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INTRODUCTION

The early history of solvent extraction in coal research has been reviewed by Van Krevelen. (1) From the beginning, solvent extraction has been used to isolate and characterize both soluble and insoluble coal fractions. The recent studies covered in this report fall into four broad areas: 1) Improvement in extraction yields or selectivity; 2) Correlation of solvent swelling and extraction behavior to structural models for the insoluble organic portion of coal; 3) Analyses of extracts to identify and perhaps quantify organic compounds in the raw coal and 4) Use of solvent extraction to predict or influence coal behavior in some other process such as liquefaction. To cover this active area in a brief Preprint, references were chosen to illustrate both the current status of the field and cite related studies.

The availability of the pristine Argonne Premium Coal Samples (2) has led to a significant improvement in the reproducibility of solvent extraction as an analytical tool. In 1984, Triolo and Child cautioned that solvent extraction may be an inherently unreproducible process. (3) Based on studies of how weathering affects solvent extraction, that was a fair statement at the time. (4) With the improvements and standardization of solvent extraction practices developed since then, it is now possible to obtain reproducible and reliable information from the solvent extraction of coal.

EXPERIMENTAL

Protection of pristine coal samples and solvent extracts from air is necessary if colloid-free extract solutions are to be isolated. (4) Solvents must be of high purity if large volumes are to be concentrated by evaporation or distillation for product isolation. Soxhlet extraction, stirring -100 mesh coal with a large volume of solvent for several days or ultrasonic irradiation for 30-90 minutes at room temperature have all been reported to give the same extract yield for a given solvent/coal combination. (4) (5) (6) (7) Complete separation of extract from insoluble residue requires either membrane filtration (Nylon or Teflon of 0.45 μ pore size, pre-filter needed if colloids are present) or centrifugation at 24,000g or greater. Removal of hydrocarbon solvents such as toluene from extract and residue can be accomplished by drying to constant weight at elevated temperature and reduced pressure (100°, 0.1 Torr). Removal of nitrogen containing solvents requires washing with specific solvents such as 80% methanol/water for pyridine or DMF (4) or acetone/water for N-methyl-2-pyrrolidinone (NMP) (6) before vacuum drying.

DISCUSSION

1) Improvement in yield or selectivity. "Solvent Extract" is an operational definition for material isolated from the complex and inhomogeneous mixture which is coal. Unless the separation process is specified, including filter pore size or centrifugation clearing factor, the material isolated is not well defined and may not be the same as that isolated by other workers. This is especially true for coals subject to weathering. We showed that insoluble colloids were present in polar solvent extracts of Argonne coals which were exposed to air during or after extraction. The colloids passed ordinary filter paper or fritted glass funnels but were removed by 0.45 μ membrane filtration or ultracentrifugation. (4) Weathered coals are less prone to colloid formation, presumably because the reactive material is no longer present. Additional insight into the effect of weathering and moisture removal on the accessibility of coals to solvents was given by Kispert using intercalation of epr spin probes. (8) Even brief air exposure caused measurable changes in the retention of polar probes by Ill. No. 6 coal. Most workers dry coal before extraction in order to determine extract yields and material balances; however this may collapse pore structure in low-rank coals and produce other changes in high-rank coals. Even drying at 100° can induce cross-linking reactions in low-rank coals which reduce pyridine swellability. (9)

Pyridine is a good solvent for many coals and has been extensively studied. Selected extraction data for the Argonne Premium Coals are given in Table 1. All material balances are 94-102% and the lab to lab variation in yield is typical of recent studies. Pyridine cannot be completely removed from coal or extracts by heating, either under reduced pressure or in a flow of nitrogen. In our experience, 80% methanol/water washing followed by vacuum drying is the most effective method to remove pyridine or DMF in terms of minimizing the time and volume of wash solvent used - which minimizes chances for air oxidation or loss of slightly soluble minerals. This wash solvent has a high heat of wetting for coal surfaces. (10) Trace amounts of either DMF or pyridine can be detected by FT-IR spectroscopy (4) and the human nose is quite sensitive to traces of pyridine on coal fractions.

