The effects of coal rank, temperature and residence time on the chemical composition of tar condensates

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Abstract Experiments involving coal pyrolysis with subsequent capture and analysis of the devolatilised 'tar' products is presented, with the aim of providing information pertinent to developing groundwater risk assessments for underground coal gasification (and similar in-situ thermal process). Different coals were pyrolysed at different temperatures and for different lengths of time within a reactor, and the resultant volatilised components were captured by condensation and analysed by GC-MS for PAHs and phenols. Whilst a clear correlation was found between temperature and amounts of potential contaminants in the condensates, there was no clear correlation with the residence time of the parent coal within the furnace.

Key Words UCG, Groundwater, Coal condensates

Introduction

Underground Coal Gasification (UCG) is the process by which coal is converted in the coal seam into a combustible gas. The basic UCG process involves a coal panel being ignited, and oxidants being introduced to gasify the panel. A potentially valuable product gas is produced that once brought to the surface and cleaned can be combusted for power generation or further processed to produce a range of products including fertilizers, liquid hydrocarbon fuels, hydrogen, and ammonia. However, concerns over the influence of UCG projects on groundwater integrity are very high. There have been numerous examples of groundwater pollution since the technology has emerged, with major contamination events occurring in the former Soviet Union and in various US experimental sites. The maximum recorded benzene concentrations in groundwater after one US trial exceeded 3000µg/L.[1] Current (2011) UK threshold values are 0.75µg/L).[2]

Considering this, there have been a number of laboratory investigations into potential pollution of groundwater from the UCG process. Most studies have concentrated on the influence of ash-leaching on groundwater,[5 – 13] and this process is relatively well understood. However, the role of organic condensates on groundwater has been less thoroughly investigated, which is potentially attributable to the complexity of compounds in any post-gasification organic condensate (often referred to as tar). Research has been carried out on the cavity water from UCG field trials, including Humenick et al.,[5] who concluded that the condensed vapours contributed the organic contaminants, identified mostly as Polycyclic Aromatic Hydrocarbons (PAHs). Campbell[7] analysed the liquid products from pyrolysis of coal (in an argon stream) at differing temperatures, but stated that individual analysis was beyond the scope of the study. Boysen et al[10] analysed laboratory UCG condensates for phenols and Total Organic Carbon. Kapusta et al[14] found that hard coal produced a higher total load of organics, although lignite produced a greater proportion of complex PAHs.

As outlined above, the majority of UCG contamination problems have been attributable to organic condensate contamination, but there has been a lack of research into this area; this paper describes preliminary experiments that capture and analyse coal-derived tar condensates.

Materials and Methods
Materials
The samples used for this experiment were two coals – anthracite and steam coal – sourced from different mines in the Welsh coalfields. The physicochemical characteristics are given below in Table 1.

Experiments
A vapour sample of the condensate pyrolysis products of coal was captured in an organic sol-

Table 1 *Physicochemical characteristics of utilised coals*

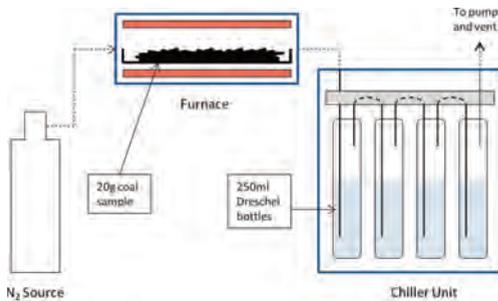| Coal Rank	Mine	Particle Size*	Proximate Analysis			
			Moisture %	Ash %	Volatiles %	Fixed Carbon %
Steam Coal	East Merthyr	2mm>1mm	0.5	4.4	13.6	81.5
Anthracite	Glynneath	5mm>4mm	0.9	2.2	6.3	90.6
* - Coal was dried at 105°C for 4 hrs before processing						

Figure 1 *Schematic of experimental capture of tar condensates from coal.*

vent using a bespoke system designed by the authors. A 300mm tube furnace, operated using a Eurotherm 815 controller, was heated to a set temperature (600, 800 or 1000 °C), then nitrogen gas (2 L/min) was allowed to flow into the furnace, purging the atmosphere of air such that no oxidation reactions could occur. Four hundred millilitres of isopropanol that had been divided into 4 x 250ml Dreschel gas washing bottles were used to trap the organic condensate. Isopropanol was chosen as it is the most appropriate solvent for tar condensate capture, based on similar results from combustion and gasification testing.[15 – 17] 20.00g of coal (+/-0.02g) on a steel boat were introduced into the furnace, a vacuum pump started to aid product gas flow and venting, and the experiment was run for a set time (5, 15 or 30 minutes), this is what is referred to as 'residence time' in the text, i.e. residence time of the parent coal within the furnace. A schematic diagram of the experiment is shown below in Figure 1.

