UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

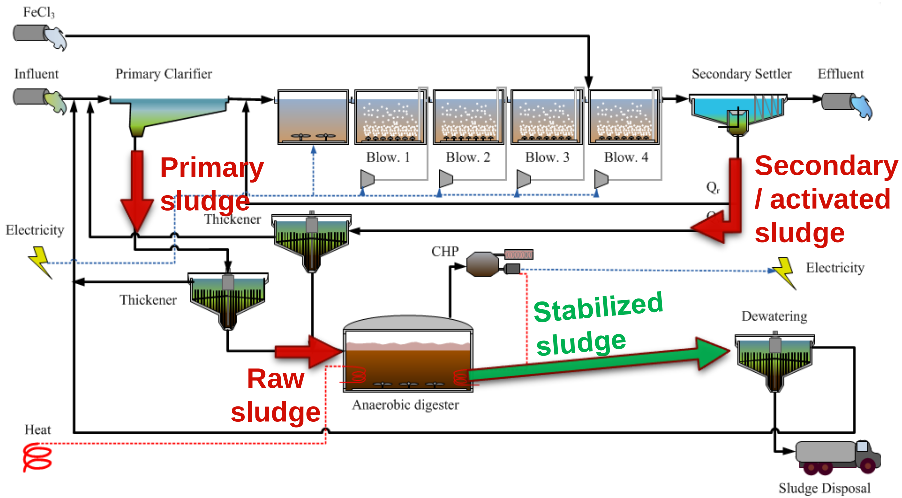
Institute of Chemical Process Fundamentals of the CAS, v. v. i.

Multiple Analyses Assessment of Properties of Biochar Based on Dry Stabilized Sewage Sludge

Jaroslav Moško

Sewage sludge

- inevitable waste (product) of wastewater treatment
- suspension of organic and inorganic particulates in water



Adapted from: Conaqua -Online: http://www.conaqua.es/estudio-de-simulacion-sobre-la-recuperacion-de-p-en-la-edar-sur-de-madrid/ (accessed 31.05.2018)

Stabilized sludge disposal I

Landfill disposal

- Advantages: basically no advantages

- Disadvantages:
  - leaching of pollutants at the deposit
  - smell
  - legislative restrictions

Stabilized sludge disposal II

Disposal on agricultural soil, composting

- Advantages:
  - fertilizer like substance
    - recirculation of organic matter and nutrients (N, P, K)
- Disadvantages:
  - legislative restrictions
    - limits on heavy metals content
    - limits on pathogens content => hygienization of sludge
  - precautionary principle
    - apprehension about content of POPs & PPCPs
  - smell

Stabilized sludge disposal III

Thermal treatment

- Advantages:
  - significant reduction in volume of waste
  - destruction of organic pollutants
  - concentration of P, K, Ca, Mg in solid residue – possible recycling/recovery?
  - gain of energy for production of heat and electricity
  - long-term storage of solid products
- Disadvantages:
  - need for drying
  - additional technologies for treatment of products needed
  - expensive
  - public awareness

Stabilized sludge disposal IV

Czech Republic

Year	2010	2012	2014	2016	2018
Sludge disposal	% of total sludge disposed				
agricultural use	36	31	30	36	44
composting	27	32	38	38	32
landfilling	3.6	5.6	3.3	5.9	8.8
thermal treatment	2.0	2.1	2.1	2.8	9.6
other[1]	32	30	27	18	5.8
sum total	*100*	*100*	*100*	*100*	*100*

[1] For instance technical landfill layer

Adapted from: Czech Statistical Office. Water Supply Systems, Sewerage and Watercourses - 2010-2018. Online: https://www.czso.cz/csu/czso/water-supply-systems-sewerage-and-watercourses-2018 (accessed 15.06.2019)

Ash for production of P-products

- It must be ash from sludge mono-incineration
  - typical P content of the ash ≈ 8 wt. %
- It is intermediate product
- Low phosphorus bioavailability
- Treatment is needed:
  - to separate P from pollutants (heavy metals)
  - to transfer P into bioavailable form or product for P-based fertilizers production
- Processes for ash treatment

