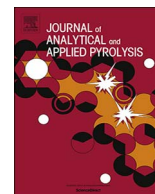




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Evaluation and prediction of slow pyrolysis products derived from coals of different rank

Gustav N. Pretorius^a, John R. Bunt^{a,*}, Martin Gräbner^b, Hein Neomagus^a, Frans B. Waanders^a, Ray C. Everson^a, Christien A. Strydom^c

^a Coal Research Group, Unit for Energy and Technology Systems, School of Chemical and Minerals Engineering, North West-University, Potchefstroom 2520, South Africa

^b Air Liquide Forschung und Entwicklung GmbH, Gwinnerstraße 27-33, 60388 Frankfurt am Main, Germany

^c Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa

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ABSTRACT

When coal is heated slowly ($< 10\text{ }^{\circ}\text{C}/\text{min}$), as in the Lurgi Fixed Bed Dry Bottom (FBDB) gasification process, products formed in the pyrolysis region of the gasifier include gas liquor, condensable tar, oil and non-condensable gases. Knowledge of the temperature profile together with the coal decomposition behaviour is of great importance when designing a fixed bed gasification plant, and although the characterisation of tar and the composition thereof has been reported extensively, there is limited literature available on the prediction of tar composition formed during slow pyrolysis. The focus of this study was to investigate temperature and coal rank effects on pyrolysis product yield, and to predict (using FLASHCHAIN[®]) the char, tar, water and gas yields when heated at slow heating rates for coals of different rank (ranging from lignite B to bituminous C). A modified Fischer Assay setup was used to investigate pyrolysis at temperatures higher than that of the ISO 647 standard, i.e. 520, 720 and 920 °C and the tar quality was determined via SEC–UV (size exclusion chromatography–ultraviolet), GC–MS (gas chromatography–mass spectrometry), SimDis (simulated distillation) and ultimate analysis. Only the char yield was found to be rank dependent and the average molecular weight of the coal derived tars (212–415 Da) compared well with previous studies. The rank dependence based on the composition of the evolved volatiles (tar and gas), showed a linear relationship with elemental oxygen and carbon contents of the derived tar, as well as for the oxygen containing gases (CO and CO₂). FLASHCHAIN[®] was able to provide a relatively accurate prediction of the char yield, poorer predictions of the tar and water yields and no correlation with the gas yield. The simulated results on tar composition showed poor promise. Statistical regression was also applied in order to determine correlations between coal properties and the pyrolysis product yields and composition. It was found that the mineral elements (Na₂O, MgO, CaO, TiO₂ and Fe₂O₃) have strong correlations with tar yield, thus implying that catalytic effects of the mineral matter appear to play a significant role in the formation and decomposition of coal derived tar, which is a limitation in all pyrolysis predictive models.

1. Introduction

Coal provides 30% of the world's energy needs and contributes to 40% and 70% of the world's electricity and steel production, respectively [1]. Coal pyrolysis is an important sub-process that occurs during coal conversion processes, not only for the application in the petrochemical feedstock industry, but also as the first step in combustion and gasification processes [2–4]. In Lurgi gasification the pyrolysis zone is defined as the zone with temperatures of 300–900 °C, where as much as 15% of the total gas production is formed [2]. Knowledge of coal

behaviour in this zone is therefore important from a gas and tar formation perspective. In-depth studies have therefore been conducted on the effect of pyrolysis conditions on pyrolysis products [5–8]. An extensive study and critical review on coal pyrolysis experiments and product formation for heated grid experiments, entrained flow experiments, thermo gravimetric analysis (TGA) and other slow heating experiments, fluidised beds, etc. have been reported by Gräbner [3]. A large number of products are formed during pyrolysis due to the intricate structure of coal and by the several chemical reactions that may occur [3,9,10].

Abbreviations: d.b., dry basis; d.a.f., dry, ash free basis; GC, Gas chromatography; XRD, X-ray powder diffraction; XRF, X-ray fluorescence spectroscopy; SEC–UV, size exclusion chromatography–ultraviolet; GC–MS, gas chromatography–mass spectrometry; RoV, random value of vitrinite reflectance

* Corresponding author.

E-mail address: john.bunt@nwu.ac.za (J.R. Bunt).

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Pyrolysis products are largely determined by the coal rank, coal type, inorganic matter present in the coal and operating conditions [11–13]. A few pyrolysis models, founded using analytical methods, have been proposed based on an understanding of coal structure, which is determined by the type of coal. These models include FG-DVC (functional group-depolymerization, vapourisation, cross-linking), FLASHCHAIN® and CPD (chemical percolation devolatilisation), [14–16]. With the knowledge of only raw coal properties, tar, char and gas yields can be estimated by the utilisation of these models [17]. Zhao et al. [18] used and extended the FG-DVC model and validated the model for selected coals based on the elemental composition, and also reported that the model can be improved by implementing additional parameters such as sulphur content and/or maceral composition.

Tar liquid products are also dependent on the chemical characteristics of the coal [3] and due to consensus regarding the effect of the volatility of tar molecules on the molecular weight distributions of tar models, progress has been made for the quantitative description of tar formation during pyrolysis. These models correlate liquid fragments and the occurrence of the plastic phase of the coal when undergoing pyrolysis [12]. Although reporting on the characterisation of tar and the composition thereof exists [19,20], there is limited literature available on the prediction of tar composition formed during slow pyrolysis, which is applicable to technologies such as fixed-bed gasification. The focus of this study was therefore to investigate temperature and coal rank effects on pyrolysis product yields and to predict (using FLASHCHAIN®) the char, tar, water and gas yields when heated at slow heating rates (< 10 °C/min) for coals of different rank and from different origins of the world (ranging from lignite B to bituminous C). No literature regarding slow heating rate modelling using FLASHCHAIN® for fixed bed gasification exists, and this was identified as a shortcoming needing further work. The FLASHCHAIN® modelling package was used solely due to its availability at the North-West University.

