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REVIEW PAPER

Advances in the biological treatment of coal for synthetic natural gas and chemicals

Pamidimarri D.V.N. Sudheer*,‡, Yokimiko David,‡, Cheol Gi Chae**, You Jin Kim**, Mary Grace Baylon**, Kei-Anne Baritugo**, Tae Wan Kim***, Min-Sik Kim*, Jeong Geol Na*,†, and Si Jae Park**,†**

*Clean Fuel Department, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Korea
**Department of Environmental Engineering and Energy, Myongji University,
116 Myongji-ro, Cheoin-gu, Yongin-si, Gyeonggido 17058, Korea
***Marine Biotechnology Research Center, Korea Institute of Ocean Science and Technology,
787 Haean-ro, Sangnok-gu, Ansan-si, Gyeonggido 15627, Korea
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Abstract−Coal, the most primitive fossil fuel, has been exploited for ages, and reserves dictate the economies of many countries. Presently, most energy is generated by direct combustion, raising concerns over global warming. Biological pretreatment of fossil resources and generation of alternative green energy can address the environmental issues associated with global coal utilization. Biological coal treatment can produce industrially important chemicals and bio-methane by employing microorganisms able to depolymerize/degrade coal. This review discusses current advances in microbial coal conversion, such as the efforts made to comprehend microbial processes, significant outputs of coal conversion, principle components responsible for coal conversion, and factors affecting the biological processes to convert coal. Development of these biological processes can be a stepping stone for greener coal; however, integration of multidisciplinary technologies is needed to increase the efficiency of economic coal utilization and production of economically and industrially feasible biomethane.

Keywords: Coal, Coal Biodegradation, Coal Depolymerization, Biological Treatment, Biomethane

INTRODUCTION

Among fossil fuel reserves, coal is one of the key and most primitive sources [1,2]. It plays a major part in metallurgical applications, power generation, and transportation, in which coal accounts for approximately 30% of global energy production in various sectors [3]. Coal can be converted into several useful products through chemical processing [4], in which different strategies are applied to various kinds of coal as summarized in Table 1 [5]. For the past two decades, increasing concerns with regards to the depletion of petroleum reserves have led us to search for alternative sources of energy. Coal, accounting for approximately 70% of total world fossil fuel reserves, has been considered the next major fuel source with potential to sustain energy needs for the coming decades; however, not all coal reserves are suitable for direct energy generation, such as low rank coal with high moisture and low calorific value. Additionally, use of high rank coal suitable for energy production may result in several environmental problems such as particulate emissions and release of greenhouse gases (GHGs) contributing to global warming. Thus, development of green processes to convert coal to a green energy source is becoming more essential. Although several microbial and biological processes have been developed for removing pyritic sulfur from coal in earlier research, only a few biological processes have been found for liquefying or gasifying coal [6-9].

One of the most promising technologies for greener coal utilization can be developed biologically with several advantages for treatment of coal rich in carbon. For instance, methanogenic microorganisms can produce methane from coal by using chemical components as substrates, which are obtained by biosolubilization, or anaerobic digestion of coal. Fig. 1 provides an overview and comparison of chemical and biological process for coal degradation.

Overall, the present review discusses the biological mechanisms of greener coal utilization and their applications for the production of valuable industrial products. Much emphasis is given to biological methane production since it may provide an answer to the present context of environmental issues and it is a potential candidate for green energy production from coal.

BIOLOGICAL PROCESSING OF COAL

Over time, plant matter is degraded and amalgamated to form very large complex molecules of coal. This renewable resource accounts for almost 71.4% of all fossil fuels [10]. Because of its carbon content, coal seems to be a promising source of various compounds, from fuel to biogas, alcohols, and other industrially important chemicals [11-13]. However, several factors that limit the availability of this polymer must first be overcome to maximize its full potential [14]. Among these, the high recalcitrance of coal restricts degradation to hazardous chemical processes, which require

†To whom correspondence should be addressed.
E-mail: narosu@kier.re.kr, parksj93@mju.ac.kr
‡Pamidimarri D.V.N. Sudheer and Yokimiko David contributed equally to this work.

Table 1. Composition of carbon, hydrogen, nitrogen, sulfur, and oxygen in different types of coal, and transformation reactions during degradation of different types of coal [5]

	Type of coal	C%	H%	N%	S%	O%	Main transformation reactions
Low rank coal	Lignite	67.7	5.6	0.4	0.7	25.5	• Cleavage of aryl ether bonds • Alkylation • Loss of methoxyl groups through demethylation and dihydroxylation • Loss of cellulose and lignin • Side-chain dehydroxylation • Dehydroxylation of catechols
Bituminous coal	High vol. C bituminous	79.9	5.7	1.7	2.9	9.9	• Loss of cellulose and lignin • Side-chain dehydroxylation • Dehydroxylation of catechols • Gradual loss of alkyl carbons • Enrichment in aromatic carbons • Increase in aromatic cluster size
	High vol. B bituminous	86.9	5.5	1.7	0.6	5.4	• Gradual loss of alkyl carbons • Enrichment in aromatic carbons • Increase in aromatic cluster size •Transformation of catechols to phenols • Condensation of phenols • Aromatic ring closure and aromatization of alkyl side chains • Condensation of aromatic ring chains • Loss of phenolic structures • Condensation of benzene-like structures to a polycyclic aromatic ring system
	High vol. A bituminous	87.3	5.7	1.7	0.7	4.5	• Transformation of catechols to phenols • Condensation of phenols • Aromatic ring closure and aromatization of alkyl side chains • Condensation of aromatic ring chains • Loss of phenolic structures • Condensation of benzene-like structures to form a polycyclic aromatic ring system
	Medium vol. bituminous	89.9	5.2	1.5	0.7	2.7	• Transformation of catechols to phenols • Condensation of phenols • Aromatic ring closure and aromatization of alkyl side chains • Condensation of aromatic ring chains • Loss of phenolic structures • Condensation of benzene-like structures to form a polycyclic aromatic ring system
	Low vol. bituminous	92.4	3.1	1.5	0.5	2.6	• Transformation of catechols to phenols • Condensation of phenols • Aromatic ring closure and aromatization of alkyl side chains • Condensation of aromatic ring chains • Loss of phenolic structures • Condensation of benzene-like structures to form a polycyclic aromatic ring system • Polyaromatic ring structure • Development of molecular orientation • Decrease in interlayer spacing • Development of strong optical anisotropy
High rank coal	anthracite	94.6	2	0.9	0.4	1.3	• Polyaromatic ring structure • Development of molecular orientation • Decrease in interlayer spacing • Development of strong optical anisotropy

*Coal elemental composition and transformation reactions are adopted from Hatcher and Clifford [2], Drobniak and Mastalerz [87], Cao et al. [88], and Strąpoć et al. [5]