When the experiment was completed, the pump was turned off, the pyrolysed coal was removed from the furnace, and the isopropanol was circulated around the condenser unit to dissolve any remaining tars. Acetone was circulated around the condensate unit after each experiment to clean the system.

Analyses
Each collected sample was first filtered through paper glass fibre 1.2μm filters. An accelerated solvent extraction (ASE) was performed on each filter residue using a DIONEX ASE100 with isopropanol as the solvent, and this additional solution was added to the original sample. A sub-sample of 100ml was then taken, and reduced under nitrogen on a heated plate at 78 °C , until 1ml remained. This reduced sample was then analysed using a PerkinElmer Clarius 500 GC-MS, with isopropanol blanks run between each sample. When reducing the steam coal samples taken at 800 °C, and 1000 °C, some of the condensate products condensed out of solution to form a liquid deposit on the sample vials, and therefore it was not possible to run these through the GC-MS. Instead, a direct 1ml sample was taken from the filtered 'total' sample. The resultant spectrometry graphs (counts versus retention time) were compared to calibrations prepared with proprietary phenol and PAH standards.

Results and Discussion
Coal Rank
Of the compounds within the proprietary standards, fifteen of the thirty-four were found within the samples analysed; their maximum concentrations are shown in Table 2. Where concentration is shown as mg/kg, this is expressing the concentration of the organic compound per unit mass of parent coal. Twelve compounds were detected in

Table 2 *Compounds identified in the GC-MS traces of condensate and action values for contaminated groundwater*

Compound	Max. Conc. (mg/kg)	Detected	Action Values (mg/L)
Naphthalene	135.964	a, sc	0.0132[T]
Acenaphthylene	6.065	a, sc	
Fluorene	21.104	a, sc	
Phenanthrene	27.607	a, sc	0.005[D]
Fluoranthene	1.955	a, sc	0.0006[T]
Pyrene	1.538	a, sc	
Chrysene	3.614	sc	0.00005[D]
Benzo(b)fluoranthene	0.031	a, sc	
Phenol	15.851	a, sc	0.0828[T]
3-Methylphenol (m-cresol)	11.478	a, sc	
2,4-Dichlorophenol	0.001	a	0.03[D]
4-Chloro-3-methylphenol	0.0007	a	
2-Chlorophenol	6.329	sc	
2-Methylphenol (o-creosol)	1.796	sc	
2,4-Dimethylphenol	185.021	sc	

a – identified in anthracite condensate, sc – identified in steam coal condensate, T – [2] Maximum Threshold Value, D – [18] Action Levels

Table 3 *Mass loss and total mass of contaminant per mass parent coal with temperature and time*

Coal Type	Temperature (°C)	Time (minutes)	Coal Mass Loss (g)	Total mass of contaminants[*] (mg/kg)
Anthracite	600	5	0.31	5.043
Anthracite	600	15	0.41	5.273
Anthracite	600	30	0.50	4.870
Anthracite	800	5	0.87	6.045
Anthracite	800	15	1.06	1.715
Anthracite	800	30	1.15	0.622
Anthracite	1000	5	1.45	1.057
Anthracite	1000	15	1.52	1.118
Anthracite	1000	30	1.70	1.648
Steam Coal	600	5	0.48	0.976
Steam Coal	600	15	1.07	9.750
Steam Coal	600	30	1.41	16.202
Steam Coal	800	5	2.60	141.298
Steam Coal	800	15	2.96	232.770
Steam Coal	800	30	3.13	219.502
Steam Coal	1000	5	3.79	279.218
Steam Coal	1000	15	3.96	409.126
Steam Coal	1000	30	4.11	359.963

[*] - of compounds identified

each coal. In anthracite, acenaphthylene was the most prevalent compound detected, followed by naphthalene, and then phenol. For steam coal, 2,4-dimethylphenol (which was not detected in the anthracite condensate) then naphthalene were over five times more prevalent than phenanthrene (third), then fluorene.

