



Lower emission plant using processed low-rank coals

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ABSTRACT

Low-rank coals can be processed into non-fouling coal, ultra-low ash coal, and coals containing catalysts. Systematic studies of the action of acid to reduce ash in a number of low-rank coals have shown total ash reduction varied from 96% to 30%; the extent of ash reduction was limited by the nature of minerals, which may be removed using various acids, including HF, to produce ultra-low ash coal. A commercial process must operate at elevated temperatures, but this must not produce toxic wastewater; data are provided to show that wastewater may be treated and water recycled without polluting the environment. The addition of effective catalysts results in enhanced reactivity of the coal to oxygen and steam; experimental data show high yield of H₂ from char and steam, and accompanying post-gasification chemistry. Development of catalytic steam gasification requires an understanding of aqua-chemistry and the thermal transformations of inorganics as the coal is heated. The scientific basis exists for processing low-rank coals, but commercial application requires: (i) high production rates, (ii) treating wastewater produced from coal treatment plant, (iii) catalysts that increase the yield of H₂ from steam gasification, and (iv) plant that achieves high power and thermal efficiencies. Modelling studies for super-critical plant, and for direct coal-fuelled turbine in combined cycle, illustrate the potential for lower-emission technology; catalytic steam gasification offers the cleanest option for future coal-fuelled plant.

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1. Introduction

A worldwide effort has been underway to develop new coal-based technologies for cleaner power generation. Impetus for this has stemmed from environmental concerns for global warming and climate change due to increasing levels of Greenhouse gases. Present power generation using low-rank coals is the least efficient and thus the largest emitter of CO₂ per unit of electricity produced. Low-rank coals, however, are generally cheaper and consequently are commercially attractive for use in power generation and gasification plant. The as-mined coals have a low calorific value, typically at 5–10 MJ/kg, because of high water content, and usually contain aggressive ash which causes fouling, slagging, and fireside corrosion. The ash-forming constituents undergo aggressive chemical reactions at elevated temperatures, forming vapour phase sodium, chloride and sulfur species, and molten silicate slag, which deposit on boiler surfaces, causing fouling and corrosion [1–5]. As a result of these properties, as-mined low-rank coal is the fuel of last choice for new coal utilizing plant. The low cost of these coals has been exploited by locating base load power generation plant close to open-cut mining.

A new approach to using these coals, and to improve their environmental footprint while maintaining the economic advantages, is

to process them into a fuel with properties suitable for use in higher efficiency plant. Simple moisture reduction of low-rank coals would generally increase the fouling, slagging and corrosion, because the dry coal would increase the coal flame temperatures, which in turn would increase the aggressive chemistry of the inorganic ash-forming species. A general coal treatment process must also be suitable for all low-rank coals; such a process must be sufficiently flexible to take advantage of the low cost of mining. Generally, these hydrophilic coals may be treated with acid to remove ash and produce non-fouling coal, and also, they may be mixed with inorganic solutions to add catalysts for coal gasification. To maximise the commercial potential of a coal processing technology, it must be able to: (i) remove all ash related problems, (ii) increase the heating value of the non-fouling coal, and (iii) add effective catalysts to the coal for catalytic steam gasification. The environmental aspects of the coal treatment are also extremely important; for example, it must not produce toxic wastewater. The non-fouling coal may be used in high-efficiency super-critical boilers, and ultra-low ash coal may be used for direct coal-fuelled turbine in combined cycle; such plant would substantially reduce the amount of CO₂ produced per unit of power. Coal containing catalysts could be used in lower temperature gasification using a mixture of oxygen and steam, to increase the hydrogen content of syngas.

Ash reduction for coals may be achieved by treatment with alkali or acids. Examples of ash reduction for high-rank coals using alkali treatment include the CSIRO black coal process [6,7]; ash reduction for high-rank coals using HCl, HNO₃ and HF has been discussed in [8–10]

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and ash reduction of low-rank coals using HCl and H₂SO₄ in [1,11,12]. The reduction of mineral matter in coal using HCl and HF has been discussed in [13,14]. Numerous other treatment methods for low-rank coals has been discussed, but most of these have been of moisture reduction [15,16]; additionally, methods have been developed that heat coal/water mixture to high temperatures, and these produce large quantities of toxic wastewater [17].

The assessment of effective catalysts for steam gasification is complicated by the thermal transformations in coal which eventually create the catalytic species; thus it may be difficult to predict if a particular inorganic added to the coal would be an effective catalyst. Research is needed to provide insights on the methodology that may be used to add effective catalysts to low-rank coals, and also on methods that may be used to ascertain the catalytic activity of treated coals.

Development of a coal processing technology on a commercial scale is predicated on both a comprehensive understanding of the process (acid washing and adding inorganics), and on the economic viability of the coal-fuelled plant within a carbon constrained framework. The scientific basis must be well established before the technology may be developed into full scale plant to ultimately prove its commercial viability. The objectives of this paper are to: (1) examine conditions for ash reduction of a wide range of low-rank coals to show that non-fouling coal may be obtained using acid treatment, (2) examine conditions that may be used to add inorganics, and methods to assess how effective these are for catalytic gasification of low-rank coals, (3) show that polluting wastewater may be produced and examine ways to clean the wastewater for re-use, and (4) use computer models of coal-fuelled power generation plant to illustrate the potential for improved environmental performance using treated low-rank coals.

