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Biologically Derived Value-Added Products from Coal

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ABSTRACT

The Idaho National Engineering Laboratory (INEL) has for several years conducted research in the area of coal bioprocessing. Fundamental and exploratory research has been directed toward the conversion of coal to cleaner fuels and the remediation of harmful byproducts of coal utilization. Specific research projects have involved coal depolymerization, coal solubilization, removal of organosulfur and pyritic sulfur from coal, the molecular biology of coal-modifying microorganisms, removal of ash-forming minerals from coal, conversion of coal combustion gases, and the development of novel coal bioreactors. Notable research accomplishments include elucidation of mechanisms by which microorganisms solubilize different portions of coal, discovery and characterization of microorganisms capable of depolymerizing macromolecular coal, discovery of microorganisms capable of removing organosulfur from coal, development of technologies critical to analyzing biologically mediated depolymerization and organosulfur removal, novel methods of pyritic sulfur removal, novel methods of removal (and conversion) of CO_2, SO_x, and NO_x from combustion gases, and new technologies for bioconversion of waste gypsum generated in coal combustion gas scrubbers.

Index Entries: Coal; lignite; bioprocessing; depolymerization; desulfurization.

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INTRODUCTION

The overall purposes of coal bioprocessing research at the INEL are to (1) determine fundamental interactions between biocatalysts (whole cells and enzymes) and coal, and (2) define fundamental properties of coal bioprocess engineering. INEL studies have been conducted with an eye on the impetus behind the research—the eventual production of environmentally clean, high-value coal products. Clean coal products that are desirable include desulfurized coal, fermentation products (such as ethanol), and demineralized coal. In addition, the bioremediation of coal combustion gases could make the burning of coal a more valuable process, since major atmospheric pollutants would be neutralized.

Bioprocessing of coal to create a variety of value-added products requires that research be performed in many different areas ranging from the most basic microbiological and molecular biological work to development and application of unique bioreactors. The INEL has been involved in all aspects of coal bioprocessing research, including the following: fundamental chemistry and biochemistry of microbial solubilization and liquefaction of coal (*1–3*), biological removal of ash-forming minerals in coal (*4–6*), biological removal of pyritic and organic sulfur from coal (*6,7*), coal bioprocess engineering (*8,9*), bioremediation of CO_2, gaseous sulfoxides (SO_x), and gaseous nitroxides (NO_x) from coal combustion gases (*10*), molecular genetics of biodesulfurization of coal (*11–13*), biocatalysts for non-aqueous and biomimetic reactions with coal (*14*), and bioconversion of waste gypsum (calcium sulfate) from coal combustion gas scrubbers (*15*).

Five specific coal research projects at the INEL are presented below; these are directed toward the production of value-added products. The projects concern coal solubilization, coal depolymerization, prediction of coal bioprocess product yields, reactors for coal bioprocessing, and biological coal depyritization.

BIOSOLUBILIZATION OF COAL

The mechanisms by which biocatalysts liquefy or solubilize coal are under investigation. The driving force behind this research is the hope that liquid coal products may be alternative, cleaner fuels. Another possible benefit of the research is that solubilizing agents might remove portions of coal that contain disproportionately high amounts of pollutants, leaving behind a cleaner burning coal. Recent research has shown that chemically synthesized surfactants (such as Tween 80) solubilize portions of lignite coal and reduce the sulfur and nitrogen content of the dissolved coal; biosurfactants may also be able to clean coal in this fashion (*3*).

