



The effect of syngas on tar quality and quantity in pyrolysis of a typical South African inertinite-rich coal



Beatriz Fidalgo^a, Daniel van Niekerk^b, Marcos Millan^{a,*}

^aDepartment of Chemical Engineering, Imperial College, London SW7 2AZ, UK

^bSasol Technology (Pty) Ltd., R&D Division, 1 Klasie Havenga Road, Sasolburg 1947, South Africa

HIGHLIGHTS

- Thermochemical processing of an inertinite-rich South African coal is investigated.
- Effect of syngas and addition of steam on quantity and quality of tar is studied.
- Tar yield increases when H₂/CO atmosphere is used and with the addition of steam.
- Tars with lighter MW distribution and larger aromaticity are obtained under H₂/CO.
- Tars with slightly broader and heavier MW distribution are obtained when adding steam.

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ABSTRACT

The influence of gas atmosphere on the quantity and quality of tar obtained from thermochemical processing of an inertinite-rich South African coal is reported in this work. The effect of syngas and steam on the produced tar is addressed. Experiments were carried out in a fixed bed reactor at 30 bar and four gas atmospheres: N₂, N₂ + steam, H₂/CO and H₂/CO + steam. Tar yield increased when H₂/CO was used instead of N₂. Additionally, the introduction of steam to the reaction atmosphere together with N₂ or H₂/CO gave rise to higher tar yields than those obtained under dry N₂ or H₂/CO alone. Tar quality was evaluated by size exclusion chromatography, simulated distillation, gas chromatography–mass spectrometry and infrared spectrometry. Tar evolved under H₂/CO atmosphere presented lighter molecular weight distribution than that obtained under N₂ atmosphere. Moreover, the presence of steam in the reaction atmosphere gave rise to tars with slightly broader molecular weight distribution, shifted towards heavier species. Although all tars exhibited wide variety of aromatic compounds, tar from H₂/CO experiment showed the largest degree of aromatization. The addition of steam to H₂/CO atmosphere yielded tar with lower degree of aromatization and oxygenated groups. In contrast, tar with higher degree of aromatization and oxygen functional groups were obtained when steam was added to N₂ atmosphere.

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1. Introduction

Pyrolysis is one of the first steps undergone by a solid fuel in a gasification process, and gives rise to char, tar and gas products, which will further react in the gasifier. Both in pyrolysis and gasification, yield and composition of the solid, liquid and gaseous fractions depend on the raw material, reactor design and the operating conditions, such as temperature, heating rate, residence time and pressure [1–5]. In general, tar yield is enhanced by high heating rates and low vapour residence times to avoid secondary

reactions whereas char formation increases by slow heating and moderate temperatures [4,6,7].

The composition of the reaction atmosphere also has influence on the product distribution. Several studies have focused on the effect of different components in the pyrolysis atmosphere, such as H₂, CO₂ or steam. The addition of the reactive gas H₂ to an inert atmosphere has been found to change the course of coal pyrolysis due to the occurrence of hydrolysis, having significant influence on tar formation and gasification reactions [1,2,8–14]. It has been reported that partly shifting inert atmosphere to CO₂ has no influence on the tar yield and composition during the initial pyrolysis step. However, depending on the operating conditions, CO₂ may react with the nascent char and/or the evolved tar in subsequent stages and may lead to larger yields of non-condensable

* Corresponding author. Tel.: +44 (0)20 7594 1633; fax: +44 20 7594 5638.

E-mail address: marcos.millan@imperial.ac.uk (M. Millan).

gases [15–18]. The addition of steam to the pyrolysis atmosphere may enhance the production of tars [19,20]. Moreover, steam can react with the nascent char more rapidly than CO₂ and lead to non-condensable gases richer in H₂ and CO₂ [15,21,22]. Additionally, the influence of other gases, such as CH₄ and CO, on pyrolysis and gasification processes has been investigated [19,23,24].

The influence of synthesis gas and its mixture with steam in coal gasification has not been extensively studied. In updraft moving bed gasification, pyrolysis takes place in an atmosphere of syngas due to the countercurrent flow configuration between the coal feedstock and the syngas-rich evolved volatiles. Novel results on the effect of synthesis gas and its mixture with steam at high pressure on coal pyrolysis and gasification may provide an insight on tar formation and tar properties in moving bed gasifiers. The presence of syngas and/or steam may modify product distribution and composition inside the gasifier itself. Moreover, tar quantity and quality may affect process and equipment downstream.

The main objective of this work is to investigate the influence of syngas and steam on the tar quantity and quality obtained from thermochemical processing of an inertinite-rich South African coal. In order to assess the effect of reaction atmosphere, experiments were conducted at 30 bar in a fixed bed reactor employing four different gas compositions: N₂, N₂ + steam, H₂/CO and H₂/CO + steam. The quality of the tars produced was evaluated using size exclusion chromatography (SEC), simulated distillation (Simdis), gas chromatography–mass spectrometry (GC–MS) and infrared spectrometry (FTIR).

2. Materials and methods

2.1. Reaction system

A fixed bed reactor, also described as “hot-rod” in the literature, has been used in this work [4,7]. The original reactor has undergone modifications to accomplish the requirements for different applications. A schematic diagram of the configuration of the “hot-rod” reactor is shown in Fig. 1.