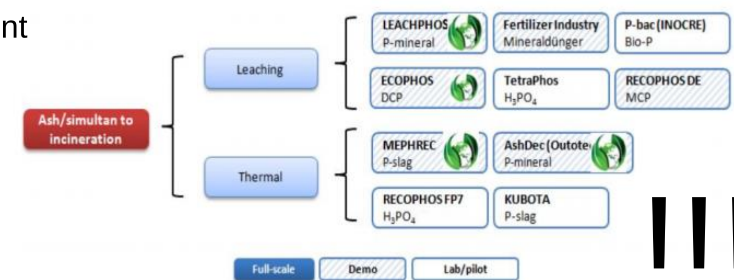


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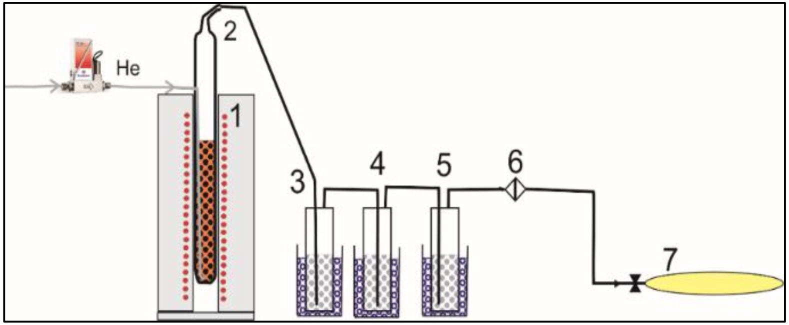
Figure adapted from: Šyc M., et al: Recyklace fosforu z popelu po spalování čistírenských kalů. online at: http://www.odpadoveforum.cz/TVIP2016/prispevky/304.pdf (accessed 04.12.2018)

Sludge pyrolysis as alternative to incineration?

Sludge-char is carbonaceous material which may provide several advantages if used on soil in terms of its fertility.

- Increases water retention
- Prevents leaching of nutrients (N, P, K) from fertilizers to groundwater
- Loosens/aerates the soil
- Sequestrates carbon dioxide (C form)

Experimental campaign



1 – oven, 2 – quartz reactor,
3 – 5 ice-cooled impingers,
6 – porous filter,
7 – tedlar bag

Inert carrier gas: helium – 150 ml min^{-1}
Pyrolysis temperature: 400–800 °C
Heating time: 2 hours

After pyrolysis

Before pyrolysis

Sewage sludge

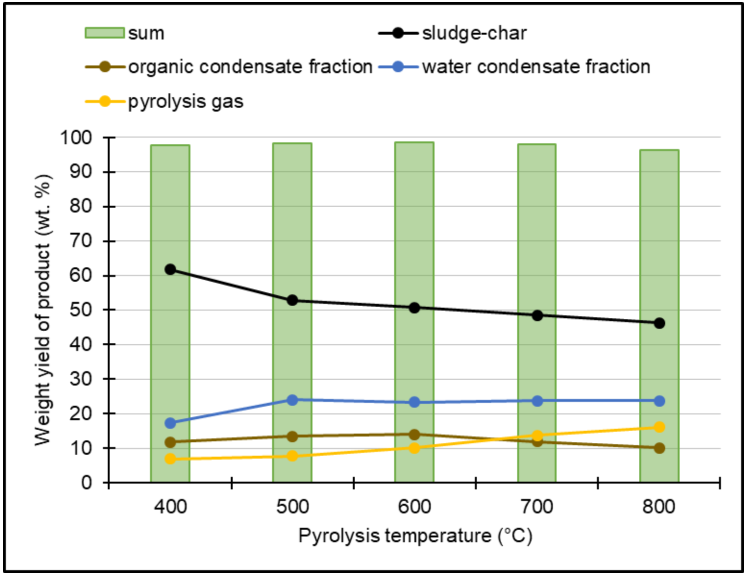
Stabilized sewage sludge from municipal wastewater treatment plant (with mesophilic anaerobic stabilization of the sludge) in the Czech Republic.