Three specific research directions have arisen in this area: solubilization of coal by microbially produced alkali, microbially produced metal

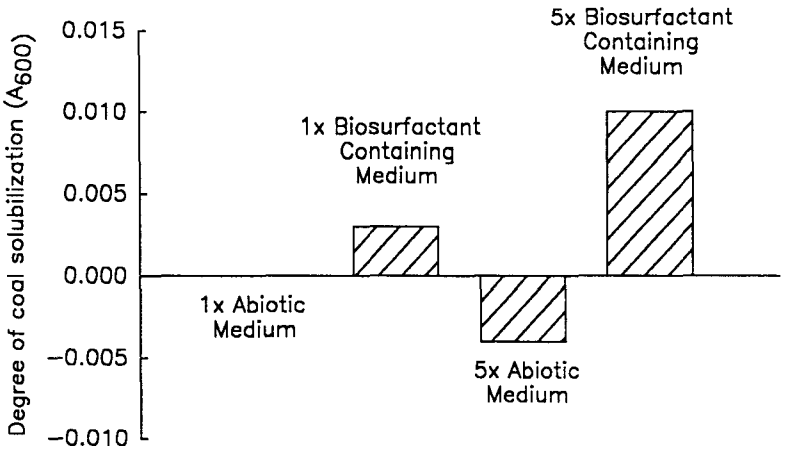

Fig. 1. Biosurfactant-mediated coal solubilization. Unconcentrated and concentrated surfactant-containing cell-free extracts derived from *Candida bombicola* cultures were mixed with granular lignite coal overnight. Controls that did not contain surfactant were included. After removing undissolved coal by centrifugation, supernatants were analyzed for the presence of dissolved coal by measuring optical absorbance.

chelators, and biosurfactants (*1–3*). Research at the INEL has been instrumental in elucidating mechanisms for these three modes of coal biosolubilization. Microbial alkali-mediated solubilization is predominant for those coals that are susceptible to solubilization by NaOH (e.g., leonardite and lignite coals). In addition, removal of coal-associated metal ions by microorganisms also renders coal more soluble in water. Recent data indicate that biosurfactant produced by *Candida bombicola* is capable of solubilizing a portion of lignite coal (Fig. 1). Future research will focus on characterizing the effects of biosurfactant solubilization on coal chemistry.

BIOLOGICAL DEPOLYMERIZATION OF COAL

The discovery and investigation of biocatalysts that depolymerize alkali-soluble macromolecular coal may lead to utilization of coal as a cheap source of carbon feedstock for the fermentative production of clean biofuels, such as ethanol. The type of process envisioned is analogous to the bioconversion of cellulosic biomass to ethanol, which has been proposed and studied for many years.

Specific research tasks include:

1. Fungal and bacterial in vivo depolymerization of alkali-soluble coal;
2. Enzymatic depolymerization of alkali-soluble coal; and
3. Development of methods for analysis and purification of coal depolymerization products.

Table 1
Timing of Veratryl Alcohol Oxidation, Alkali-Soluble Coal Modification, and Lignin Modification by *Penicillium citrinum* Strain 26[a]

	Observance of conversion activities at different times, hours, after the introduction of substrate[b]				
Activity type	0	8	19	24	45
Veratryl alcohol oxidation	N	N/Y	Y	Y	Y
Alkali-soluble coal modification	N	N	Y	Y	Y
Lignin modification	N	N	Y	Y	Y

[a]Growth conditions and veratryl alcohol, coal, and lignin assay procedures are described in detail in ref. (*20*).
[b]N, no activity; N/Y, marginal activity; Y, activity present.

Major accomplishments and discoveries include the discovery of several coal depolymerizing microorganisms and the development of liquid chromatography and high-performance liquid chromatography methods for analyzing coal-derived products (*16–19*). In particular, an INEL isolate designated as *Penicillium citrinum* strain 26 is capable of significant alteration of coal macromolecular structure (*20*). Strain 26 is reactive with both North Dakota Beulah Zap lignite and Ugljevik lignite. The fungus produces depolymerization products with molecular weights of 185, 5000, and 14,000, and polymerization products with molecular weights of 71,000 and 220,000 from Beulah Zap lignite (original mol wt = 25,000). The 5000-mol-wt product has an optical absorption maximum at 300 nm, the 185-mol-wt product has absorption maxima at 300 and 400 nm, and the 220,000-mol-wt product has absorption maxima at 240 and 280 nm. Strain 26 is even more reactive with Ugljevik lignite (original mol wt = 53,000), producing depolymerization products with molecular weights of 100, 200, 6000, 11,000, and 24,000, and polymerization products with molecular weights of 73,000 and 213,000. Comparisons of chromatographic peak areas for untreated coal with those for treated coals indicate that there is a 90–100% conversion of these two lignite coals to the aforementioned coal-derived products. The mechanism of conversion appears to be primarily enzymatic, and may involve an enzyme similar to lignin peroxidase since the chronologies of veratryl alcohol oxidation, coal modification, and lignin modification activities are similar in the growth cycle of the organism (Table 1).

