REVIEW ARTICLE

Coal biodesulfurization processes

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Abstract

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Sulfur emission from coal combustion presents many environmental problems. It is believed that the best method to limit the amount of sulfur oxides emitted into the atmosphere is to reduce the amount of sulfur in coal before combustion. The techniques used include physical, chemical and biological processes. Biological processes based on degradation of sulfur compounds by microorganisms offer many advantages over the conventional physical and chemical processes. The processes are performed under mild conditions with no harmful reaction products and the value of coal is not affected. In this article the progress achieved to date in coal biodesulfurization processes is reviewed. The barriers for biodesulfurization processes to scale up to commercial applications are highlighted. In addition, the future needs of research for the development of efficient biodesulfurization processes are included.

Key words : coal, biodesulfurization, sulfur

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บทคัดย่อ

ผกามาศ ประยืนยง

การกำจัดกำมะถันจากถ่านหินด้วยกระบวนการทางชีวภาพ

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การแพร่กระจายของก๊าซซัลเฟอร์ออกไซด์ซึ่งเกิดจากการเผาไหม้ถ่านหิน ก่อให้เกิดปัญหามลภาวะต่อสิ่งแวดล้อมต่าง ๆ มากมาย เชื่อกันว่า วิธีที่จะจำกัดปริมาณของก๊าซซัลเฟอร์ออกไซด์ที่แพร่สู่บรรยากาศได้ดีที่สุด คือ การลดปริมาณกำมะถันในถ่านหินก่อนที่จะนำถ่านหินมาเผาไหม้ ซึ่งวิธีการลดกำมะถันจากถ่านหินนี้ประกอบไปด้วย กระบวนการทางฟิสิกส์ เคมี และชีวภาพ โดยกระบวนการทางชีวภาพซึ่งคือการลดกำมะถันโดยจุลินทรีย์นั้น มีข้อเด่นเหนือกระบวนการทางฟิสิกส์ และเคมี ที่ใช้อยู่ก่อนหน้าแล้วหลายข้อด้วยกัน เช่น กระบวนการทางชีวภาพจะดำเนินที่สภาวะความดันและอุณหภูมิไม่สูงมากนัก ผลผลิตจากปฏิกิริยาจะไม่เป็นพิษ และคุณค่าของถ่านหินจะไม่ลดลง บทความนี้จะสรุปความก้าวหน้าจนถึงปัจจุบันของการลดกำมะถันจากถ่านหินโดยกระบวนการทางชีวภาพ รวมทั้งระบุอุปสรรคในการที่กระบวนการทางชีวภาพจะถูกนำไปใช้เป็นกระบวนการทางการค้าจริง ๆ และความต้องการงานวิจัยต่อเนื่องที่จะช่วยพัฒนากระบวนการทางชีวภาพให้เป็นกระบวนการที่มีประสิทธิภาพต่อไป

ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112

Coal has been accepted as a major source of energy for centuries. In addition, the International Energy Agency has forecast a substantial increase in coal use over the next few years, rising from 3.5×10^{12} tonnes at present to over 5.3×10^{12} tonnes per year (IEA, 1998). When coal is burnt its sulfur content combines with oxygen to form sulfur dioxide (SO_2), which contributes to both pollution and acid rain. Governments throughout the world have recognized the problems and moved to reduce the amount of SO_2 emission through legislation. To meet the legislation standard, flue gas desulfurization (FGD) has been retrofitted to existing coal combustion plants in many countries (UK Clean Coal Technology, 1998). In the FGD process, the flue gas is sprayed with slurry made up of water and alkaline agent, usually lime or limestone. The SO_2 is converted into calcium sulfate (gypsum) and disposed of as a wet sludge. Fluidized bed combustion (FBC) has been used in another instance. This method cleans coal inside the furnace where the coal is actually burned. Coal is ground into small particles, mixed with limestone and injected with hot air into the boiler. This mixture, a bed of coal and limestone, is suspended on jets of air and resembles a boiling liquid. As the coal burns, the limestone acts as a sponge and captures the sulfur. Nevertheless, both FGD and FBC are too expensive and impractical for users of small to intermediate volumes of coal.

It is believed that the best method to limit the amount of sulfur dioxide emitted into the atmosphere is to reduce the amount of sulfur in coal before combustion. The techniques include physical, chemical and biological processes. In physical processes coal is crushed, ground and washed. This allows for up to 90% of pyrite (predominant form of inorganic sulfur in coal) to be removed. However, depending on the type of coal, a considerable amount of finely distributed pyrite as well as organic sulfur can remain in and attach to the coal particles (Klein, 1998). The inability of physical methods to completely remove even the inorganic sulfur has led to the development of many chemical desulfurization processes. These include carbonization in different atmospheres, air oxidation, wet oxidation, Meyers process, chlorination and extraction with sodium hydroxide, copper chloride and ethanol solutions (Yaman *et al.*, 1995). Hydrodesulfurization, a physicochemical technique, has been applied as

a conventional method for sulfur removal worldwide. It is a high-pressure (10-17 atm) and high-temperature (200-425 °C) process in which sulfur is converted to hydrogen sulfide (Monticello, 1998). Although high reaction rates are given when chemical or hydrodesulfurization processes are used, they are costly, producing hazardous products and the structural integrity of the coal is affected. In addition, the processes do not work well on organosulfur, particularly the polyaromatic sulfur heterocycles. This has tempted researchers to move to the biological methods, which offer many advantages. The processes are performed under mild conditions with no harmful reaction products and the value of coal is not affected (Monticello, 1998). This paper is intended to review the progress achieved to date in coal biodesulfurization processes.

