

Investigation of carriers of lustrous carbon at high temperatures by infrared spectroscopy (FTIR)

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Abstract

Lustrous carbon is very important in processes of iron casting in green sand. Lustrous carbon (pirografit) is a microcrystalline carbon form, which evolves from a gaseous phase. In the case of applying additions, generating lustrous carbon, for sands with bentonite, there is always a danger of emitting – due to a high temperature of liquid cast iron and a humidity - compounds hazardous for a human health. There can be: CO, SO₂, benzene, toluene, ethylbenzene, xylene (the so-called: BTEX) as well as polycyclic aromatic hydrocarbons (PAHs). In order to assess the selected mixtures: bentonite – carrier of lustrous carbon, in which a coal dust fraction was limited, the thermogravimetric analysis and the analysis of evolving gases were performed. Examinations were carried out in the Applications Laboratory NITZSCH-Gerätebau GmbH, Selb/Bavaria, Germany. The NETZSCH TG 209 *FI Iris*[®] thermal analyzer coupled to the BRUKER Optics FTIR *TENSOR™* was used to measure.

Keywords: Green sands, Carriers of lustrous carbon, Thermal analysis, Infrared spectroscopy, FTIR

1. Introduction

Lustrous carbon is very important in processes of iron casting in green sand. Lustrous carbon (pirografit) is a microcrystalline carbon form, which evolves from a gaseous phase [1, 2]. Its main task is a protection of a casting surface against sand scorching and obtaining the required surface smoothness. Lustrous carbon is formed, during pouring liquid metal into moulds, from additions containing carbon, which are being introduced together with bentonite into sands. The main source of lustrous carbon in sands with bentonite was, until recently, coal dust. However, mainly because of the environment protection and improvement of work conditions, the world companies producing additions for sands

with bentonite are searching for coal dust substitutes being more environmentally friendly [2, 3, 4]. Such additions can be: graphite dust, coke dust, carbon black, granulated tar, synthetic resin, gilsonite, lignite, aliphatic oils etc. [5, 6, 7, 8].

Product of the Hüttenes-Albertus Company of a trade name Carbofluid, which is able to form lustrous carbon in an amount of 12 to 25% is an example of a coal dust alternative. Very broad successful investigations in the field of development ecological substitutes for coal dust are carried out in the S&B Industrial Minerals Company in cooperation with the Faculty of Foundry Engineering, of the AGH - University of Science and Technology, the Faculty of Chemistry of the Jagiellonian University and Bergakademie Freiberg. The developed

technology of the name ENVIBOND utilizes microcrystalline graphite as such substitute [9, 10, 11, 12, 13].

In the case of applying additions, generating lustrous carbon, for sands with bentonite, there is always a danger of emitting – due to a high temperature of liquid cast iron and a humidity -compounds hazardous for a human health. There can be: CO, SO₂, benzene, toluene, ethylbenzene, xylene (the so-called: BTEX) as well as polycyclic aromatic hydrocarbons.

In order to assess the selected mixtures: bentonite – carrier of lustrous carbon, in which a coal dust fraction was limited, the thermogravimetric analysis and the analysis of evolving gases were performed.

Examinations were carried out in the Applications Laboratory NITZSCH-Gerätebau GmbH, Selb/Bavaria, Germany.

2. Materials and the applied method

Two mixtures, being applied in domestic foundry plants as additions to sands with bentonite, were selected.

They were:

1. Kormix 75 produced by ZGH Zębice
2. Ekosil produced by Süd-Chemie.

For the assessment of the selected mixtures: bentonite – carrier of lustrous carbon, in which a fraction of coal dust was limited, the thermo gravimetric analysis as well as infrared spectroscopic analysis, FTIR, of evolving gases was performed. These investigations constitute the continuation of the previous ones performed by the authors for mixtures Ekosil and Kormix at the application of the thermo analyser coupled with the mass spectrometer [14, 15].

Examinations were carried out in the Applications Laboratory NITZSCH-Gerätebau GmbH, Selb/Bavaria, Germany. For measurement of the temperature-dependent mass changes including gas analysis employing the NETZSCH TG 209 *FI Iris*[®] simultaneously coupled to the BRUKER Optics FTIR *SENSOR*[™] was used (fig. 1).