Proximate analysis		
Ash, A^d	wt. %	43.3
Volatiles, V^{daf}	wt. %	86.8
Fixed Carbon, FC^{daf}	wt. %	13.2
Calorific values		
Higher Heating Value, HHV^d	MJ kg^{-1}	12.7
Lower Heating Value, LHV^d	MJ kg^{-1}	11.8
Ultimate analysis		
C^d	wt. %	28.8
H^d	wt. %	4.20
N^d	wt. %	4.22
O^d	wt. %	18.4
S^d	wt. %	1.10
Cl^d	mg kg^{-1}	433
F^d	mg kg^{-1}	255

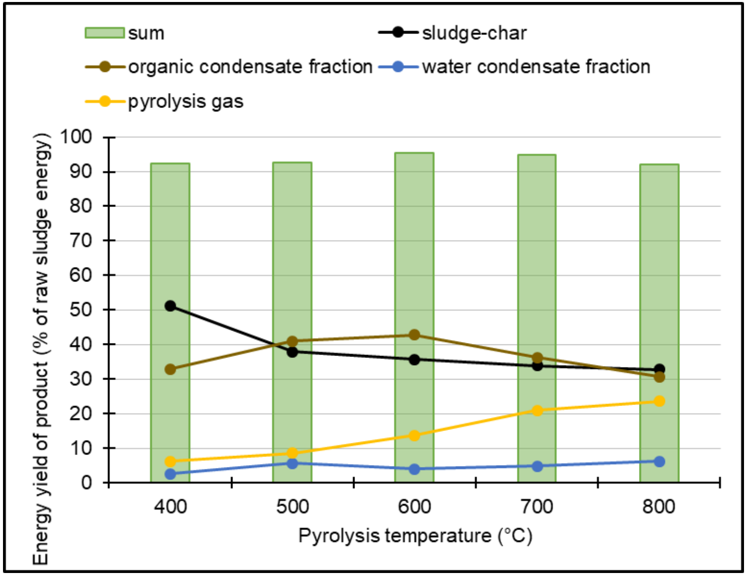
Sludge ash composition determined by XRF analysis

Species	wt. %
Al_2O_3	16.0
CaO	14.0
Fe_2O_3	13.9
K_2O	1.64
MgO	2.64
P_2O_5	18.2
SiO_2	28.5
Sum	94.9

Material balance



Energy balance



Sludge-char properties

Conventional analytical measurements

Property	A^d	V^d	C^d	H^d	N^d	S^d_{total}	H/C^d	HHV^d	pH_{H_2O}	EC_{H_2O}
Unit	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	mol mol^{-1}	MJ kg^{-1}	-	μS cm^{-1}
SC 400/He	67.9	21.5	23.1	1.62	3.04	0.76	0.839	9.49	7.34	583
SC 500/He	72.7	15.9	21.4	1.04	2.66	0.81	0.580	8.23	8.12	564
SC 600/He	75.8	11.7	20.5	0.716	2.26	0.77	0.419	8.04	10.11	521
SC 700/He	77.8	5.93	19.3	0.497	1.55	0.85	0.309	8.01	11.5	1400
SC 800/He	80.8	0.922	17.2	0.310	0.939	0.84	0.217	8.10	11.0	876