Types of sulfur present in coal

Sulfur in coal is present in both inorganic and organic forms. The inorganic sulfur in coal consists predominantly of sulfides and sulfates. Sulfide minerals include pyrite (FeS_2), sphalerite (ZnS), galena (PbS), arsenopyrite (FeAsS) and others. The sulfate minerals include barite ($BaSO_4$), gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), and a number of iron sulfates and others (Calkins, 1994). The pyrite is generally the preponderant inorganic sulfur in coal. Particles of pyrite are randomly distributed as crystals throughout the coal but are not bound to it as shown in Figure 1 (Wise, 1981).

The organic sulfur in coal is covalently bound into its large complex structure and is difficult to remove physically or chemically, in contrast to pyritic or inorganic sulfur (Constanti *et al*., 1994). The organic sulfur in coal exists as both aliphatic and aromatic or heterocyclic forms, which can be classified into four groups (Klein *et al*., 1994) as shown in Figure 2:

1) aliphatic or aromatic thiols (mercaptans, thiophenols);
2) aliphatic, aromatic, or mixed sulfides (thioethers);

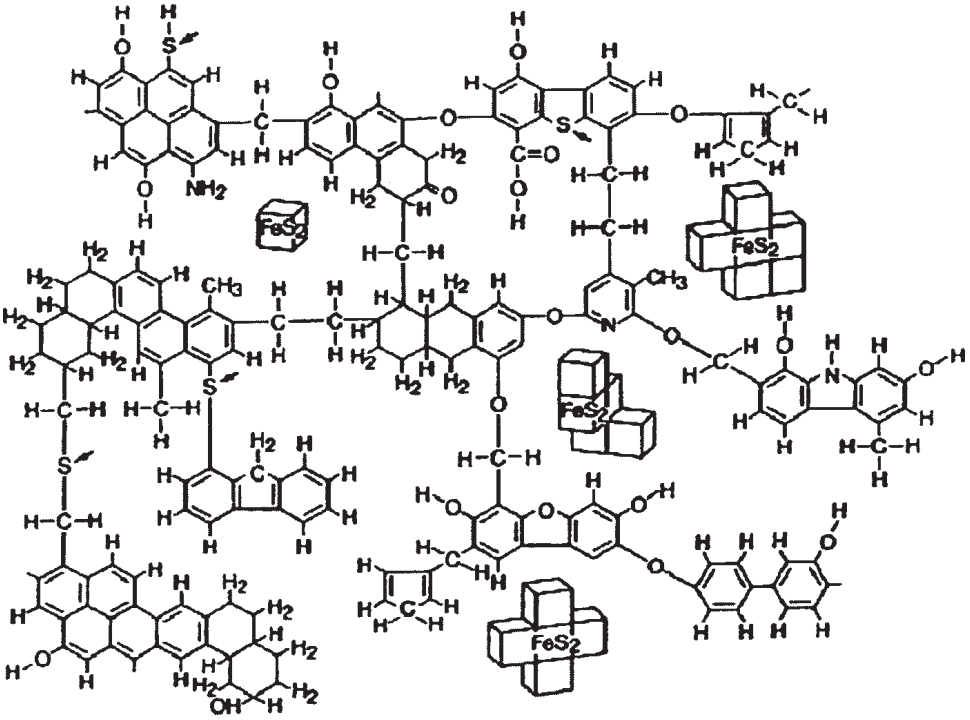

Figure 1. Structural model of hard coal (Wise, 1981).