With a far higher percentage of volatile matter, there was a marked increase in the mass loss of the steam coal, as well as the mass of detected compounds in the condensate (discussed later), as compared to the anthracite (see Table 3), although the condensates produced at 600 °C are of a similar mass.

Regarding the differences between temperatures, it can be seen that over 2.5 times (averaged) more mass was lost than at 800 °C than 600 °C when pyrolysing anthracite; the difference in steam coal is greater, at nearly 3.5 times. Between the temperatures of 800 °C and 1000 °C, the figures were more similar, averaging around a 1.5 times greater loss at the higher temperature. Visibly, the recovered steam coal samples showed an increase in dissolved condensate, as shown in Figure 2.

The average mass of volatilised products produced by each coal differs in trend, with a greater mass of detectable compounds produced by anthracite at lower temperatures, and the converse for steam coal (see Figure 3). Concerning residence time, the correlation is less clear, with little change in the mass of detectable compounds (see Figure 4).

Figure 2 *Dissolved steam coal condensate in solvent (time increasing – horizontal, temperature decreasing – vertical).*
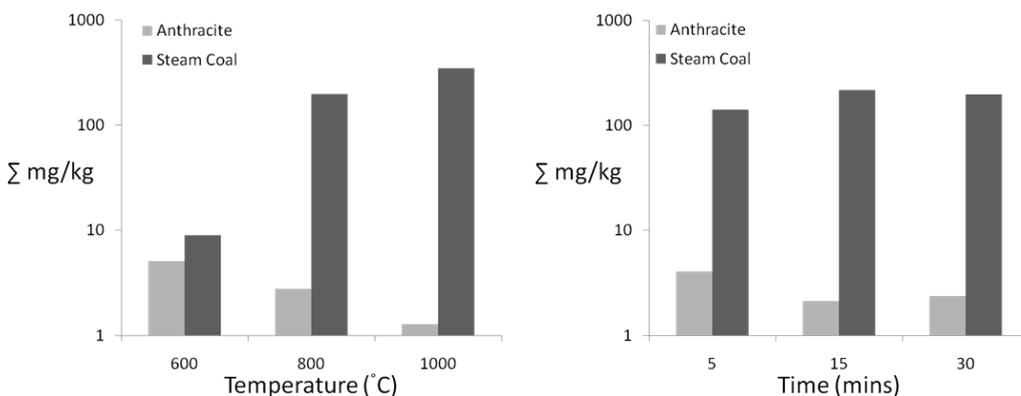
Figures 3 & 4 *Levels (averaged) of detected PAH and Phenols in condensate from anthracite and steam coal based on temperature (left) and residence time (right) (NB logarithmic scale)*

Temperature

Anthracite: The majority of naphthalene and acenaphthylene (the most prevalent compounds) were volatilised at 600 °C; acenaphthylene was almost below the detection level limit at 1000 °C. Volatilised fluorene also displayed a general downward trend with rising temperature. Conversely, phenanthrene has a definite upward trend with temperature; the majority was detected at 1000 °C. Benzo(a)fluoranthene and 2,4-dichlorophenol were only detected at 800 °C and higher, and fluoranthene, chrysene and pyrene are only detectable in the condensate taken at 1000 °C. At all temperatures, PAHs made up over 75% of the identified compounds (>95% at 600 °C).

Steam coal: Compared to the downward trend of naphthalene in anthracite, steam coal displayed a definite upward trend, like the majority of volatilised compounds. However, acenaphthylene, very prevalent in anthracite, was only detected at temperatures of 1000 °C from the steam coal. Chrysene was only detected at 800 °C and higher, whereas 2-methylphenol was only detected at 600 °C. It is worth noting that more individual compounds were detected at 800 °C than at any other temperature, which perhaps could be attributable to the higher temperature thermally decomposing the compounds. Finally, phenols made up a greater proportion of identified compounds in the majority of steam coal samples than anthracite samples (samples ranged from 46 to 67% phenolic compounds).

Residence Time

Anthracite: As stated above, the correlation between residence time of the coal within the furnace and contaminant production is not clear. At 600 °C, the majority of mass had volatilised within 5 minutes of contact with the tube furnace;

the negligible difference between the produced masses with the longer residence times could be simple sample heterogeneity, or experimental error. Of all compounds, only 2,4-dichlorophenol is found at the higher residence times and not at the 5 minute mark.

