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Transformation of nitrogen functional forms and the accompanying chemical-structural properties emanating from pyrolysis of bituminous coals

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HIGHLIGHTS

- Transformations in N functionalities and carbon crystallite structures were examined.
- Pyrolysis caused the change in aromaticity to correlate with quarternary-N of chars.
- Diminishing pyrrolic-N in chars correlated with the degree of disorder index (DOI).
- Total reactive macerals in coal influence morphological changes at high temperatures.
- Vitrinite- and inertinite-rich coal chars displayed similar and varying N forms.

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ABSTRACT

Characterisation of simultaneous changes in nitrogen functionalities and condensed aromatic crystallites during pyrolysis of bituminous coals was conducted. X-ray photoelectron spectroscopy (XPS) was utilised to determine nitrogen functional forms in three South African bituminous coals and the subsequent transformation in respective chars. Corresponding structural properties of coal and char were deduced through X-ray diffraction (XRD) analysis. Carbon structural properties in parent coals were also determined by solid state ^{13}C nuclear magnetic resonance (ss NMR). The chars were prepared by pyrolysis at 740–980 °C in a bench-scale fluidised-bed (FB) and at 1000–1400 °C in a drop-tube furnace (DTF). The changes in XPS N 1s spectra of the coals through the respective chars were used to determine the nitrogen functionality transformations. Deconvolution of the XPS N 1s spectra revealed that pyrrolic nitrogen decreased with increasing pyrolysis temperature while quaternary nitrogen increased appreciably. Simultaneously, information deduced from XRD spectra showed that aromaticity (f_a) and average crystallite diameter (L_a) increased with severity of pyrolysis temperature in all the chars, while the fraction of amorphous carbon (X_A) and degree of disorder index (*DOI*) decreased significantly. Chars derived from the vitrinite-rich (also high in total reactive macerals) coal were more susceptible to thermal treatment with regard to nitrogen functional forms and other carbon crystallite transformations; high temperature chars only contained pyridinic and quaternary nitrogen, and exhibited a significant increase in crystallite height (L_c) and the average number of aromatic carbons (N_{ave}). Aromaticity of coals determined from ss ^{13}C NMR and XRD corresponded. Comparison of structural changes brought by pyrolysis, as measured by XPS and XRD, showed that a good correlation existed between increasing quaternary nitrogen and f_a. In a marked contrast, the diminishing of pyrrolic nitrogen displayed a good efficacy with *DOI* and X_A. The reported concomitant transformations of nitrogen functional forms with char morphological changes are considered precursors to nitrogen release. This will inform future detailed studies on the conversion of coal nitrogen in solid fuel fired systems, such as in the applications of low-NOx burner technologies towards the release and reduction of nitrogen oxides in pulverised coal combustion.

1. Introduction

Coal is integral to the economies of several countries and regions around the world as it provides reliable and affordable power required to meet electricity demand and fuel economic growth. Bituminous coals are mostly used for steam production in the electric power generation

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industry across the globe. When coal is introduced into a combustion or gasification chamber it goes through pyrolysis (devolatilisation) during the primary stage of combustion or gasification which results in coal nitrogen to be partitioned into char nitrogen and volatile nitrogen, of which the volatile-N consist of NH_3, HCN and tar-N [1–4]. Nitrogen oxides are formed during the subsequent combustion. Coal-N is the dominating source of nitrogen oxides in most solid fuel combustion systems [5], contributing more than 80% from pulverised coal combustion [6], and almost all the NOx (NO and NO_2) and nitrous oxide (N_2O) emissions from fluidised bed combustion [7]. Once devolatilisation is complete, char-N becomes the source of subsequent nitrogen release during pyrolysis/combustion/gasification [4,8]. NOx has been condemned for causing acid rain, ground level ozone and photochemical smog, while N_2O is a potent greenhouse gas that has been blamed for indirectly depleting the ozone layer [9].

The complexity and heterogeneity of coal and its subsequent products presents the most persistent difficulty in characterisation endeavours. A variety of coal structural models have been proposed as a result of its inherent heterogeneous nature [10]. Hence the need to employ different conventional and novel advanced characterisation techniques to elucidate the structure of coal and related substances. Some of the advanced analytical techniques that have been utilised by many researchers to elucidate coal or char molecular chemical structure include XPS, solid state nuclear magnetic resonance (ss ^{13}C and ^{15}N NMR), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. These analytical methods have been applied on coal and char analyses with variable outputs [11–16]. Nonetheless, coal structure and related substances which include coal chars are still yet to be fully understood. The comprehension of chemical and physical processes that determine formation of nitrogen oxides during combustion of solid fuels continue to pose a challenge despite considerable research having been conducted in the past four decades [5]. Quite a number of studies have tried to correlate NOx emissions to coal properties, however, so far there is no generic relationship or model that precisely predicts the level of nitrogen oxides beyond the data set upon which it was established. Almost all of the correlations were dependent on the application of basic coal attributes determined by the standard proximate and ultimate analyses [17–19]. There are issues that limit the potential reduction of nitrogen oxides that still require to be resolved. Further enlightenment of nitrogen chemistry in solid fuel fired systems is beneficial towards the improvement of primary measures for the control of nitrogen oxides.

