Substance Scheme
Thermolysis Oil

Product name:	Thermolysis oil
Precurser:	Tyre rubber
Production process:	Pyrum-Thermolysis

Author	Dipl.-Chem. David Hafner	**Issued**	06/11/2018
Dok.-No.	902	**Version**	5
Page count	19		

Revision index	Date	Description
Version 1	05.07.2017	First draft of substance scheme
Version 2	18.07.2017	New Logo
Version 3	25.09.2017	Update
Version 4	06.07.2018	NMR-, UV-Vis and IR- spectroscopy
Version 5	06.11.2018	Two-dimensional gas chromatography

Table of contents

1 Safety information

Table 1: Relevant hazard notes for packaging and safety data sheet according to GHS

			
H225; H226; H228	H312; H315; H319; H332; H335; H336	H340; H350; H351; H361d; H373	H400; H410; H411; H412

Precautionary statements: P201; P210; P260; P261; P273; P280; P301+P310; P301+P312; P304+P340+P312P304+P340+P312; P331; P370+P378; P391; P403+P235; P501

Table 2: Recommended personal protection equipment

			
PPE - long clothing	Safety shoes	Safety goggles	Resistant gloves

Table 3: Relevant warning signals and prohibitions for technical applications

			
Toxic	Danger of explosive atmosphere	No open flames	Do not extinguish with water

Dangerous goods ADR/RID/AND UN1993 LAMMABLE LIQUID, N.O.S. (BENZENE, TOLUENE), ENVIRONMENTALLY HAZARDOUS

All safety information is based on experience and is merely intended to assist and sensibilize the user. It does not replace the user's risk and danger assessment in any way.

2 Physical properties

state of aggregation:	liquid (under atmospheric conditions)		
colour:	brown-yellow		
pH-Wert:	7,5 to 9		DIN 38404C5
density (20°C):	810 to 910	kg/m³	pycnometric
gross calorific value:	35 to 45	MJ/kg	DIN EN 15400
kin. viscosity at 20 °C:	2,5 to 4,5	mm²/s	NF RN ISO3104
kin. viscosity at 40 °C:	1,1 to 2,6	mm²/s	NF RN ISO3104
kin. viscosity at 50 °C:	1,6	mm²/s	DIN 51366
kin. viscosity at 60 °C:	2,0 to 2,6	mm²/s	NF RN ISO3104
kin. viscosity at 75 °C:	1,1	mm²/s	NF RN ISO3104
dyn. viscosity at 20 °C:	2,5 bis 5,5	mPas	ASTM D7042
dyn. viscosity at 40 °C:	2,6	mPas	ASTM D7042
dyn. viscosity at 40 °C:	0,8 bis 1,5	mPas	Ph. Eur. 2.2.10
dyn. viscosity at 60 °C:	1,7 bis 2,1	mPas	ASTM D7042
flash point:	<-20 to 40	°C	Pensky Martens, DIN51755, EN22719
boiling range:	70 to 550	°C	ASTM D2887 Extended

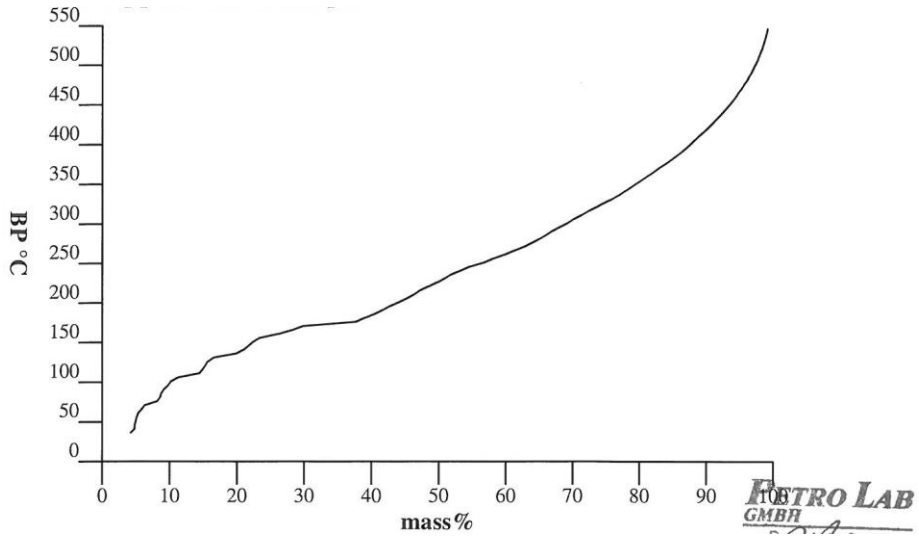


Figure 1: Boiling point distribution by simulated distillation in accordance with ASTM D2887 Ext.

The proportions of the boiling fractions are shown in Figure 1.

