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The Biotechnology of Coal

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Biotechnology is a multidisciplinary field with its roots in the biological, chemical and engineering sciences. It arises from the combination of a number of specialist subjects such as molecular genetics, microbial physiology and biochemical engineering. It has been variously described and is defined for the Organization of Economic Cooperation and Developments as, “the application of scientific and engineering principles to the processing of materials by biological agents to provide goods and services.” This subject is complex due to its multidisciplinary approach.

Because of the many advances in the field of biotechnology, these techniques are finding application in number of novel areas. One of these novel areas is the Coal bioprocessing. Coal does not appear to be an ideal material for biological attack. It is highly variable and heterogeneous mixture with varying properties in different regions on this earth. It is basically carbonaceous material with mineral inclusions and it is such a heterogeneous substance that microorganisms may be able to attack, degrade or use a number of different constituents present in it. Bioprocesses might have significant advantages over the conventional technologies of breakdown or cleaning currently in use, and they might open up the possibility of the economic production of new products. This is because the reaction conditions involved would be much “milder” than the required for the equivalent chemical transformations and removal of certain impurities might be maximized. The use of biotechnology could provide alternative process routes for coal conversion and/or could provide alternate and viable pathways for the cleaning of coal (Desulfurization).

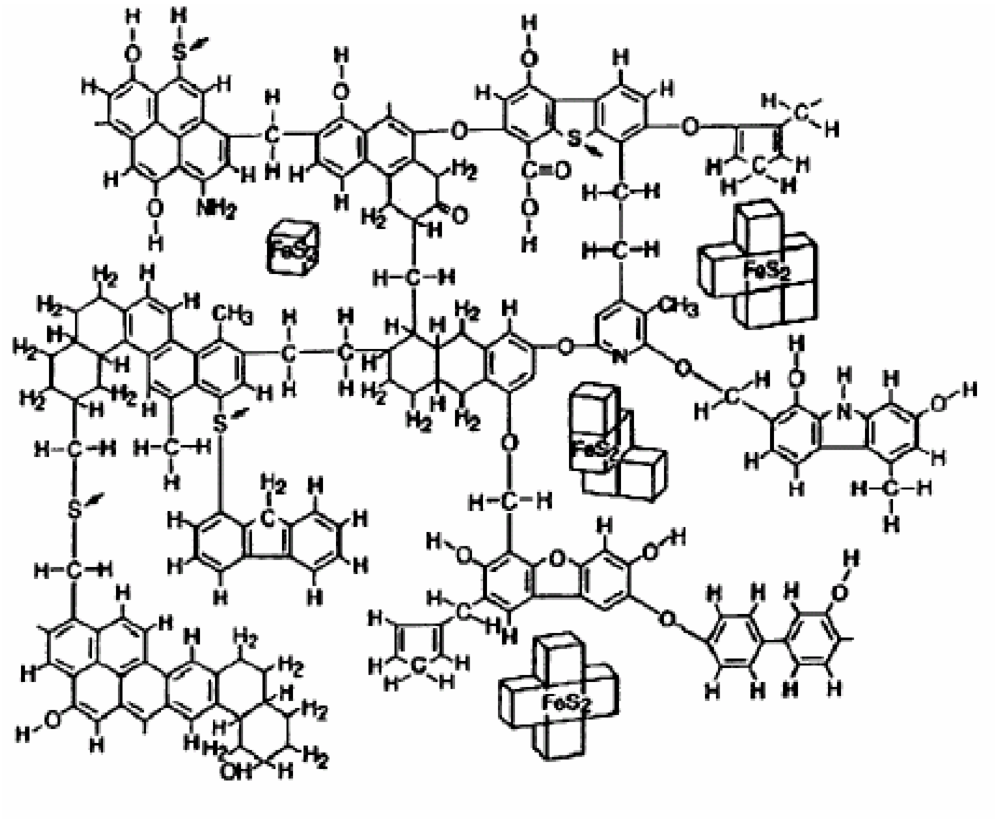
The vast amount of coal in the world exists because the carbon present in the precursor of coal was not degraded. This was the result of imposed temperature and pressure and the limited amount of the oxygen due to which complete oxidation was not possible. Coal has biological origins and is largely insoluble both in water and many organic solvents, except under extreme conditions. The small size of the porous structure in most coals presents an obstacle to the ingress of microorganisms and the outer surface is the main area for the biological attack. In addition, there are substantial quantities of inorganic impurities present in the form of clays, quartz, sulfur compounds and others. There may be trace elements that will be toxic to the various microorganisms.

Several routes for microbial coal beneficiation are possible. Microorganism may attack either carbonaceous coal or the interspersed inorganic materials. One route is the depolymerization of coal polymer and the breakage of various key links. This could provide the basis for the liquefaction processes. A second route would be reduction in oxygen content either through reduction of C=O to CH_2 or perhaps by decarboxylation to CO_2. This could improve the heating value. A third would be the removal of sulfur, nitrogen or metals from the coal before combustion which would lead to the reduction of unwanted emissions and residues.

High sulfur containing coals present many environmental problems. When coal is burnt its sulfur content combines with oxygen to produce sulfur oxides which contributes to both pollution and acid rain. The best possible way to prevent our environment from sulfur oxides is to reduce the amount of sulfur in coal before combustion. Different techniques are used for the desulphurization of coal which includes physical, chemical and biological processes. Biological processes are based on the degradation of coal using microorganisms. These processes are performed under mild conditions with no harmful products. Moreover, the value of coal is not affected.

