Study of Evolved Gases from Pitch Combustion Using the TGA-FT-IR Technique

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Introduction

Pitch, a complex carbonaceous material derived from the distillation of organic substances such as coal tar or petroleum, is widely used in industries ranging from metallurgy to carbon fiber production. Understanding the thermal stability and decomposition behavior of pitch is critical, as these properties directly influence its performance in high-temperature applications, such as the manufacture of carbon-based materials and composites.

Measurement Conditions

In this study, we explore the thermal stability of pitch samples and conduct detailed gas analysis to better understand the decomposition pathways and the nature of the volatile species released. Through these analyses, we aim to elucidate the thermal behavior of pitch, providing valuable data that can inform both the development of new materials and the enhancement of existing industrial processes.

The measurement was performed with a NETZSCH PERSEUS® STA *Jupiter®* system. The measurement parameters are detailed in table 1.

Table 1 Measurement parameters

Sample mode	TG-FT-IR
Heating rate	10 K/min
Sample mass	77.19 mg in an 0.3-ml Al_2O_3 crucible
Temperatur program	RT - 1000°C
Purge gas atmosphere	14% oxygen in nitrogen
Purge gas amount	70 ml/min
Spectral measurement range	4400 - 650 cm^{-1}
Resolution	4 cm^{-1}

NGB · Application Note 340 · EN · 1124 · Technical specifications are subject to change.

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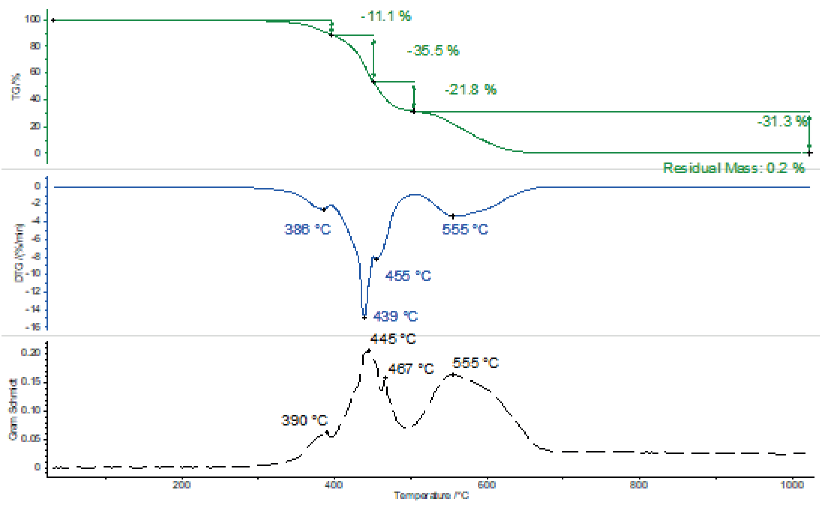
Results and Discussion

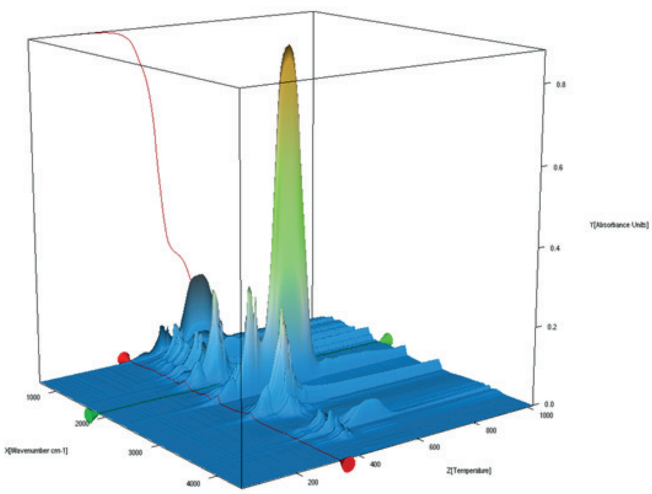
From the TGA and DTG curves, it was found that there were four mass-loss steps in the pitch sample; see figure 1. The first mass-loss step was detected between RT and 400°C with a mass change of 11.1%. The second step occurred between 400°C and 450°C with a mass change of 35.5%. The third mass-loss interval between 450°C and 500°C resulted in a mass change of 21.8%. The fourth step was observed between 500°C and 1000°C with a mass change of 31.3%. The residual mass amounted to 0.2%. The DTG curve is the first-order derivative of the TGA curve, which reflects the rate of mass loss. The DTG peak temperatures for these four mass changes occur at 386°C, 439°C, 455°C and 555°C.