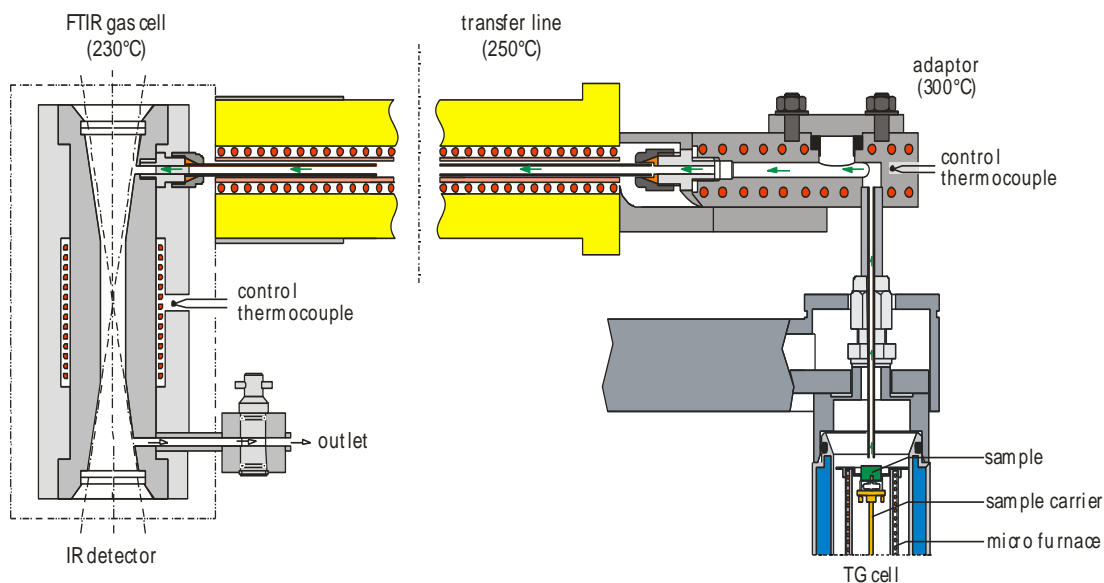


Fig. 1: Schematic design of the FT-IR coupling and the gas cell

The Thermo-Microbalance NETZSCH TG 209 *FI Iris*[®] with an effective resolution of 0.1 µg enables highly precise measurements under pure gas atmospheres from ambient temperatures up to 1000°C. Internal mass flow controllers (MFC) guarantee a highly precise gas flow adjustment of three different gases. For control of the measurements as well as for data acquisition, modern digital electronics and the well established NETZSCH *PROTEUS*[®] 32-bit Software are employed. Several *Advanced Software* packages like *c-DTA*[®] (calculated DTA-signal), *Super-Res*[®] (rate-controlled mass change) or *Thermokinetics*[®] are available. Combining both thermogravimetric and spectroscopic methods such as FTIR and/or MS, enables furthermore identification of the evolved gases. Data exchange between NETZSCH *PROTEUS*[®] software

and Bruker *OPUS*[™] software is done online during the measurement. This guarantees simultaneous start and stop of the measurement as well as data exchange during the measurement.

Experimental conditions:

temperature range	RT – 1000°C,
heating rate	20 K/min,
atmosphere	nitrogen,
flow rate	40 ml/min,
crucible	Al ₂ O ₃
sample mass	about 10 mg

3. Results of examinations

Kormix sample

Figure 2 shows the TG results of the measurement of sample "Kormix 75" in a temperature range from room temperature to

1000°C under nitrogen atmosphere. TG depicts the relative mass change of the sample (black), the mass-loss rate signal as the first derivative of TG (DTG, green) and the Gram-Schmidt trace (blue curve) as the overall IR intensities. Three mass loss steps can be detected: 1.2%, 8.0% and 5.2% with maximum at temperature 68°C, 468°C and 673°C respectively.