2. Experimental

2.1. Coal sample and preparation

A wide range of coal samples were chosen in order to represent a suite of coals typically considered for use in fixed bed gasification. The following basis was therefore used for the coal selection:

- 1) The potential use of the coal in commercial fixed-bed dry bottom gasifiers.
- 2) The coals should be of different rank ranging from lignite to bituminous.
- 3) The coals should be from different parts of the world.

Five coals (labelled A–E) were selected by Air Liquide as a result of the above criteria and were sourced from different countries of origin. The coal samples were crushed to the desired particle size for Fischer Assay experimentation as stipulated by ISO 647 [21], where 90% of particles pass a sieve of 1 mm aperture and no more than 50% pass a sieve of 0.2 mm aperture. The crushed samples were sieved and homogenised using a riffle splitter and stored in a sealed container under an inert atmosphere. Conventional characterisation methods (proximate and ultimate analysis) together with more advanced characterisation methods (XRF, XRD and petrography) were used to characterise the five coals using the standard ISO/ASTM methods.

2.2. Fischer assay operating procedure

A modified Fischer Assay setup [22] (Fig. 1) was used for the pyrolysis product preparation at 3 different temperatures (520 °C, 720 °C and 920 °C). This setup was developed in order to perform Fischer Assay experiments at elevated temperatures above the ISO 647 [21] temperature of 520 °C. Modifications made included the use of stainless steel retorts instead of aluminium in order to operate at temperatures close to 1 000 °C, and for the capture of non-condensable gases in gas

sampling bags, automated temperature control and direct retort bed-temperature measurements.

Two stainless steel retorts, built according to ISO 647 [21] dimensions were used to load the 50 g coal samples with particle size: 90% passing a 0.5 mm sieve, and no more than 50% passing a 0.2 mm sieve. Argon was used to create an inert atmosphere before the coal was heated in order to prevent combustion of the coal. This was done by purging each of the retorts with a low flow of Argon for 5 min. The retorts were heated in a Lenton oven (22 amp–48 kW rating over 220 V) fitted with a TOHO TTM-P4 temperature controller and a Shinko LMD-100 Console/Data Logger. Two K-type thermocouples were fitted within each of the two retorts, one measuring the bed temperature and the other the environment temperature inside the oven chamber. A lag in temperature increase between the oven chamber temperature and the bed temperature existed, therefore the bed temperature was used for temperature control. The heating rate ranged between 8.5 °C/min and 9.5 °C/min, depending on the final pyrolysis temperature.

The gas formed during the heating of the coal and pyrolysis flowed through stainless steel pipes and was bubbled through a tar trap and two gas wash bottles. This was done in order to capture the condensable gases (tar and water) before the non-condensable gases were captured in 10 L Tedlar gas sampling bags. Toluene was used as solvent in the tar trap and gas wash bottles, and was kept at 0 °C by immersion in an ice bath. Char, tar, water and gas yields were determined according to ISO 647 [21]. The water yield was determined first by means of Dean-Stark distillation of the water, tar, toluene mixture. Thereafter the toluene and tar was separated by means of a rotary evaporation at 60 °C using a Büchi Rotavapor R II with Büchi Vacuum pump V 700. Gas yields were determined by difference, according to the ISO 647 procedure.

2.3. Pyrolysis product analyses

Tars obtained from the Dean-Stark separation were kept in air tight glass bottles and in cool conditions prior to analyses. Analyses conducted on the tar samples included: simulated distillation (Simdis), qualitative gas chromatography–mass spectrometry (GC–MS), size exclusion chromatography (SEC), performed by Imperial College (London), and the determination of elemental C, H, O, N and S, performed by Elementar Application Laboratory (Germany).

Petrochemical products can be categorised into boiling point ranges using simulated distillation, a standard used for fractions with a boiling range between 55.5 °C and 538 °C [23]. A Perkin Elmer Clarus 500 HT5 aluminium clad fused silica capillary column with 2.5 m length and an ID of 0.32 mm was used for this analysis. An FID detector was used and helium was applied as the carrier gas at a flow rate of 100 mL/min. The program was set to an injection temperature of 350 °C and the detector temperature at 370 °C. The first ramp was at 15 °C/min from 35 °C to 350 °C and was held for 2 min. A second ramp was introduced at a heating rate of 25 °C/min to 380 °C and was held for 10 min. Fractions of samples of coal derived tar having boiling points higher than 450 °C were not analysed. The fractions with boiling points lower than 450 °C were analysed as summarised in Fig. 2.

The same tar samples, which were used for the previously mentioned Simdis analysis, were used in the SEC analysis in order to estimate the molecular weight distributions of the liquid tar samples. A polystyrene/polydivinylbenzene mixed D packed column fitted with a Knauer 2600 UV detector was used. N-methyl pyrrolidone was used as carrier and analyses were done at 80 °C [23].

The GC–MS analysis was performed using a Varian star 2400 equipment fitted with an HT5 aluminium clad fused silica capillary column with 25 mm length and an ID of 0.32 mm. A Saturn 2000 MS detector was used with helium as carrier gas at a flow rate of 100 mL/min. The program was set to an injection temperature of 350 °C and the detector temperature at 370 °C. The first ramp was at 15 °C/min from 35 °C to 350 °C and was held for 2 min. A second ramp was introduced with a heating rate of 25 °C/min to 380 °C and was held for 10 min. The

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