The Gram Schmidt curve displays the overall IR intensities and behaves as a mirror image of the mass-loss rate (DTG). It also shows maximum intensities during mass-loss steps. This proves the interaction of the evolved gases with the IR beam.

Figure 2 shows a 3D graph of the evolved gas from the TGA-FT-IR coupling test of pitch under air atmosphere between RT and 1000°C. In the OPUS software of the FT-IR device, this cube display of the measurement can be rotated in all directions to obtain an exact view of the recorded gases released.



1 Temperature-dependent mass change (TGA, green), rate of mass change (DTG, blue), Gram Schmidt curve (black, dashed).



2 3D plot of all detected IR spectra of the pitch sample; TGA curve plotted in red at the back of the cube.

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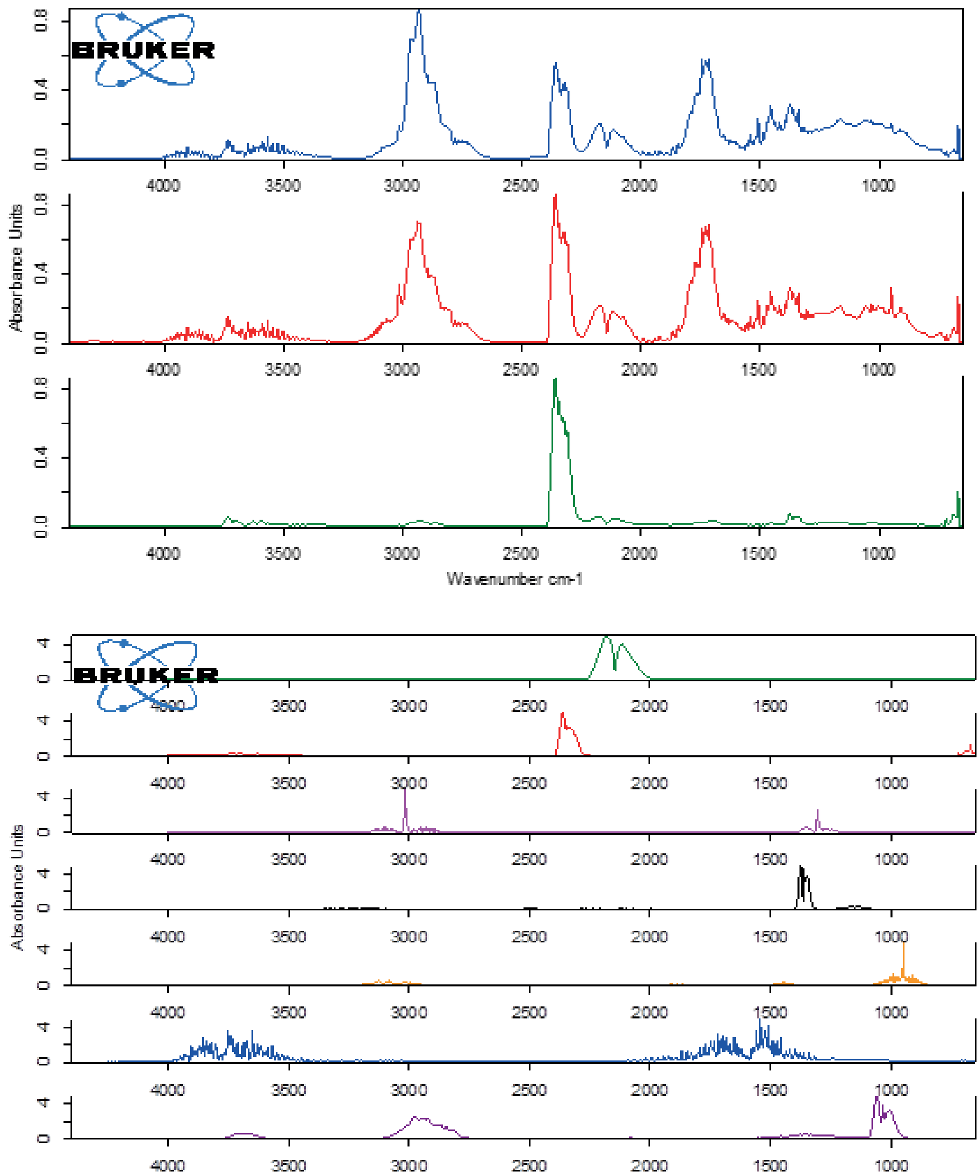
It can be assumed from the infrared spectra of figure 3 that the gaseous products of pitch at 400°C to 500°C mainly include the release of CH_4, CO_2, CO, and H_2O. Traces of methanol and ethene, aldehydes (significant IR vibration between 1600 and 1800 cm^{-1}) and hydrocarbons (significant IR vibration between 2700 and 3000 cm^{-1}) could also be detected. Of course, aromatic compounds are also released. However, they are not identified here. This indicates that many aliphatic and aromatic substances are released at the same time. The residual products are probably dehydrogenated and polymerized into long-chain macromolecules, which belong to the aerobic thermal cracking stage of asphalt binder [1].