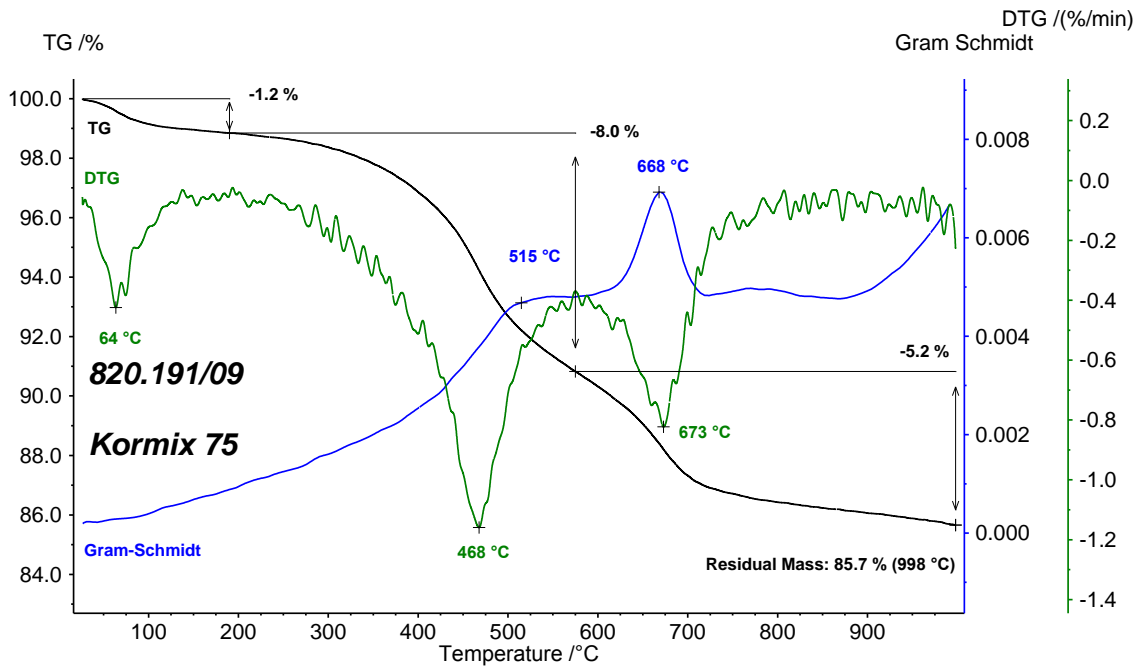


Fig. 2. Temperature-dependent mass change (TG), rate of mass change (DTG) and heat flow rate (DSC) of the sample Ekosil

Corresponding to the DTG curve, the intensities of the Gram-Schmidt trace increase as soon as a mass loss is detected. It is more or less the mirrored view of the DTG curve and this shows that the gases are interacting with the infrared beam as soon as they are released and transferred to the gas cell.

A collection of all detected IR-spectra is shown exemplary in figure 3. The 3D-cube is temperature-scaled and additionally displays the TG signal at the side face. From the 3D cube, single spectra at the DTG minima were extracted (figure 4) and compared to library data (figures 5 to 7).