The reactor is made from Incoloy 800 HT, which makes it suitable for running high temperature and pressure experiments, and has an internal diameter of 12 mm, 2 mm wall thickness and a length of 250 mm. The reactor is fitted with a ‘T’ piece at the top to allow a thermocouple to be placed inside it and gas to be supplied. The thermocouple is imbedded in the coal bed to ensure that the temperature reading represents the actual pyrolysis temperature. A CM4000 HPLC pump, capable of delivering flow rates from 10 μL min⁻¹ to 10 mL min⁻¹ at pressures to 670 bar, has been used to inject the water flow needed when steam supply is required. The pressurized water line is connected to the gas inlet. The mixture of water and gas is preheated before reaching the coal bed, allowing the water to evaporate. A controlled electrical current drawn along the reactor body between two copper electrodes serves as heater during the experiments. The system is programmed to follow a pre-established heating profile. The bottom of the reactor is connected to a trap system through a reduction fitting. When no steam is introduced, the tar trap is directly connected to the reactor. The trap is immersed in a liquid nitrogen bath, so that the volatiles released from the reactor are condensed. Stainless steel mesh is packed in the outlet arm of the trap to ensure efficient trapping of the condensed material in the form of aerosol droplets. When steam is fed, a trap immersed in an ice bath is placed between the reactor and the tar trap, to allow the non-reacted steam to condense.

2.2. Experimental procedure

A standard suite of operating conditions was used in the experiments. A high-volatile bituminous South African Highveld

inertinite-rich coal was used in these experiments (random reflectance of 0.61–0.67). These coals are typically inertinite rich (>70 wt.%, mineral-matter free basis) and contain significant amounts of mineral matter (~30 wt.% dry basis ash in proximate analysis). A typical proximate analysis for this coal shows 22 wt.% volatile matter and 48 wt.% fixed carbon (dry basis). 1 g of this inertinite-rich South African coal was placed inside the reactor before each test and supported by a wire-mesh plug. Previously, the coal sample had been crushed to less than 300 μm and stored under N₂ in a freezer. The reactor was pressurized at 30 bar under a flow of the gas used in the experiment and heated up to 700 °C at a heating rate of 10 °C min⁻¹. Peak temperature was held for 15 min, before ending the test and allowing the reactor to cool to ambient temperature. Four different gas atmospheres were used and duplicate experiments were performed for each condition: (i) N₂ (100 vol.%), N₂ + steam (70:30 vol.%), syngas (100 vol.% with a H₂/CO ratio of 2:1) and syngas + steam (70:30 vol.%). During the experiments, a low flow of gas through the reactor (0.005 m s⁻¹ at 700 °C and 30 bar of N₂ or H₂/CO) was used to sweep the released volatiles into the traps. The required steam flow rate was calculated at the reaction conditions (700 °C and 30 bar). Char was recovered and weighed in order to calculate the char yield as a percentage of the initial coal weight. Condensed steam was retrieved from the steam trap and its volume measured. Tars were recovered by washing the reactor and the steam and tar traps with a mixture of chloroform and methanol in the ratio 4:1 (v/v). The solution was filtered using a Whatman no. 1 filter paper and collected in a flask. A BUCHI Rotavapor R-3000 was used to evaporate most of the solvent. The rotavapor was operated at 90 °C (water bath temperature) and 40 rpm for 15 min. The remaining solution was then dried in a re-circulating oven operated at 50 °C for 1 h to evaporate the residual solvent and allow the tar to be isolated. The tar was weighed and its yield was determined as a percentage of the initial weight of coal.

2.3. Characterization techniques

The quality of the tar produced in each experiment was evaluated using size exclusion chromatography, simulated distillation performed in a gas chromatograph, gas chromatography–mass spectrometry and infrared spectrometry.

Size exclusion chromatography was carried out in a 300 mm long, 7.5 mm i.d. polystyrene/polydivinylbenzene-packed Mixed-D column with 5 μm particles (Polymer Laboratories). The column was operated at 80 °C and a flow rate of 0.5 mL min⁻¹. NMP was used as the mobile phase. Detection was carried out using a Knauer Smartline diode array UV-absorbance detector. As NMP is opaque at 254 nm, detection of standard compounds and samples was performed at 300 nm, where NMP is partially transparent. A calibration of the Mixed-D column was carried out using two sets of standards, polystyrene (PS) and polyaromatic hydrocarbons (PAH). The PS-based calibration is applied to the 11–20.5 min time range, while the PAH-based calibration is used in 20.5–24 min region, resulting in the following calibration equations:

$$15\text{--}20.5 \text{ min region: } \log_{10} [\text{MM}] = 9.6827 - 0.3456 [\text{elution time (min)}]$$

$$20.5\text{--}24 \text{ min region: } \log_{10} [\text{MM}] = 6.9022 - 0.2095 [\text{elution time (min)}]$$

Simulated distillation was performed in a Perkin Elmer “Clarus 500” chromatograph with flame ionization detector (FID). The GC was equipped with a non-polar capillary column HT5 (SGE Analytical Science, 25 m × 0.32 mm and 0.1 μm film thickness). A flow rate of 10 mL min⁻¹ of He was used as carrier gas with a split ratio of 1:20. The initial oven temperature was 35 °C, which was held for

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