The influence of imidazolium-based ionic liquids on the spontaneous combustion characteristic of hydrothermal hydrochars and hydrochar/coal blends.

Prepared by:

Ethel Tsholofelo Matsobane (888743)

Masters dissertation submitted to:

The School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Supervisor and Co-Supervisor:

Prof. Samson O. Bada and Prof. Bekir Genc

February 2023

ABSTRACT

Spontaneous combustion is a major problem facing South African coal mines. It is caused by the build-up of heat during oxidation, which eventually leads to the temperature of the coal reaching the point of ignition. The adverse effects of spontaneous combustion, such as the release of large toxic gases into the environment and the loss of valuable materials, called for a solution to the problem and for further new fuels to be explored. Biomass, hydrochar and hydrochar/coal blends have been proposed as alternative energy sources to coal to reduce greenhouse gas emissions. However, given that the new fuels are derived from biomass, which is highly reactive, there is a need to investigate their susceptibility to spontaneous combustion and preventative measures thereof.

This study assessed the factors that contribute to the spontaneous combustion of 100% coal discard, 100% biomass, 100% hydrochar, 25% hydrochar + 75% discard coal, 50% hydrochar + 50% discard coal and 75% hydrochar + 25% discard coal through their characteristics. The thermogravimetric analysis (TGA) and the Wits-Ehac apparatus were used to predict the spontaneous combustion susceptibility of the fuels. Those that were found to be highly susceptible to spontaneous combustion from the six were treated with three imidazolium-based ionic liquids, 1-butyl-3-methyl-imidazolium hydrogen sulphate [$Bmim^+HSO_4^-$] (IL-A), 1-ethyl-3-methyl-imidazolium hydrogen sulphate [$Emim^+HSO_4^-$] (IL-B) and 1-Butyl-3-methyl-imidazolium acetate [$Bmim^+OAc^-$] (IL-C), to inhibit their spontaneous combustion characteristic.

The physicochemical analysis results for the samples revealed an increase in the energy characteristic of the hydrochar produced from 100% biomass. In addition, the 100% discard coal was found to have low energy characteristics, however, the quality improved when it was blended with 100% hydrochar at different ratios. 100% biomass was found to have the highest moisture content, volatile matter and oxygen content at 8.01%, 60.52% and 37.67%, respectively. Additionally, the sample was also found to have the lowest ash content, fixed carbon, and total carbon at 2.92%, 19.54% and 44.60%, respectively. As a result, 100% biomass is highly susceptible to spontaneous combustion compared to other fuels. The Fourier Transform Infrared Spectroscopy (FTIR) analysis results revealed that all samples had a transmittance of the C=O stretch, which is known to promote spontaneous combustion. The fingerprint region of the FTIR spectra of the samples showed that the 100% discard coal had the highest mineral content, which

tends to inhibit spontaneous combustion. Whereas 100% biomass had the lowest mineral content in comparison to other fuels, making it more susceptible to spontaneous combustion.

The TGA results showed that 100% biomass is highly reactive with a TG_{spc} index of 0.1457 %/ ˚C.min, while 100% discard coal was found to be non-reactive with a TG_{spc} index of 0.0135 %/ ˚C.min. The remaining fuels were classified as low reactive given that their TG_{spc} index was between 0.02 and 0.03 %/ ˚C.min. A significant correlation was seen between the TGA susceptibility data and the physiochemical properties of the samples. The Wits-Ehac results showed that the 100% biomass had the lowest spontaneous combustion susceptibility index of 3.49, while the 50% hydrochar/50% discard coal blend was found to have the highest spontaneous combustion susceptibility index of 4.79. The remaining fuel was classified as medium risk as their Wits-Ehac values ranged from 3 to 5. No correlation was found between the TGA and Wits-Ehac spontaneous combustion results, as the Wits-Ehac results showed some inconsistencies, especially for samples derived from 100% biomass. In addition, the Wits-Ehac results were inconsistent with the characterisation results from the samples.

The three imidazolium-based ionic liquids were used to treat 100% biomass to inhibit its spontaneous combustion characteristic, as it was the only sample that was highly susceptible to spontaneous combustion. The TGA results from the treated biomass showed that 1-butyl-3-methyl-imidazolium hydrogen sulfate [$Bmim^+HSO_4^-$] (IL-A) and 1-ethyl-3-methyl-imidazolium hydrogen sulfate [$Emim^+HSO_4^-$] (IL-B) reduced the TG_{spc} index of 100% biomass from 0.1457 %/ ˚C.min to 0.0839 and 0.0576 %/ ˚C.min, respectively at a lower heating rate. The two imidazolium-based ionic liquids were found to be inefficient in inhibiting the spontaneous combustion of 100% biomass, as the samples were still classified as highly reactive after treatment. 1-Butyl-3-methyl-imidazolium acetate [$Bmim^+OAc^-$] (IL-C) showed the best inhibitory effects given that the TG_{spc} index of 100% was reduced to 0.0207 %/ ˚C.min, and the sample was classified as low reactive after treatment. The results of the physicochemical analysis showed that after IL-C treatment, the physicochemical properties, textural properties and microstructure of the 100% biomass improved significantly.