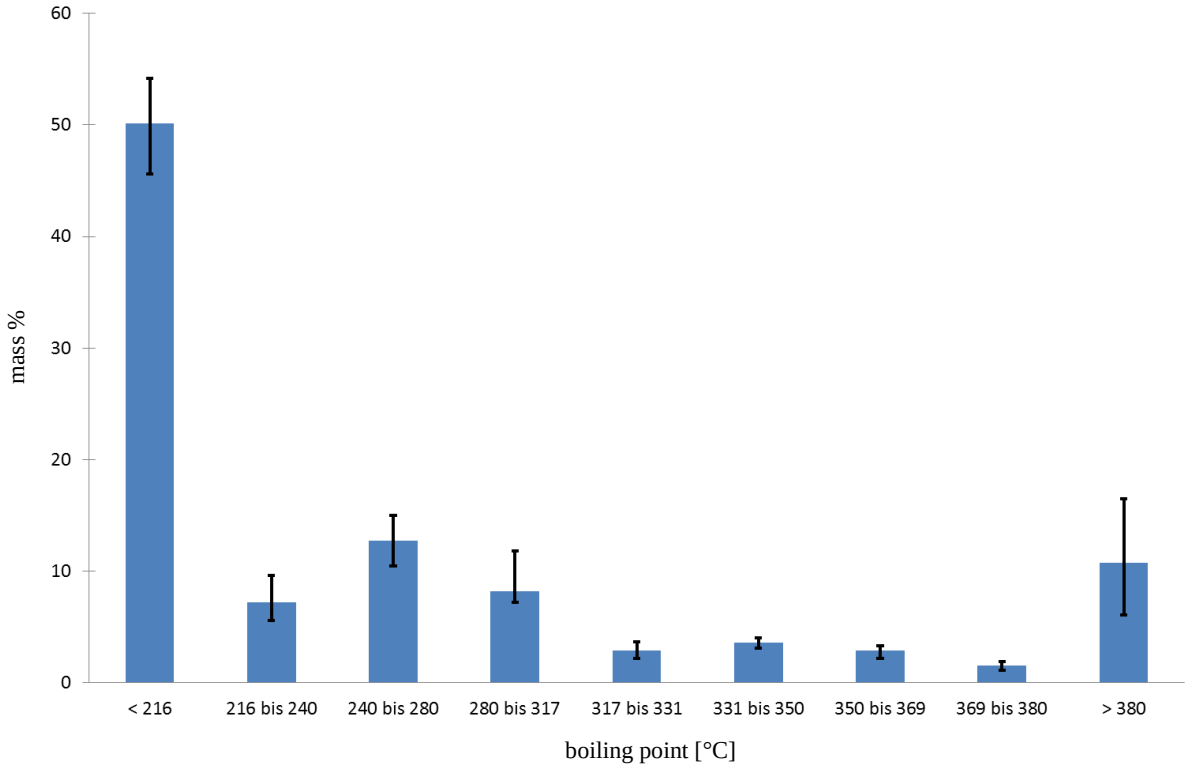


Figure 2: Proportions of the boiling fraction

3 Chemical properties

- Corrosive towards non-passified steel
- Dissolves polystyrene
- Expands many plastics

4 Chemical analysis

4.1 NMR-Spectroscopy

4.1.1 ^{1}H-NMR Spectroscopy

4.1.1.1 Method description

NMR-Spectrometer: Jeol JNM ECS400 with 5 mm probe 40TH5AT/FG, Fieldgradient-System and Auto-Tuning

Parameters:

Frequency/Field:	400 MHz / 9.38 Tesla
X_offset:	7.0 ppm
X_sweep:	8.5 kHz
X_points:	32768
X_angle:	45°
Relaxation delay:	1 sec
X_acq_time:	3.85 sec
Repetition_time:	4.85 sec
Scans:	16
Temperature	room temperature, see spectra
Solvent:	(Chloroform) $CDCl_3$
Reference:	Tetramethylsilane (TMS) is the internal reference for the chemical shift (TMS = 0.00 ppm).
Sample preparation*:*	Solution of about 0.2 mL sample in 2 mL solvent