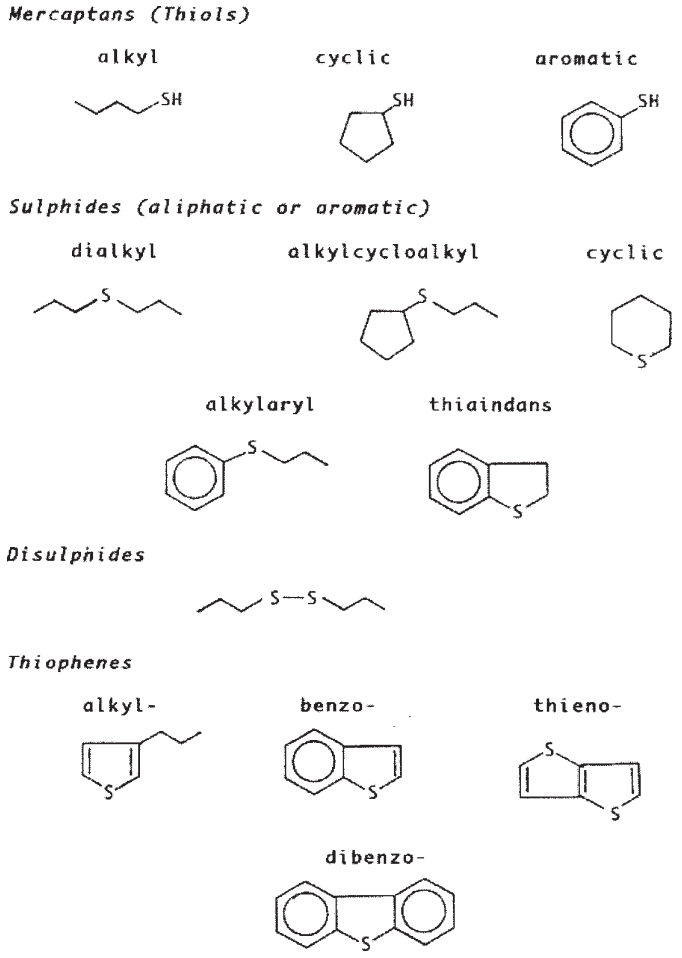

Figure 2. The types of sulfur-containing organic compounds identified in coal (Shennan, 1996) .

3) aliphatic, aromatic, or mixed disulfides (dithioethers); and
4) heterocyclic compounds or the thiophene type (dibenzothiophenes).

Methods of analyzing and identifying sulfur compounds

Whilst there is a need for coal desulfurization, techniques to quantify and identify sulfur compounds in coal are also required. The customary methods used are the standard methods of the American Society of Testing Materials (ASTM): a coal sample is analyzed chemically to determine total sulfur (ASTM, 1993) and sulfate sulfur; pyritic sulfur is calculated from pyritic iron (ASTM, 1994); and organic sulfur is obtained indirectly by subtracting the sulfate and pyritic sulfur contents from total sulfur content. The techniques are time-consuming and not consistent. Many errors can be introduced in each stage of the analysis. Thus, it is difficult to monitor accurately the efficiency of the different desulfurization processes.

Recently, the sequential digestion method has been reported for the direct determination of sulfate, pyritic and organic sulfur concentrations in coal (Laban and Atikin, 2000). A three-stage extraction was developed, using acid digestion in a microwave oven. In the first stage, 5M HCl was used to dissolve sulfate phases in coal. Pyrite

was then extracted using 2M HNO_3. The final stage, for the determination of organic sulfur, involved the use of concentrated HNO_3, HCl, hydrofluoric acid (HF) and boric acid for the complete decomposition of residue that remained following stage 2. The extract solutions from each stage were analyzed for sulfur by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sums of the three forms of sulfur have shown consistent agreement with certified total sulfur data for most of the coals studied. The good precision achieved by this technique suggests that the process has an acceptable degree of reliability. However, the use of HF poses a potential hazard which should be avoided.

All of the procedures described above are destructive methods. Non-destructive methods for sulfur determination are preferable. The instrumental techniques which have been predominant in sulfur determination in coal are based on electron microscopy, such as X-ray photoelectron spectroscopy and X-ray absorption near edge spectroscopy (Davidson, 1994). However, to date, uses of the non-invasive methods suffer from inadequate resolution. In addition, the techniques are highly specialized. Further studies and development of the analytical methods of sulfur in coal are required.

Mechanisms of inorganic sulfur removal

Microbiological removal of inorganic sulfur from coal has been demonstrated in numerous laboratory studied over the past 30 years (Klein *et al*., 1994). Pyrite bioleaching occurs in a three-phase system, the suspension of coal in an aqueous solution through which a stream of air + CO_2 is dispersed by suitable injectors (Rossi, 1993). The presence of certain microbial strains, which can be mesophilic or thermophilic, in aqueous suspensions of finely ground pyrite in suitable inorganic salt solutions enhances the dissolution kinetics of the mineral. Two mechanisms have been proposed for the biologically catalyzed oxidation of pyrite by *Thiobacillus ferrooxidans*: a direct mechanism, and an indirect mechanism. In the direct mechanism, the pyrite is oxidized biologically and it requires physical contact between the bacterium and the pyrite particles as represented in Equation 1 (Klein, 1998).

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. With certain coals, the direct mechanism for oxidation of pyrite may be limited because the microorganisms are too large to enter most of the coal pores as shown in Figure 3 (Hone *et al*., 1987). This suggests that pyrite oxidation in coal to a large extent must rely on the indirect mechanism. In the indirect mechanism, the bacteria oxidize ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}); the regenerated Fe^{3+} ions are then used for chemical oxidation of pyrite. Equations 2 and 3 describe the indirect oxidation mediated by Fe^{3+} and *T. ferrooxidans* (Larsson *et al*., 1994):

The oxidation of ferrous iron in the absence of microorganisms is a slow process. It is considered to be the rate-limiting step for the oxidation of pyrite with ferric iron. Another option for the indirect mechanism is that the ferric iron oxidizes the ferrous iron in the pyrite, leaving elemental sulfur behind as in Equation 4. The

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \xrightarrow{\textit{T. ferrooxidans}} 2\,FeSO_4 + 2\,H_2SO_4 \qquad \text{(Equation 1)}$$

