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Effect of Polymer Blending on the Properties of Coal Tars Produced by Pyrolysis

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Abstract

Pyrolysis of coals to produce cokes is an important part of the ironmaking process. Coal pyrolysis to coke is an energy-intensive process and involves the transformation of the coal from a soft carbonaceous material to a hard coking structure. During this process, volatiles present in the coke are released and coal tar is extracted, and this has numerous applications as a source of various chemicals for different industries as well as carbon for anodes. This work investigates the effect of blending different amounts and proportions of waste polymers with coals in order to enhance the coal tar yield and to modify the chemical product characteristics. Coal and polymer blends were pyrolysed at 500°C and the tar and volatile compounds were collected by condensation. The collected tars (solid and liquid) were characterised using gas chromatography-mass spectrometry (GC-MS) to determine the major components. Further analysis of the proportions of the major organic components was conducted using solution NMR analysis. When blended with the polymers, all the coals showed a proportional increase in their tar yields. The highest yields were observed with the addition of polystyrene (PS), followed by rubber tyres (RT), while polymers with aliphatic chains produced lower yields. This work has shown potential for enhancing the coal tar yield and for modifying coal tar properties through polymer addition, which can add further value by providing additional uses for pyrolysis products and by removing waste polymers from the disposal stream.

Keywords: Coal pyrolysis, Polymer addition, Coal tar, Ironmaking

1. INTRODUCTION

Coke quality is very important for blast furnace steelmaking or smelting processes; the coke performance is strongly influenced by the properties of the parent coals. The coke has to be sufficiently strong to support significant loads in the blast furnace and reactive to act as a reducing agent to convert ferrous ores to hot metal, while also providing structural support to ensure good permeability that allows the flow of gases and discharge of slag and hot metal. Different coal types are formed naturally owing to variations in physical and chemical changes that occur with temperature, time, and pressure over long periods of time. Coal formation occurs via the transformation from peat to lignite to bituminous coal and finally to anthracite. A narrow range of bituminous coals with mean maximal vitrinite reflectance (R_0 mean) values of 0.6 to 1.6% are generally classified as coking coals owing to their unique ability to melt when heated in the absence of air. Generally, lignites, sub-bituminous, semi-anthracites, anthracites, and meta-anthracites do not melt and are hence categorized as non-coking coals. Coal also consists of different microscopic constituents known as macerals. Vitrinite, semi-vitrinite, and exinite components are reactive macerals as they produce plastic mass in a temperature range of 330°-360°C while inertinites generally exhibit negligible or no plasticity and are hence referred as inert macerals. Fluidity is controlled by the relative proportions of plastic (vitrinite + liptinites) and inert components (inertinite + mineral grains) **(Gray et al 1988).**

In the coke-making process, coal is pyrolysed at about 1100°C in an oxygen deficient atmosphere. The softening and flow properties (rheology) of the coal are strongly influenced by the coal rank and maceral composition. Coal pyrolysis involves carbonisation, gasification, and combustion. During carbonisation at ~350°C, coal starts to lose moisture and forms unstable plastic phase (metaplast). This phase then forms semi-cokes by losing primary volatiles at temperatures of 350°-450°C, which then intensifies at temperatures of 450°-550°C. This process causes an increase in the density of the semi-coke and releases secondary volatiles such as methane and hydrogen (**Habermehl et al 1981**). During the primary pyrolysis stage, the coal starts to soften as the weak aliphatic bridges connecting large aromatic clusters in the coal matrix are cleaved to produce metaplast (**Fitzgerald 1956; Krevelen 1993).** The fluidity increases with an increase in the concentration of metaplast (**Rouzaud et al 1988**). At the same time, these molecular fragments containing one to several aromatic ring structures are released as tar. Some functional groups as well as labile bridges attached to aromatic clusters will be released as gases such as CO, CO_2, and low molecular weight hydrocarbons. At the higher temperatures, the coal loses its fluidity, and condensation reactions start as aromatic structures repolymerise to form larger aromatic structures.

Coal fluidity increases with the total percentage of reactive macerals, depending on the rank range, and this effect is most likely attributed to the differences in hydrogen levels of vitrinite grains of coals of different ranks **(Ryan et al 1998)**. Often inert macerals decrease the maximal fluidity as well as the plastic temperature range **(Predeanu et al 2009)**. However, the inertinites do not have a significant influence on the fluidity within the plastic temperature range, due to large aromatic cluster size, lower substitution of alkyl- and oxygen functional groups in aromatic rings, and higher density of cross-linking **(Kidena et al 2002)**. Ash phases also play a role in the fluidity. Iron oxides can increase the total surface area of inert phases and also it can catalyse the polymerisation reactions of the intermediate products to produce char at the expense of tar and gases **(Mochida et al 1976)**.