4.1.1.2 Results

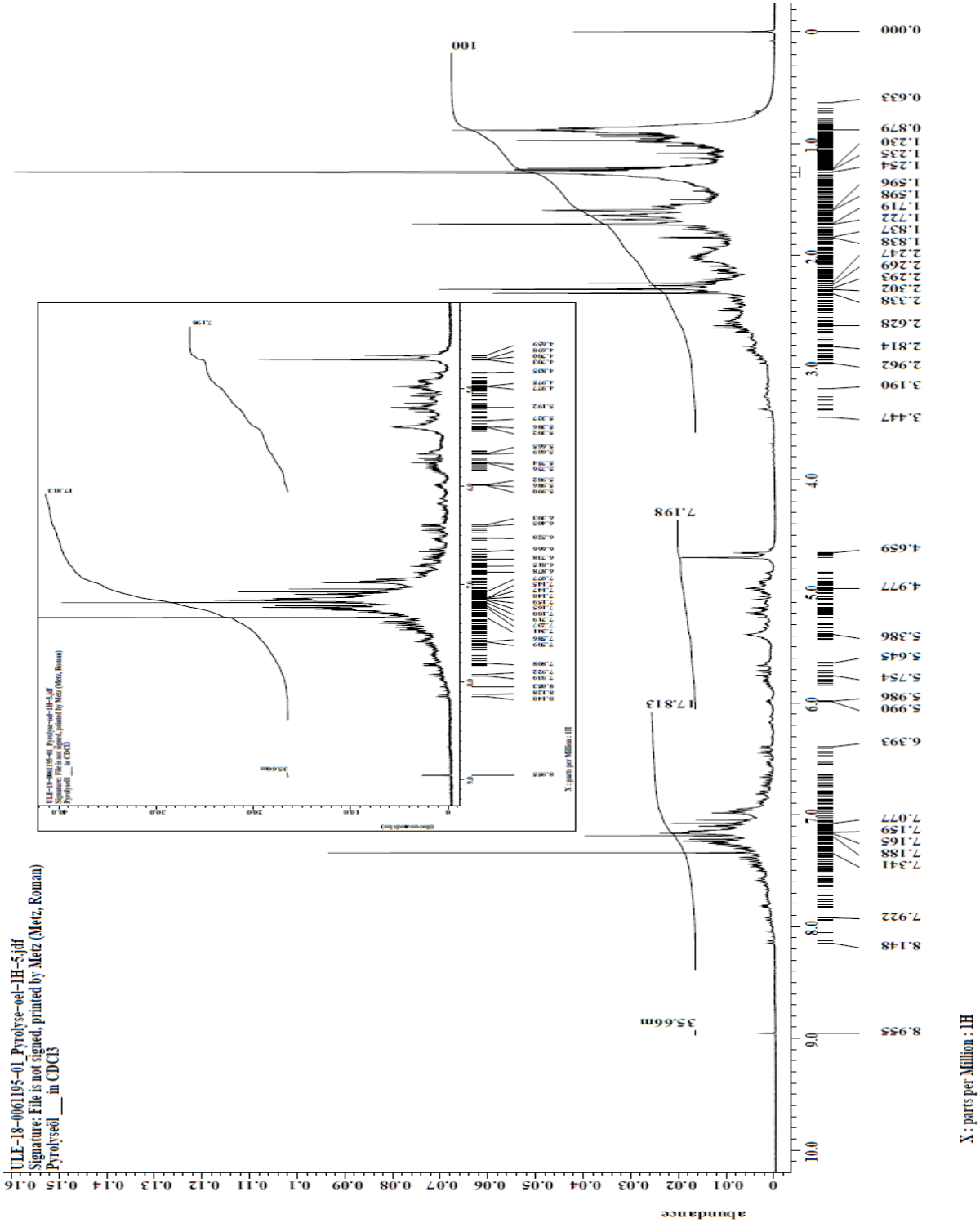


Figure 3: ^{1}H-NMR spectrum of the pyrolysis oil with $CDCl_3$ as solvent

Table 4: Results and the signal assignment of the ^{1}H-NMR spectroscopy

	Chemical shift [ppm]	Signal splitting	Integration of the signal [/]	Assignment
Pyrolysis oil	6.2 – 8.2 4.5 – 6.2	Overlapping signals, multiplets	18 7.2	Aromatic protons Olefinic protons
	0.5 – 3.5	Overlapping signals, multiplets	100	C-H aliphatic
	7.1 – 7.6	Singulet	---	Solvent $CDCl_3$ overlapping signal with sample

The complexity of the spectrum does not allow to assign single signals to special chemical formulas/isomers. There are signals in the complete range of the spectrum (aromatic, saturated and unsaturated aliphatic hydrocarbons) detectable.
The chemical shift of the signals corresponds to the expected signals of an UVCB-substance, which was generated by pyrolysis.

4.1.2 ^{13}C-NMR Spectroscopy

4.1.2.1 Method description

NMR-Spectrometer*:* Jeol JNM ECS400 with 5 mm probe 40TH5AT/FG,Fieldgradient-System and Auto-Tuning

Parameters:

Frequency/Field:	100 MHz / 9.38 Tesla
X_offset:	105 ppm
X_sweep:	28.9 kHz
X_points:	32768
X_angle:	45°
Relaxation delay:	2 sec
X_acq_time:	1.13 sec
Repetition_time:	3.13 sec
Scans:	256
Temperature:	room temperature, see spectra
Solvent:	$CDCl_3$
Reference:	solvent
Sample preparation:	Solution of about 0.2 mL sample in 2 mL solvent