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \longrightarrow 15\,Fe^{2+} + 16\,H^{+} + 2\,SO_4^{2-} \qquad \text{(Equation 2)}$$

$$2\,Fe^{2+} + 2\,H^{+} + 0.5\,O_2 \xrightarrow{\textit{T. ferrooxidans}} 2\,Fe^{3+} + H_2O \qquad \text{(Equation 3)}$$

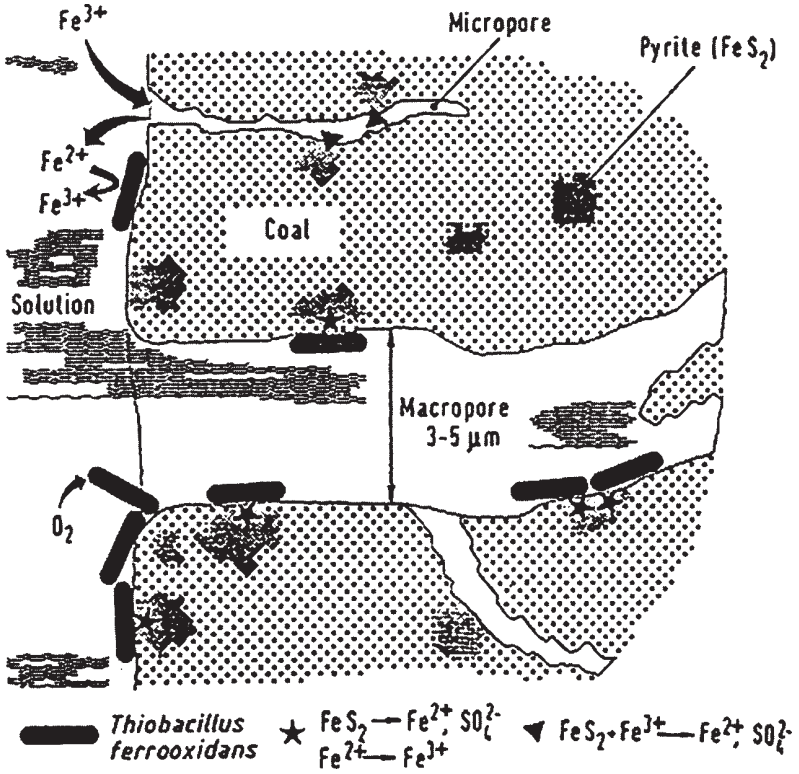

Figure 3. Bimodal pore structure of coal and pyrite oxidation (Hone *et al.*, 1987).

$$FeS_2 + 2\ Fe^{3+} \dashrightarrow 3\ Fe^{2+} + 2\ S^0 \qquad \text{(Equation 4)}$$

$$2\ S^0 + 3\ O_2 + 2\ H_2O \xrightarrow{\textit{T. ferrooxidans}} 2\ H_2SO_4 \qquad \text{(Equation 5)}$$

elemental sulfur is then oxidized to sulfate by the microorganisms as shown in Equation 5.

The formation of iron precipitates, mainly jarosites ($MFe_3(SO_4)_2(OH)_6$ where M stands for either hydronium, potassium, sodium or ammonium) is a problem in oxidation of pyrite. At the elevated temperatures used for the thermophilic bacteria, the chemical reactions are faster and the overall pyrite oxidation rate is higher than at temperatures applied for the mesophilic bacteria. However, elevated temperatures also increase the formation of jarosites which counteracts the desulfurization as the precipitates stick to the coal even after the washing step. The concentration of soluble ferric iron also decreases. These conditions have a large impact on the chemical reactions involved in the indirect mechanism (Larsson *et al*., 1994).

Mechanisms of organic sulfur removal

Early attempts on biodesulfurization of organic sulfur were considered failures because the bacteria that were isolated could not specifically remove sulfur and moreover the fuel value of coal was decreased. Initial attention has focused on bioremoval of sulfur from dibenzothiophene (DBT) since it represents a major proportion of thiophenic sulfur found in most fuels. The isolation and characterization of *Rhodococcus erythropolis* IGTS8 (formerly called

Rhodococcus rhodochrous IGTS8) led to major advancements in the investigations of DBT-biodesulfurization. A sulfur specific pathway, sometimes called 4S pathway was proposed (Kilbane, 1990). The pathway presents the sequential metabolism of DBT to DBT-sulfoxide, DBT-sulfone, DBT-sulfinate, hydroxybiphenyl (HBP) and sulfite as shown in Figure 4. According to 4S pathway, bacteria selectively oxidize the sulfur atom in DBT with no cleavage of C-C bonds, thereby maintaining the caloric value of the fuel (Bressler *et al*., 1998).