Polymeric additives can modify the chemical compositions of the tars as well as improve their rheological behaviour. The addition of macromolecular polymers such as polyester resin or polyethylene glycol could decrease the benzo-a-pyrene (BAP) content in coal tar pitches by more than 90%. Researchers **(Brzozowska et al 1998)** examined the effect of addition of 10 wt% of a range of polymers including PVC, PS, PP, PET and PEG on the coke quality in a temperature range of 100°-350°C. These polymers were shown to modify the softening point, penetration, and toluene insoluble content even though no clear correlation was established with the product yield; moreover polystyrene, PET, polypropylene and polysaccharide addition increased the semi-coke yield. **Grzyb et al (2003)** studied the co-pyrolysis of coal tar pitch with polyacrylonitrile (PAN); the carbonization behaviour of the pitch was modified such that the resultant semi-cokes contained pyridinic or pyridonic nitrogen-containing groups. The present work focusses on the effect of adding different polymers to coals to determine the changes in the coal tar yield and characteristics during pyrolysis.

2. EXPERIMENTAL

2.1 Sample selection

Three coal samples (A, B, C) and six polymers (PET, PS, HDPE, LDPE, PP, Rubber tyres (RT)) were used for this work. The properties of the coals and the polymers are not listed owing to proprietary issues. Different blends were prepared with weight proportions ranging from 0-30 wt%. The coals were crushed in a tungsten carbide ring mill while the polymers were crushed cryogenically in a Spex Cryo Mill; then the particles were sieved to ensure a size range of 200-425 μm for the particles.

2.2 Low Temperature Pyrolysis

A horizontal tube furnace with a quartz tube reactor was used for the pyrolysis of the coal blends. 10 g of the samples (coal or coal + polymer blend) was placed at the closed end of the quartz tube, while the other end was designed to go into a sealed collecting vessel. The temperature at the open end was close to room temperature. The furnace had a rapid heating system; so it was possible to reach the target temperature within 30 min. This removed any potential of tar formation at lower temperatures which might affect the measurements. The tar portion produced from the coal pyrolysis experiments was found to be a mixture of a black solid portion in a clear liquid portion. This was collected in the vessel and subjected to GC-MS analysis. The char residue found in the reactor tube was extracted by firstly breaking the tube, and the removing the char into another collection vessel.

2.3 Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

The GC-MS analysis was conducted at the Bioanalytical Mass Spectrometry Unit at UNSW using a Thermo DSQ II mass spectrometer interfaced to a Thermo Trace gas chromatograph and Triplus autosampler (Thermo Fisher Scientific, Waltham, MA). This was operated in electron impact GC-MS mode for all analyses. A Restek Rxi-Sil MS 30 m x 0.25 mm inner diameter, 0.25 µm film, GC column (Restek Corp., Bellefonte, PA) was installed in the split inlet of the gas chromatograph with an SGE split Focus liner. The inlet was maintained at 305°C and the helium carrier gas set to a constant flow rate of 1.8 mL/min. The ion source of the MS was maintained at 200°C and the detector gain set to $3x10_5$. The autosampler used 10% dichloromethane in acetone (v/v) as a syringe wash.

The samples consisted of a mass of semi-solid black tar immersed in a clear viscous liquid. The solid and liquid phases were analysed separately, using slightly differing methods. In the case of the tar, 20 mg of the solid was weighed and then extracted in 2 mL of 10% dichloromethane in acetone (v/v). After vortexing for 5 min, the samples were allowed to settle and then the upper 1 mL of tar solution was decanted into GC-MS vials. The clear liquid phase surrounding the tar in the original samples was decanted directly to GC-MS vials. 0.5 µL of the liquid phase was injected into the heated GC inlet at a split ratio of 75:1. The initial oven temperature was 40°C and the sample was held for 6 min. The oven temperature was then increased at a rate of 3.5°C/min to 190°C, then at 15°C/min to 290°C, where it was held for 4 min. The GC transfer line was maintained at 295°C throughout the run and the MS was programmed to scan from m/z 34-350 at a rate of 3.5 scans per second. The MS was switched off during the first 1.8 min of the run to protect the filament. 1.0 µL of the tar extract was injected into the heated GC inlet at a split ratio of 20:1. The initial oven temperature was 40°C, held for 6 min. The oven temperature was then increased at a rate of 3.5°C/min to 190°C, then at 15°C/min to 305°C, where it was held for 7 min. The GC transfer line was maintained at 310°C throughout the run and the MS was programmed to scan from m/z 34-550 at a rate of 3.5 scans per second.