4.1.2.2 Results

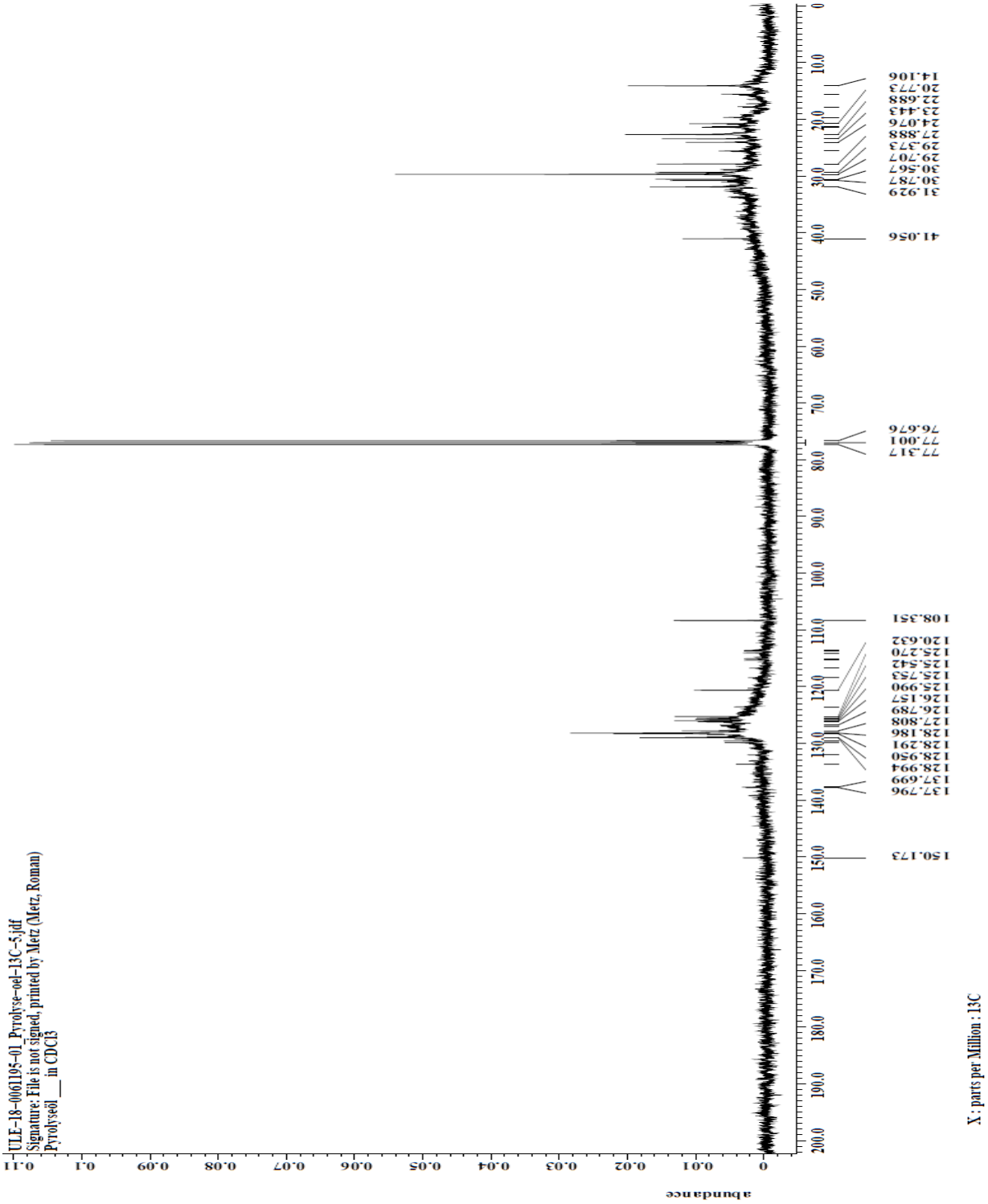


Figure 4: ^{13}C-NMR spectrum of the pyrolysis oil with $CDCl_3$ as solvent

Table 5: Results and the signal assignment of the ^{13}C-NMR spectroscopy

	Chemical Shift [ppm]	**Assignment**
Pyrolysis oil	100 - 150	Aromatic + Olefinic Carbon
	10 - 50	CH, CH_2, CH_3
	77	Solvent $CDCl_3$

The complexity of the spectrum does not allow to assign single signals to special chemical formulas/isomers. There are signals in the complete range of the spectrum (aromatic-aliphatic) detectable. The chemical shift of the signals corresponds to the expected signals of an UVCB-substance, which was generated by pyrolysis.

4.2 UV-Vis Spectroscopy

4.2.1 Method description

The analysis was carried out via UV/Vis spectroscopy.
Spectrometer: Specord 50 Analytik Jena GmbH
For the UV-Vis measurement the sample was diluted with *n*-hexane in the relation 1 : 50000.
There was a small insoluble part. An improvement could not be achieved by the use of cyclohexane. Other solvents would have partially overlaid the UV-Range.
The reference cuvette contained *n*-hexane.

Spectral bandwidth: 1.4 nm
Increments: 1 nm
Cuvettes: 10 mm quartz glass
Software: WinASPECT®

The sample was applied to the spectrometer and the UV/Vis spectra were recorded via the spectrometer software.

4.2.2 Results

Results are presented as a spectrum of the sample. At first a spectrum between 200 and 800 nm in the 1:50000 was recorded.