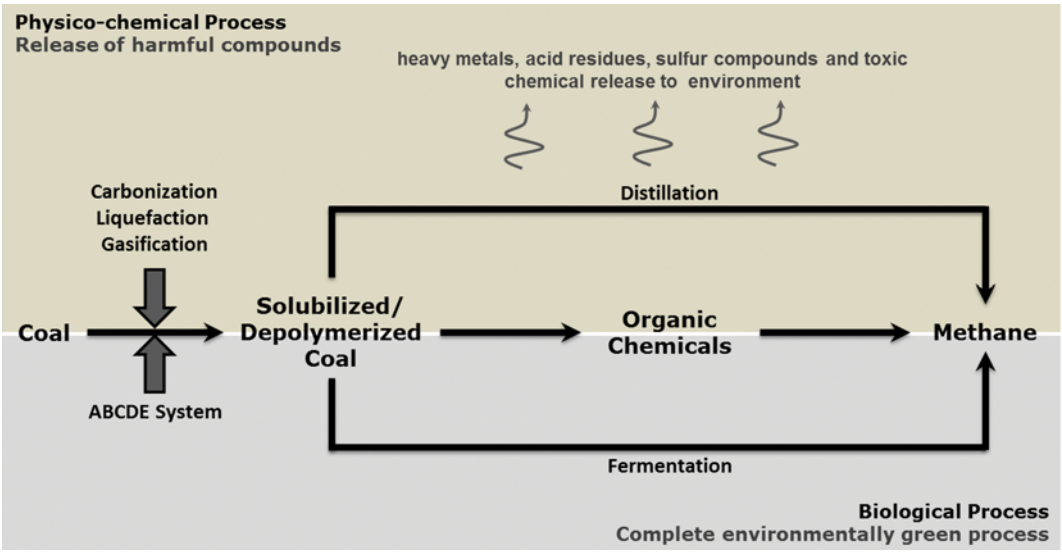

Fig. 1. Comparison of the biological and chemical process of coal degradation. Coal can be degraded by chemical methods, including carbonization, liquefaction and gasification, or biological methods, including the ABCDE system. Solubilized and degraded coal undergoes distillation or microbial fermentation to produce methane gas.

extreme conditions, such as high pressure, high temperature, and sometimes, use of expensive solvents, all of which are not ideal for large scale production. Therefore, replacement of these methods with biological processes will be ideal and economically feasible [15]. Although initial reports of biological strategies started during the 1920's, major findings have recently been reported in the past couple of decades. Periodic breakthroughs are summarized in Fig. 2 [16,17]. Many strategies and techniques have been applied to overcome the recalcitration of coal. The limited amount of functional groups present in coal can be highly susceptible to degradation by pretreatment, such as chemical oxidation (using nitric acid and hydrogen peroxide) and methylation prior to biodegradation [12,18]. Increased solubility of hydrophobic substrates, such as coal, can enhance the accessibility of microorganisms to degrade

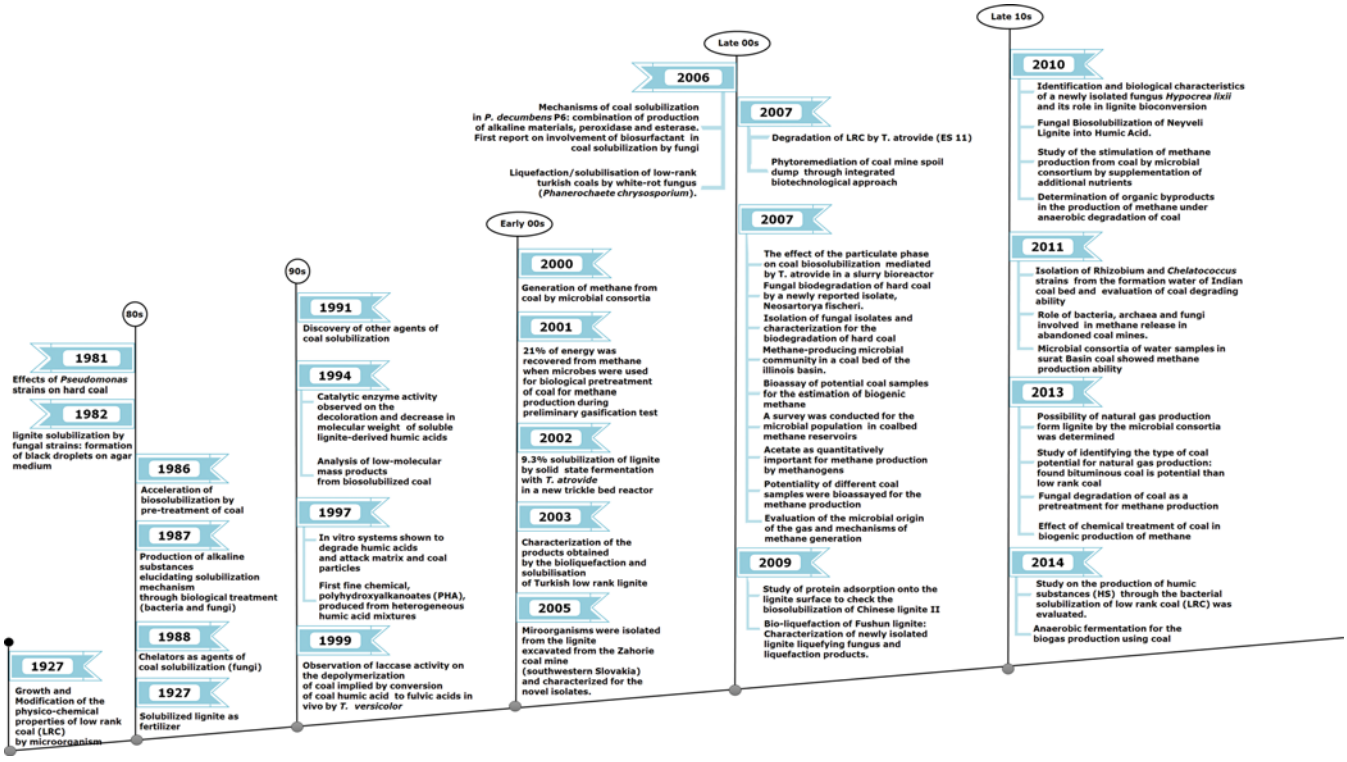

Fig. 2. Developments in coal conversion by employing biological processes presented in chronological order [16,17].

the substrate. It has been reported that the solubility of coal is directly proportional to coal oxidation, as well as pH [14,18,19] nitrogen, and ash content [20].

