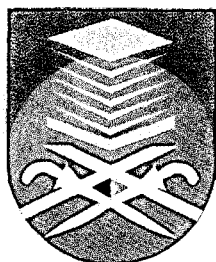


**SPECIATION AND DESULPHURISATION OF
SULPHUR FORMS IN COALS AND DERIVATIVES
AND PETROLEUM RESIDUES**



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JUNE 2001

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ABSTRACT

Combustion of coals to produce electricity has created environmental problems, one of which is sulphur which is converted to SO_2 and SO_3 gases. In order to produce a “clean coal”, the pretreatment processes of sulphur removal from coal have to be effective to remove the inorganic (pyrite) and organic sulphur forms (thiolic, sulphidic and thiophenic).

High pressure Temperature-Programmed Reduction (TPR) has been used for specifying the distribution of organic sulphur forms in both pyrite-free Malaysian (Mukah Balingian) and Indonesian coals (Banjarmasin Hj. Ali-Aliansar and Banjarmasin Coal A). The results obtained thus far, indicate that *ca.* 95% and 75% of sulphidic functionalities are present in Mukah Balingian (MB) and Banjarmasin Coal A (BMA), respectively, with 70% thiophenic forms are present in Banjarmasin Hj. Ali-Aliansar (BMHAA).

In this study, several methods have been developed to remove the inorganic sulphur forms from local coals. Two reducing agents namely lithium aluminium hydride and chromous chloride and the use of hydrogen peroxide as an oxidising agent, have been identified to successfully remove the pyrite from Malaysian sub-bituminous and bituminous coals. About 10 to 50 weight % and 10 to 20% of sulphur and ashes are reduced respectively, using both reducing and oxidising agents. The acidic chromous chloride and lithium aluminium hydride procedures offer an improve method for pyrite removal in coal. The Scanning Electron Microscopy (SEM) micrographs show a minor alteration to the coal microstructure as a result of acidic chromous chloride and lithium aluminium hydride chemical reducing treatments. However, with hydrogen peroxide

treatment, the SEM micrograph reveals the formation of depressions, microfissures and fragmentation of the coal microstructure into smaller particles. Further, the Energy Dispersive X-ray (EDX) analysis indicates that the concentration of iron (Fe) is greatly reduced in treated coal indicating that pyrite has been removed from the coal by the reagents.

The chemical desulphurisation of both inorganic and organic sulphur forms from high sulphur sub-bituminous BMHAA coal was investigated using the mild oxidising and reducing agents. The mild oxidising agent that used was peroxyacetic acid; a mixture of hydrogen peroxide in acetic acid, which is known to produce PAA in situ, is capable of removing up to *ca.* 62% of the total sulphur; both the inorganic (majority pyrite) and organic sulphur forms (*ca.* 42%) and approximately 10 – 50% of ashes in the coal. These organic sulphur reduction might be due to sulphides and disulphides, based on TPR analysis. The simultaneous removal of both inorganic and organic sulphur were measured with respect to time, reaction temperatures and reagent mixture ratios. The success of desulphurisation was measured by the reduction of the total sulphur content of the desulphurised product, its S/C atomic ratios. In general, desulphurisation from coal using mild conditions showed that the coal molecular structure were not severely affected. This was shown from results based on SEM-EDX, infra-red analyses and the slight reduction (1.1%) in the heating value. Consistent results were also achieved when PAA was applied on BMA coal, whereby 66% of the total sulphur is being reduced. Based on TPR results, 16% of the organic sulphur removal is probably due to simple sulphides functionalities. The optimum conditions for PAA was achieved by using 70 ml CH₃COOH : 30 ml H₂O₂ (concentration O₂ of 6%), reaction temperature at 50 °C with duration time of 24 hours.

Two reductive techniques were carried out for the removal of organic sulphur namely Single Electron Transfer (SET) and Nickel complex reducing agent (Nicra). The percentages of organic sulphur removal achieved using SET on BMHAA and BMA coals, were *ca* 52% and 10%, respectively. Further, the SEM-EDX analyses on the SET treated BMHAA coal at reflux temperature showed that, more fragmentation with an increase in porosity to the coal surfaces has occurred. The nickel complex reactions were carried out using nickel-THF (method A) and nickel-Bpy (method B). Initial results show that the ability of these reagents to remove mainly the inorganic (pyrite) sulphur from both of the Indonesian sub-bituminous coals.

Finally, further desulphurisation 46% and 30% were achieved using sodium benzoxide (NB) on the PAA-treated BMHAA and BMA coals, respectively. This proved the ability of NB to remove additional organic sulphur from both coals. These results strengthen the assumption that C-S bonds have been broken due to the weakening of the bonds during pretreatment oxidation (PAA) by the formation of sulphones, sulphoxides or sulphonic acid from the divalent sulphur species present in the coal after NB treatment.