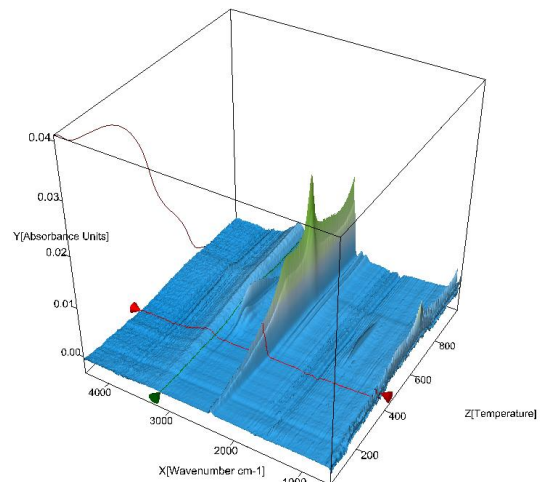
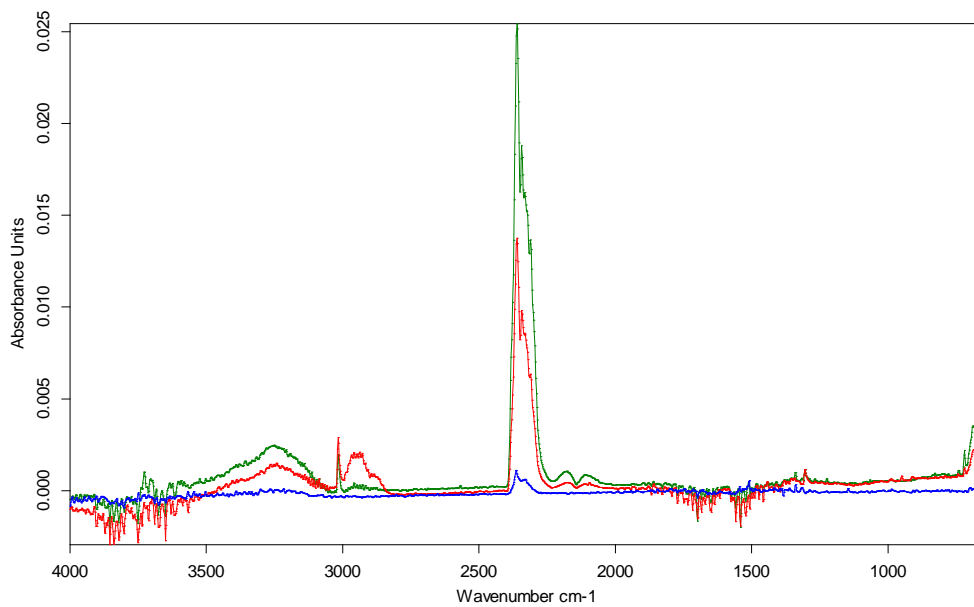
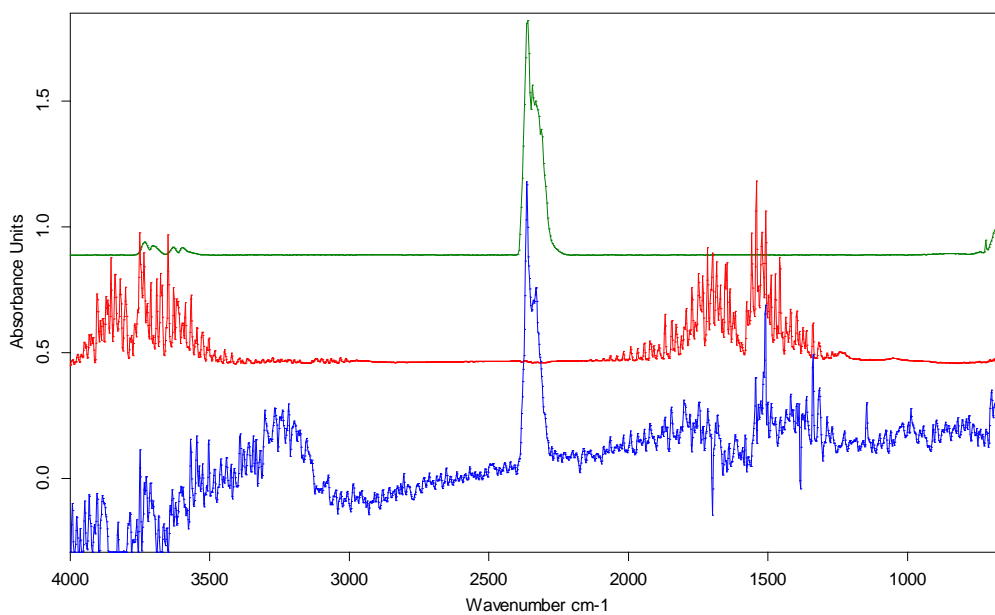


Fig. 3: 3D view of all detected IR-spectra versus temperature including the TG results at the side face for Kormix sample



M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-05 66C.0	Kormix 75	8.466 NETZSCH TG 209 F1	27/08/2009
M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-05 487C.0	Kormix 75	8.466 NETZSCH TG 209 F1	27/08/2009
M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-05 672C.0	Kormix 75	8.466 NETZSCH TG 209 F1	27/08/2009