Some bacteria and fungi are able to release coal solubilizing substances that yield either enzymatic or non-enzymatic products. Most biological treatments of coal have used different kinds of fungi. Among fungal strains reported for coal degradation, *Phanerochaete chrysosporium* [13] and *Colorius versicolor* (formerly known as *Polyporus versicolor*) [21] have long been known for biological treatment. Other fungal strains reported include *Poria monticola* [22] and *Aspergillus niger* [23]. On the other hand, only a few bacteria, such as *Streptomyces setonii* 75Vi2, *Bacillus cereus*, *Bacillus pumilus*, and *B. subtilis* have been reported for their capability to degrade or solubilize coal [18,24].

BIOLOGICAL DEGRADATION OF COAL: SEVERAL MECHANISMS PROPOSED TO DATE

Biological coal conversion/degradation can be classified into three mechanisms: solubilization, depolymerization, and utilization. Coal solubilization occurs in the presence of alkaline substances, chelators, and surfactants, resulting in a black liquid. Coal depolymerization utilizes enzymes that function at a pH lower than 6. On the other hand, some microorganisms utilize the mobile part of the coal serving as its source of carbon [25]. Previously, the microbial coal degradation mechanism was summarized and denoted as the ABCDE system. Several microorganisms were found to have either one or a combination of these mechanisms [26-28]. In this section, the ABCDE mechanism is further described in detail.

1. Excretion of Alkaline Substances: Coal Solubilization Caused by Increase in pH

The majority of studies conducted on the biosolubilization of coal applied enzyme based methods. However, some reports have suggested that there are active, non-protein coal solubilizing substances secreted by some microorganisms such as *Streptomyces setonii* 75Vi2, which release an extracellular coal solubilizing component that is very stable under high temperature and pH, and is unaffected by proteases [24]. These non-enzymatic chemicals, alkaline substances and chelators, have been suggested to play a significant role in the solubilization of coal. Microbes reported to secrete non-enzymatic secretions are summarized in Fig. 3. Additionally, the coal solubilizing activity of the alkaline substances by the fungal strains was identified to be proportional to the increase in pH [19]. These alkaline substances, such as ammonia and biogene amines [26], increase the oxidation and neutralize the carboxylic acids present in coal, which ultimately results in coal solubilization. This mechanism has also been supported by the biosolubilization of lignin accompanied by an increase in pH in the medium by *Streptomyces viridosporus* [29]. *Bacillus* sp. Y7 [30] and *Penicillium decumbens* [31] have been reported to release alkaline material, resulting in an increase in pH as well as coal solubility. Initial weathering, chemical oxidation, and peroxidation seem to enhance coal solubility, which suggests that pretreatment of coal prior to biosolubilization would be beneficial for efficient utilization of coal by microorganisms.

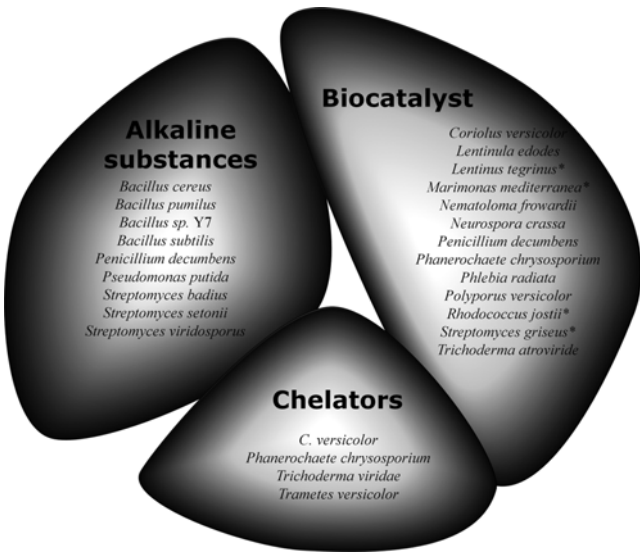

Fig. 3. List of representative microorganisms that secrete solubilizing agents, alkaline substances, biocatalysts, and chelators that aid in coal biosolubilization.

2. Enzyme Biocatalyst for Oxidative Depolymerization of Coal

The proposed mechanism for enzymatic coal degradation is based on the enzymatic mechanism used in lignin degradation because the structure of lignin is very similar to that of lignite (low rank coal). Several microorganisms have been reported to secrete ligninolytic enzymes on the culture medium (Fig. 3). One well-known enzyme of coal depolymerization is laccase, a phenol oxidase with a wide variety of substrates, which initiates depolymerization of lignin and lignin-like polymers by either of following three reactions: Cα oxidation, Cα-Cβ cleavage, or aryl-aryl cleavage [32]. Laccases are known to oxidize a variety of substrates by one-electron oxidation along with the reduction of O_2 to H_2O_2. As a result, radicals are formed to promote degradation. Laccase requires mediators, such as ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) and 3-HAA (3-hydroxy-anthranilic acid), to oxidize non-phenolic substrates [26]. The four copper ion regions in the enzyme allow oxidation of compounds with high redox potential. The molecular mechanism of laccase to degrade coal consists of three major steps as shown in Fig. 4 [33]. The best evidence for a similar mechanism of laccase towards lignin and lignite coal has been demonstrated by yellow laccase during solid-state fermentation of *Trametes versicolor* on coal humic acid [26], which clearly supports the role of laccase in coal degradation.

Peroxidases able to depolymerize lignin and lignite include lignin peroxidase (LiP) and manganese peroxidase (MnP). LiP is a glycoprotein, containing heme (iron protoporphyrin IX) as a prosthetic group. LiP also has broad substrate specificity towards many aromatic compounds and oxidizes both phenolic and non-phenolic structures. Even though the co-substrates, H_2O_2 or phenolic substances, show potent inhibitory action to LiP during enzymatic reactions, LiPs have been suggested to be potent enzymes that can play a significant role in the biological degradation of coal. For example, LiP was successfully employed in a process where 85% of coal was converted into lower molecular components that could be recovered with alkali washing and acid precipitation [13,34,35]. Since

