Title: **Regulation of Coal Polymer Degradation by Fungi**

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Abstract

Certain low rank coals are partially solubilized by fungi. Early research showed that lignin degrading fungi have the ability to solubilize these coals and a substantial amount of research interest focused on the role of lignin degrading enzymes in this process. The selection of lignin degrading fungi for study appeared to be a logical choice as lignin and low rank coals such as lignite appear to have some similarities. However, it is important to note that there are also several differences. For example, the aromatic substructures of lignite and other low rank coals appear to be somewhat more condensed than aromatic substructures in lignin. Furthermore, phenylether linkages do not appear to be as important in the structure of lignites as they are in lignin. A major difference between lignin and lignite is that, in lignites polyvalent cations form ionic linkages between coal substructures. Although some of the early research suggested that extracellular oxidases that are produced by lignin degrading fungi have a role in coal solubilization, it is now generally accepted that the major mechanism by which such coals are solubilized involves chelation of metals in these coals by oxalate ion (and possibly by other metal chelators). Chelation breaks the ionic linkages between coal macromolecules (*i.e.,* coal derived humic acids and other materials) which are relatively polar and soluble in water once these linkages are broken. In addition to lignin degrading fungi, several other fungi, such as *Aspergillus spp.* and *Penicillium spp*. have been shown to be able to solubilize low rank coal. In retrospect, this is not surprising as it is known that these fungi are able to produce large amounts of oxalate. Furthermore, we have shown that a number of Krebs cycle intermediates are also able to solubilize leonardite, an oxidized lignite. The ability of certain low rank coals to be solubilized by metal chelators is a phenomenon that has been described relatively recently. In contrast, the ability of such coals to be solubilized by a strong base (*e.g.*, sodium hydroxide) has been known for over thirty-five years. We have very recently shown that Lewis bases (*e.g.,* bicarbonate/carbonate ions and phosphate/hydrogen phosphate ions) are also able to mediate substantial solubilization of leonardite, but at considerably lower pH (*i.e.*, pH 7-9) than is required to effect solubilization by strong bases such as sodium hydroxide. Although the role of extracellular oxidases secreted by wood rotting fungi is minimal in the initial solubilization of coal macromolecules, it appears that they may have a role in subsequent degradation of this material. We have shown that ligninolytic cultures of *Phanerochaete chrysosporium* are able to mediate decolorization/degradation of soluble coal macromolecule and we have shown

that lignin peroxidases are involved in the decolorization process. Depolymerization of soluble coal macromolecule by lignin peroxidase and other extracellular enzymes is somewhat difficult to thoroughly document because water soluble coal does not appear to be a simple mixture of noninteracting macromolecules. Instead this material is a mixture of macromolecules that tend to form aggregates. Furthermore, the composition of the aqueous solution in which coal macromolecules are dissolved tends to affect aggregation phenomena as assessed by gel permeation high performance liquid chromatography. Results to date from our laboratory and by others suggest that ligninolytic cultures of wood rotting fungi and their extracellular oxidases do appear to degrade soluble coal macromolecule and the peak molecular weight of such mixtures does appear to be decreased. Unfortunately, existing processes do not yet seem promising for production of industrially important chemical feedstocks. Of potential industrial importance, however, is the observation that treatment of leonardite with readily available and inexpensive Lewis bases results in solubilization of coal macromolecule at physiological pH. This fact may facilitate subsequent bacterial methane production from leonardite and other low rank coals that are amenable to solubilization by this treatment. (Supported by DOE Grant DE-FG22-94PC94209)

Published Journal Articles, Completed Presentations and Students Receiving Support from Grant DE-FG22-94PC94209.

Peer Reviewed Publications

Bumpus, J.A., J. Senko, G. Lynd, R. Morgan, K. Sturm, J. Stimpson and S. Roe, (1998) Biomimetic solubilization of a low rank coal: Implications for its use in methane production. Energy & Fuels. In Press.

Bumpus, J. A., J. Senko, S. Roe, R. Morgan, K. Sturm and J. Stimpson (1998) Biological and biomimetic solubilization of a low rank coal and its chemical characterization: Experiments in coal chemistry for undergraduates (Manuscript Completed).

Other Publications

Sturm, K. (1995) Investigations of solubilization and depolymerization of leonardite by *Trametes versicolor.* University Coal Research Internship Program Final Report. pp187-196.

Senko, J. (1996) Investigating solubilization and depolymerization of leonardite by *Trametes versicolor* and *Phanerochaete chrysosporium.* University Coal Research Internship Program Final Report. pp 195-203.

Poster Presentations

Stimpson, J., J.A. Bumpus, K. Sturm, J. Senko, S. Roe and R. Morgan (1996) Biological and Biomimetic Solubilization of a Low Rank Coal and its Chemical Characterization: Experiments in Coal Chemistry for Undergraduates. 31st Midwest Regional Meeting, American Chemical Society, November 6-8, 1996, Ramkota Inn, Sioux Falls, SD.

Bumpus, J.A., J. Senko, G. Lynd, R. Morgan, K. Sturm, J. Stimpson and S. Roe, (1997) Biomimetic solubilization of a low rank coal: Implications for its use in methane production. Department of Energy University Coal Researchers Annual Meeting, Pittsburgh, PA, June, 1997.

Speaking Engagements

Bumpus, J.A. (1996) Department of Energy University Coal Researchers Annual Meeting, Pittsburgh, PA, June, 1996, Title: Regulation of Coal Degradation by Fungi.

Students who have received support.

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Chamindra Dassanayeke (University of Notre Dame)
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Undergraduates students (The following students also participated in the UCR Internship Program)

Kimberly Sturm (Thiel College)
John Senko (St. Vincent's College)
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