Fig. 4: Extracted IR spectra of the specimen at 66°C (blue), 487°C (red) and 672°C (green)



M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-05 66C.0	Kormix 75	8.466 NETZSCH TG 209 F1	27/08/2009
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C:\Dokumente und Einstellungen\Sonja.Eichholz\Eigene Dateien\NGB Bibliothek\CO2.01	CARBON DIOXIDE		

Fig. 5: Comparison of the extracted IR-spectrum at 66°C (blue) with the library spectra of CO₂ (green) and water (red)

Small amounts of water and CO₂ are detectable at 66°C (figure 5). At 487°C (figure 6) CO₂, CO, methane and additional vibrations at about 3000 cm⁻¹ can be detected. This gives a hint of saturated

carbohydrates. No unsaturated vibrations can be measured. At 672°C the carbohydrate vibrations disappear and only CO, CO₂ and methane are detectable (figure 7).

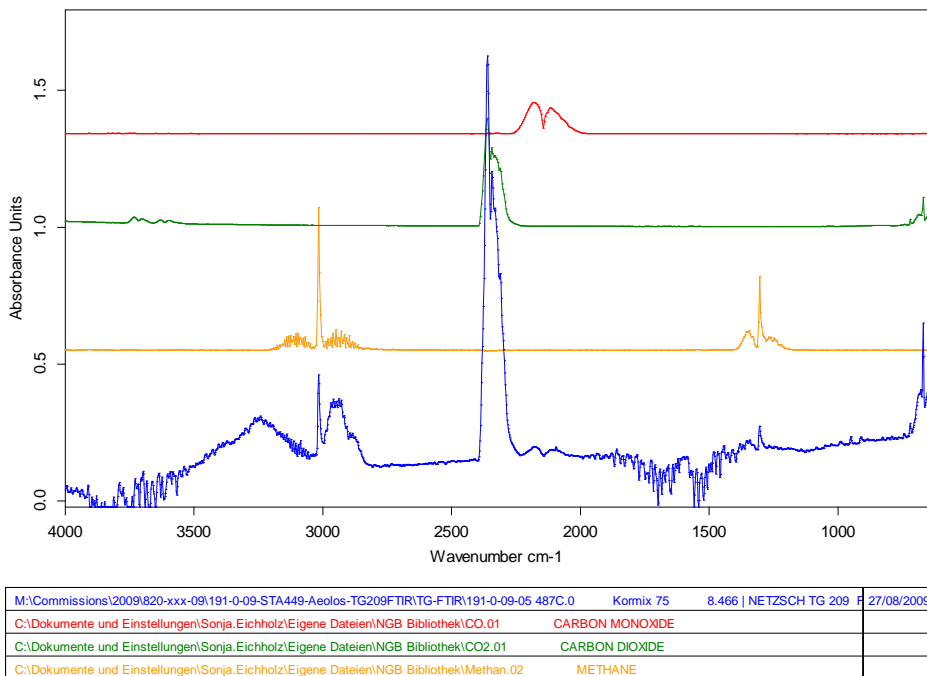


Fig. 6: Comparison of the extracted IR-spectrum at 487°C (blue) with the library spectra of CO (red), CO₂ (green) and methane (orange)