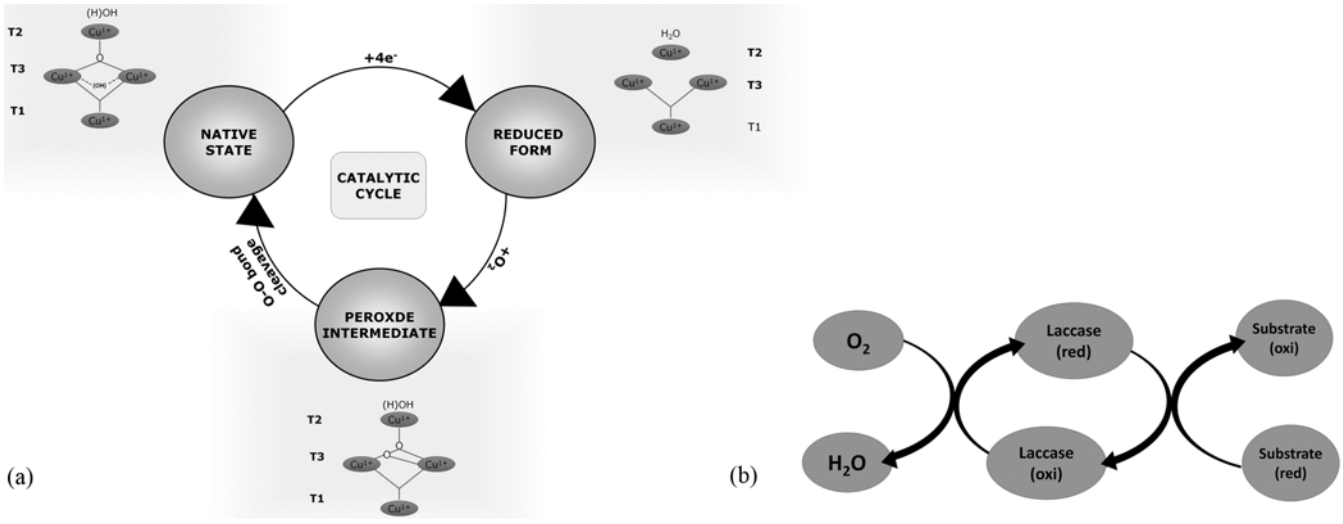

Fig. 4. (a) Schematic diagram of the laccase catalytic mechanism showing the three major steps of redox reactions. (1) Reduction of type I copper, (2) transfer of electrons from type 1 copper to the T_2T_3 cluster, and (3) activation of molecular oxygen and formation of water at the T_2T_3 cluster (b) substrate oxidation-reduction by Laccase [33].

LiP considers the substrate's size and redox potential before it attacks its aromatic substrates, it uses mostly phenols as decent substrates, but also can act on complex substrates like lignin or lignites [26,36]. Phenolic compounds generate phenoxy radicals, whereas non-phenolic compounds generate aryl cation radicals [26]. On the other hand, manganese peroxidase (MnP) is an extracellular glycosylated enzyme that contains heme as a prosthetic group. MnP has a wide substrate range, but prefers complexed Mn(II) as its reducing substrate [36] and Mn(III) as a mediator [26]. The relatively small size of the Mn(II)-Mn(III) redox mediator couple provides easy access to coal subunits; thus it can attack the polymer where larger molecules cannot reach by generating radical substrates [26]. MnP also tends to produce radicals that attack and break covalent bonds present in coal, which can be maintained for several weeks, and releases CO_2 gas as the process continues [26]. Considering the mechanisms of LiP and MnP, both share similar redox catalytic cycles in the degradation of coal. The catalytic cycle (Fig. 5) starts from the oxidation of Fe(III) in LiP and Mn(II) in MnP, respectively. Compound I generated by the enzymes through hydrogen peroxide is followed by one-electron oxidation with an aromatic compound (mediator: veratryl alcohol), which results in compound II and a radical aromatic compound. The resulting compound reverts to its original form via reduction of the products [26,37-39]. Compound I present in the enzymes is responsible for the oxidation of substrates with higher redox potential. LiP has a higher redox potential than MnP; therefore, it is easier for LiP to oxidize PAHs (polycyclic aromatic hydrocarbons) than MnP [36]. Addition of veratryl alcohol may also induce oxidation activity as a mediator and reductant of compound II [36]. Additionally, both of these peroxidases contain three regions consisting of a distal residue, where enzymatic reactions with hydrogen peroxide and acid-base catalysis occur, a proximal region, and a substrate-binding site [40].

Extracellular oxidative enzymes can alter the structure of coal, which ultimately results in coal depolymerization. These enzymes are involved in indirect coal degradation, in which cation radicals released via enzymatic action diffuse into complex coal structures and attack carbon-oxygen and carbon-carbon bonds. This avoids

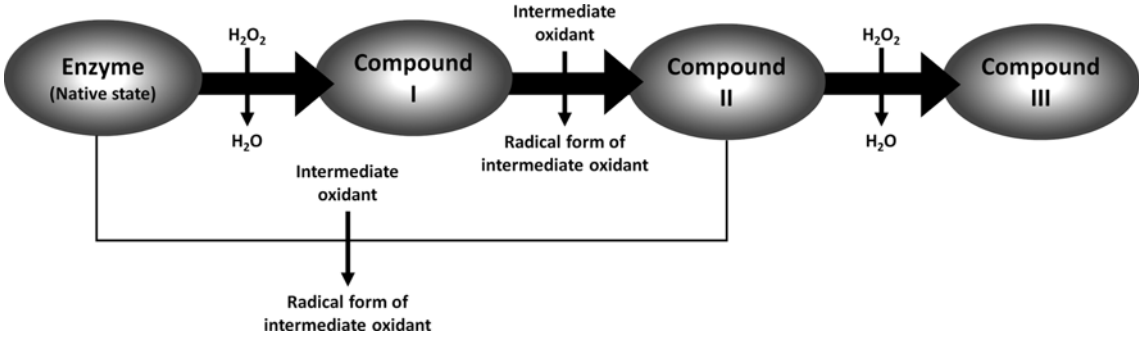

Fig. 5. Schematic diagram of the redox cycles catalyzed by lignin peroxidase and manganese peroxidase. Briefly, compound I is generated from the oxidation of Fe(III) and Mn(II) catalyzed by LiP and MnP in the presence of hydrogen peroxide. Then, compound I undergoes one-electron oxidation with an aromatic compound as a mediator generating a radical compound. Reduction of the products reverts the resulting compound to its native state [26,37-39].

the need for direct enzyme-substrate interaction for the general enzymatic action. Both LiP and MnP catalyze the depolymerization of coal by peroxide radicals. These enzymatic activities depend on the components produced after depolymerization, which is highly dependent on the type of coal and process employed [34,35]. It has been suggested that LiP and MnP actively break macromolecular bonds by releasing hydrophilic and hydrophobic aromatic components leading to the non-specific binding and inhibition of proteins [14].

The amount of extracellular enzymes released during coal degradation is highly dependent on the type of coal and coal-derivative products. Initial studies showed that adding different coal-derived substances can affect the production of the type and amount of exoenzymes [12,20]. The strain used in the studies showed enhanced secretion of peroxidase when lignite powder or lignite-extracted derivatives like bitumen, matrix B, and humic acids were added. Up to a six-fold increase in enzyme production was observed upon induction with lignite or its derivatives [12,20]. The studies employing *Penicillium decumbens* strain P6 as a host suggested that lignite or lignin is needed for induction of the peroxidase or esterases. Upon induction, a variety of isoenzymes of peroxidases and esterases were released into medium and helped in solubilizing lignite by increasing the surface tension of the culture medium [31]. In another study, very low concentrations of humic substances (0.001%) chemically extracted from low rank coal were used in culture medium to induce coal degrading enzymes in *Bacillus mycoides* str. BGSC1-DN3, *Mycobacterium* sp. *Acinetobacter* sp. str. CCGE2017, and *Enterobacter aerogenes* str. JCM1235 [41].