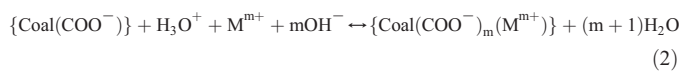
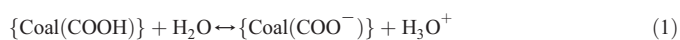
2. Experimental

2.1. Coal samples

Victorian brown coal was obtained from the Loy Yang and Yallourn open-cut mines, German brown coal was provided by Rheinbraun GBT, Lochiel, Bowman, and Leigh Creek coals were obtained from deposits in South Australia, Collie and Esperance coals from Western Australia, and Wyoming coal from the USA. Batches of as-received (ar) brown coal were prepared in the laboratory, by crushing a 5 kg batch of each coal sample using a MF basic IKA Werke laboratory hammer mill with a 1.68 mm mesh sieve. The crushed coal was mixed thoroughly until the amount of ash in three randomly selected ten gram coal samples agreed to within ± 0.2 wt.%. The coals were stored in closed polyethylene containers. Leigh Creek, Collie, and Wyoming coals were supplied crushed and dried as used ar.

2.2. Laboratory treatment of coal samples

The basis for any acid treatment technology is the removal of inorganic species by the action of acid added to the hydrophilic coal and water. The general equations may be written as (M^{m+} is any aqua-inorganic species):



Eq. (1) illustrates the weakly acidic nature of coal/water mixtures, and Eq. (2) shows that acidic conditions would render all M^{m+} species bound in the coal matrix into solution species (Eq. (2) also illustrates

that aqua-inorganic species may be added to the coal matrix by adjusting the pH of the mixture with alkali).

The action of acids can differ between hydrophobic high-rank coals and hydrophilic low-rank coals; the physical and chemical properties of these two categories of coal are sufficiently different as to necessitate different treatment methods for ash reduction. High-rank coals contain ash-forming constituents as occluded particles within the coal matrix and the coal needs to be crushed to liberate the mineral particles and expose them to the action of acids. Low-rank coal samples are mined with inorganic species in the coal matrix, and with extraneous mineral particles and clays; these can readily be mixed with water and acids to remove cations from the coal matrix and from the extraneous particles. Low-rank coals, however, compress under pressure and a coal bed can be compressed into a non-permeable solid when subjected to pressure, rendering it impossible for effective acid treatment. This makes it extremely difficult to treat large quantities of low-rank coal at elevated temperatures and pressures using conventional technology.

Separate coal samples were prepared from each of the as-received (ar) well mixed coal samples by: (i) washing with water, and (ii) washing with HCl at a number of pH values. Acid-washed (aw) coals were prepared by heating a mixture of water, HCl, and the coal samples, at given values of pH 0–4; some samples were also treated with H₂SO₄, as described previously [1,18]. A sample of ultra-low ash coal obtained by the CCT process has been included to illustrate the removal of silicates; this was prepared by washing with a mixture of acids; removal of silicates and clays was done by treating the coal samples with hydrofluoric acid (HF).

The addition of various inorganics to prepare coal samples for catalytic steam gasification was carried out using the step-wise addition method discussed in [18,19]. Briefly, the acid-washed coal was mixed with a solution of the inorganic salt, and the pH of the mixture adjusted using a solution of NaOH. Samples of coal were prepared containing various amounts of Fe, Co, Ni, Ca and K salts.

2.3. Assessment of catalytic activity

All data were obtained by carrying out experiments using identical conditions for aw coal and the same coal containing the particular inorganic. Enhanced reactivity in air was assessed by measuring the weight loss of the treated coal sample when heated in air; enhanced reactivity was indicated by complete weight loss of the coal sample at 120–200 °C (this may be compared to a relatively small weight loss was observed for untreated coal samples until they were heated to above 300 °C, with volatiles lost at ~ 400 °C).

Pyrolysis experiments were performed to obtain a distribution of char, tar and gases using a closed glass retort vessel which could be weighed before and after each experiment, as described in [20]. Detailed experiments were also carried out to obtain weight losses under a stream of Helium (pyrolysis), and Helium and steam (gasification), for aw coal samples, and aw coal samples with added inorganics; the weight loss under steam over 10 and 15 min, was used as a measure catalytic activity. These pyrolysis and gasification experiments were performed by placing a porcelain boat holding the coal sample into the quartz reactor at a set temperature of between 200 °C and 900 °C, and Helium gas passed at an accurate rate through a round bottom flask containing gently boiling water, the vapour of which then flowed through the quartz reactor, as discussed in [21]. The product gases exiting the quartz reactor were passed through a water trap cooled in an ice bath, and a sample obtained in an IR gas cell for FTIR analyses. Gas was obtained using a sampling loop for on-line GC analysis. GC analysis was performed using a double column Shimadzu GC-4B PTF, with a silica gel 60/80 packed column, specific for H₂, CO, CO₂, and CH₄, and a thermal conductivity detector. The temperature of the column was kept constant at 65 °C, the detector at 50 °C, and the injection loop at 120 °C; the flow rate of gases was 80 ml/min. Data

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