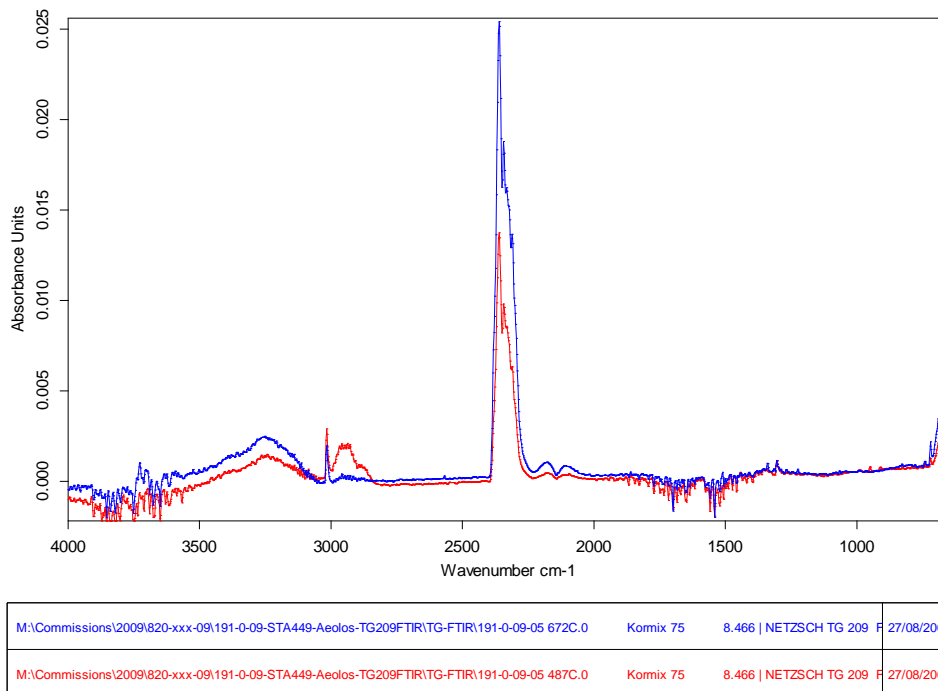


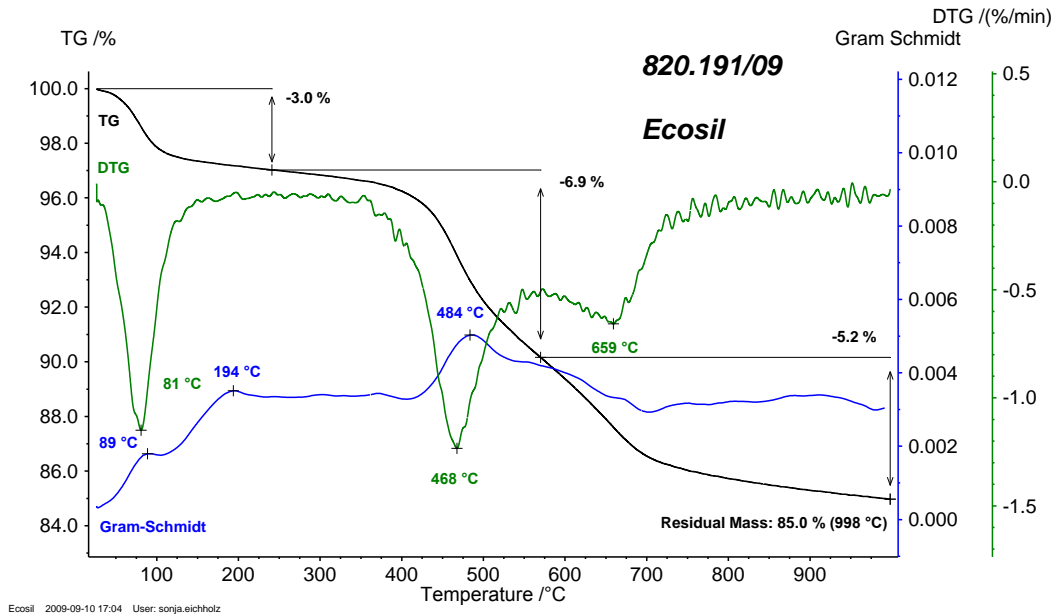
Fig. 7: Comparison of the extracted IR-spectrum at 672°C (blue) with the spectrum at 487°C (red)

Ekosil sample

Figure 8 depicts the TG results of the measurement of sample “Ekosil” in a temperature range from room temperature to 1000°C under nitrogen atmosphere. Three mass loss steps can be detected: 3.0%, 6.9% and 5.2% with maximum at temperature 81°C, 468°C and 659°C respectively.