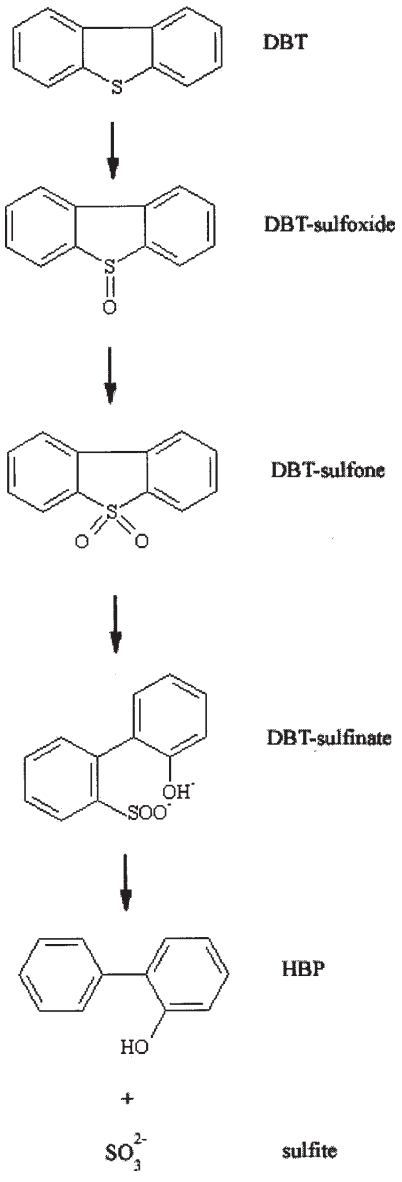

Figure 4. 4S pathway of DBT degradation (Bressler *et al*., 1998).

Biodesulfurization of alkylated dibenzothiophenes has also been reported. For instance, two strains of *Arthrobacter* species (Lee *et al*., 1995), reclassified as *Rhodococcus erythropolis* strain X309 and strain X310 (Denis-Larose *et al*., 1997) or strain ECRD-1 (Grossman *et al*., 1999) were demonstrated to desulfurize the sterically hindered compound 4,6-diethyldibenzothiophene, yielding 2-hydroxy-3,3'-diethylbiphenyl as the sulfur-free product (Lee *et al*., 1995). Similarly, *R. erythropolis* H-2 was able to remove the sulfur atom from 3,4-benzo DBT, 2,8-dimethy DBT and 4,6-dimethyl DBT (Ohshiro *et al*., 1996). The reaction product from 3,4-benzo DBT was identified as an α-hydroxy-β-phenylnaphthalene whereas the reaction products from structurally symmetrical 2,8 and 4,6-dimethyl DBTs were identified as the corresponding monohydroxy dimethyl biphenyls. In addition, *Mycobacterium* sp. strain G3 was reported to degrade 4,6-dimethyl DBT (Nekodzuka *et al*., 1997).

To date, a mechanism to selectively remove sulfur from unsubstituted thiophene to that found in the 4S pathway for dibenzothiophenes has not been published. Attempts to isolate microorganisms capable of degrading thiophene substituted in the 2-position have been undertaken. *Flavobacterium* sp. (Amphlett and Callely, 1969), *Rhodococcus* sp. (Kanagawa and Kelly, 1987), *Vibrio* YC1 (Evans and Venables, 1990), and yellow gram-negative rod (Cripps, 1973) isolated by enrichment on thiophene-2-carboxylic acid (T2C) were reported to release the sulfur as sulfate but they utilized the rest of the compound as a source of carbon for growth. In addition, there is no successful article yet on bioremoval of sulfur from thiophenes substituted in the 3-position (Shennan, 1996). To achieve significant sulfur removal from thiophene, strain manipulations might be involved. A genetically modified strain of *Pseudomonas alcaligenes* was shown to be

capable of oxidizing thiophene (Hartdegen *et al*., 1983). Successive mutations of the facultative anaerobe *E. coli* yielded a strain able to degrade thiophene. However, even with these strains, the sulfur was not completely removed and the reaction was slow (Alam and Clark, 1991).

Similarly, initial attempts on bioremoval of sulfur from benzothiophene (BT) were not successful. The first reported bacterium capable of removal sulfur from BT via 4S pathway was called *Gordonia* sp. strain 213E (Gilbert *et al*., 1998), now recognized as a new species, *Gordonia desulfuricans* (Kim *et al*., 1999). Interestingly, even with the obvious chemical similarity of DBT and BT, the *Rhodococcus* species able to desulfurize DBT such as *R. erythropolis* IGTS8 were unable to desulfurize BT. Likewise, the *Gordonia* species able to desulfurize BT were unable to desulfurize DBT (Gilbert *et al*., 1998). Therefore, some researchers proposed that the enzymatic system responsible for BT desulfurization should be different from that for DBT desulfurization. Recently, a single bacterial strain able to desulfurize alkylated forms of both DBT and BT has been reported (Kobayashi *et al*., 2000). The bacterium was isolated from soil sample enrichment in DBT. It was classified as *R. erythropolis* strain KA2-5-1. The strain KA2-5-1 was quite similar to the strain IGTS8. The *DszABC* genes in IGTS8 ware also found in KA2-5-1. The bacterium grew well in medium containing 3-methyl, 2-ethyl or 2,7-diethyl benzothiophene as the sole sulfur source, suggesting that KA2-5-1 may release sulfur from some benzothiophene derivatives. However, no significant growth was observed when BT, 2-methyl BT, 5-methyl BT, 7-methyl BT, 7-ethyl BT or 5,7-dimethyl BT was added to the medium as the sole sulfur source. In conformity, the resting cells of KA2-5-1 also did not significantly attack BT and 5-methyl BT. Nevertheless, the monooxygenase *DszC* from KA2-5-1 converted these all benzothiophenes to corresponding sulfones. These results show that there is the possible involvement of the same enzyme in the bacterial degradation of benzothiophenes and dibenzothiophenes (Kobayashi *et al*., 2000).

