# The Influence of Coal Tars over the Environment

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## Abstract

*Coal is a macromolecular compound. At high temperatures, by coal pyrogenesis, coke and volatile products will result. The volatile products from coal form the coke gas and coke tar from which a very large number of aromatic compounds can be extracted. The aromatic compounds extracted from domestic and foreign coal tar were compared in this paper, together with their effects over the human and animal health.*

**Keywords:** *compounds, macromolecular, coke gas*

### Introduction

The standard methods which are used during coal processing are very important in defining the subsequent potential of coal chemical treatment because the processes employed in the destructive processing of coal have provided the raw material base for the chemical synthesis and the fundamental principles for laying the base of upcoming technologies.

Coal pyrogenation at low temperatures (400–600°C), in the absence of air, leads to the simultaneous formation of some products with smaller molecular weight and of some products with a molecular weight higher than the primary coal. The products with a smaller molecular weight form the volatile matters, released as tar vapors, water and gases and the products with a higher molecular weight that gives the solid residue of carbonization (semi-coke and coke).

### Coal chemical treatment

Basically, coal pyrogenation at low temperatures (semi-coking) takes place as follows:

- Up to 100–150°C hygroscopic water and adsorbed gases are being emitted;
- Between 200°C and 250°C occurs a thermal decomposition revealed by the coming of the pyrogenetic water and of some gases, such as: $CO_2$, CO and $H_2S$;
- At around 300°C starts the emission of tar vapors;
- Between 350°C and 400°C takes place an intense decomposition and the amount of the emitted gases increases abruptly; the gases become combustible because there increases highly the content of hydrocarbons (methane and homologues), as well they start to have increasing amounts of hydrogen;

At high temperatures (coking), the following processes take place:

- Between 50°C and 150°C coal dries out and gases are being emitted;
- Between 150°C and 300°C the marginal functional groups, carboxyl, hydroxyl, tionil break up and $CO_2$, $H_2O$ and $H_2S$ are being emitted;
- Between 400°C and 550°C, full aliphatic chains and heterocycles with oxygen and nitrogen break up and aliphatic, hydro aromatic hydrocarbons and superior phenols are being formed;
- The maximum temperature for tar emission is between 400°C and 550°C and tar formation ends at 500°C and 550°C;
- Above 600°C there are emitted gaseous products ($CH_4$ and especially $H_2$) that are being formed by breaking the bonds C–H and the breaking off the groups $CH_3$. The emission of condensable products (tars) ends at around 550–600°C. There also occur conversions that lead to the formation of pyridinic and kinoleic alkali, to the occurrence of phenol, of ammonia and even of the elementary nitrogen.

As a result, both the structure and the percentage weighting of the co-products acquired from the coal pyrogenation shall depend on the quality of the raw material that is being used and on the parameters of the processing method: temperature, pressure and the operating period of temperature over the coaly mass, also called the standstill period.

Figures 1a, 1b and 1c show the variation in the structure of gaseous phase, liquid phase and solid phase in relation to the carbonization temperature.

Table 1 shows, by comparison, the products acquired through hard coal pyrogenation, during semi-coking at 500°C and during cooking at 1000°C.

The analysis of charts and of data submitted shows that a process of secondary carbonization occurs simultaneously with the temperature rise together with the diminution of the tar efficiency and increasing the efficiency for formation of gaseous components. Pyrogenation at higher temperatures increases the weight of aromatic hydrocarbons from the tar and of hydrogen from the gaseous phase.

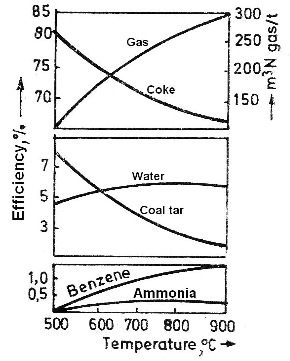


Fig. 1a. Variation in the efficiency of hard coal pyrogenation depending on temperature
Rys. 1a. Zróżnicowanie wydajności pirogenizacji węgla kamiennego w zależności od temperatury

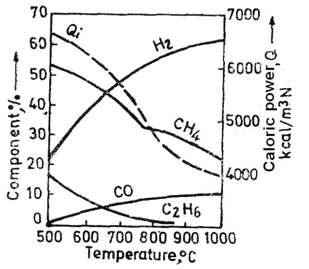


Fig. 1b. Variation in the gas structure depending on temperature
Rys. 1b. Zmienność struktury gazu w zależności od temperatury