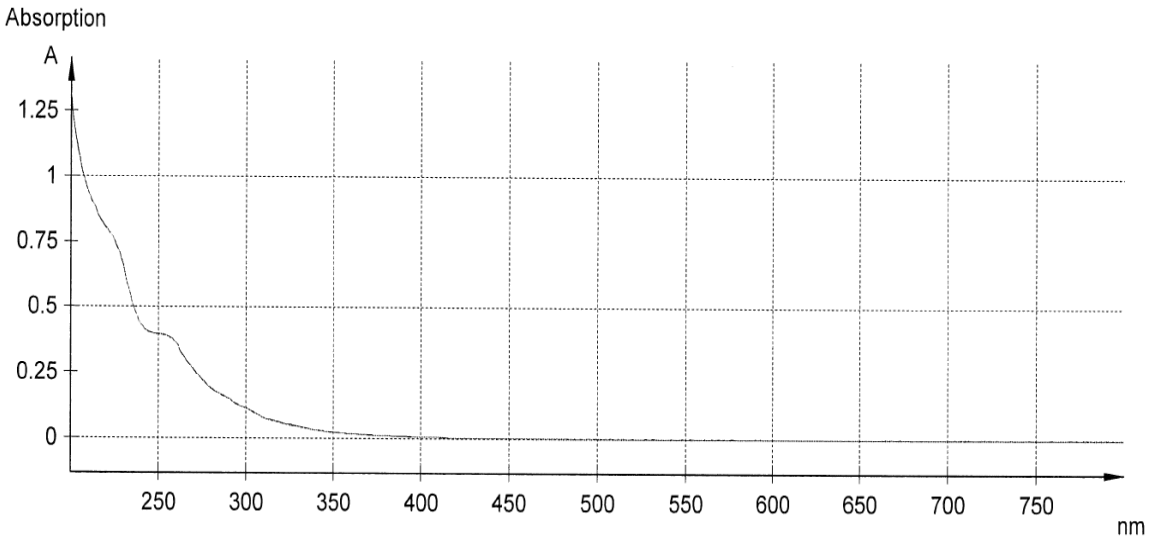


Figure 5: UV-Vis spectrum of the pyrolysis oil

In this dilution was no adsorption in the visual range (400-800 nm) observed. Another measurement was carried out only in the area with the greatest absorption between 200 to 300 nm.

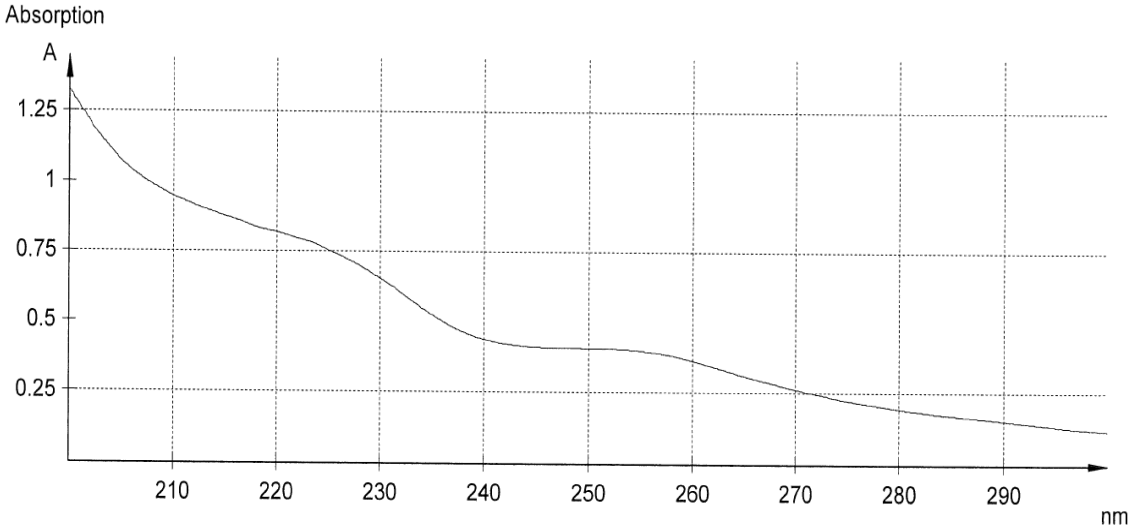


Figure 6: UV-Vis spectrum of the pyrolysis oil (200 nm-300 nm)

In the UV-Range the absorption bands lie between 200 and 350 nm. Between 240 and 270 nm, the typical fine structure for aromatic compounds is included. The maximum is theoretical approximately 255 nm. This is a banned $\pi \rightarrow \pi^*$ transition. Due to overlays, the typical aromatic spectrum is not visible under the measurement conditions.

4.3 IR-Spectroscopy

4.3.1 Method description

The qualitative IR analysis was carried out via (ATR) IR spectroscopy.

Spectrometer:	Alpha with sample compartment RT-DLaTGS, Bruker
Accessory:	ATR platinum Diamond 1 Refl
Software:	OPUS 7.5