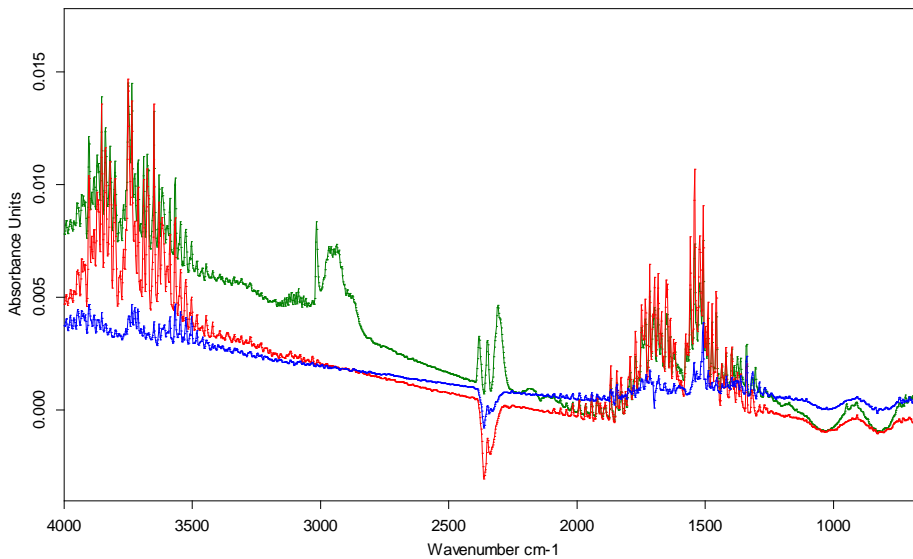
The extracted IR spectra of sample “Ekosil” are shown in figure 9.

At 89°C and 197°C mostly water is detectable (figure 10). At 483°C (figure 11) CO, CO₂, methane and water can be measured. Additionally, saturated CH-stretching vibrations at about 2900 cm⁻¹ are shown, and other vibrations at 2300 cm⁻¹, 910 cm⁻¹ and 719 cm⁻¹ which should provide an indication of nitrile or alkynes derivatives.



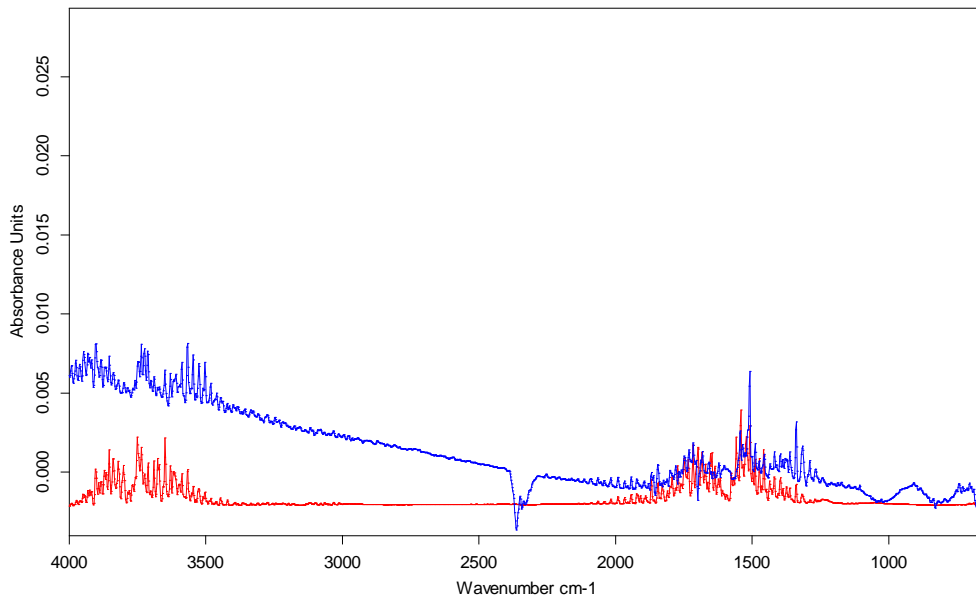
Ekosil 2009-09-10 17:04 User: sonja.eichholz

Fig. 8: TG- (black), DTG- (green) and Gram-Schmidt-(blue) results of sample “Ekosil”