Sulfur in coal is present in both forms i.e., organic and inorganic. The inorganic sulfur in coal is predominantly in the form of metal sulfides and sulfates. The pyrite is generally the most abundant inorganic sulfur in coal. The crystals of pyrite are randomly distributed throughout the coal matrix.

In the following diagram structural model of coal has been shown having the crystals of pyrite disseminated in the whole coal matrix. These pyrite particles are distributed randomly and not attached to coal.



Structural Model of Hard Coal (Wise, 1981)

The organic sulfur in coal is covalently bound into its large complex structure which is difficult to remove from the coal structure. The organic sulfur in coal exists in both forms i.e., aliphatic and aromatic or heterocyclic forms, which can be classified into four groups.

1. Aliphatic or aromatic thiols (mercaptans, thiophenols)
2. Aliphatic, aromatic or mixed sulfides (thioethers)
3. Aliphatic, aromatic or mixed disulfides (dithioethers)
4. Heterocyclic compounds or the thiophene type (Dibenzothiophene)

Microbial desulphurization of coal is a wet process; therefore, the process also provides a cleaning step in preparation of coal slurries for combustion. 70% coal slurry has approximately the same bulk calorific value as dry coal. Under supercritical conditions, viscosity of such slurry approaches infinitely and the slurry behaves as a solid. Water provides hydroxyl radicals that react with carbon monoxide formed during burning, thereby decreasing the amount of carbon monoxide for reaction with oxygen and increasing the amount of oxygen that can burn the carbon.

Certain microorganisms oxidize pyrite and marcasite and have been considered as potential agents for a coal desulfurization process. Microbial desulfurization of coal has shown various advantages including a higher pyrite removal efficiency and lower coal wastage than with physical methods and reduced costs compared to chemical methods because microbial methods operate at ambient conditions with fewer reagents. However, microbial processes are slower, requiring days to complete.

The best known of the pyrite-oxidizing bacteria is *Thiobacillus ferrooxidans*, a gram-negative iron-, sulfur and metal sulfide-oxidizing bacterium. This organism is acidophilic and chemoautotrophic, and is a common inhabitant of acidic environments associated with metal sulfide weathering. Indeed, this organism is important in the production of acidic coal mine drainage that results from uncontrolled pyrite oxidation during and following mining.

Certain thermophilic bacteria have also shown to remove pyritic sulfur from coal. These include *Sulfolobus acidocaldarius*. *Sulfolobus,* a member of archaebacteria, oxidizes pyrite, elemental sulfur, certain metal sulfides and organic compounds at temperature of upto 85ºC. Thermophilic bacterial processes may result in faster coal desulfurization rates as associated chemical reactions are accelerated at elevated temperatures, although this has yet to be demonstrated conclusively.

Two mechanisms have been proposed for biologically catalyzed oxidation of pyrite by *Thiobacillus ferrooxidans*: a direct mechanism and indirect mechanism. In the direct mechanism, the pyrite is oxidized biologically and it requires physical contact between the bacterium and pyrite particles. Several attempts have been made to demonstrate the direct attack of *T. ferrooxidans* on metal sulfides. It can be considered as a heterogeneous process in which the bacterial cell attaches itself to the sulfide crystal surface and the corrosion occurs in a thin film located in the interspace between the bacterial outer membrane and the sulfide surface.

In the indirect mechanism pyrite slowly oxidizes on exposure to air and water to produce acid and ferrous ion:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

Thiobacillus ferrooxidans oxidizes soluble ferrous ions to ferric ions at low pH as a source of metabolic energy:

$$4FeSO_4 + O_2 + H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

The above reaction is considered the rate-limiting step in pyrite dissolution and bacteria accelerate the dissolution by a factor of up to 10^6.

Under acidic conditions, ferrous ion is relative stable to chemical oxidation. However, the bacteria catalyze this reaction, generating ferric ions that react with additional pyrite:

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^0$$

The literature is conflicting as to whether S^0 is formed in the reaction of ferric ion with pyrite. Other metal sulfides are also oxidized and solubilized in ferric sulfate solutions:

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0$$

Elemental sulfur is also oxidized by *Thiobacillus ferrooxidans* and other thiobacilli to sulfuric acid.

The overall biological pyrite oxidation sequence can be summarized as

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4$$

In the indirect mechanism the role of bacteria is considered not to attack the pyrite directly but to catalyze aerobic oxidation of ferrous ion in solution to the ferric state. The ferric ion in solution then oxidizes pyrite to the ferrous state and additional acidity is produced due to protons released in this reaction.

Experimental results indicated that the removal of pyritic sulfur from coal in batch systems is governed by first-order reaction kinetics as described by the following equation:

$$\frac{d(FeS_2)}{dt} = -k(FeS_2)$$

The relative ease of coal desulfurization follows the order bituminous>subbituminous>lignite depending upon the neutralizing capacity of coals.

Several different microorganisms have been suggested for the process and these microorganisms behave differently. Advancement in genetic engineering could perhaps fulfill the need for microbial cultures that present more complete and rapid sulfur removal activities. It can be seen that a wide range of further studies on coal biodesulfurization process are required, e.g. investigation in sulfur removal mechanisms and rate enhancement; and investigation of the effects of many parameters, such as, substrate type in the growth medium, substrate concentration, type of reactor, type of coal, initial pH, growth temperature, shaking rate and aeration rate on the process efficiency. In addition, the key engineering issues include reactor design, separation processes, by-product deposition and product quality. Therefore, the cooperation of scientists and engineers is certainly needed for the process improvement.