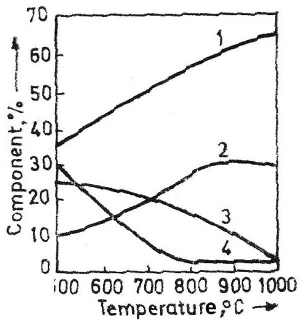


Fig.1 c. Variation in the tar composition in relation to temperature: 1. pitch; 2. aromatic oils; 3. acids an phenols; 4. saturated hydrocarbons
Rys. 1 c. Zróżnicowanie składu smoły w zależności od temperatury: 1. pak 2. oleje aromatyczne; 3. kwasy i fenole; 4. nasycone węglowodory

**Chemical structure of tar resulted after hard coal coking and semi-coking**

High and low temperature tar comprises a large array of fractions that can be separated in accordance with the needs and opportunities related to their trading.

Table 2 shows the main products separated from the high temperature tar (coking tar) that are being used by the chemical synthesis technology.

The table shows that the coking tar is a complex mixture of aromatic hydrocarbons, phenols, derivatives with nitrogen, oxygen, sulphur, etc.

The capitalization of the coking tars can be made through direct processing, meaning the separation of relatively homogenous fractions and getting some components of different purity degrees and through chemical treatment, hydrogenation, cracking, processes that lead to the acquiring of new fractions that comprise intermediate products for the petrochemical industry.

The methods that are being used for a direct capitalization of tars implement traditional physical operations, such as decanting, filtering, distillation, rectification, crystallization, sublimation and selective extractions, refining with acids, alkali, chemical operations, etc. As a result, there are being used substances of different purity degrees necessary for the chemical industry: benzene, toluene, xylene, naphthalene, antracene, pyridinic alkali, components with nitrogen, components with sulphur, etc.

Tars derived from semi-coking display specific structures and features that differentiate them from the tar acquired through the coking process. These tars include mainly alkenes and aromatic hydrocarbons in very small quantities. Nevertheless, there can be noticed high concentrations of oxygenated compounds from the category of phenols and especially, through the contents of phenols.

The processing of semi-coking tar shall give products similar to the ones that result through oil processing: gasoline, diesel oil, mineral oils, phenols and a solid distillation residue, asphalt.

Tab. 1. Products acquired during hard coal semi-coking and coking
Tab. 1. Produkty uzyskane podczas półkoksowania i koksowania węgla kamiennego

| Products and specific features | U.M. | Semi – coking (500°C) | Coking (1000°C) |
|---|---|---|---|
| **Solid product** | - | Semi - coke | Coke |
| - efficiency | % | 70 - 81 | 65 – 70 |
| - volatile matters | % | 10 - 18 | 0.5 – 1.5 |
| **Tar** | - | Alkaline | Aromatic |
| - efficiency | % | 7 – 12 | 2 – 4 |
| - content of phenols | % | 20 | 2 |
| - content of phenol | % | - | 1 – 1.7 |
| - content of tar | % | 40 | 60 |
| - density | $Kg/m^3$ | $0.9 – 1.0 \times 10^3$ | $1.1 – 1.2 \times 10^3$ |
| **Gas** | - | of semi – coke | of coke |
| - efficiency | $Nm^3/t$ | 60 - 80 | 330 – 350 |
| - superior calorific power | $Kcal/Nm^3$ | 6000 - 8000 | 3800 – 4500 |
| - density | $Kg/m^3$ | 0.85- 0.95 | 0.4 – 0.4 |
| **Light oils in gas** | - | gasoline from gas | raw benzene |
| - efficiency | % | 0.3 – 0.5 | 1.0 – 1.2 |
| - content of benzene ($C_6H_6$) | % | traces | 50 – 75 |
| Ammonia | - | From semi – coke gas | From coke gas |
| - efficiency | % | Traces | 0.20 – 0.35 |

