NATURAL COAL TARS: A GEOLOGICAL CONTAMINANT

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Keywords

Coal Fire
Natural Coal Tar
Polycyclic Aromatic Hydrocarbons
Background

Abstract

Burning coal beds formed natural coal tars for thousands of years in the United States, India, China, and many other countries. The hydrocarbon mixtures in natural and industrial coal tars are very similar and easily confused. Coal-fire vents liberate pyrogenic PAHs and other contaminants commonly attributed to MGPs, coke plants and wood treating facilities.

This paper compares and contrasts natural and industrial coal tars in the United States. The presentation demonstrates the forensic features used to differentiate coal tar sources; specifically, properties associated with the coal feedstock, the conditions of formation, and the degree of environmental weathering. While it is theoretically possible to completely degrade all of the hydrocarbons in coal during carbonization, real world samples of natural and industrial coal tars demonstrate high concentrations of semivolatile hydrocarbons with source specific signatures.

Of particular importance are: (1) the high resolution hydrocarbon fingerprints, (2) the parent and alkylated PAHs, (3) the saturated hydrocarbon feedstock signatures, and (4) the geochemical biomarkers. The growing collection of reference samples helps recognize and interpret hydrocarbon signatures in the environment.

Coal Feedstock

Sedimentary Rock (More than 50% OM)
Lithified Plants
- Marshes
- Swamps
- Bogs

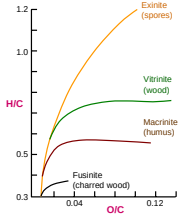
Coalification
- Temperature (<200°C)
- Geological Time Scale
- Pressure

Transformation
- Lignin and Cellulose
- Moisture and Hydrogen Loss
- Aromatization
- Increasing Reflectance

Bituminous

Anthracite

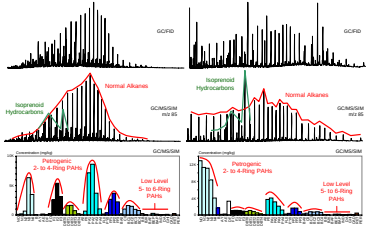
van Krevelen Diagram



Modified from Stach et al., 1982

High Resolution Hydrocarbon Fingerprints

HV Bituminous (Low Sulfur) HV Bituminous (High Sulfur)



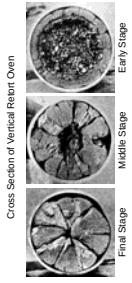
Modified from Emsbo-Mattingly et al., 2003
Research Funded by Battelle

Industrial Coal Tars

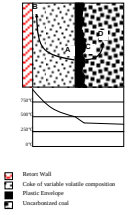
Gas Plant Coal
- 30-40% Volatile Matter
- Smaller Ovens
- Cook Time: 6-12 hrs

Coke Plant Coal
- 15-25% Volatile Matter
- Large Ovens (tons)
- Cook Time: 24-60 hrs

Temperatures
- About 1,000°C



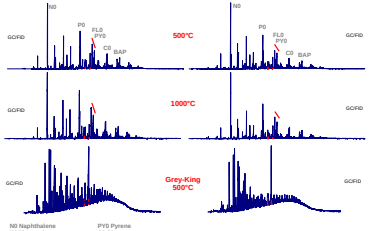
Reprinted from Porter 1924



Modified from Morgan 1926

High Resolution Hydrocarbon Fingerprints

HV Bituminous (Low Sulfur) HV Bituminous (High Sulfur)



Modified from Emsbo-Mattingly et al., 2003
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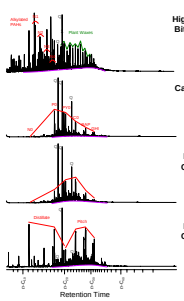
Natural Coal Tars

Coal Fire
- Hazard County KY
- High Volatile Bituminous Coal
- Breathitt Formation
- Former Mine
- Ignited by Lightening Strike
- Environmental Investigation Underway
- Monitoring Vent Emissions
- Off Site Effects Under Investigation

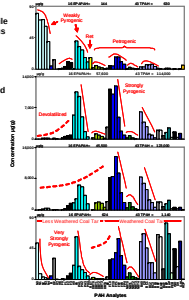
Coal

Coke

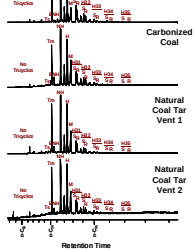
High Resolution Hydrocarbon Fingerprints