Recently, new peroxidases, such as manganese-oxidizing enzymes CotA (Coat protein A) and DypB (Dye peroxidase B), have been reported in lignin and PAH degradation. Since lignite is composed of aromatic structures similar to lignin, DypB [42,43] and CotA from *Bacillus pumilus* WH4 [44] have potential applications in coal degradation. Despite extensive research, the detailed mechanism of the mentioned ligninolytic enzymes towards coal has not been fully understood, but the proposed mechanism may be useful in understanding the coal solubilization process [36,45].

3. Chelators and Detergents

The overall structural integrity of coal depends on the multivalent cations bridging the active acid or other side chain active group. Thus, destabilization of the structure by chelating the multivalent metal cations assists in coal solubilization [11,22]. *T. versicolor* secretes metal chelators such as ammonium oxalate and siderophores, which promote coal solubilization. Similarly, *Penicillium* sp. also secretes oxalate, which may have participated in solubilization of subbituminous coal [46]. Decreasing the surface tension of coal with biosurfactants will also enhance coal solubilization.

4. Esterases

Aside from the peroxidases, hydrolases also contribute to coal solubilization. LiP from *P. chrysosporium* has esterase activity, but less coal solubilization activity compared to that of other peroxidases and chelating agents [47]. The function of esterase in coal solubilization was first described by Crawford and Gupta [7], in which they identified esterase as a non-oxidative enzyme with an ability to depolymerize humic acids derived from lignite. Unlike peroxidases, esterases are not known to be activated by mediators, and steric hindrance becomes an obstacle in postulating a mechanism by which the enzyme as a whole cannot invade the macromolecular coal network and act up on it. Therefore, more research is needed to determine the actual role by which esterases show solubilization on lignin and coal materials.

Table 2 displays a list of organisms showing coal solubilization, the mechanisms involved, elemental content, and changes in functional group [48-55].

BIOLOGICAL METHANE PRODUCTION FROM COAL

The main target of biological coal degradation is to replace conventional methods of industrial chemical production with a conventional energy source while maintaining environmental sustainability. Methane is a gas that can be utilized as a fuel source. Many microorganisms such as methanogens produce methane when they are cultured on dead debris or decayed matter. Coal, a fossil material with high carbon content, can be utilized by the microorganisms to produce beneficial eco-friendly fuel reserves, such as methane.

With the growing concern of greenhouse gases (GHGs), there has been an increasing development of biological processes for the generation of energy from fossil fuels. The stepping stone in the utilization of coal for alternative clean fuel started in the late 1980's and the majority of the work has been focused on identifying organisms capable of liquefaction and transformation of coal to a simple carbon source. Biological coal transformation depends on many factors, including the microorganism used, culture condition, coal type, involvement of alkaline agents, chelation, type of acting enzyme, and peptides and amines used, which suggests that there are several mechanisms involved in the process. These mechanisms may be applied for the production of methane from coal.

Biological methane can be produced by a microbial consortium-based process. Here, complex polymers of coal are depolymerized and utilized by anaerobic bacteria through fermentation, which can convert it into substrates for methanogens to produce methane [56].

1. Pathway for Bio-methane Production from Coal

The biogenic origin of methane within coal makes it plausible in theory to stimulate the formation of new methane in existing wells or split process systems. On the other hand, coal is a recalcitrant geopolymer, and may not be readily degradable by microorganisms, especially by methanogens. Mechanisms by which bacteria degrade coal to methanogenic substrates and finally into methane for biogenic generation should be well understood to establish a process of beneficiation.

On the production of bio-methane, complex mixtures of aromatic, heterocyclic, and aliphatic constituents of coal provide short-chain organic acids (e.g. acetate), alcohols, and H_2 for acetoclastic, methylotrophic, and hydrogenotrophic methanogenesis, respectively. These compounds released from the primary and secondary fermentation of coal are utilized by methanogens to produce methane gas [56-58]. By combining the different mechanisms of coal degradation, a suitable model can be proposed for the process of converting coal into methane gas. The process of forming biogenic methane from coal (Fig. 6) can be divided into three events:

Table 2. Representative microorganisms for the solubilization of coal. Their substrates, elemental content changes in biosolubilized coal, changes in functional groups of biosolubilized coal, reported mechanisms, and enzymes involved in coal degradation are summarized

Organism	Source of organism	Substrate	Changes in elemental content of biosolubilized coal	Changes in functional groups of biosolubilized coal	Mechanism	Enzyme	Products	Reference(s)
Bacillus licheniformis (dominant bacteria in the consortium)	Single bacterial community (MCSL-2)	Untreated leonardite	Increase in N, C and O content; decrease in sulfur content	Increase in carboxyl groups and decrease in aromatic carbons	Desulfurization; alkylation	Alkaline substance, MnP, esterase	Humic acids with higher nitrogen content than leonardite and cHA	[47]
Bacillus mycoides	Petrochemical plant sewage	Crude or nitric acid pretreated lignite	Increase in O and N; decrease in C and S	Presence of hydroxyl groups of alcohols, phenols and N-H groups; degradation of aliphatic chains; less aromatics	Oxidation	Alkaline substance		[48]
Gordonia alkanivorans S7	Petrochemical plant sewage	Crude or nitric acid pretreated lignite	Increase O and N; decrease in C and S	Presence of hydroxyl groups of alcohols, phenols and N-H groups; degradation of aliphatic chains; less aromatic rings	Oxidation	Alkaline, thermostable substances		[48]
Neosartorya fischeri	Environmental coal	Untreated and nitric acid-treated hard coal	Increase in O and N	Oxidation of coal surface and nitration of the condensed aromatic structure	Depolymerization and solubilization reactions: oxidation, nitration		Humic acid extract from Coal (GC/MS): phenol, benzoic acid, methyl ester, benzyl nitrile, indole, N-methyl pthalamide, 3-phenylpiridine, dibenzofuran, fluorene	[49]
Neosartorya fischeri ECCN 84	Coal environment	Waste coal (mixture of low-grade roof coal and discards, following the extraction of high-grade coal seams	Increase in O and decrease in C		Oxidation	Laccase		[50]
Phanerochaete chrysosporium	Lab strain	Untreated lignite		IR-Spectra: absence of bands representing carboxylate species, aromatic structures X-ray diffraction (liquefied matl): non-crystalline, amorphous structure COD: methane production; no CO_2 produced loss of carboxyl groups	Oxidation, strong decarboxylation; ring opening of the aromatic structures	Ligninase enzyme	Methane	[51]

