

ENVIRONMENTAL SIGNIFICANCE OF FUEL - DERIVED ORGANIC COMPOUNDS

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Summary

Volatile organic compounds (VOC) are emitted during the combustion process. They originate from the organic components of fossil fuels, or are formed during the combustion process. For example, the addition of smaller aliphatic compounds, cyclization, and transformation into aromatic hydrocarbons leads to polycyclic aromatic compound (PAH) formation. Some PAHs are known to be carcinogenic. The degree of emissions of VOC in the combustion process depends on its conditions.

Considerably higher concentrations of VOC are emitted from small furnaces (residential heating, municipal waste incineration plants etc.). Organic pollutants occur in both the solid phase (adsorbed and associated by fly ash) and the gaseous-vapor phase. Some of them have relatively long lifetimes in the environment. Combustion processes involving chlorine are the source of dioxins.

Volatile organic compounds interact with nitrogen oxide, leading to its oxidation and ozone formation. When nitrogen dioxide concentration and ozone formation are high, photochemical smog of Los Angeles-type is formed. Polycyclic aromatic hydrocarbons are among the compounds showing the highest mutagenic, teratogenic, and carcinogenic properties.

1. Emission of Organic Compounds in the Combustion Process of Fossil Fuels

It is a widely accepted fact that the organic component of coal actually consists of two structures. The main one is a macromolecular insoluble three-dimensional lattice, whose structure involves aromatic and hydroaromatic units bound with ether and thioether chains and short alkyl bridges. The second constituent consists of particles representing a low and medium molecular weight, usually soluble in organic solvents. This molecular component is assumed to contain a varying distribution of aliphatic

hydrocarbons, hydroxylated polycyclic, aromatic compounds, and heterocyclic compounds.

If hydrocarbons are not totally oxidized during combustion, a variety of substances can appear in exhaust gas; for example, alcohols, aldehydes, or organic acids. Hydrocarbons can be oxidized to carbon dioxide and water via stable oxidation states (methanol, formaldehyde, formic acid, carbon monoxide etc.), which are also possible emission components. During incomplete combustion or insufficient mixing of fuel and air in the flame, part of the fuel can escape unburned along with the exhaust gas. In contrast, if there is a lack of air, thermal decomposition (pyrolysis) can set in. This decomposition process either takes place via the reaction of partial oxidation or it leads to the formation of new hydrocarbons not originally contained in the fuel. This is a path through which aromatic (e.g. benzene, toluene, xylenes, and polycyclic aromatic hydrocarbons (PAH)), some of which are known to be carcinogenic, are formed. In the first stage of PAH formation, the addition of smaller aliphatic compounds and cyclization into hydroaromatic hydrocarbons with medium-sized molecules occurs. Then, transformation of hydroaromatic hydrocarbons into fully aromatic hydrocarbons takes place. Finally, the formation of larger polycyclic aromatic hydrocarbons from smaller ones occurs. The PAH family of hydrocarbons consists of molecules containing two or more fused six-carbon aromatic rings. Two common members of the group are naphthalene and benzo(a)pyrene with two and five fused rings, respectively.

The degree of emission of Volatile Organic Compounds (VOC) in the combustion process depends on its conditions. Considerably higher concentrations of VOC are emitted from furnaces used by the communal/social sectors operating low-capacity heating plants. In large power stations the combustion process is constantly monitored, and it is also run at higher temperatures. Research of the coal combustion process conducted in many centers for different combustion conditions has shown that among the emitted pollutants many organic compounds of low boiling point occur: benzene, toluene, aldehydes, phenols, aliphatic compounds C₅-C₂₀, furanes, dioxins, and significant amounts of PAH, just to mention a few.

PAH can also be contained in the matrix fossil fuel: oil or coal. At medium temperatures (approx. 200°C) and under increased pressure PAH can be formed from biological material constituting exploitable fossil deposits. Although the process following this path is rather slow, comparably large quantities of polycyclic compounds can be formed. These compounds are released unchanged or undergo certain transformations during the combustion of coal or oil. Their emission with flue gases from a coal-fired power plant amounts to 30–930 mg/m³, from a municipal waste incineration plant it amounts to 17–2700 mg/m³, and from a bonfire, 2800–173 000 mg/m³. Particularly large quantities are released during tobacco smoking, reaching the value 0.8–2.0 µg/g tobacco. Organic pollutants occur in both solid phase (adsorbed and associated by ash) and the gaseous-vapor phase. Distribution of these pollutants between ash and gaseous states depends on the type of furnace and combustion condition. Generally, it can be assumed that approximately 20–30% of pollutants exist in adsorbed and ash-associated forms. It has been observed that two- and three-ring hydrocarbons prevail in the gaseous phase while the four- and five-ring ones are present in the solid matter (ash).