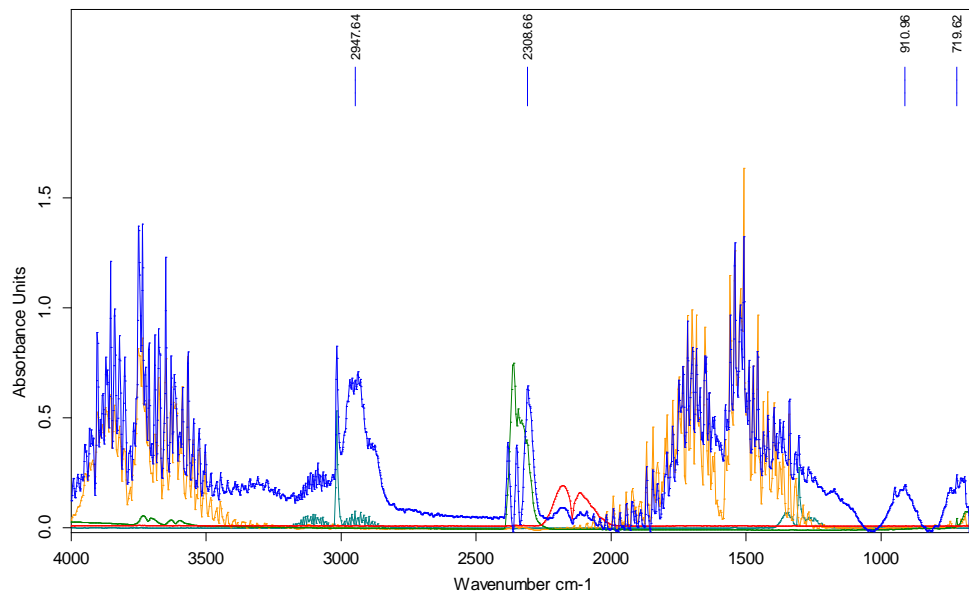
M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-06 89C.0	Ekosil	11.529 NETZSCH TG 209 F1	27/08/2009
M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-06 197C.0	Ekosil	11.529 NETZSCH TG 209 F1	27/08/2009
M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-06 483C.0	Ekosil	11.529 NETZSCH TG 209 F1	27/08/2009

Fig. 9: Extracted IR spectra of the specimen at 89°C (blue), 197°C (red) and 483°C (green)



M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-06 89C.0	Ecosil	11.529 NETZSCH TG 209 F1	27/08/2009
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Fig. 10: Comparison of the extracted IR-spectrum at 89°C (blue) with the library spectrum of water (red)



M:\Commissions\2009\820-xxx-09\191-0-09-STA449-Aeolos-TG209FTIR\TG-FTIR\191-0-09-06 483C.0	Ecosil	11.529 NETZSCH TG 209 F1	27/08/2009
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C:\Dokumente und Einstellungen\Sonja.Eichholz\Eigene Dateien\NGB Bibliothek\CO2.01	CARBON DIOXIDE		
C:\Dokumente und Einstellungen\Sonja.Eichholz\Eigene Dateien\NGB Bibliothek\water.1	WATER DISTILLED		
C:\Dokumente und Einstellungen\Sonja.Eichholz\Eigene Dateien\NGB Bibliothek\Methan.02	METHANE		

Fig. 11: Comparison of the extracted IR-spectrum at 483°C (blue) with the library spectra of CO (red), CO₂ (green), water (orange) and methane (turquoise)

4. Conclusions

1. During heating of both samples (Kormix and Ekosil) three maximums of a mass loss occurred at very similar temperatures.
2. The main components evolving during heating were: H₂O, CO, CO₂ and CH₄. In addition, at higher temperatures vibrations corresponding probably to saturated hydrocarbons were recorded. In the case of Ekosil, vibrations probably corresponding to compounds from nitrile (RCN) or alkynes (CH_{2n-2}) group were observed.
3. Application of the thermal analysis coupled with the infrared spectrometry constitutes a valuable supplement of investigations carried out in a system: thermal analysis – mass spectrometry at the identification of substances evolving during heating of samples, which undergo decomposition. However, for the complete analysis of evolving compounds the gas chromatography application is necessary.

Acknowledgements

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