Table 2. Continued

Organism	Source of organism	Substrate	Changes in elemental content of biosolubilized coal	Changes in functional groups of biosolubilized coal	Mechanism	Enzyme	Products	Reference(s)
Pseudomonas stutzeri	Ormation water of Indian coal bed	Lignite			Emulsification	Rhamnolipid (biosurfactant)		[42]
Trametes hirsuta	Lab strain	Leonardite and its humic substances (HS)	Decrease in O and C content	Decrease in relative content of aliphatic and carboxyl group carbons; increase in ketone and chinone	Reduction and dehydration			[52]
Trametes hirsuta	Lab strain	Lignite		Introduction of brown coal led to a higher biomass and higher MnP and LiP activity	Biosolubilization	LiP, MnP, laccase	Humic substances	[53]
Trametes maxima	Lab strain	Leonardite and its humic substances (HS)	Decrease in C content and H/C ratio and increase in O/C ratio	Decrease in relative content of aliphatic carbon and increase in ketone and	Oxidation (carboxylation)	LiP, MnP, laccase	Humic substances	[52,53]
Trichoderma atroviride	Lignite	HCl-pretreated lignite labeled with 14C-alkyl iodide		Hydrolysis of carboxylic esters and phenolic ether bonds	Solubilization, hydrolysis, oxidation	Esterases, oxidative enzymes (laccase)		[54]
Trichoderma atroviride	Soil	Sub-bituminous coal		Degradation of aromatic compounds	Oxidation; depolymerization	Phenol hydroxylase; 2,3-dihydrobiphenyl-2,3-diol dehydrogenase, 3,4-dihydro phenanthrene-3,4-diol dehydrogenase, 1,2-dihydro-1,2-dihydroxynaphthalene dehydrogenase, 1,2-dihydro-1,2-dihydroxyanthracene dehydrogenase	4-Hydroxyphenylethanol, 1,2-benzenediol, 2-octenoic acid	[55]

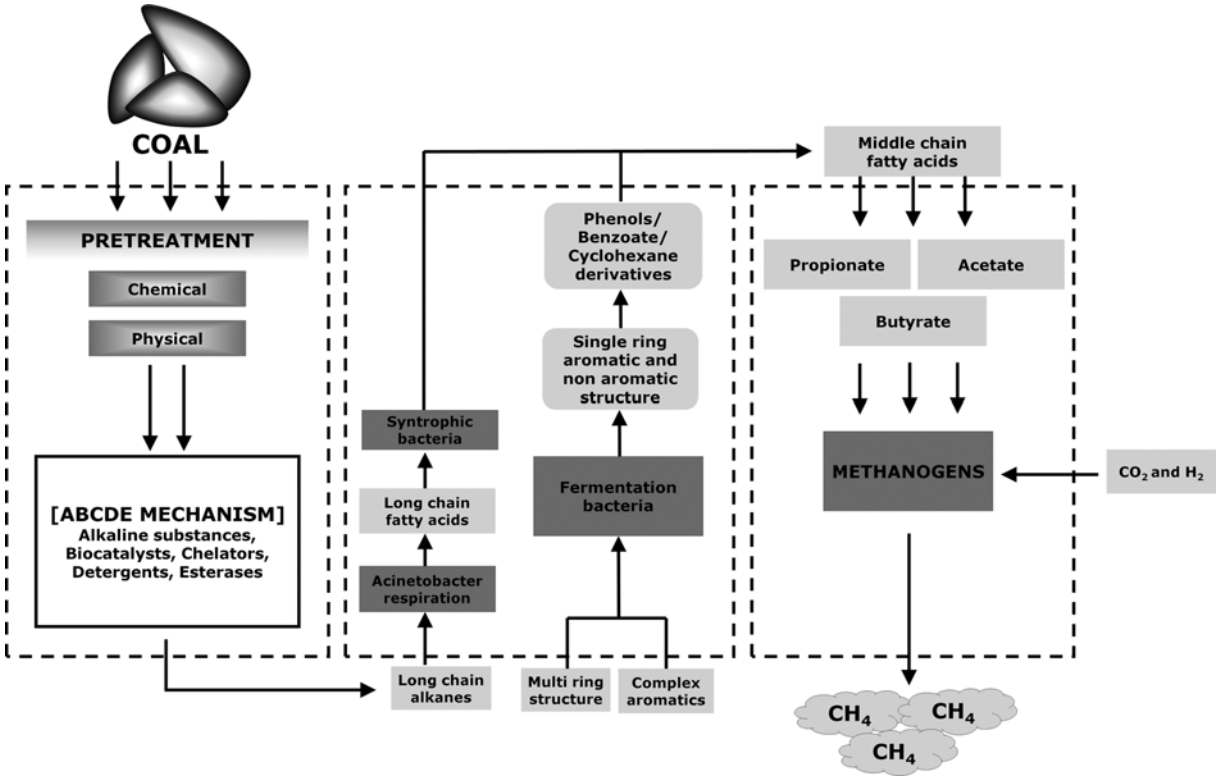

Fig. 6. The production of bio-methane from coal includes three major stages: (1) Pretreatment of coal by chemical or physical methods, such as crushing and oxidation with acid catalyst producing smaller molecules of coal, which can be used as substrate in ABCDE mechanism, (2) conversion of depolymerized coal molecules, such as long chain alkanes, multi ring structure compounds and complex aromatics, into fatty acids by various microorganisms, and (3) fermentation of fatty acids by methanogens producing bio-methane.

(i) the release of soluble organic intermediates from coal geopolymer, (ii) the degradation of soluble intermediates into substrates utilizable by methanogens, and (iii) methanogenesis [59]. Generally, the complex aromatic hydrocarbons are converted into simpler molecules that can be used by methanogens. In this process, fermentative bacteria use these intermediate components and provide simple carbon sources such as acetate, simple organic derivatives, or CO_2 and H_2. Then, the produced substrates are used by methanogens to produce methane from coal. Intermediate components of coal degradation during the biological production of methane from the coal are acetate, long chain fatty acids, alkanes (C19-C36), and various low molecular weight aromatics, including phenols, all of which are primary intermediates in the biodegradation pathway from coal-derived geopolymers to methane [60]. All models of microbial production of methane from coal suggest that the rate-limiting step is the degradation of coal to the substrates. The degradation of lignite (low rank coal) and subsequent breakdown into low-molecular weight aromatic and aliphatic compounds can be an indirect option for extracting some material capable of being fermented by anaerobic microorganisms [59,61]. The precursors of biogenic methane formation are limited to simple compounds, primarily acetate and H_2 [62].