At 500°C to 700°C, it is assumed to be the combustion stage of pitch in combination with the results of the infrared spectral analysis in figure 3. Compared to 300°C to 500°C, it can be found that the release of inorganic gases H_2O, CO_2, SO_2 and CO increased significantly, but at the same time, the release of organic compounds such as CH_4, aldehydes, C-C and C=C decreased significantly or even disappeared [2]. This proves that the oxidation reaction dominates as the temperature increases.



3 (a) upper part: infrared spectra of the pitch sample at 399°C (blue), 455°C (red) and 575°C (green);
(b) lower part: library spectra of CO (green), CO_2 (red), methane (pink), SO_2 (black), methanol (orange), water (blue) and ethylene (purple).

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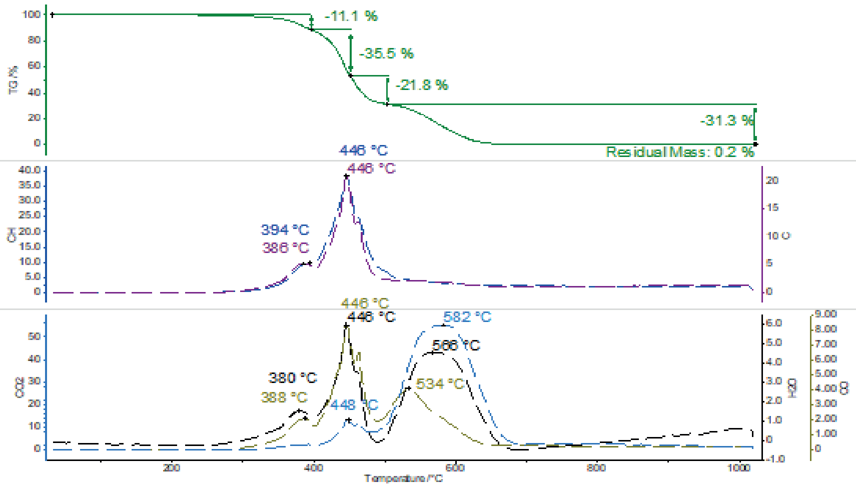
Integrating the wavenumbers of different substances or functional groups, it was possible to obtain a temperature-dependent release of the substance or functional group. Figure 4 shows the TGA curves of pitch and the wavenumber integration curves of three substances and two functional groups. It can be seen that hydrocarbons and aldehydes are present in the first three mass-loss steps, while CO, CO_2 and water are present in all four mass-loss steps; further, CO_2 shows its maximum release in the fourth mass-loss step.



4 Pitch TGA curve and temperature dependence of different substances/functional group integrals

Table 2 Integral wavenumber intervals for different substances/functional groups

Substances/functional group	Integral wave number range
C-H (dark blue)	3200 - 2600 cm^{-1}
C=O (purple)	1900 - 1600 cm^{-1}
CO_2 (light blue)	2400 - 2250 cm^{-1}
H_2O (black)	4000 - 3800 cm^{-1}
CO (olive)	2200 - 2000 cm^{-1}

Conclusion

The application of thermal analysis techniques in combination with infrared spectroscopy (FT-IR) in this study of pitch materials is extensive and in-depth. TGA allows for the measurement of the mass change of a sample under controlled temperature procedures, which can reveal the thermal decomposition temperature and volatile content of the pitch.

Combined with FT-IR analysis, it can further identify changes in the molecular structure of pitch at different temperatures, such as the formation or fracture of functional groups, thus providing a comprehensive assessment of the thermal stability and aging mechanism as well as providing a solid theoretical basis and technical support for the in-depth research and innovative development of pitch materials.

References

[1] Zhu K, Qin X, Wang Y, et al. Effect of the oxygen concentration on the combustion of asphalt binder[J]. Journal of Analytical and Applied Pyrolysis, 2021, 160:105370-.DOI:10.1016/j.jaap.2021.105370.
[2] Xu T, Huang X. Study on combustion mechanism of asphalt binder by using TG–FTIR technique[J]. Fuel, 2010, 89(9): 2185-2190.

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