Extracted ion chromatograms for the desired m/z range were plotted. This approach was preferred to analysis of total ion chromatograms (TIC) because some argon (m/z 40) was seen in the samples that produced baseline lift in the early part of the chromatograms, complicating visualisation of the relevant compounds and their intensities. Eluting compounds were identified by comparison of their baseline-subtracted mass spectra with those contained in the Wiley 9 / NIST 2011 Mass Spectral Library. Identifications with a match score greater than 900/1000 were considered valid.

2.4 Nuclear Magnetic Resonance (NMR) Analysis

NMR spectroscopy was performed on a Bruker Avance III HD 600 (600.13 MHz, ^1H) equipped with a 5 mm TCI probe cryoprobe. NMR spectra were processed using the Bruker TOPSPIN 3.5 software. Samples were dissolved in D_2O and solvent suppression was performed with a presaturation pulse program modified with a composite pulse used for the suppression. Spectra were obtained with a sweep width of 7195 Hz yielding an acquisition time of 4.55 s. A delay of 5 s was used and 56 scans were recorded.

3. RESULTS AND DISCUSSION

In general, the addition of polymers was seen to cause an increase in the amount of tar-containing extract from the coals. Polystyrene, rubber tyres, and polypropylene were observed to be the most promising additives in enhancing the yield of the tar-containing extract from the coals. Blending with HDPE, LDPE, and PET were observed to produce the lowest volumes of tar-containing extract. However, in the case of HDPE and LDPE, the chars could not be removed easily owing to it being bonded to the surface of the quartz reactor tube with some tarry substance and thus this resulted in an error in the calculation of the yields of the chars. Coal B produced the highest amount of tar, while Coals A and B showed similar amounts.

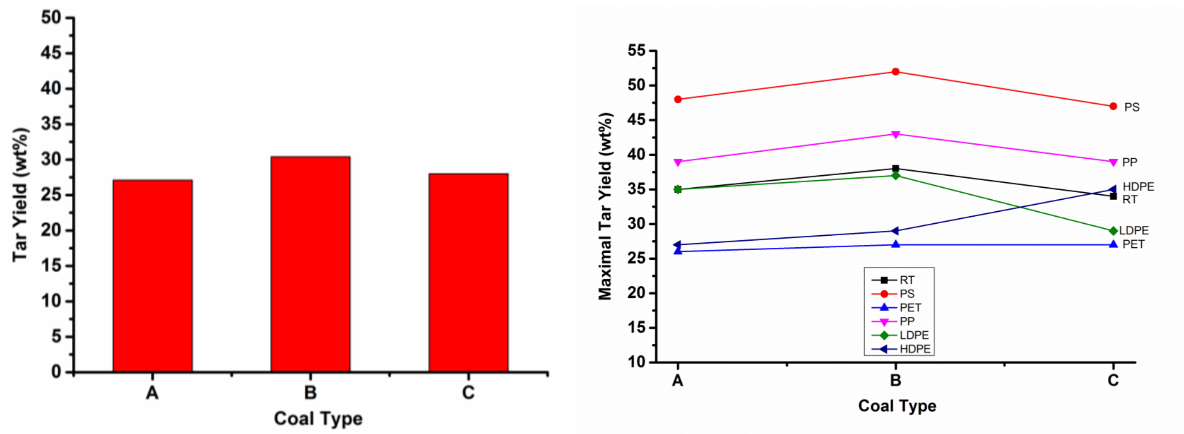

Figure 1. ***Comparison of maximal tar yield for each coal and for each of the coal/polymer blends***

For the liquid portion, phenol was the major component in most cases, with catechol being in quite high levels as well; there were generally substantial levels of cresols, dimethyl benzendiols, and minor amounts of acetic acid, benzoic acid, methyl catechol in most samples. For the solid portion, toluene was the major component in all samples; styrene and ethyl benzene were the additional major phases in blends containing PS while hydoxy methyl pentanone was the additional substantial phase in PP containing samples. Minor amounts of decanol, monoterphthalate, limonene, cymerene, biphenyl, naphthalene based products, aliphatic and aromatic compounds (with 22-28 carbons) were found in some of the tar samples. For the liquid portion,
PET addition resulted in a substantial increase in acetic acid and benzoic acid; rubber tyre addition caused a substantial increase in cresols and minor increases in styrene and benzaldehyde, PS addition resulted in a minor increase in ethyl benzene and styrene; PP addition resulted in a minor increase in catechol and benzenediols, LDPE addition resulted in substantial increase in cresol, and HDPE addition resulted in a minor increase in acetic acid and cyclopentanone.