2. Factors Influencing the Biological Methane Production of Coal

As described earlier, coal with different ranks has different complexities. As the rank of coal increases, the structure becomes more compact and highly aromatic with fewer oxygenated side chains. The biogenic generation of methane from low rank coal has been a subject of interest because of its potential for combustible fuel [1].

Production of biological methane is highly dependent on the coal type, quality, size, pretreatment conditions, and microbial consortia. Low rank coals such as lignite and subbituminous coal consist of largely branched components with oxygen-containing side chains, wherein these structural aspects are thought to be suitable for microbial communities to produce methane in a laboratory setup [5,63,64]. Although low rank coal seems to be more suitable for supporting the efficient production of biogenic methane than higher-rank coals that have a greater proportion of aromatic and compact structures with high recalcitrant components, highly volatile bituminous coals have been used for the production of methane [62,65,66]. Some studies have suggested that the use of bituminous coal (2.47 CH_4/g coal/day) on biological methane production is better than subbituminous (1.41 CH_4/g coal/day) and lignite coal (0.24 CH_4/g coal/day) [56]. This might be due to liberated volatile compounds or the release of more adsorbed methane from bituminous coal. Another report also suggested that adding nutrients and minerals in the growth medium can improve culture conditions to achieve comparable amounts of methane from low rank coal [57]. Methane production might be also dependent on the parent source from which the coal was formed, since Indonesian lignite gave the best results for methane production among samples derived from

Table 3. Major advances in the conversion of coal to methane

Year	Process achieved in production of bio-methane from coal	Microbial source and/or species identified	Coal source and/or coal rank	Bio-methane yield	Reference(s)
1994	Biological production of methane from bituminous coal	Anaerobically collected coal mine underwater, Sewage treatment sludge and Termite gut consortia	Bituminous coal from the Penn State Coal Sample Bank	0.2008 mmol/65 g coal (3.07 μmol/g coal)	[82]
1997	Preliminary demonstration of the mechanism of biologically mediated methane production from black coal	Microbial consortia from termite guts, aquatic sediments coal mine and piggery grower-finisher	Black coal (Bulli seam of the Illawara coal, New South Wales, Australia)	~9 cc/g coal	[83]
2000	Biogas production from different sources of micro-organisms	Cow dung, insect, algae and fungi grown over wood, mine sludge, mixed consortia, Jitpur, India	Indian coal	Cow dung-42.5 mL, insect 19.6 mL, algae and fungi-39.5 mL, Mixed consortia-11.6 mL (yield coal 25 g)	[74]
2001	Investigated biogenic methane origin and derived mechanism of CBM in from Australian Permian coal	N/A	Permian coal-seams from Sydney and Bowen basins, Darwub basin, Australia	N/A	[84]
2008	Identified the microbes responsible for the coalbed methane reservoirs in Australia	*Archaeoglobus* sp.	Tertiary brown coals and Permian bituminous coals	N/A	[75]
2008	Identified and compared the ability of CMB methanogen consortia to produce methane	CBM methanogenic consortia	Powder River Basin (subbituminous type), Wyoming, USA	~10 μmol/g coal	[58]
2008	Characterization of the methanogen consortium enriched from coalbed methane well	Methanogenic consortia includes; acetogens, Acidaminobacter, hydrogenoformans, *Syntrophomonas* sp., OUT (operational taxonomic units) similar to *Methanosarcina* sp.	Powder River Basin (subbituminous type), Wyoming, USA	0.084 m^3/t coal/day	[78]
2008	Designed a bio assay for estimation of the biogenic methane-generating potentials of different coal samples	Enriched mixed culture, WBC2; sp. includes *Clostridiumsp, Bacteroides* sp., *Acetobacterium* sp., *Desulfobulbus* sp. & Methane-forming *Archae*	Powder River Basin (subbituminous type), Wyoming, USA	0-23 μmol/g coal	[64]
2008	Derived the mechanism of methanogenic pathway of coal bed methane gas in Powder River Basin	Consortia collected from different places in the Powder River Basin	Powder River Basin (subbituminous type), Wyoming, USA	N/A	[80]
2008	Studied the chemical and microbial factors influencing the Bio-methane production from low rank coal	Coal slurry prepared from the collected coal	Coal samples collected indifferent sediments like Cook Wall Pawnee Alaska shallow Alaska deep from Powder River Basin (subbituminous type), Wyoming, USA	Powder River Basin- 140.5-374.6 mL; Cook Wall Pawnee Alaska-131.1-284.0 mL (CH_4/kg coal)	[63]

Table 3. Continued

Year	Process achieved in production of bio-methane from coal	Microbial source and/or species identified	Coal source and/or coal rank	Bio-methane yield	Reference(s)
2010	Characterized the microbial community associated with deep coal seam methane reservoir	Mixed consortia with major methanogen *Methanobacterium* sp.	Gippsland Basin, Australia (Brown coal)	N/A	[85]
2010	Identified the organic intermediates in the anaerobic digestion and conversion of coal to bio-methane	Bioassay microbial consortium WBC2	Wilcox coal (ub-bituminous)Zavala County, Texas	78 µmol/g coal	[60]
2010	Studied the stimulation of the bio-methane production from coal by addition of nutrients or microbial consortium	Microcosm from coal and enriched mixed culture WBC2	Wilcox coal (sub-bituminous)Zavala County, Texas	Microcosm from coal- 60 µmol WBC2- 80 µmol (CH_4/g coal)	[57]
2011	Biogenic methane potential for Surat Basin, Queensland coal seams	Microbial consortia, Surat Basin Queensland, Australia.	Subbituminous to high-volatile bituminous	1.0 m^3/t coal/day	[69]
2012	Comparative studies on field and laboratory bioconversion of coal to methane	Actinomycete, Firmicute, Proteobacterial lineages, Thermoanaerobacterales, Methanosarcinales and Methanomicrobiales	San Juan Basin	0.37 µmol/g/day	[66]
2013	Biogas production from chemically pretreated coal	*P. putida* F1 (ATCC strain 700007)	Powder River Basin (subbituminous type), Wyoming, USA	N/A	[71]
2013	Studied the coal rank on ability of bio-methane production	Powder River Basin adopted consortia WBC2	Lignite, subbituminous, high-volatile bituminous and low-volatile bituminous coal	Lignite- 0.24 µmol, subbituminous, high-volatile bituminous- 1.41 µmol and low-volatile- 2.47 µmol, bituminous coal- 0.38 µmol (Yield CH_4/g coal/day)	[56]
2013	Demonstrated the bio-methane production from coal by chemical stimulation by potassium permanganate	Coal-derived microbial consortia (21-32 γ)	Powder River Basin (subbituminous type), Wyoming, USA	93.41 µmol/g coal	[71]
2013	Enhanced production of methane from the coal by addition of ethanol	Powder River Basin adopted consortia WBC2	Powder River Basin coals, US (sub-bituminous)	124.2±25.6 µmol/10 g coal	[86]
2013	Demonstrated the fungal degradation as pretreatment to produce bio-methane from coal	*Penicillium chrysogenum* MW1	Sindh Province coals (rank lignite to subbituminous coal)	7-11 µmol/g coal	[73]
2013	Demonstrated the feasibility of bio-methane production from non-gas-production lignite	Mixed consortia collected from coal bead lignite seam southern Sumatra island	Lignite from Indonesia, China and Australia	Indonesia-4.46×10^{-3} China-3.24×10^{-3} Australia-3.30×10^{-3} (Yield CH_4 mol/kg/day)	[67]
2014	Biogas production from coal via anaerobic fermentation	Jitpur coal mine derived consortia	Indian coal (sub-bituminous s)	479.3 cc/100 g coal	[70]