4.3.2 Results

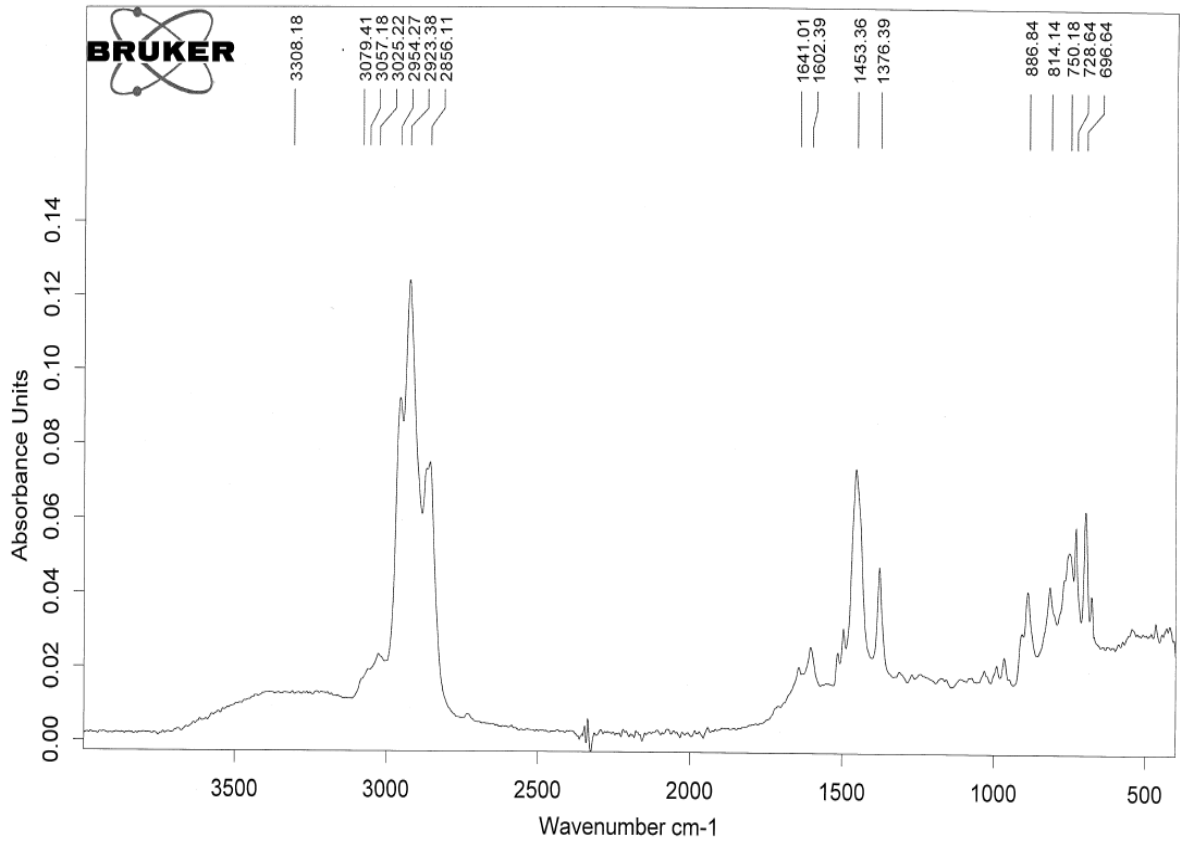


Figure 7: IR-spectrum of the pyrolysis oil

Table 6: Typical bands of the pyrolysis oil

Wavenumber (cm^{-1})	Structural unit
3057.18	=C-H (Stretching, Olefine)
3025.22	=C-H (Stretching, Aromaten)
2954.27	CH_3 (Stretching)
2923.38	CH_2 (Stretching)
2856.11	CH (Stretching)
1641.01	C=C (Stretching, Olefine)
1602.39	C=C (Stretching, Aromaten)
1453.36	CH_3, CH_2, CH (Bending)
1376.39	CH_3 (Bending)
990-660	=C-H (Bending, Olefine)
900-600	C-H (Bending, Aromaten)

The IR spectrum showed the expected absorptions according to the sample composition. Both aromatics and saturated and unsaturated aliphatic hydrocarbons were detected.

Table 7: Experience based values for the chemical stability of chosen substances toward thermolysis oil; good chem. stability (+); moderate chem. stability (o); low to no chem. stability (-)

Material	Stability	Long term stability
Stainless steel: 1.4571, 1.4828, or similar	+	affirmative
Graphite (e.g. in flat gasket)	+	affirmative
NBR	-	
Polystyrene	-	
Oxime-silicone	o	n.e.
PTFE	+	affirmative
Copper	+	affirmative
S235JR (construction steel)	-	Prone to corrosion

5 Physiological properties

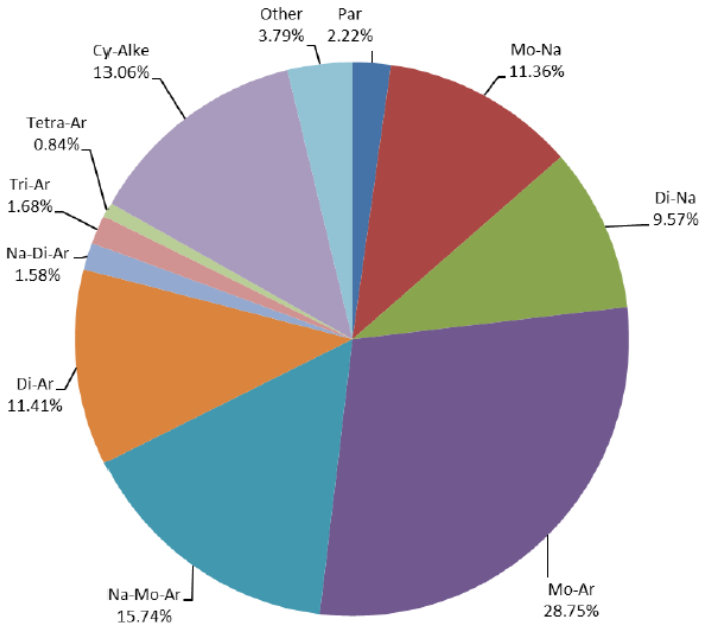
Odour: sent of mineral oil, sulfidic

Toxicity: see table 1 and chapter 8

6 Composition

The values represent a measured maximum if not specified differently.