Efforts to increase extraction yields include Liotta's addition of (n-Bu)₄NOH in methanol for ultrasonic pyridine extraction of several coals. (11) For Argonne coal 301 the yield increased from 28 to 70% only when the good swelling agent, (n-Bu)₄NOH in methanol, was present. Our results on the effect of acid demineralization on pyridine extraction yields of Argonne coals 201, 301, 401 and 801 are shown in Figure 1. The increase in yield for low-rank coals may be, in part, the effect of converting carboxylic acid salts into pyridine soluble acids. Our preliminary results on the effect of demineralization on toluene extraction yields for Ill. No. 6 coals show that, although the absolute yield is much smaller, the relative increase after demineralization is greater than with pyridine. This is consistent with the view that, given enough time for mass transport, a good swelling solvent such as pyridine can remove soluble material by diffusion through the organic matrix but a poorly swelling solvent such as toluene removes material only via the interconnected pore network, portions of which may be blocked by minerals.

Iino used CS₂/NMP mixed solvent, with and without ultrasonic irradiation, to remove from 30-66% by weight of soluble material from 29 of the 59 coals they studied. (6) Results for the Argonne coals are also listed in Table 1. Based on analyses of coals, extracts and residues as well as extraction of separated macerals, they suggest a synergistic effect due to the good solvent and swelling character of the NMP and high diffusibility of the CS₂. Morgan has recently reported that KOH or NaOH added to NMP or DMF extractions of South African and the Argonne coals gave extracts containing up to 80% of the carbon from the feed coals. (12) However, from the information given, the absence of colloids or material balances cannot be determined. Other strong base treatments of pyridine extract residues also lead to high total yields of extract at modest temperatures. (13)

Supercritical solvent extraction has been used by several groups to study coal porosity (14) or to remove organic (15) or elemental sulfur (16) from coal, either as a prototype desulfurization process or as an analytical method. For the isolation of analytical samples for GC or HPLC analyses the method is quick and equipment requirements modest. (17)

2) Correlation of solvent swelling and extraction with structure. Solvent extraction is often used to prepare the insoluble residue for solvent swelling studies which are used to infer structural information by reference to the literature on solvent swelling of cross-linked polymers. Access to this active field can be gained from recent papers by Green, (18) Iino, (19) Larsen, (20) Nishioka, (21) Painter (22) and Snape. (23) Current work shows that brief heating of coals with solvents in which they are not soluble, such as water or chlorobenzene, causes irreversible changes in swelling and extraction yields with good solvents (defined as those such as pyridine which swell and extract coal to the greatest extent.) The suggestion that new cross-links such as hydrogen bonds have been established (19) has been criticized by Painter who notes that hydrogen bonds are dynamic and cannot serve as true cross-links as do the covalent bonds in cross-linked polymers. (22) Physical association with strong concentration and temperature dependence is suggested as a better representation than a cross-linked network for the insoluble portion of most coals. (21) The implications for coal liquefaction if this model is substantiated are profound.

3) Analyses of Extracts. Modern size exclusion chromatography (SEC) is a powerful method for determining molecular weight

distributions of mixtures. Because coal fractions usually contain both polar and non-polar molecules, interpretation of SEC data is difficult. Advantages and problems with THF(24), NMP(25) and pyridine(26) as SEC mobile phases for coal fractions are discussed in the references cited. Solvents which prevent self-association of coal molecules (pyridine, DMF, NMP) give more realistic molecular weights but limit the choice of SEC detectors. The common refractive index detector over-estimates the contribution of oxygen rich species such as phenols and gives average molecular weights which are too high unless calibrated with appropriate compounds. Changes in SEC molecular size distributions find use in studies of the progress of coal liquefaction and other processes. A novel recent use is the screening of microorganisms which bio-degrade coal.(27)

Among the methods which have the possibility for identification of specific compounds in solvent extracts, GC/MS has been the most studied. For this purpose, solvents such as benzene/methanol(28) have the advantage of extracting only molecules which can be volatilized in a typical GC or MS inlet and thus need no fractionation before analysis. In contrast, during FIMS analysis of the toluene insoluble portion of a pyridine extract, only 34% of the sample was volatilized.(4) A disadvantage to non-polar solvents is that potentially soluble molecules may not be accessible to the solvent and their absence may bias the conclusions drawn. To avoid this problem, chromatographic fractionation of pyridine extracts is often used to isolate fractions which can be analyzed by mass spectroscopy. In the usual methods, elution from a silica gel(29) or alumina column(5)(30) produces increasingly polar coal extract fractions which may be further fractionated on other supports for specific analyses. A typical application is the study of terpenoid biomarkers in coal to better understand the progress of the coalification process.(31)(5)