N/A data not available

different countries such as Australia, Indonesia, and China. On the other hand, Australian lignite supported the production of methane with low CO_2 composition in the final gas mixture [67-69]. The development of methane production from different sources of coal, coal type, microbial source and production yields is summarized in detail in Table 3. The biogas production ability depends not only on the properties of coal, but also on the mesh size of coal used. It was found that biogas production is inversely proportional to particle size, which might be because smaller particle size provides microorganisms with more chances for access to coal-degrading substances and more available substrates for biogas production [70]. Several models of methane production have been proposed based on the results obtained in various laboratory conditions, in which the rate-limiting step is the degradation of coal by microorganisms. As mentioned, chemical or biological pretreatment of coal may increase the reaction rates mediated by microorganisms in the coal biosolubilization process and carbon substrates released from coal available for the host microbial consortia.

Similar to the conversion of coal to other chemicals, initial pretreatment of coal prior to utilization as a carbon source for methane production has been reported to enhance the efficiency of biogas production as compared with untreated coal [3]. Various chemical pretreatments applied for different aspects of coal utilization have recently been applied for the production of methane. For example, potassium permanganate ($KMnO_4$) employed for many pretreatment processes, such as contaminated hazardous waste, has been suggested to also be useful for treatment of coal in alkaline media resulting in the oxidation of phenolic rings and the release of CO_2, acetate, and oxalic acids from polynuclear aromatics and heteroaromatic structures [3,71]. Low molecular compounds resulting from the degradation of coal are more ideal carbon sources for microorganisms to utilize for efficient production of methane than untreated coal, as was supported by successful demonstration of enhanced biogenic methane production using potassium permanganate as a pretreatment [3]. Chemical reagents representing acids (HNO_3), bases (NaOH), and oxidants ($KMnO_4$ and H_2O_2) were also used for pretreatment to examine the biogas ability of pretreated coal. Here, nitric acid and sodium hydroxide were found to solubilize coal up to 14%. Approximately 20% of the soluble carbon was produced when high concentrations of permanganate were used. Thus, at higher concentrations, $KMnO_4$ is the most efficient pretreatment for biogenic gas production [71]. Though biological pretreatment for methane production has yet to be attempted, the combination of the pretreatment reported for coal solubilization and anaerobic methane production can enhance the efficiency of biogenic methane production. As discussed, biological pretreatment with *Penicillum decumbens* [31] or similar species reported to degrade coal listed in Fig. 3 can enhance degradation and make simple monomers that are easily accessible to microcosm and methanotrophs to produce methane. However, there are still many issues to deal with in combining these aerobic and anaerobic systems. On the other hand, oxidation pretreatment of low rank coal with microwaves has been suggested to enhance their water solubility [72]. In this process, oxidizing free radical species (●OH, HO_2●, ●O_2, H_2O_2) are generated via radiolysis of water and serve as important intermediates for coal decomposition. This depolymerized coal can act as good substrate for many biological processes [72]. Other than chemical and physical pretreatment, microorganisms able to solubilize coal can also be used for pretreatment, such as *Penicillium chrysogenum*, in which extracts showed the release of complex components such as single ring aromatics, polyaromatic hydrocarbons, aromatic nitrogen compounds, and aliphatics [73].

The microbial source and microcosm are two important factors that need to be considered to establish a process for methane production. Usually, coal mines are good sources of microcosms. Mine water seems to be a potential source for microcosms [70,74]. The microbial populations on some dominant coalbed methane reservoirs have also been investigated for a consortium of microbes that naturally produce methane. In this study, we analyzed the prokaryotic diversity of water and coal samples derived from the target reservoirs. Gram-negative bacteria were predominant, followed by Archaea and gram-positive bacteria [75]. Microbial communities associated with CBM (coal bead methane) are generally colonized by an array of bacterial taxa that commonly include members of the *Proteobacteria*, *Comamonadaceae*, and *Geobacteraceae* families [75-77]. Apart from these numerous *Firmicutes*, the order *Clostridiales* has also been detected [76,78]. Moreover, coals are also colonized with archaea such as methanogens, e.g., Methanocorpusculaceae, which are common in the Illinois coal basin [79]. In the study on powder river basin coals, the methanogenesis involved more than two pathways, taking acetic acid as the base source, and was converted to methane either by acetoclastic methanogenesis, hydrogenotrophic methanogenesis, or syntrophic acetate oxidation to H_2 and CO_2 and followed by hydrogenotrophic methanogenesis [58,80]. Recently, various sources of microbial consortia from different natural sources such as cow dung, paddy field soil, termite nests, and mine waters have been examined for methane production from coal. Proper enrichment of the microbial source is essential for obtaining efficient production of methane from coal.

CONCLUSIONS

Coal is a main entity for major industrial needs and will continue to be significant in world energy requirements. Coal is not only a key energy source, but is also a major contributor of GHGs. With the depletion of liquid fossil fuel, coal is going to be an increasingly important energy source and great efforts are needed to produce greener coal. Though other biomasses available for green biomethane production exist, coal has been found to be more efficient. Treatment of coal also provides other useful coal-derived chemicals and products not achievable with other biomasses. Although the concept of green fuel conversion of coal has been demonstrated at a laboratory scale via biological means, the feasibility of large-scale applications has yet to be demonstrated. Biological processes for the generation of green energy, such as coal biosolubilization and utilization by microorganisms, will be a great achievement in the fuel industry [24]. However, there have only been limited studies regarding the microbial degradation of coal. Thus, more studies are needed to derive an efficient process. A combination of successful microbial strains and processes designed in various stages will minimize the production cost and enhance productivity for

converting coal to fuel, chemicals, and energy [81].

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