General Information: Dichloromethane was added to a small amount of the samples and was subsequently analyzed with two-dimensional gas chromatography (GCxGC) followed by a mass spectrometry (MS) detection and a flame ionization (FID) detection.
The gas chromatograph was equipped with a Rxi-1ms column with dimensions 30 m x 0.25 mm x 0.25 µm and a BPX50 column with dimensions 1 m x 0.15 mm x 0.15 µm. Quantification was performed in area percentage by using GCxGC-FID.



C-nr	Carbon number	Mo-Ar	Mono-aromatics	Results in % w/w (based on the FID respons factors)
Par	Normal paraffins	Na-Mo-Ar	Naphthenic-mono-aromatics	
Me-Br	Methyl branched paraffins	Di-Ar	Di-aromatics	
Et-Br	Ethyl branched paraffins	Na-Di-Ar	Naphthenic-di-aromatics	
H-Br	Heavily branched paraffins	Tri-Ar	Tri-aromatics	
Mo-Na	Mono-Naphthenics	Tetra-Ar	Terta-aromatics	
Di-Na	Di-naphthenics	Cy-Alke	Cycloalkenes	

Figure 8: Composition of the thermolysis oil, characterized by two-dimensional gas chromatography

6.1 Substance groups

TPH (C5-C50):	350	mg/L	DIN EN 93677-2
PCB:	< 0,01	mg/kg	DIN EN 15308
PAH total:	1500	mg/kg	DIN EN 15527
PAH total:	12	wt.-%	EN 590

6.1.1 Aromatic content

Phenols:	150	mg/L	DIN 38409H16

Table 8: Content of aromatic hydrocarbons

	Min. [m%]	Max. [m%]	typical [m%]
Mono-aromates	10	60	45
Di-aromates	5	25	13
Tri+-aromates	0	15	3
Polyaromates	10	25	15
Total aromates	15	75	60

6.1.2 Non aromatic components

Table 9: Content of non aromatic hydrocarbons

	Min. [m%]	Max. [m%]	typical [m%]
Paraffins	0	10	2
Mono-Naphthenics	0	20	10
Di-Naphthenics	0	20	10
Cycloalkenes	0	25	13
Other	0	15	4

The biggest parts of the oil are aromatic compounds, olefins and paraffins. The chain length proportions were shown in figure 9.