Tab. 2. Separable products from coal tar
Tab. 2. Produkty, które można oddzielić od smoły węglowej

| No. | Name | Boiling temperature °C | Melting temperature °C | % (g) |
|---|---|---|---|---|
| 0 | 1 | 2 | 3 | 4 |
| 1 | Components above 1% | | | |
| | naphthalene | 217,95 | 80,29 | 10,0 |
| | fenantrene | 338,4 | 100 | 5,0 |
| | fluoroantrene | 383,5 | 111 | 5,3 |
| | pyrene | 393,5 | 150 | 2,1 |
| | acenaftylene | 270 | 93 | 2,0 |
| | fluorene | 297,9 | 115 | 2,0 |
| | chrysene | 441 | 256 | 2,0 |
| | antracene | 340 | 218 | 1,9 |
| | carbazole | 354,76 | 244,4 | 1,5 |
| | 2 – methylnaphthalene | 241,05 | 34,58 | 1,5 |
| | diphenylenoxide | 285,1 | 85 | 1,0 |
| | indene | 182,44 | -1,5 | 1,0 |
| | | | | |
| 2 | Components below 1% | | | |
| | acridine | 343,9 | 111 | 0,6 |
| | 1 - methylnaphthalene | 244,68 | -30,8 | 0,5 |
| | phenol | 181,83 | 40,9 | 0,4 |
| | m - cresol | 202,23 | 12,22 | 0,4 |
| | benzene | 80,1 | 5,53 | 0,4 |
| | diphenyl | 255,0 | 69,2 | 0,4 |
| | acenaphthene | 227,0 | 95 | 0,3 |
| | 2 - phenylnaphthalene | 359,8 | 101 | 0,3 |
| | toluene | 110,62 | -94,99 | 0,3 |
| | quinoline | 237,1 | -14,2 | 0,3 |
| | diphenyl sulphide | 331,4 | 97 | 0,3 |
| | tionaphtene | 219,0 | 31,32 | 0,3 |
| | m – xylene | 139,10 | -47,87 | 0,2 |
| | o - cresol | 191,00 | 30,99 | 0,2 |
| | p - cresol | 201,94 | 34,69 | 0,2 |
| | isoquinoline | 243,25 | 26,48 | 0,2 |
| | quinidine | 247,6 | -1 | 0,2 |
| | fenantridine | 349,5 | 107 | 0,2 |
| | 7, 8 - benzoquinoline | 340,2 | 52 | 0,2 |
| | 2, 3 – benzo diphenyl oxide | 394,5 | 208 | 0,2 |
| | indole | 254,7 | 52,5 | 0,2 |
| | 3, 5 - dimetylphenol | 221,69 | 63,27 | 0,1 |
| | 2, 4 - dimetylphenol | 210,93 | 24,54 | 0,1 |
| | 2 – methylpyridine (α – picoline) | 129,40 | -66,7 | 0,02 |
| | 3 – methylpyridine (β – picoline) | 144,14 | -18,25 | 0,01 |
| | 4 – methylpyridine (γ – picoline) | 145,35 | 3,65 | 0,01 |
| | 2, 6 – dimetylpyridine (2,6 - lutidine | 144,04 | -6,1 | 0,01 |
| | 2, 4 – dimetylpyridine (2,4 - lutidine | 158,40 | -63,96 | 0,01 |
| | pyridine | 115,25 | -41,8 | 0,02 |

Tab. 3. Classification of toxicity
Tab. 3. Klasyfikacja toksyczności

| LD (mg / kg) | Classification |
|---|---|
| < 25 | Very toxic substances |
| Between 25 and 200 | Toxic substances |
| Between 200 and 2000 | Hazardous substances |
| 2000 > | Substances which are not toxic |

Tab. 4. LD and $LD_{50}$ for the compounds come from the hard coal tar
Tab. 4. LD i $LD_{50}$ dla związków pochodzących ze smoły węglowej

| Name of the aromatic compound | LD (oral ingestion, at rats) (mg / kg) | $LD_{50}$ (oral ingestion, at rats) (mg / kg) |
|---|---|---|
| Aniline | | 440 |
| Antracene | > 16000 | |
| Benzene | | 3800 |
| Ethylbenzene | | 3500 |
| O - cresol | | 121 |
| Naphthalene | > 16000 | |
| Fenantrene | > 16000 | |
| Phenol | | 414 |
| Pyrene | > 16000 | |
| Styrene | | 5000 |
| Toluene | | 5000 |
| o – xylene | | 5000 |
| m – xylene | | 5000 |
| p – xylene | | 5000 |