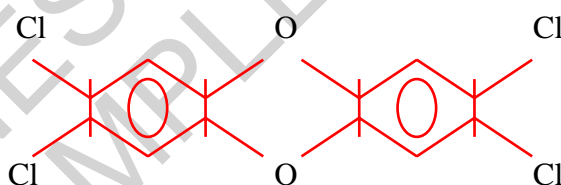
	USA	Sweden	Norway
Residential heating combustion (wood, coal, oil, gas)	1380	132	62.5
Municipal plants, bonfires, forest fires, agricultural waste	1150	3.5	13.7
Power generation (coal, oil, peat)	401	13	1.3

Table 1. Production of volatile organic compounds from combustion, in selected countries. (Units: tons per unit)

Organic pollutants, which have a long environmental residence time, are generally called persistent organic pollutants (POPs). These include polycyclic aromatic compounds and a host of chlorinated organic compounds. PAHs feature strong UV and visible light absorption. It leads to photochemical modification and transformation of these substances. PAHs in clear water with high oxygen concentration exposed to sunlight have a half-life shorter than an hour (e.g. benzo(a)pyrene of then order of one year).

For PAHs with lower molecular weight, the half-life is much shorter in sediment water but much longer in the first described conditions. In the first case, photolytic degradation and biodegradation in the second case take place. On the other hand, PAHs deposited in the soil or water undergo biological degradation by microorganisms. Combustion processes involving chlorine are the source of dioxins as well. Dioxins, or PCDDs (polychlorinated dibenzo(1,4)dioxins) are widely distributed in relatively low concentrations in the atmosphere, soil, sediments, plants, animals and in humans.

For example, the 2,3,7,8-tetrachlorodibenzo(1,4)dioxin has the following structural formula:



Other halogenoderivatives formed in the combustion process are polychlorinated dibenzofurans (PCDFs).

Combustion sources produce a variety of PCDD and PCDF congener profiles. Even for a single source, the profile will vary with the fuel used and the combustion temperature. Combustion sources include municipal waste incineration plants, coal-fired power plants and others.

Dioxins associated with particulates from combustion processes may reside in the atmosphere for considerable periods. For dioxins and PCDFs phototransformation of vapor phase material is quite important. As for reaction of OH radical with dioxins, an estimate of the tropospheric lifetime is approximately seven hours.

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Biographical Sketch

Andrzej Grzegorz Chmielewski was born in Warsaw in 1943. In 1967 he graduated from the Warsaw University of Technology where he obtained his Ph.D. (1974) and D.Sc. (1984) in chemical engineering. He was appointed Professor in 1992. Six Ph.D. theses and 15 M.Sc. diploma theses were performed under his supervision. In 1967-1983 he was employed at the Warsaw University of Technology (Institute of Process and Chemical Engineering). In 1976-1977 he worked as Postdoc. Res. Assoc. at the Chemistry Department, University of Tennessee, Knoxville, USA.

Since 1983 he has been working at the Institute of Nuclear Chemistry and Technology, at the beginning as Head of the Department and since 1986 till 2001 as Scientific Director of the Institute. Recently he is a Head of the Department at the Institute and holds position of the Professor at the Warsaw University of Technology (Department of Chemical and Process Engineering). He has lectured in Japan, Brazil, Syria and Saudi Arabia and served as UN expert to China, the Philippines, Iran, Brazil, Ukraine, Chile, Malaysia and South Korea. He is author and co-author of over 100 papers, two textbooks and over 45 patents (including patents in the USA(3), Germany(2), Canada, Japan, China, Russia, Ukraine). Many of invented solutions were implemented in industry. Among them new type wastewater equalizer-clarifier constructed at the biggest Polish refinery Orlen, Plock and the installation for electron beam flue gas purification from SO₂ and NO_x for 100 MW_e block at EPS Pomorzany, Szczecin (second plant in the world using this process). In 1999 he was awarded with the title "Engineer of the Year" by prestigious Polish professional journal "Technical Review".

Professor Chmielewski is the Editor-in Chief of the scientific journal "Nukleonika." Vice-chairman of the Atomic Energy Council, a member of the Board and in the years 1999-2001 President of the Polish Nuclear Society, vice-president of the Council of the Radiation Research Foundation, member of the Advisory Board of the "Europe Nuclear Worldscan" (ENS, Switzerland), a member of the Scientific Council of many Institutes.