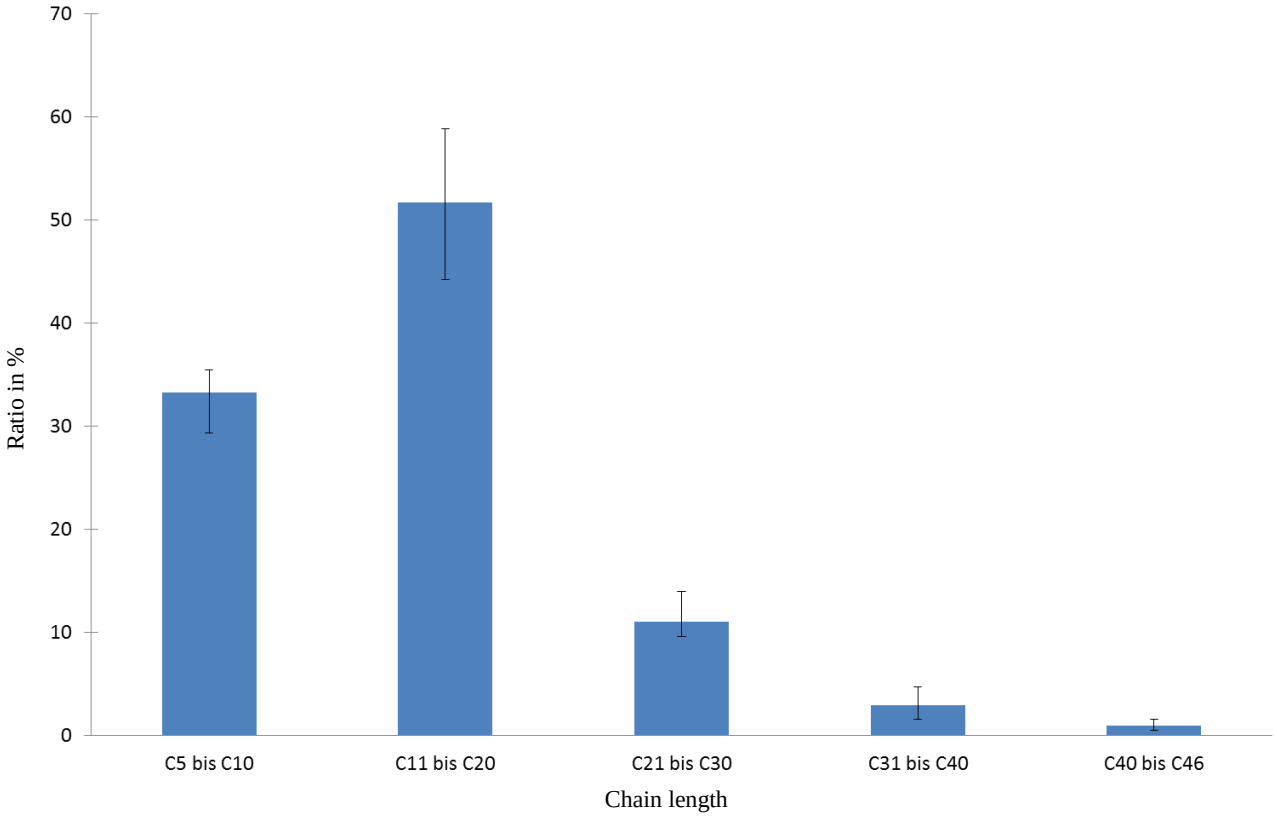


Figure 9: Content depending on the chain length

6.1.3 Single substances and molecules

Table 10: Content of single-ring aromatic hydrocarbons

	Min. [m%]	Max. [m%]	typical [m%]	DIN Norm
BTEX	5	25	15	DIN 38407F9
Benzene	1	5	2.5	DIN 38407F9
Toluene	2	10	5	DIN 38407F9
Ethylbenzene	0	5	1,5	DIN 38407F9
Xylene	0	10	5	DIN 38407F9
Styrene	0	0,4	1	DIN 38407F9

Table 11: Content of polycyclic aromatic hydrocarbons (PAH)

	Quantity [mg/kg]	**DIN EN Norm**
Naphthalene:	900	DIN EN 15527
Acenaphthylene:	15	DIN EN 15527
Acenaphthene:	15	DIN EN 15527
Fluorene:	45	DIN EN 15527
Phenanthrene:	250	DIN EN 15527
Anthracene:	65	DIN EN 15527
Fluoranthene:	40	DIN EN 15527
Pyrene:	65	DIN EN 15527
Benz(a)anthracene:	45	DIN EN 15527
Chrysene:	40	DIN EN 15527
Benzo(b)fluoranth	15	DIN EN 15527
Benzo(k)fluoranth	15	DIN EN 15527
Benzo(a)pyrene:	15	DIN EN 15527
Indeno(1,2,3-c,d)pyrene	5	DIN EN 15527
Dibenzo(a,h)anthr.:	5	DIN EN 15527
Benzo(g,h,i)perylene	5	DIN EN 15527
Limonene	n.e.	

6.2 Nuclear composition

C:	85	wt.-%	elementary analysis
H:	12	wt.-%	elementary analysis
N:	2	wt.-%	elementary analysis
O:	n.b.		
S:	1	wt.-%	elementary analysis
Cl:	< 0,4	g/kg	„Altöl Anlage 2 Nr.3“

6.3 Impurity

Water:	possible in low quantaties
Carbon Black:	possible in low quantities

7 Examples for application

- Fuel for asphalt burner
- Crude oil supplement for usage in refineries
- Fuel in general for generation of energy

8 Hazard and precautionary statements

8.1 Relevant hazard warnings

H225	Highly flammable liquid and vapour.
H226	Flammable liquid and vapour.
H228	Flammable solid.
H302	Harmful if swallowed.
H304	May be fatal if swallowed and enters airways.
H312	Harmful in contact with skin.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H332	Toxic if inhaled.
H335	May cause respiratory irritation.
H336	May cause drowsiness or dizziness.
H340	May cause genetic defects.
H350	May cause cancer.
H351	Suspected of causing cancer.
H361	Suspected of damaging fertility or the unborn child.

H372	Causes damage to organs through prolonged or repeated exposure.
H373	May cause damage to organs through prolonged or repeated exposure.
H400	Very toxic to aquatic life.
H410	Very toxic to aquatic life with long lasting effects.
H411	Toxic to aquatic life with long lasting effects.
H412	Harmful to aquatic life with long lasting effects.

8.2 Relevant precautionary information

P201	Obtain special instructions before use.
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P260	Do not breathe dust/fume/gas/mist/vapours/spray.
P261	Avoid breathing dust/fume/gas/mist/vapours/spray.
P273	Avoid release to the environment.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P301+P310	If swallowed: Immediately call a POISON CENTER/ doctor
P301+P312+P330	If swallowed: Call a POISON CENTER/ doctor if you feel unwell.
P304+P340+P312	If swallowed: rinse mouth. Do NOT induce vomiting.
P308+P313	If exposed or concerned: Get medical advice/attention.
P331	Do not induce vomiting.
P370+P378	In case of fire: Use extinguishing powder to extinguish.
P391	Collect spillage.
P403+P235	Store in a well ventilated place. Keep cool.
P501	Dispose of contents/container to waste disposal facility