In general, coal contains about 1–2% nitrogen by weight (daf) [20,21], most of which exists as organically bound N-containing heteroatomic ring structures [21,22]. Nitrogen in coal organic fraction originates from proteins of plants and micro-organisms, of which most of the proteins were transformed by biological reactions during the early stages of coalification resulting in different types of nitrogenous compounds being formed [23]. X-ray photoelectron spectroscopy (XPS) analyses on coals and chars have revealed that these heteroatomic structures mainly exists in the form of pyrrolic (N-5), pyridinic (N-6), quaternary (N-Q) and to a lesser extent, as protonated and/or oxidised pyridinic (N-X) nitrogen structures [24–26]. In exceptional circumstances a fifth nitrogen form, nitro type complexes (-NO_2), with binding energy above 405 eV has been reported in chars and model compounds [25,27].

XRD has traditionally been utilised for qualitatively and quantitatively analysing the mineral constitution of coal. However, the technique has also proven to be a powerful tool in elucidating carbon crystallite properties of demineralised coals and structural transformations occurring in respective de-ashed chars due to heat treatment [28–32]. ^{13}C NMR spectroscopy has been utilised to elucidate the structural differences between coals, tar and char [33–35]. XPS has been widely utilised for determining and quantifying nitrogen functional forms in complex solid and non-volatile carbonaceous systems, including in the transformation of nitrogen species during pyrolysis of coal and model compounds [24,25,27,36–38]. The distribution of nitrogen functional forms varies with increasing intensity of pyrolysis conditions [25,39].

During pyrolysis, the heteroatoms are removed through devolatilisation of nitrogen, sulphur, and oxygen compounds, decreasing the number of these edge-located atoms and causing carbon structure rearrangement [40]. In high temperature chars, N-Q becomes the prominent form of nitrogen. The edge-located nitrogen species (N-5 and N-6) are liberated into the volatile stream as NH_3, HCN, N_2 or conveyed as part of the tar molecules [41–43]. Pels et al. [25] showed that carbazole, a rich source of N-5, at temperatures exceeding 800 °C a significant portion of N-5 was transformed into N-6 and N-Q. In addition, acridine which is a source of N-6, lead to the conclusion that heat treatment transforms a portion of N-6 into N-Q. Quaternary nitrogen can emanate from both organic and inorganic origins [44–46].

A great portion of Gondwana coals of the Permian age are bituminous coals and an infrequent existence of anthracites [47,48]. Some of the coals in the southern Africa region share similar attributes with the coals that also emanated from the splinter Gondwana regions that encompass India, Madagascar, Australia, Antarctica and South America [48,49]. These coals are characterised by high levels of mineral matter and inertinite content [47,50]. However, there is contrast that is exhibited by the age and basins of the coals. The Carboniferous coals of the Laurasian region (northern hemisphere) are generally high in vitrinite and contain low mineral matter [51]. The North Atlantic coals of the Palaeozoic and Mesozoic age show an average petrographic composition that is dominated by vitrinite with averages of 70% and 74% (mmf) respectively. Nonetheless, the Gondwana counterparts of the same age also displayed maceral compositions dominated by vitrinite, but much less, averaging 52% and 65% (mmf) respectively [52]. In further comparisons, Vasconcelos [52] stated that coals of the Tertiary emanating from both the North Atlantic and Gondwana territories have similar petrographic compositions with vitrinite ≈80% and inertinite ≈10% (mmf). Generally, coals in South Africa (SA) are Permian, apart from a very small deposit in the Molteno area, which is Tertiary. The Main Karoo Basin hosts the Free State-, Witbank-, Highveld-, Ermelo- and KZN coal deposits, which formed around a large inland delta. Coals are typically inertinite-rich and mineral matter content that is quite high [49]. The Limpopo Province Coalfields, which includes the Waterberg Coalfield, were formed in small basins tectonically different in that they were half grabens or grabens [47]. The coals in these coalfields are typically vitrinite-rich and high in mineral matter content. South Africa is one of the countries that are heavily dependent on coal, a substantial portion of the SA's liquid fuels are produced from bituminous coals, the coals are also utilised to generate more than 90% of the country's electricity [53].

The behaviour of nitrogen that is inherently present in coal, which is the major source of nitrogen oxides, needs to be closely monitored during coal conversion processes to enable coal optimum utilisation with minimum environmental implications. The manifestation of such achievements, that will ensure prolonged usage of coal, require close examination on the transformation of nitrogen within the immediate carbonaceous environment of coal-chars towards aspirations to gain an in-depth insight into the release of nitrogen species. There appear to be a need for systematic studies that simultaneously monitor the association of nitrogen functional forms with the accompanying changes of carbon crystallite properties during coal pyrolysis. Previous studies by other researchers were exclusively focusing on either nitrogen functionalities using XPS or the elucidation carbon structural properties deduced from XRD. This study aims at evaluating the simultaneous transformation of nitrogen functionalities and condensed aromatic crystallites during pyrolysis of SA bituminous coals in a bench-scale bubbling fluidised bed (FB) and drop-tube furnace (DTF) through the application of a battery of analytical methods, mainly incorporating XPS and XRD, respectively. The crux of the matter is to establish an