PREDICTION OF COAL BIOPROCESS PRODUCT YIELDS

Research was performed to establish yields of microbially derived products from coal and to determine ideal products and processes. The

research efforts are contingent on the assumption that coal is a cheap source of fermentable carbon that might be used as a microbial substrate to make higher-value products. Two types of results were obtained: (1) determinations of yield coefficients for cells and products from coal, and (2) interpretation of yield data (*21,22*). The results provided a means of deriving the constancy of product yield based on available coal electrons. Calculations also set the theoretical potential yield limits for anaerobic processes that produce two products (methane and hydrogen; ethanol and acetic acid). Various potential fermentation products that might be derived from coal were rated according to the profitability of their production from coal. The profitability analysis was based on theoretical product yield (in terms of carbon and electron equivalents) and the current prices of coal and products. Four products were analyzed in this fashion. The products, in order from highest possible economic return down to lowest possible return, were: propionic acid (return = 43 cents/lb coal), ethanol (28 cents/lb coal), butanediol (16 cents/lb coal), and methane (3.5 cents/lb coal).

REACTORS FOR COAL BIOPROCESSING

The efficiency of any coal bioprocessing scheme is dependent on sound process design. Therefore, fundamental engineering research is being conducted on general topics arising from the bioprocessing of coal. Specific research tasks involve (1) the investigation of oxygen transfer in three-phase bioreactors and (2) the modeling of pyritic inclusion-size distribution effects on depyritization of coal (*8,9,23*). It was discovered that oxygen transfer limits (1) the size of coal particles that can be used in a heap bioreactor and (2) the slurry concentration in a slurry reactor. A potential application of this type of modeling is the design of efficient bioreactors, such as the one developed for coal desulfurization, described below.

BIOLOGICAL COAL DEPYRITIZATION

As one of the most applied projects in INEL coal bioprocessing research, the depyritization task is directed toward the development of bioreactors and process flowsheets for the microbial removal of pyrite from coal. Removal of pyritic sulfur from coal is necessary because it gives rise to harmful SO_x gases during coal combustion. The major research project (and accomplishment) was the development of an aerated trough slurry reactor that combines physical removal of large pyritic inclusions (and other liberated matter) with microbial degradation of micropyrite. Tests using a 150-L reactor demonstrated that this combination removed 90% of coal pyrite and 35% of coal ash-forming minerals, while retaining 90% of the coal heating value (*6*). This was attained using the following reactor

parameters: hydraulic residence time = 8.8 d, reactor residence time = 5 d, mass fraction of coal = 0.2, dry coal feed rate = 4.37 kg/d. These conditions resulted in a product coal flow rate of 4.14 kg dry coal/d. Preliminary economic evaluations indicate that the cost of treatment is $10–15/T coal (unpublished data, G. Andrews). This price is favorable in light of the high cost of processing coal combustion gases.

CONCLUSION

The INEL has conducted (and continues to conduct) considerable research in the area of coal processing. Reputable and successful studies have spanned several disciplines of science and technology, involving microbiology, molecular biology, biochemistry, chemistry, chemical engineering, mechanical engineering, and biochemical engineering. These studies have all been focused on one ideal—making the utilization of coal environmentally and economically sound.

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