Property	WHC	ρ_L	ρ_{Hg}	ρ_{He}	ε	V_{intr}	S_{BET}	S_{meso}	V_{tot}	V_{micro}
Unit	%	kg m^{-3}	kg m^{-3}	kg m^{-3}	%	mm^3 g^{-1}	m^2 g^{-1}	m^2 g^{-1}	mm^3_{liq} g^{-1}	mm^3_{liq} g^{-1}
SC 400/He	63.5	771	1348	2123	36.5	238	15	11	66	1.9
SC 500/He	76.4	777	1290	2268	43.1	290	50	23	101	13
SC 600/He	53.7	756	1281	2359	45.7	305	55	24	103	16
SC 700/He	60.9	767	1273	2480	48.7	344	60	26	105	18
SC 800/He	62.1	750	1205	2581	53.3	350	86	49	121	18

A – Ash, V – Volatiles, H/C – Hydrogen to Carbon molar ratio, HHV – Higher Heating Value, EC – Electrical Conductivity, WHC – Water Holding Capacity, ρ_L – Loose poured bulk density, ρ_{Hg} – Apparent density, ρ_{He} – True solid density, ε – porosity determined as $\varepsilon = 1 - (\rho_{Hg}/\rho_{He})$, V_{intr} – Intrusion volume determined by mercury porosimetry, S_{BET} – Specific surface area determined from adsorption isotherm of N_2 at T=77 K, S_{meso} – Specific surface area of mesopores determined by t-plot method, V_{tot} – Total pore volume determined from adsorption isotherm of N_2 at $P/P_0 = 0.99$, V_{micro} – Micropores volume determined by t-plot method; ^{d} – in dry matter

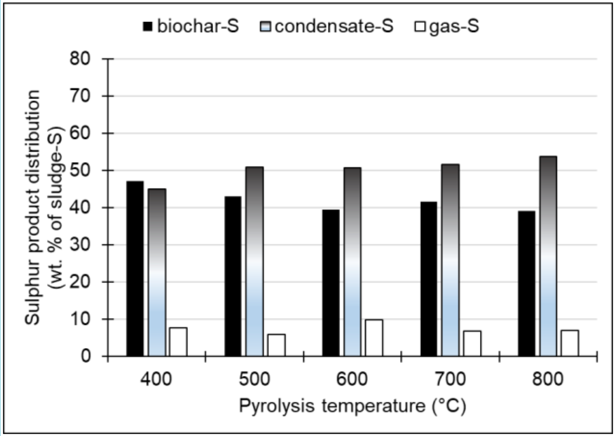
Additional analytical measurements:

SEM/EDX

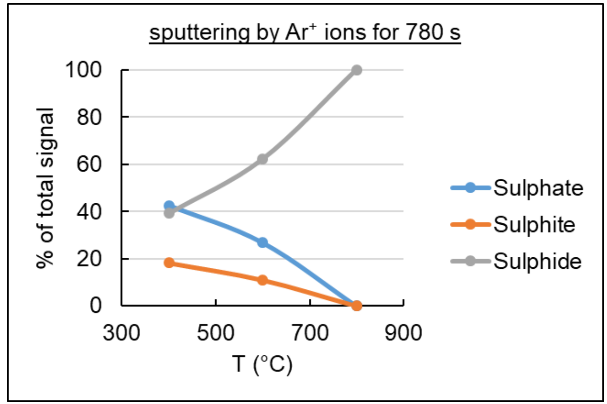
FTIR, NMR, Raman, and XPS spectroscopy

S analyses

Sulphur balance



S XPS



Property	S^d_{total}	$S^d_{organic}$	$S^d_{sulfate}$	S^d_{pyrite}	$S^d_{sulfide}$
Unit	wt. %	wt. %	wt. %	wt. %	wt. %
Sewage sludge	1.10	0.55	0.45	0.10	-
SC 400/He	0.76	0.47	0.14	0.10	0.05
SC 500/He	0.81	0.67	0.04	0.01	0.09
SC 600/He	0.77	0.62	0.04	0.04	0.07
SC 700/He	0.85	0.43	0.02	-	0.40
SC 800/He	0.84	0.21	0.03	-	0.60