Alkylated PAHs



Geochemical Biomarkers



Target Analytes

Analytes	Abbrev
Naphthalene +	N0
C1-Naphthalenes	N1
C2-Naphthalenes	N2
C3-Naphthalenes	N3
C4-Naphthalenes	N4
Biphenyl	B
Dibenzofuran	DF
Acenaphthylene +	AY
Acenaphthene +	AE
Fluorene +	F0
C1-Fluorenes	F1
C2-Fluorenes	F2
C3-Fluorenes	F3
Anthracene +	AC
Phenanthrene +	P0
C1-Phenanthrenes/Anthracenes	P1
C2-Phenanthrenes/Anthracenes	P2
C3-Phenanthrenes/Anthracenes	P3
Dibenzothiophene	DBT
C1-Dibenzothiophenes	DBT1
C2-Dibenzothiophenes	DBT2
C3-Dibenzothiophenes	DBT3
Fluoranthene +	FL0
Acephenanthrylene	AP
Cyclopenta[c,d]pyrene	CPP
Pyrene +	PY0
C1-Fluoranthenes/Pyrenes	PY1
C2-Fluoranthenes/Pyrenes	PY2
C3-Fluoranthenes/Pyrenes	PY3
Benzo[a]fluorene +	BAF
Benzo[b]fluorene +	BBF
Benzo[c]phenanthrene +	BCP
Benz[a]anthracene +	BA0
C1-Benz[a]anthracenes/Chrysenes	BA1
C2-Benz[a]anthracenes/Chrysenes	BA2
C3-Benz[a]anthracenes/Chrysenes	BA3
Cyclopenta[cd]fluoranthene +	CPF
Benzo[b]fluoranthene +	BBF
Benzo[j]fluoranthene +	BJF
Benzo[k]fluoranthene +	BKF
Benzo[e]pyrene +	BE
Benzo[a]pyrene +	BAP
Perylene	PER
Indeno[1,2,3-cd]pyrene +	IND
Dibenz[a,h]anthracene +	DA
Benzo[g,h,i]perylene +	BPE

Analytes	Abbrev
C24 Tricyclic Terpane	c24
C25 Tricyclic Terpane	c25
C26 Tricyclic Terpane	c26
C24 Tetracyclic Terpane	tc24
C28 Tricyclic Terpane-22S	c28S
C28 Tricyclic Terpane-22R	c28R
C29 Tricyclic Terpane-22S	c29S
C29 Tricyclic Terpane-22R	c29R
C30 Tricyclic Terpane-22S	c30S
C30 Tricyclic Terpane-22R	c30R
C28 Bisnorhopane	BH
C29 Hopane	H29
C30 Hopane	H30
C31 Homohopane-22S	H31S
C31 Homohopane-22R	H31R
C32 Bishomohopane-22S	H32S
C32 Bishomohopane-22R	H32R
C33 Trishomohopane-22S	H33S
C33 Trishomohopane-22R	H33R
C34 Tetrakishomohopane-22S	H34S
C34 Tetrakishomohopane-22R	H34R
C35 Pentakishomohopane-22S	H35S
C35 Pentakishomohopane-22R	H35R

* EPA 16 Priority Pollutant PAHs

Discussion

Conventional wisdom dictates that coal tars are industrial byproducts. This study demonstrates that coal fires also produce coal tars, naturally. The hydrocarbon signature of coal varies, but is quite different from coal tar. However, the pyrogenic PAH patterns of coal tars – both industrial and natural - are very similar, especially when detected by conventional lab methods. Natural coal tars resemble industrial coal tar distillates or pitch. Coal-tar sources can be differentiated with advanced chemical testing methods; specifically, high-resolution, hydrocarbon fingerprints; alkylated PAHs; and geochemical biomarkers. Identifying the source of coal tars can be important at MGPs, coke plants, tar refineries, and wood treaters, especially when there is a history of coal fires in the area.

Conclusion

Coal tars form naturally in coal fires.

Industrial and natural coal tars contain high concentrations of pyrogenic PAHs and incompletely carbonized feedstocks.

Advanced chemistry methods can help differentiate pyrogenic PAH sources.

Reference:

Emsbo-Mattingly, S.D. and Stout, S.A., 2010, Semivolatile hydrocarbon residues of coal and coal tar, in Stracher, G.B., Sokol, E.V., and Prakash, A., eds., The World Atlas of Coal Fires and Combustion Metamorphism, Accepted for Publication by Elsevier, Chapter 11.