Steam coal: Again, as anthracite, a trend concerning residence time is difficult to ascertain. However, comparing samples taken from differing temperatures, four compounds had not been detected in the 5 minute sample were detected in later samples: 4,2-chlorophenol, fluorene, pyrene and chrysene.

Consequences for Groundwater

From Table 2, it can be seen that the condensate produced by pyrolysing coal has the potential to pose a serious threat to groundwater as it contains numerous 'priority' contaminants. A typical UCG plant operates at temperatures around 700 – 900 °C.[20] Looking at Figures 3 & 4, the majority of potentially polluting mass will be volatilised from the steam coal at these temperatures, although this temperature is advantageous with regards to anthracite. Looking closer, of most importance to groundwater is the solubility of the produced contaminants in groundwater. Of the identified compounds, phenols are the most soluble, and have been identified as contaminants in a number of plants and trials in the former Soviet Union,[21] and the USA.[1, 20, 21] Figures 5 and 6 show total phenols detected in the condensate samples.

It can be seen from above that steam coal produces a much greater mass (in three orders of magnitude) of phenols than anthracite, and both coals volatilise a greater mass at the higher temperatures associated with UCG. Considering this, the total amount of phenols 'available' for contamination is considerable but would depend
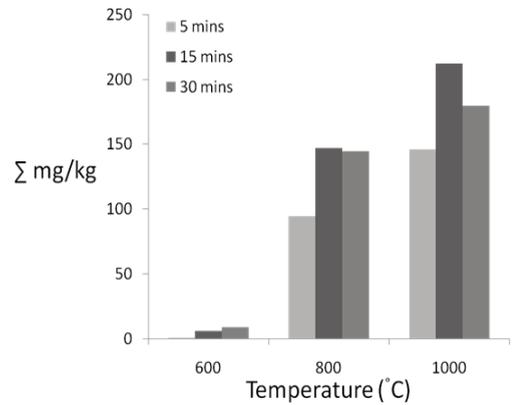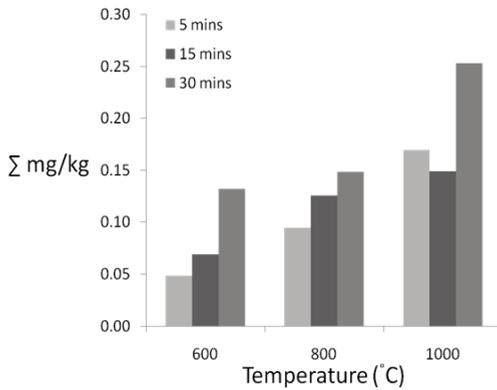
Figures 5 & 6 *Levels of detected Phenols in condensate from anthracite (left) and steam coal (right) based on temperature and residence time (NB different vertical scales).*

upon various factors such as how much condensate stays underground, the prevailing groundwater regime and the operating regime (e.g. pressure differential) for the UCG operation (which can greatly influence the escape of vapours into the surrounding strata).

Conclusions

The work above shows that the method of collecting condensate from pyrolysing coals is effective, although there is scope to experiment with differing solvents and flow rates to achieve a greater absorption of pyrolysis products. Also, with a wider range of GC-MS standards, more compounds could be identified and compared. Of the coal samples, temperatures and furnace residence times studied, the following observations were made for the coal samples tested:

Steam coal experiences a larger mass loss when pyrolysed than anthracite, and produces a greater mass of detected compounds (although the difference was negligible at 600 °C).

In anthracite, acenaphthylene was the most prevalent compound detected (highest detection – 3.44mg/kg), followed by naphthalene, and then phenanthrene; PAHs are more prevalent in the captured condensate.

For steam coal, 2—4dimethylphenol (highest detection – 185.02mg/kg), then naphthalene (135.96mg/kg) were over four times more prevalent than phenanthrene; Phenols are slightly more prevalent in the captured condensate.

Considering temperature, the average mass of detectable volatilised products produced by each coal differs in trend, with anthracite producing more PAH and Phenol mass at the lower temperature, and the converse for steam coal.

Residence time of the coal within the furnace does not seem to have such a large influence on

contaminant release (at least up to the 5 minute mark) than temperature, although this needs further investigation with respect to the test repeatability.

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