Total sulphur (ISO 334:1992)
– Eschka method

S forms (ISO 157:1996)
– extraction methods

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Sludge-char properties

Conventional analytical measurements

Property	A^d	V^d	C^d	H^d	N^d	S^d_{total}	H/C^d	HHV^d	pH_{H_2O}	EC_{H_2O}
Unit	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	mol mol^{-1}	MJ kg^{-1}	-	µS cm^{-1}
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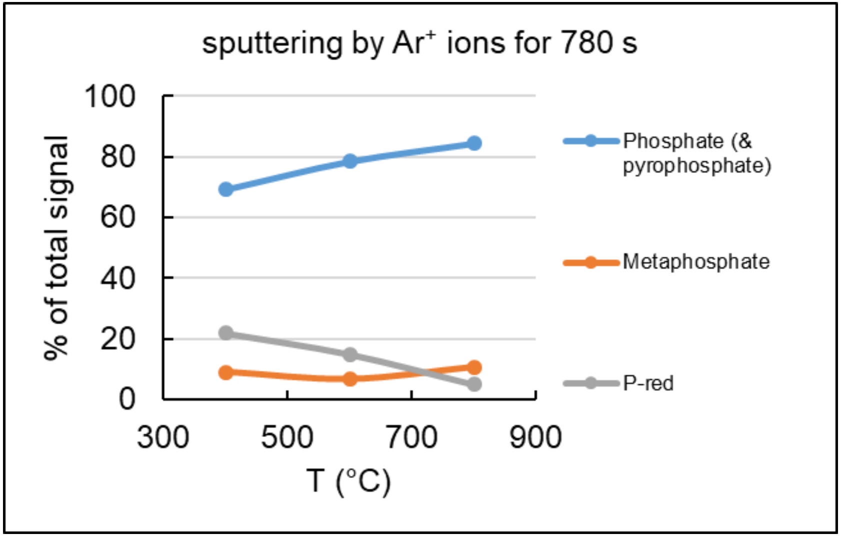
Additional analytical measurements:

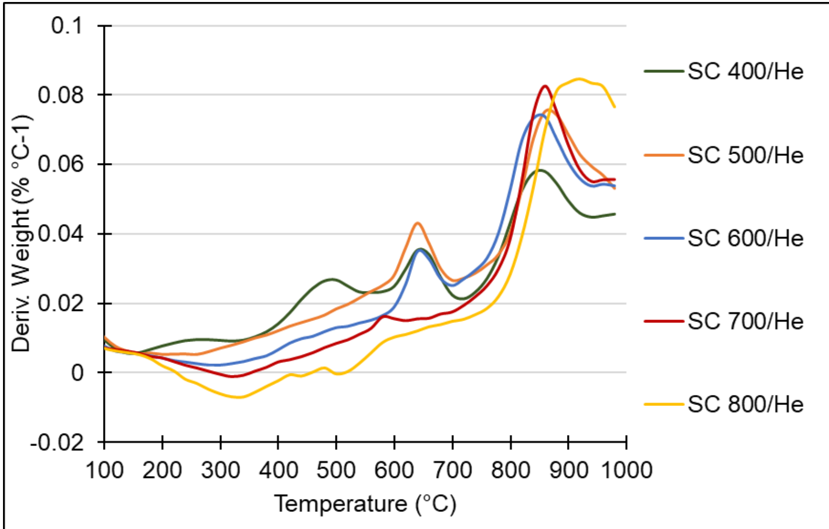
SEM/EDX

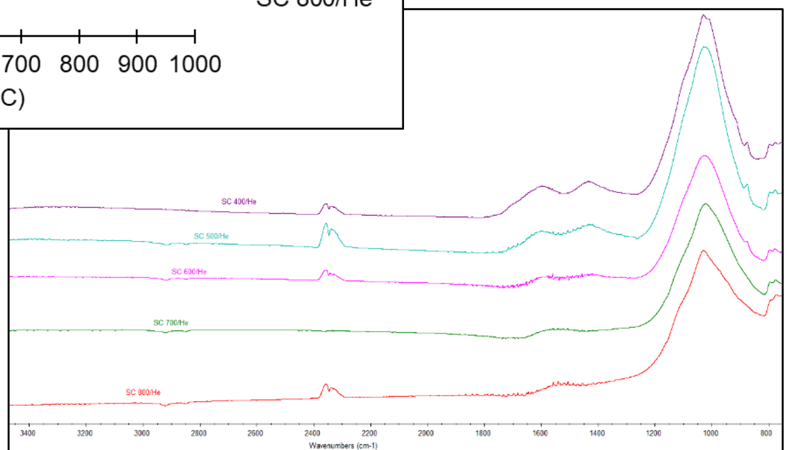
FTIR, NMR, Raman, and XPS spectroscopy

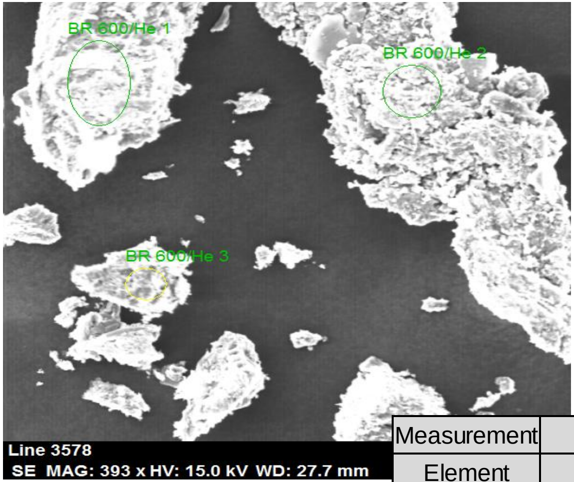
P XPS analysis



TGA/DTG & FTIR analyses







SEM/EDX

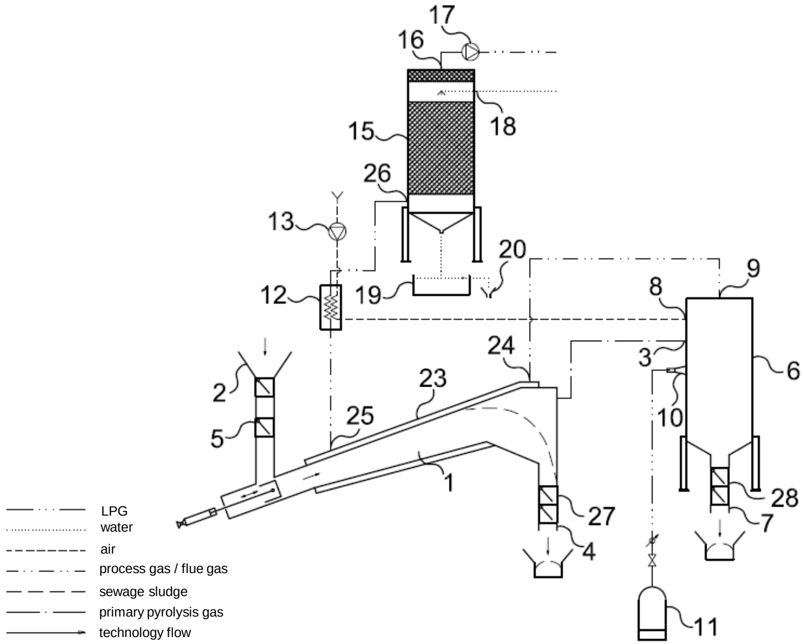
Ultimate analysis:

C^d = 20.5 wt. %
S^d = 0.77 wt. %

SC 600/He

Measurement	1	2	3	Average	StDev	ConfT
Element	concentration (wt. %)					
C	23.8	29.9	29.9	27.9	2.88	7.14
O	42.5	36.9	35.1	38.1	3.16	7.84
Na	0.91	0.70	0.51	0.71	0.16	0.41
Mg	2.00	1.24	1.08	1.44	0.40	1.00
Al	3.38	3.30	3.60	3.43	0.13	0.32
Si	11.8	5.99	7.63	8.47	2.44	6.06
P	4.03	4.38	5.85	4.75	0.79	1.96
S	0.59	1.33	0.64	0.85	0.34	0.84
Cl	0.06	0.29	0.07	0.14	0.11	0.26
K	0.46	0.62	0.46	0.51	0.08	0.19
Ca	4.66	6.66	7.20	6.17	1.09	2.71
Fe	5.64	8.27	7.51	7.14	1.11	2.75
Ba	0.21	0.48	0.45	0.38	0.12	0.30

Semi-conclusion



Adapted from: Pohořelý M., Picek I., Skoblia S., Beňo Z., Bičáková O. Equipment and method for energy treatment of dried sewage sludge. Patent PV 2019-150.

Thank You for your kind attention!

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Gas composition

	Pyrolysis temperature (°C)				
	400	500	600	700	800
S containing gases (g_S m^{-3})					
H_2S	6.85	4.32	5.30	2.49	2.11
COS	1.89	1.14	1.24	0.761	0.654
MeSH	6.65	3.68	4.19	1.79	1.56
CS_2	0.277	0.190	0.146	0.0919	0.0717
others	2.57	1.20	1.03	0.570	0.289
sum	18.2	10.5	11.9	5.70	4.69

Pyrolysis temperature	°C	400	500	600	700	800
Gas production	m^3 t_{sludge}^{-1}	42.3	55.7	82.3	119	149
Gas composition (vol. %)						
CO_2		62.3	49.5	38.1	29.1	23.6
H_2		10.0	20.6	25.3	26.5	27.9
CO		8.24	8.59	12.6	18.4	24.5
CH_4		7.81	11.2	12.7	12.2	10.7
N_2		0.0930	0.0424	1.62	3.61	5.00
ethane		2.14	2.33	2.09	1.87	1.46
ethylene		1.13	1.34	1.52	2.53	2.59
acetylene		< 0.01	< 0.01	< 0.01	0.0328	0.0535
propane		1.38	1.15	0.953	0.682	0.490
propene		1.18	1.23	1.31	1.80	1.57
propyne		0.147	0.108	0.111	0.096	0.067
butanes		0.574	0.411	0.194	0.204	0.147
pentanes		0.180	0.171	0.131	0.0742	0.0506
hexanes		0.0722	0.0502	0.0417	0.0246	0.0155
C_4 (=)		1.20	0.975	0.922	0.900	0.697
1,3-butadiene		0.0406	0.0597	0.111	0.267	0.262
1-buten-3-yne		0.0469	0.0484	0.0674	0.0320	0.0232
cyklopentadiene		0.0936	0.0643	0.114	0.174	0.136
benzene		0.221	0.118	0.0854	0.142	0.0391
toluene		0.528	0.236	0.237	0.185	0.0223
others (FID)		2.70	1.81	1.86	1.21	0.73
HHV (MJ m^{-3})		17.0	17.8	19.1	20.1	18.2

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Ultimate analysis of condensate fractions

organic fraction

Pyrolysis temperature	C	H	N	S	O	HHV
°C	wt. %					MJ kg^{-1}
400	66.9	10.3	6.48	1.23	15.1	32.0
500	71.2	9.86	7.23	0.694	11.0	34.7
600	71.4	9.85	7.08	0.629	11.1	34.8
700	71.9	9.35	7.74	0.804	10.2	34.7
800	71.7	9.21	7.48	1.10	10.5	34.9

water fraction

Pyrolysis temperature	C	H	N	S	O	HHV
°C	wt. %					MJ kg^{-1}
400	8.27	9.70	4.44	0.161	77.4	1.69
500	9.92	9.68	5.16	0.239	75.0	2.67
600	10.0	9.30	5.48	0.227	75.0	1.93
700	9.32	9.48	5.43	0.293	75.5	2.35
800	9.69	9.44	5.71	0.283	74.9	2.98