petroleum asphaltenes under a variety of conditions can produce similar amounts of distillate, but the amount of retrograde product (coke) generated in conjunction with these volatiles is critically dependent on conditions of catalyst, medium, and hydrogen pressure.³⁵⁻³⁷ Thus the impact of retrograde processes can be quite obvious, but the detailed nature of

Scheme V. Ring Recombination of Phenoxy Radicals and Subsequent Tautomerization to a More Refractory Linkage

the responsible bond-forming reactions remains to be determined.

Recombination of radicals has traditionally been considered the main reaction leading to retrogression. However, the most abundant radicals during coal liquefaction will be resonance-stabilized radicals, whose recombination can result only in the formation of weak bonds, providing only temporary retrograde products. Thus, truly retrograde products must result from some pathway other than recombination, except in the case of ring recombination of phenoxy radicals (Scheme V). In this case we suggest that successful retrograde reaction is possible because the highly unstable initial adduct is able to rapidly rearrange through facile intermolecular proton-transfer reactions that are known³⁸ to be accessible to phenolic structures at coal liquefaction temperatures even in hydrocarbon solvents. Studies with the model compound benzyl phenyl ether have shown that the presence of scavengers can decrease but cannot easily eliminate the formation of diarylmethane linkages through this route. This example illustrates an interplay of radical and ionic reactions, a phenomenon we expect may be commonly important in retrograde reactions of oxygen-containing structures.

Recognition of the fact that hydrogen-transfer is a prerequisite to strong bond cleavage (rather than merely a subsequent step necessary to limit recombination) leads, via consideration of microscopic reversibility, to the conclusion that hydrogen-transfer is also necessary to the formation of strong bonds, or retrograde reaction. Tracing Scheme I backwards, for instance, illustrates that the link between the "coal" pieces is not "locked" into place until some agent removes the ipso H atom in what amounts to the reverse of the first step. In the absence of a suitable H-transfer agent, the intermediate is likely to come back apart because unimolecular loss of H atom is not very favorable in these cases. Thus, the very reactions that we relied upon to transfer hydrogen to the ipso position to effect cleavage could also under certain conditions lead to cross-linking reactions. Thus, the task of increasing coal liquefaction yields may in some cases involve the dilemma that introduction of a particular H-transfer agent will increase bond formation as well as bond cleavage. It follows then that the relative utility of various H-transfer agents in liquefaction cannot be truly understood unless we know their proclivity for promoting both bond cleavage and bond formation.

Distinct from retrogression resulting from coupling of two aromatic moieties is retrogression resulting from growth of PAH systems. Ring growth can occur through a sequence of cyclization and aromatization. These ring

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Figure 1. FI mass spectrum of a Pittsburgh (Wilsonville run 259) recycle oil showing the prominent PAH structures in the 200–350 Da range.

growth processes are known to be very rapid on acidic surfaces, but indirect evidence^{35–37} indicates that growth of PAH can also occur in bulk petroleum process streams. Sullivan et al.³⁹ recently examined the chemical composition of products from the hydrotreating/hydrocracking of a resid-derived VGO using a careful and thorough analysis regimen of high performance liquid chromatography/field ionization mass spectrometry (HPLC-FIMS). They showed a marked correlation between decreasing catalyst performance and increasing levels of certain PAH in the product and recycle streams. The most striking increases observed from start-of-run to end-of-run were factors of 4 and 100 for benzo[ghi]perylene and coronene at m/z 276 and 300.

Evidence for the presence, and possible importance, of such structures in coal liquids comes from our recent examination by field ionization mass spectrometry (FIMS) of 15 coal liquefaction resids from the Wilsonville facility.⁴⁰ At first glance, the spectra looked very similar with only a broad, featureless envelope. Closer examination, however, revealed that the mass spectra consistently showed the same set of a few prominent peaks in the low mass end. Figure 1 shows the FI mass spectrum of one of these resids with the more prominent peaks identified. Interestingly, these prominent masses were identical with those previously associated by Sullivan et al. with increased difficulties in hydrotreating vacuum gas oils.³⁹ Because FIMS analyses on Wilsonville samples were performed on the whole resids (i.e., without any HPLC separation), we cannot be sure that the structures responsible for these very prominent peaks are the same as those implicated by Sullivan et al. However, the coincidence is remarkable and we believe that a quantitative analysis could lead to an index of resid reactivity, and moreover that judicious studies that involve the following of these structures through the hydrotreating process could lead to useful mechanistic understanding of coke-forming reactions.

