



## Full Length Article

# Analysis of pyrolysis liquids obtained from the slow pyrolysis of a German brown coal by comprehensive gas chromatography mass spectrometry



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## HIGHLIGHTS

- Resolution of more than 1000 compounds in a pyrolysis liquid from coal.
- Qualitative evaluation of observed alkanes, alkenes, alkylbenzenes, thiophenes, phenols and carboxylic acids.
- Combination of data from GC×GC and FT-ICR-MS.
- Quantification of 94 compounds.
- Evaluation of temperature dependent liberation behavior.

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## ABSTRACT

Due to the upcoming shortage of crude oil and natural gas, alternative resources for the production of chemicals are needed and long-term research should be conducted. One of the future possible methods for the production of valuable chemicals is the utilization of coal and its conversion by pyrolysis. During pyrolysis, macromolecular organic compounds are decomposed into smaller compounds, which can be utilized. The development of these processes requires compositional knowledge of the products, which are very complex mixtures of organic compounds. In this study a series of pyrolysis liquids obtained in a fixed bed reactor at different pyrolysis temperatures between 400 and 700 °C is analyzed qualitatively and quantitatively by comprehensive gas chromatography mass spectrometry (GC×GC-MS). More than thousand compounds were observed in each of the samples. Selected compound classes (alkanes, alkenes, alkylbenzenes, phenols, carboxylic acids and thiophenes) are discussed in detail. Quantification results of 94 compounds are given, visualized and discussed in relation to the pyrolysis conditions. It is demonstrated, that the application of GC×GC-MS is highly beneficial for the analysis of pyrolysis liquids from coal.

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## 1. Introduction

During the last decades it has been generally accepted, that a fundamental change in the worlds supply with energy and carbon raw materials will take place in the near future. The oil crisis in the 1970s and 1980s lead to the widespread acceptance that the depletion of readily available crude oil reservoirs will lead to a shortage in the next decades. Nevertheless, forecasts of *peak oil*, the point in time of the maximum production rate of crude oil, are uncertain

[1,2]. In the past, carbon based raw materials, which have been utilized by mankind for energetic usage or the production of chemicals, were constantly changing. After a long period of biomass utilization, coal was established as the major carbon raw material during industrialization. In the middle of the 20th century, coal itself was replaced largely by crude oil and natural gas, which had substantial advantages [3–5]. Coal derived products are still produced, but mainly as byproducts from coking, and crude oil will remain the main carbon resource for the chemical industry during the next decades. Bearing this steady change in mind, the current situation facing depleting oil reserves, is not unusual to mankind and it can be expected, that a diversification of solutions for energetic and material use of carbon raw materials will take place. For

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this, a stepwise shift from a crude oil based chemical industry to an industry with a diversified carbon feedstock must be managed during the next decades. At present there are several possible feedstocks, like e.g. biomass, coal, crude oil residues or plastic wastes, which can be converted thermochemically into chemical feedstocks. A diversification of the carbon feedstocks would be highly advantageous, since it will lower the reliance associated with the usage of only one or a few feedstocks like crude oil.

Coal is one of the possible alternative feedstocks, which will gain importance in the future [6,5], also due to its widespread appearance around the world compared to crude oil or natural gas [2]. Coal comprises monocyclic and polycyclic aromatic structures that represent ideal feedstocks for aromatic polymers and plastics, which currently show an increase in applications [6]. Existing coal conversion processes need to be developed further and adopted to modern requirements regarding rate of yield, purity and energetic aspects. A current review gives an overview on the utilization of lignites for the production of value added chemicals [7].

A general task, which can be found in several of these conversion processes, is the thermochemical conversion of the higher molecular weight feedstock into lower molecular weight products. One of the most important thermochemical conversion processes in this regard is pyrolysis. During pyrolysis, a macromolecular compound is decomposed into smaller compounds at elevated temperatures and in the absence of oxygen. Various chemical reactions like dehydration, dehydrogenation, cyclization, condensation and aromatization take place. Due to complex, usually macromolecular starting materials, and diverse reaction possibilities of the reactants, complex mixtures of lower molecular weight compounds result. Solid, liquid and gaseous compounds are produced. Depending on the usage aimed at, each of the phases can be a target product. When valuable chemicals should be produced, the liquid phase is usually referred to as the target product, and the gas is used for heating. Most studies dealing with pyrolysis aim in the investigation of biomass pyrolysis, but an increasing number of studies focusses on coal pyrolysis [7].