Desulfurizing bacteria

Several microorganisms have been suggested for the coal biodesulfurization process. Sulfate-reducing bacteria were reported to desulfurize sulfur compounds in coal to hydrogen sulfide. However, no significant reduction in the sulfur content of coal was observed in any work (McFarland, 1999). The mesoacidophilic bacteria have been considered as the most important organisms for coal depyritization. Three species including *Thiobacillus ferrooxidans*, *T. thiooxidans*, and *Leptospirillum ferrooxidans* are mainly involved. *T. ferrooxidans* (a sulfur and iron oxidizer) and *L. ferrooxidans* (an iron oxidizer) are capable of oxidizing pyrite when growing in pure culture, whereas *T. thiooxidans* (a sulfur oxidizer) is not able to oxidize pyrite alone but grows on the sulfur released after the iron is oxidized (Rawlings *et al*., 1999). In the industrial processes, *L. ferrooxidans* is thought to be more dominant than *T. ferrooxidans*. The major reason is a greater affinity for ferrous iron and a lower sensitivity to inhibition by ferric iron on prolonged aeration of *L. ferrooxidans*. In addition, the optimum pH for growth of *T. ferrooxidans* is within the range of 1.8-2.5 whereas *L. ferrooxidans* is more acid resistant since it can grow at a pH of 1.2. With regard to temperature, *T. ferrooxidans* is considered to be more tolerant of low temperature and less tolerant of high temperature than *L. ferrooxidans* (Rawlings *et al*., 1999). Some strains of *T. ferrooxidans* are able to oxidize pyrite at temperatures as low as 10 °C (Norris, 1990); however, 30-35 °C is considered to be optimal. While, *L. ferrooxidans* has an upper limit of around 45 °C (Norris *et al*., 1986) with a lower limit of about 20 °C (Sand *et al*., 1993).

Although mesoacidophilic bacteria are the most important microorganisms for inorganic sulfur removal, they do not work well for organic sulfur removal. Many bacterial species including *Pseudomonas* and *Sulfolobus* species were of great interest in the early success of organic

sulfur removal. However, some bacterial strains were no longer available to the research community due to viability loss and some were proved that only degrade C-C bond not C-S bond of organosulfur compounds. Indeed, the ability to remove both inorganic and organic sulfur has been found in *Rhodococcus* species and consequently biodesulfurization processes in a new era have been mostly carried out with these species. Desulfurizing *Rhodococcus* species include *Rhodococcus erythropolis* IGTS8 (Kayser *et al*., 1993), *R. erythropolis* D-1 (Izumi *et al*., 1994), *R. erythropolis* H-2 (Ohshiro *et al*., 1996), *R.* sp. SY1 (Omori *et al*., 1995), and *R.* sp. ECRD-1 (Grossman *et al*., 1999). Among them *R. erythropolis* IGTS8 is the most widely studied.

The potential of coal biodesulfurization processes

Compared with that of oil, biodesulfurization of coal is more difficult as permeation of highly polymeric material into the bacterial cells is fairly hard. The efficiency of microbial oxidation of pyrite depends on a number of parameters, for example the particle size of the pulverized coal, the pyrite content, nutrient media composition, pH, temperature, aeration and reactor design. Table 1 summarizes some major parameters with indications of the optimum conditions for high reaction rates (Klein, 1998). Different reactor systems for large-scale applications have been developed and proposed. A choice is generally available between heap (percolation) leaching (Beir, 1987) and slurry leaching (Beyer *et al*., 1986). Heap leaching is a less expensive approach than slurry leaching. However, reaction rates are faster in slurry leaching, but these require fine grinding of coal and long residence times with aeration in large bioreactors. Surface area limits pyrite oxidation rates in heap leaching whereas biomass, up to a point, limits rates in slurry leaching (Olsson, 1994). Alternately, froth flotation methods can be used (Attia, 1990). The principal of these methods is that the bacterium could selectively adhere to pyrite rather than to coal in coal-pyrite mixtures despite the fact that the total surface area of the pyrite was much less than that of the coal (Ohmura *et al*., 1993). Its adhesion induced the suppression of pyrite floatability by changing the surface property of pyrite from hydrophobic to hydrophilic (Ohmura and Saiki, 1994). Because pyrite does not float with coal it can be collected as tailings from the bottom along with the ash minerals during the froth flotation (Raman *et al*., 1995).

