Chemical and physical modifications of coal and torrefied biomass blends during high pressure pyrolysis

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Africa is largely reliant on bioenergy as a fuel source, while South Africa still remains heavily dependent on fossil fuels (IEA, 2019). Synthetic fuel production and electricity generation remain the major coal consuming technologies in the country, accounting for almost 86% of its coal use. The addition of renewables in these sectors can yield significant transition in the energy mix (DMR, 2016). In order to meet the envisaged energy mix, coal use in South Africa is expected to reduce by approximately 18% before 2030 and 32% by 2040 (IEA, 2019). For this reason, the South African department of energy released an integrated resource plan (IRP 2010 – 2030), proposing a 20% contribution by renewables in the country's 2030 energy mix, which will be motivated by mechanisms such as the allocation of carbon credits (IEA, 2018; DOE, 2019).

The fixed-bed dry bottom (FBDB) gasification technology is used to covert 30 million tonnes of coal into synthetic fuel annually (van Dyk et al., 2006). These gasifiers have the added benefit of being able to accommodate a variety of carbonaceous material as feed, allowing for the use of not only coal, but also biomass for the generation of fuel (van Dyk et al., 2006). Lignocellulosic biomass is a second generation feedstock that has enjoyed great attention in the fuels generation field, but its sole use poses some limitations, which include low energy density, seasonal availability and high tar yield. It has therefore been crucial to evaluate biomass pre-treatment along with co-utilisation with coal for industrial applications (Pinto et al., 2017; Rentizelas et al., 2009).

In a review by Gouws et al., (2021), it was shown that various authors have evaluated the use of biomass and coal, investigating the effect of temperature and pressure on the char, tar and gas produced during pyrolysis. These studies focussed predominantly on temperatures up to 600°C, when elevated pressures we employed during slow pyrolysis (Gouws et al., 2021). In this paper, the effect of pressure on the chemical and morphological characteristics of coal and torrefied biomass blends is evaluated during pyrolysis at higher temperature up to 900°C.

A South African medium rank C, bituminous coal was used, together with a blend of softwood and hardwood chips from South African Pulp and Paper Industries (SAPPI). The coal was crushed and the -1 mm fraction used for the study. The woodchips were torrefied at 280°C, using a pilot plant scale continuous rotary kiln with a diameter and length of 0.3 m and 2 m, respectively. The torrefied biomass was crushed to below 1 mm prior to use. 3 Samples were prepared, containing coal, torrefied biomass and a 50/50 char blend. The proximate analyses of the samples can be seen in Table 1, indicating that the ash yield, volatile matter and fixed carbon were additive for the blended sample.

Table 1 Proximate analyses of the coal (CL), torrefied biomass (TBM) and the blend (MX)

Sample*	**TBM**	**Coal**	**Blend**
Inherent Moisture	2.3	2.7	4.8
Ash Yield	2.0	18.0	8.6
Volatile Matter	69.7	23.6	48.3
Fixed Carbon	26.0	55.7	38.3

*air-dried basis

These samples were pelletized by means of drum rotation, rotating at 33 rpm using 1 wt% starch addition. For the study, 9.5 – 16.0 mm pellets were utilised. The pellets were placed in a sample holder, which was inserted in an 80 mm cylindrical horizontal tube. A back pressure regulator was used to pressurise the tube to 1, 15 or 30 bar using nitrogen from AFROX with a purity of 99.99% flowing at 5 nL/min. The tube was heated to 500, 700 or 900°C using a Lenton horizontal tube furnace at a heating rate of 5°C/min, and the temperature was maintained for 30 min. Nitrogen was supplied continuously, until the oven cooled to 100°C. The volatiles produced, we

trapped at pressure using stainless steel tubes supplied by Swagelok. Upon cooling, the chars were retrieved and will be referred to using the pyrolysis temperature and pressure, e.g. 1TBM700 refers to a torrefied biomass char sample produced at 1 bar and 700°C. Both the raw material and chars were characterised by means of proximate, ultimate and XRF analyses. The effect of pressure on the structural properties of the samples was evaluated by means of SEM and CO_2 adsorption, while the reactivity was evaluated by means of thermal gravimetric analysis. The effect of temperature and pressure on the char yield can be seen in Figure 1.