The first prominent peaks in all of these spectra is at m/z 242 and is identifiable as the odd-carbon aromatic derived from pyrene by completion of a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ bridge between the 1- and the 10-positions (1,10-trimethylenepyrene). As an analog of phenalene ($\text{C}_{13}\text{H}_{12}$), m/z 242 is an odd-carbon molecule that would have to lose three hydrogens to be fully aromatic and therefore cannot form a closed-shell fully aromatic PAH. However, the

radical species formed when three hydrogens are lost is among the most stable of all radicals, and earlier ESR studies have found it to be common in thermally processed petroleum even at room temperature.

FIMS analysis clearly shows that 1,10-trimethylenepyrene, m/z 242, is a commonly recurring PAH structure that builds up during catalytic processing. How important it actually is as a step in the ring-growth processes that lead to still larger PAH and eventually char is a critical question, the answer to which is not known. A partial answer appears here in the form of studies on the pyrolysis of alkylpyrenes. The formation of a product corresponding to m/z 242 has recently been reported by Savage and co-workers during the pyrolysis of 1-dodecylpyrene.^{41,42} In addition, we recently detected formation of benzo[ghi]perylene, m/z 276, in the pyrolysis of another long-chain alkylpyrene. As indicated above, this PAH has been found to be prominent in coal- and petroleum-derived resids and to be correlated with increased problems of coke formation.³⁹ Benzoperylene could conceivably be formed from the original 1-alkylpyrene by two successive ring closures proceeding through the intermediacy of the m/z 242 ring system. Thus, we suggest that 1,10-trimethylenepyrene is indeed associated with the formation of coke precursors and factors influencing its formation and subsequent reaction deserve further study.

Conclusions

We have reviewed the implications of the solvent-mediated hydrogenolysis (SMH) picture for coal liquefaction. The essence of the SMH view is that hydrogenolysis of strong bonds is a major contributor to structural fragmentation and that this hydrogenolysis results from a competition between free H-atom addition and H-transfer that is mediated by solvent H-carrier radicals or other solvent species. This view requires that the reaction medium contain not only hydrogen donors but also hydrogen acceptors such as PAH.

We have examined a number of observations in coal liquefaction and other fossil fuel upgrading technologies in light of the SMH picture for coal liquefaction. This examination has resulted in plausible explanations for phenomena that are difficult if not impossible to rationalize on the basis of the traditional weak bond homolysis-radical capping mechanisms. These difficult-to-explain shifts in rates and product distributions are understood in terms of the changes in relative importance of competing H-transfer pathways as a result of the changes in temperature, PAH structure, PAH content, degree of hydrogenation, and coal structure. We also discussed examples from catalytic liquefaction studies which show that these solvent-mediated hydrogenolyses are important even under catalytic conditions. The solvent medium helps transfer and transport the hydrogen activity generated at the catalyst surface to where it is needed for bond cleavage. This dependence on solvent quality is expected to be greater in cases where intimate contact of catalyst and coal structures is precluded, as in the case of supported catalysts, lower loadings of finely dispersed catalysts, and nonsoftening coals. Hence we expect that the liquefaction effectiveness can be increased by catalyst supports that

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can augment H-acceptor capability and suggest that more effort should be placed on the exploration of carbon-supported catalysts. Finally, we see that solvent-mediated H transfers can also be responsible for retrogressive reactions. Hence care is warranted in selecting the optimal conditions for coal liquefaction. Because the retrograde reactions become much more facile above 425 °C and under hydrogen starvation, high-temperature processing should be limited to short contact times and hydrogen-rich conditions.

Acknowledgment. The authors acknowledge the support of the Pittsburgh Energy Technology Center, U.S. Department of Energy, in various projects whose goals have included an improved understanding of the chemistry responsible for coal liquefaction. The portion of the work with buckminsterfullerene was conducted in the program Advanced Chemical Processing Technology, consigned to ACTA from NEDO, which is carried out under the Large-Scale Project enforced by the Agency of Industrial Science and Technology.