Based on laboratory results, it is proposed to treat coal slurries in an industrial scale in large Pachuca tank reactors. These are 3-phase slurry reactors, cylindrical in cross-section with a conical bottom. The main function of a slurry reactor is to maintain suitable growth conditions for the pyrite-oxidizing microorganisms in terms of temperature, pH-value, and mass transfer. The layout of an industrial-scale plant for biodepyritization of coal is shown in Figure 5. It may be pointed out that coal biodepyritization is a sufficiently well-known process, at least as far as its fundamentals are concerned, but some controversy still exists as to its technical and economic profitability, or at least its competitiveness with conventional desulfurization methods. An industrial-scale commercial operation of coal biodepyritization has not yet been performed. Published statements concerning cost-effectiveness are based on results from lab-scale and pilot-scale tests as shown in Table 2.

To date, there is no commercial biodepyritisation available since there are faster and less expensive physical and chemical methods for the removal of inorganic sulfur. Further research on biodepyritization, especially in regard to leaching rate enhancement and bioreactor design is required. More importantly, it is necessary for biodesulfurization process to remove not only inorganic sulfur but also organic sulfur, otherwise the process may not be commercially viable. Removal of organic sulfur is more difficult than removal of inorganic sulfur. There were several bacterial cultures proclaimed to be useful for removing organic sulfur; however, their abilities were unstable and the reproducibility of results was poor. Almost every research group involved

Table 1. Parameters on biodepyritization of coal (Klein, 1998).

Process Parameter	Influence on	To obtain maximum pyrite oxidation rate
Bioreactor		
Type	Mixing Mass transfer O_2-, CO_2-supply Mechanical shear stress	Pachuca tank
Operation	Efficiency	Plug flow multi-stage
Coal		
Quality	Pyrite -concentration -distribution -crystal size	Pyrite crystal of small size but accessible for micro-organisms
Pulp density	Substrate concentration Mixing Mechanical shear stress	20-30% (w/v)
Particle size	Pyrite accessibility Mixing Mechanical shear stress	Powder coal <0.5 mm
Microorganisms		
Concentration/ species	Growth rate Pyrite oxidation rate	Mixed culture, enriched from coal relevant
Reaction conditions		
Temperature	Bacterial activity Rate of chemical pyrite oxidation Oxygen/carbon dioxide solubility	*Thiobacillus* (30-35 °C) *Sulfolobus* (70-75 °C)
pH	Precipitation of jarosite Bacterial activity	pH 1.8
Nutrients	Bacterial activity Precipitation of jarosite	N-, P-alimentation
O_2-, CO_2-supply	Bacterial activity	>10% Saturation

reports of problems with stability or reproducibility. Although extensive studies have been done on bioremoval of organic sulfur, most of these were carried out using model compounds which are recognised to behave differently to sulfur in coal. Experimentation using specific coal types is undoubtedly a requirement to enable an assessment of this technology.

Regarding bioremoval of both inorganic and organic sulfur from coal, the experiments

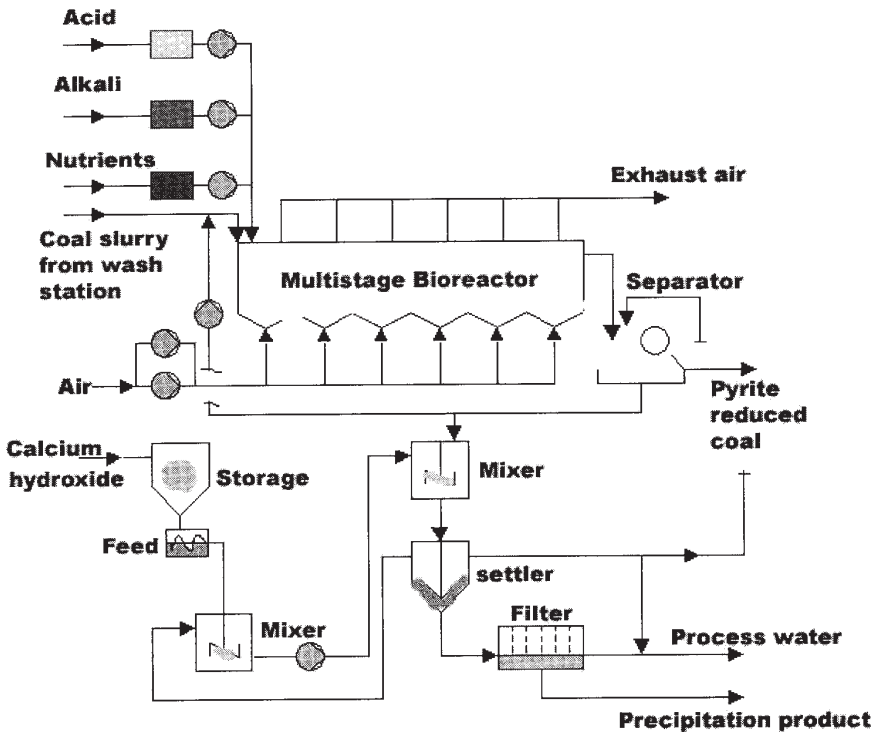

Figure 5. Process flow sheet of a plant for coal biodepyritization (Klein, 1998).

Table 2. Cost estimation for coal biodepyritization in an industrial scale (Klein, 1998) .