For the solid portion, PET addition increased the amounts of benzaldehyde, phenol, cresol, acetophenone, monoterepthalate, RT addition increased the amounts of phenol, limonene, cymenene, acetophenone, cresol, PS increased significantly the amount of styrene and ethyl benzene, phenol, and naphthalene; PP addition significantly increased the amount of hydoxymethyl pentanone; LDPE addition increased the amounts of long-chain hydrocarbons and HDPE addition increased the amounts of C28-C30 long chain hydrocarbons.

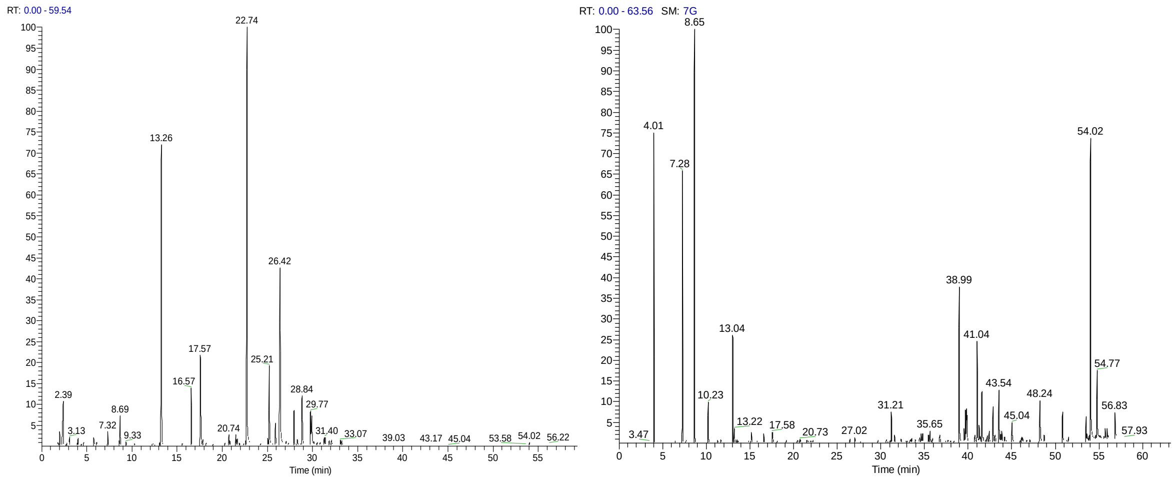

Figure 2: ***Typical GC-MS spectra for liquid fraction of blend with PS (left) and tar fraction of blend with PS (right)***

Analysis of the NMR spectra of coal samples treated with polystyrene showed the presence of phenol, p-cresol, methanol, acetate, and ethanol in significant quantities. The three samples with increasing polystyrene were virtually identical in content and with only minor variations in peak alignment attributed to pH variation between samples. The samples with increasing rubber tyre addition also contained all of the compounds listed for the coals containing polystyrene addition. The real difference between these systems is only clear at the lower concentrations where hundreds of compounds can be observed (these have not been identified). It is important to note that ethanol and methanol were not observed from the GC-MS analysis and this could be because these lighter compounds were lost from the sample during the testing process.

4. CONCLUSIONS

Polymers such PS and RT, which also contain aromatic rings in their structure are the most suitable compounds for improving tar yield and even low levels might be sufficient to cause a significant improvement. Semi-crystalline polymers with aliphatic chains such as PP and HDPE showed improvements only at high addition levels, while amorphous polymers with aliphatic chains such as LDPE showed an improvement at levels of high levels. Semi-crystalline aromatic ring-containing PET resulted in the lowest tar yields, which were generally lower than that seen for the parent unblended coals. The presence of aromatic group on the side-chain are preferable for improving the tar yields. Therefore, polymers with such characteristics are preferable for improving the tar yields. Furthermore, comparison of RT and PS shows that the relative number of benzene rings per unit monomer is higher in PS and this could be responsible for the significantly greater yield of PS-containing blends compared to RT-containing blends. The presence of O in the polymer appears to be hindering the formation of tar and this could be the reason for the low tar yields from the PET-containing samples. The higher yields of PP-containing blends compared to HDPE- and LDPE-containing blends suggests that the presence of methyl groups ($-CH_3$) could be enhancing the yield of tar, particularly at high concentration levels, compared to the presence of methylene groups ($-CH_2$) groups. The figure clearly shows that in general, the polymer addition enhanced the tar yield to a similar extent compared to the original coal. Therefore the nature of the coal has a synergistic effect on the tar yield from the blend. Phenols and Catechol were the major species in the liquid part of the tar for all the polymer additions. In addition, substantial amounts of cresol and methylated catechol were also seen in the samples. In the solid portion of the tar, toluene was the major component while ethyl benzene was seen in low to high concentrations

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