The liquids produced during pyrolysis are very complex mixtures of organic compounds, which range in dependence of the feedstock and pyrolysis conditions from apolar to polar and low to high molecular weight compounds. An analysis of these mixtures requires high resolving analytical methods, which are able to separate and give structural information of the compounds. Compounds with boiling points <400 °C are amenable to gas chromatography (GC), whereas higher boiling compounds may be analyzed by direct infusion mass spectrometry (MS) or liquid chromatography (LC).

A very powerful GC method is comprehensive gas chromatography hyphenated to mass spectrometry (GC×GC-MS) [8–12]. By utilizing the different separation principles of two GC columns, which are connected by means of a modulator, a very high separation power can be achieved in one analysis run. This setup leads to several advantages, of which the increased peak capacity is the most important. By this, minor concentrated compounds are not corrupted by higher concentrated coeluting compounds and the clean mass spectra allow structure elucidation. An appreciated side effect is the increase of the limit of detection due to the focussing effect of the modulator. GC×GC is favorably applied whenever complex mixtures have to be analyzed. Petrological samples, which are usually composed of a major amount of hydrocarbons and a minor amount of heterocyclic compounds, are a common application. A complete review of the literature of petrological analysis with GC×GC goes beyond the scope of this paper, so the following literature survey is restricted to coal derived liquids. However, the analysis of liquids from the pyrolysis of coal itself is a small group of applications from this field. A current review

by Liu et al. gives an overview of the application of mass spectrometry for the analysis of coal derived liquids including studies using GC×GC [13].

Sulfur compounds in coal tar have been analyzed by GC×GC-MS by Machado et al., who could show that frequently observed coelutions in GC can be resolved in the majority of the cases [14]. da Silva demonstrated that coal tar samples can be successfully analyzed for neutral and basic nitrogen compounds by GC×GC-MS without any prefractionation [15]. Zoccali et al. showed in a proof-of-principle study the advantages of an online prefractionation of a coal tar sample by liquid chromatography and analysis by GC×GC. The separation of the very complex sample prior to GC×GC into nonaromatic hydrocarbons, unsaturated compounds and oxygenated compounds allowed to apply optimum conditions in GC×GC for every fraction [16]. Our group contributed results on the qualitative composition of liquids from the slow pyrolysis of a German brown coal analyzed by GC×GC [17]. The number of compounds observed in these samples is usually in the range of several hundred to more than thousand peaks per sample, and manual evaluation is limited to selected compounds and compound classes. Therefore we proposed a classification method using supervised learning to group structurally related compounds. Also, we conducted a more detailed investigation on the presence of alkylbenzenes in dependence of the pyrolysis feedstock [18]. Other applications of GC×GC for coal tar related samples are forensic analyses of coal tars from former manufactured gas plants [19–21]. Koolen et al. [22] analyzed historic coal tar samples by GC×GC-MS and found ≈3000 peaks compared to ≈250 observed by GC-MS.

Samples from the direct liquefaction of coal have a comparable composition to samples from pyrolysis, and method development for GC×GC is similar. Products from liquefaction are mainly composed of aliphatic and aromatic hydrocarbons. Hamilton et al. could track in parts the fate of hydrogen shuttles. They point out the superior separation power of GC×GC compared to GC-MS, which allowed the observation of the known naphthalene derived hydrogen shuttles, but also higher molecular weight compounds [23]. Further progress in the identification of aromatic and hydroaromatic structures in direct liquefaction products was made by Stihle et al., who identified a series of hydroaromatic compounds [24]. Omais et al. investigated different column combinations for the analysis of liquefaction products [25] but also focussed on the identification and quantification of oxygen compounds in the products from the liquefaction of coal using GC×GC. The superior separation enabled the identification of phenolic compounds, benzofurans and indanols, as well as never before observed diols and naphthalenones [26–28]. Adam et al. [29] used a nitrogen chemiluminescence detector (NCD) with GC×GC for the analysis of nitrogen compounds in products from coal liquefaction. A similar experimental setup was also utilized by Dutriez et al. for the analysis of nitrogen compounds in a product from coal liquefaction [30]. Products from hydrothermal liquefaction have been analyzed by Hartman and Hatcher, who used a combination of GC×GC, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and nuclear magnetic resonance spectroscopy for comprehensive characterization of the samples [31].

The survey of the literature shows, that the application of GC×GC for the analysis of pyrolysis liquids from coal is still scarce, but the number of publications increases. Analysis methods have been developed for coal tar and products from liquefaction. Mainly qualitative results have been presented and quantitative studies are still an exception, although some workflows for a comprehensive quantification have been presented [32,33]. An important future challenge will be the development of methods for the comprehensive quantitative evaluation of GC×GC datasets.

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