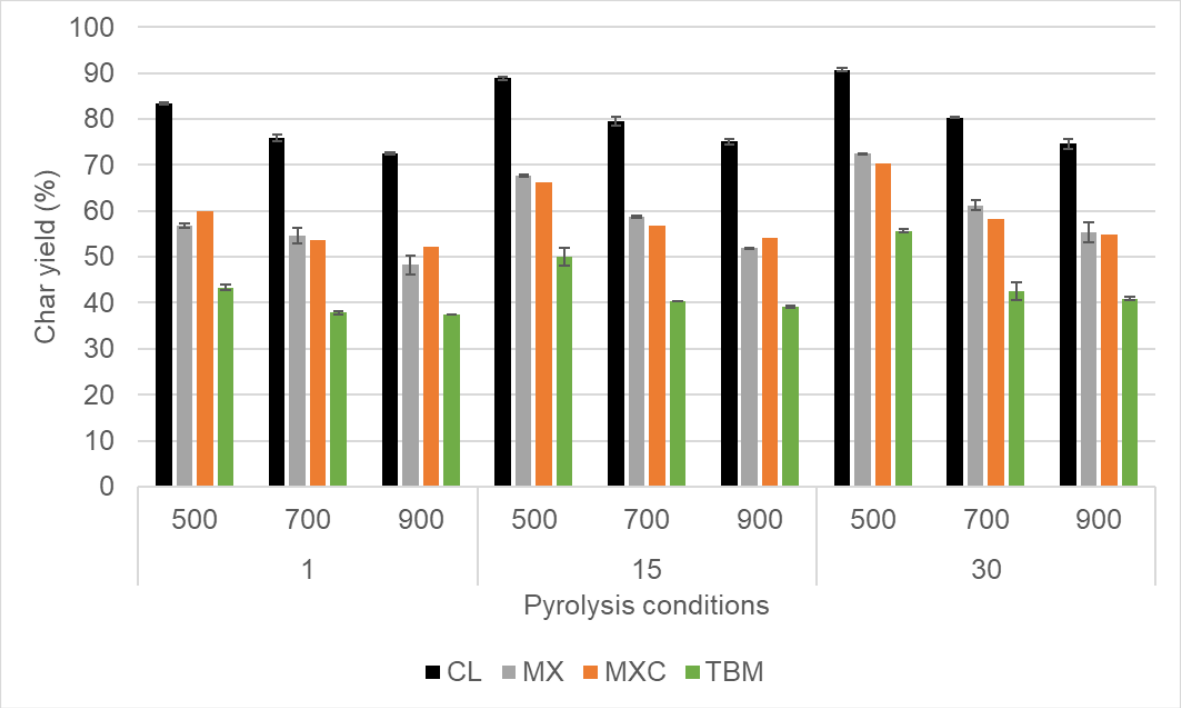

Figure 1 The effect of temperature and pressure on the char yield of coal (CL), torrefied biomass (TBM) and the blend (MX) compared to the calculated blend char yield (MXC)

It can be observed that the char yield of all the samples reduced with temperature, while increasing with pressure. The effect of pressure was less prominent after 15 bar. The increase in char yield, due to pressure, has been attributed to secondary tar reactions that lead to the retention of low molecular weight tars on the char produced (Wu et al., 2000). Similar to Gouws et.al, (2021), no synergistic effects were observed for the char yield. Preliminary CO_2 adsorption results can be seen in Table 2. From the Brunauer–Emmet–Teller (BET) and Dubinin–Radushkevich (D-R) methods, it can be seen that the micropore surface area reduced with increasing pressure, which was less pronounced at high temperatures. Cetin et al., (2004) made a similar observation, attributing it to the disappearance of the micropore structure and the increase of larger cavities.

Table 2 Effect of pressure on the BET and D-R micropore surface area

Sample	**BET micropore surface area (m^2/g)**	**D-R micropore surface area (m^2/g)**
1TB500	200	310
15TB500	143	210
30TB500	134	191
1TB900	293	414
15TB900	262	353
30TB900	235	416

Pressure (up to 15 bar) was found to have a significant effect at the lower temperature ranges. The effects of pressure on the characteristics and reactivity of the chars will be evaluated in the paper.

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