Process	Slurry 28 °C *T. f.*	Slurry 30 °C *T. f.*	Slurry 70 °C *S. a.*	Heap *T. f.*	Slurry 30 °C *T. f.*	Slurry 30 °C *T. f.*
Coal throughput (t/d)	8000	275	550	420	300	300
Particle size (µm)	< 74	< 100	-	< 50,000	< 500	< 60
Required total reactor volume (m^3)	600,000	12,500	19,000-43,000	-	14,000	14,000
Required area (m^2)	-	-	-	30,000	-	-
Concentration of pyrite (%)	2	0.5	0.8-1.6	0.6	1	2
Coal (%w/v)	20	20	20	-	20	20-40
Trickling (m^3/d)	-	-	-	241.250	-	-
Residence time (d)	18	9	10-22	28	10	5
Pyrite removal (%)	90	90	60-90	82	80	90
Specific costs						
-Investment (DM/t)	38	100-130	24-45	70	210	210
-Operation* (DM/t)	27	35-53	84-115	54	121	80

T.f.* = *Thiobacillus ferrooxidans ; ***S. a.* = *Sulfolobus acidocaldarius*** ; *** Including utilities, personnel and capital costs**

using *Rhodococcus erythropolis* IGTS8 seem to be the most successful. *R. erythropolis* IGTS8 could remove 55.2 % sulfate sulfur, 20% pyritic sulfur, 23.5% organic sulfur, and 30.2% total sulfur from Mengen lignite in 96 hours (Bozdemir *et al*., 1996). Effect of different parameters such as inoculum percentage, initial pH, growth temperature, shaking rate, substrate type, initial substrate concentration, coal type, and coal particle size on the growth kinetics of IGTS8 was also reported by Bozdemir *et al*., (1996), Durosoy *et al*., (1997), and Erincin *et al*., (1998). However, it is doubtful if the growth data presented by these experiments are reliable since the bacterial growth on coal samples was monitored by absorbance measurement at 550 nm and no information on how they separated the bacterial cells from the coal samples was provided. Moreover, it is noticed that the sulfur removal rate obtained from these experiments was still too low for a commercial application. To be used on an industrial scale, biodesulfurization processes need to enhance their sulfur removal efficiency.

There are few reports describing biodesulfurization in two-phase system (non-aqueous solvent: water). The results show that DBT-desulfurization rates were increased in the presence of 40-50% n-tetradecane or kerosine (Ohshiro *et al*., 1996), 96% hexadecane (Kaufman *et al*., 1998), or 50% diesel (Pacheco *et al*., 1999). DBT desulfurization in *Rhodococcus* appears to occur intracellularly with DBT uptake from the oil phase possibly occurring after transient adsorption to the cell (Oldfield *et al*., 1997). The oil phase and cuff layer emulsions were found to contain significant amounts of *Rhodococcus* in 1-10 μm droplets during desulfurization of DBT in high hexadecane concentration (Kaufman *et al*., 1998). Kayser *et al*. (1993) reported that the desulfurization activity of *R. erythropolis* IGTS8 is associated with the external surface of the cell wall/membrane. Since membranes are hydrophobic environments, the desulfurization enzymes should function in non-aqueous solvents, which in turn would facilitate contact with coal and increase mass transfer during biodesulfurization (Patel *et al*., 1997). In addition, Lee & Yen (1990) demonstrated biodesulfurization of coal using reverse micelle solutions (finely dispersed water in oil emulsions) containing *T. ferrooxidans* cells, or their cell-free enzyme extracts. A reduction in total sulfur as high as 48% could be achieved within 24-hour treatment; cell free enzyme extracts outperformed the whole-cell preparations. With longer times, as much as 70% of the total sulfur was removed. Therefore, desulfurization of coal using bacteria or bacterial extracts emulsified in mineral oil, or in mineral oil and solvent mixtures seems to be an enhanced biodesulfurization process.

Alternatively, biodesulfurization can be obtained in inexpensive conditions by using bacteria inherent in the coal itself. The advantages of using bacteria inherent in the coal over using the pure isolated bacterium are the immediate adaptation of the microorganisms to the coal and the reduced period of latence. The use of bacteria inherent in the coal could be of special interest for application in coal heaps in the open air. Furthermore, the complication in controlling pure microorganism will be neglected.

Conclusion

The removal of sulfur from coal before combustion by biological method is a technically feasible process. Several different microorganisms have been suggested for the process and these microorganisms behave differently. Desulfurization activities of the current desulfurizing bacteria are still too low for an economical desulfurization process. More active microbial cultures with improved desulfurization efficiency toward a wide variety of sulfur compounds are needed for process development. Advancement in genetic engineering could perhaps fulfill the need for microbial cultures that present more complete and more rapid sulfur removal activities.

To assess desulfurization processes more correctly, accurate and convenient analytical methods for measuring sulfur in coal are required. Other barriers to the scale up to commer-

cial application of biodesulfurization processes are the logistics of sanitary handling, shipment, storage, and use of living bacterial cells. However, transporting the bacterial cells as freeze-dried bacteria or using the bacteria inherent in the coal and running desulfurization at the coal sites could reduce the risk assessment of the processes.

It can be seen that a wide range of further studies on coal biodesulfurization process is 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 disposition and product quality. Therefore, the co-operation of scientists and engineers is certainly needed for the process improvement.

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