Solvent extraction is often used to prepare samples for IR, NMR, X-ray and other analyses, the results of which are discussed by other speakers at this Symposium. Elemental sulfur in coal can be determined by perchloroethylene (PCE) extraction followed by HPLC analysis(32) or GC analysis of supercritical extracts.(15)

4) Solvent extraction as related to other processes. Pre-treatment of coals with solvents prior to liquefaction often leads to increased yields of desirable products, lower conversion temperatures or both. Studies utilizing both very polar(33) and non-polar solvents(34) illustrate the complexity of the effects in that both swelling and non-swelling solvents can improve liquefaction depending on the process and coal used. Recent work using chlorobenzene(35) appears to support the view that, since solvents which disrupt molecular aggregates without bond cleavage increase liquefaction conversions, physical association is an important structural feature in coal.(21)

Removal of noxious elements such as sulfur by simple solvent extraction of coal is an attractive idea. However the claim that PCE extraction removes organic sulfur in a coal desulfurization process is controversial. ASTM organic sulfur reductions of up to 40% following PCE extraction have been reported,(36) however the effect appears to be due to removal of elemental sulfur ("organic sulfur" by ASTM) produced by pyrite oxidation.(37)

SUMMARY

With careful attention to anerobic conditions and clarification of solutions, solvent extraction of coal is a useful, reproducible technique for coal science. Studies of the extraction process itself and the related solvent swelling provide important insights into coal matrix structure while analyses of the extracts provide increasingly detailed information about the chemical species present in both extract and raw coal.

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TABLE 1. Solvent Extraction Yields of Argonne Premium Coals

| APCS # | % C MAF ^a | Wt % Toluene ^b | Wt % Pyridine ^b | Wt % Pyridine ^c | Wt % Pyridine ^d | Wt % CS ₂ /NMP ^e |
|--------|----------------------|---------------------------|----------------------------|----------------------------|----------------------------|--|
| 801 | 73 | | 2.9 | 3.1 | 3.1 | 2.3 |
| 201 | 75 | 2.3 | 7.1 | 7.4 | 6.2 | 9.9 |
| 301 | 78 | 7.0 | 25.8 | 27.5 | 27.9 | 33.1 |
| 601 | 81 | | | | 32.1 | 33.6 |
| 401 | 83 | 5.8 | 29.7 | 29.8 | 26.5 | 39.0 |
| 701 | 83 | | | | 14.7 | 27.1 |
| 101 | 86 | 0.6 | 20.9 | 6.9 | 14.9 | 59.4 |
| 501 | 91 | 0.4 | 1.2 | 0.8 | 0.5 | 2.8 |

^a Ref. 2; ^b This work; ^c Ref. 5; ^d Ref. 7; ^e Ref. 6.

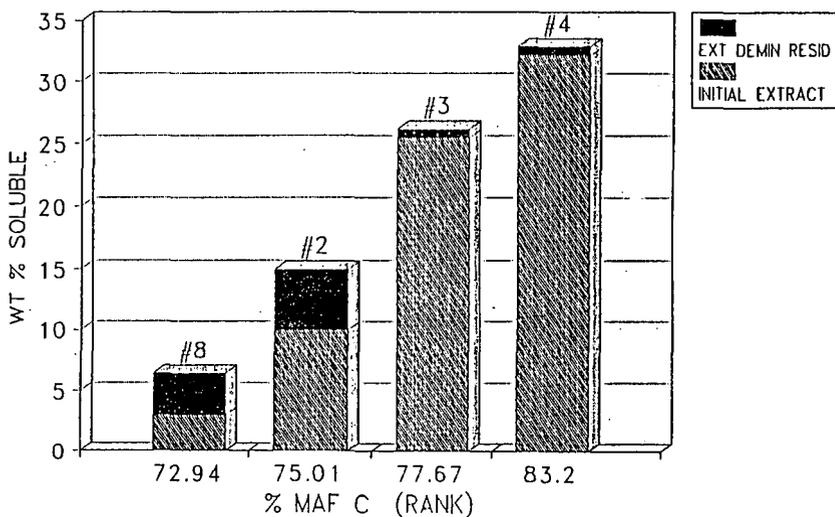


Figure 1. Yields of additional pyridine soluble material extracted from the demineralized, pyridine-insoluble residues of four Argonne Premium coals as a function of coal rank.