Tab. 5. OELV and AOELV for the compounds come from the hard coal tar
Tab. 5. OELV i AOELV dla związków pochodzących ze smoły węglowej

| Name of the compound | AOELV (mg / m$^3$) | OELV (mg / m$^3$) |
|---|---|---|
| Aniline | 10 | |
| Benzene | 16 | |
| Cresols | 22 | |
| Indene | 45 | |
| Naphthalene | 50 | |
| Diphenyl oxide | 7 | |
| Phenol | 19 | |
| Pyridine | 15 | 30 |
| Styrene | 215 | |
| Toluene | 375 | 550 |
| Xylenes | 435 | 650 |

**Toxic effect of aromatic compounds extracted from hard coal tars**

It is very important to know the compounds that result after the processing of tar coal tar because these chemical compounds are very poisonous both for the man's health and for animals health.

**Toxicity of certain aromatic compounds extracted from hard coal tars**

***Toxicological information***

*Ingestion*

The effects of toxicity due to ingestion are being tested on animal (usually on rats) and the measurement unit is the lethal dose (LD); it is expressed in mg of substance ingested per kilogram of animal body weight. (LD) represents a dose at which a given percentage of animals will die (see table 3).

$LD_{50}$ indicator allows an assessment of chronic toxicity; it is dose at which 50% of subjects will die within a determined period of time.

*Respiratory tract*

The French Ministry of Labor has settled the permissible occupational exposure values with the view to preventing the occurrence of occupational diseases triggered by the polluting substances in the atmosphere of the workplace. There are two values that evaluate the maximum permissible concentrations in the atmosphere of the workplace.

- the occupational exposure limit value (OELV) that measured all trough a maximum exposure period of 15 minutes; the observance of this value shall lead to a short - time avoidance of adverse effects due to the toxic substances;
- the average occupational exposure limit value (AOELV) measured or estimated over an 8 – hour period (see table no. 5).

This table comprises several products which are also very toxic when reaching the skin. These products are aniline, cresols and phenol.

*Water*

Phenol, cresols, xylenes and naphthalene are being classified as "marine pollutants". For cresols, for a 96 hour – period the lethal concentrations (LC50) vary between 5 and 20 mg/l, depending on the species concerned.

For naphtalene, for a 96 hour – period the lethal concentrations ($LC_{50}$) vary between 0.1 and 150 mg/l, depending on the species concerned. These products are biodegradable at low concentrations.

**Carcinogenetic risks**

Benzene and tar vapors are well – known as carcinogenic agents for man so they are subject to strict regulations in relation to the labeling of packages that contain these products.

Starting with the month of august 1997, several substances that can be found in the hard coal tar vapors have been classified as carcinogenic for man. Here are included certain compounds that have 4, 5 or 6 aromatic nuclei, the most well – known being perylene. Their boiling temperature is > 400°C and this is why they are dangerous only in certain conditions of use. Cresols are also part of this classification.

**Conclusions**

1. Coal pyrogenation gives the following main products:
   - semi-coke and coke;
   - gases that contain products which can be chemically treated, such as: ethane, ethene, propene, acetylene, methane, hydrogen, water vapors, etc.;
   - semi-coking and coking tar is a mixture of around 10,000 chemical substances, among which 350 were separated with the help of chemical treatment;
   - ammoniacal waters.

2. The chemical composition of coking tar differs from the chemical composition of semi-coking tar;
   - The coking tar is a complex mixture of aromatic hydrocarbons, phenols, derivatives with nitrogen, oxygen, sulphur, etc.;
   - The semi-coking tar includes alkenes and aromatic hydrocarbons at very low concentrations and oxygenated compounds from the category of phenols and especially of superior phenols, at high concentrations;
   - The compounds resulted from the processing of hard coal tar are very bad for the human health and for the health of the animals.

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## *Wpływ smoły węglowej na środowisko*

*Węgiel jest związkiem makrocząsteczkowym. W wysokich temperaturach, w wyniku pirogenezy węgla, powstanie koks i produkty lotne. Lotne produkty z węgla tworzą gaz koksowniczy i smołę koksową, z której można uzyskać bardzo dużą liczbę związków aromatycznych.*

*W pracy porównano związki aromatyczne uzyskane ze smoły węglowej pochodzenia krajowego i zagranicznego, wraz z ich wpływem na zdrowie ludzi i zwierząt*

***Słowa kluczowe:*** *związki, makrocząsteczki, gaz koksowniczy*