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Investigation of the properties of products of Estonian Oil Shale decomposition through the bitumen stage

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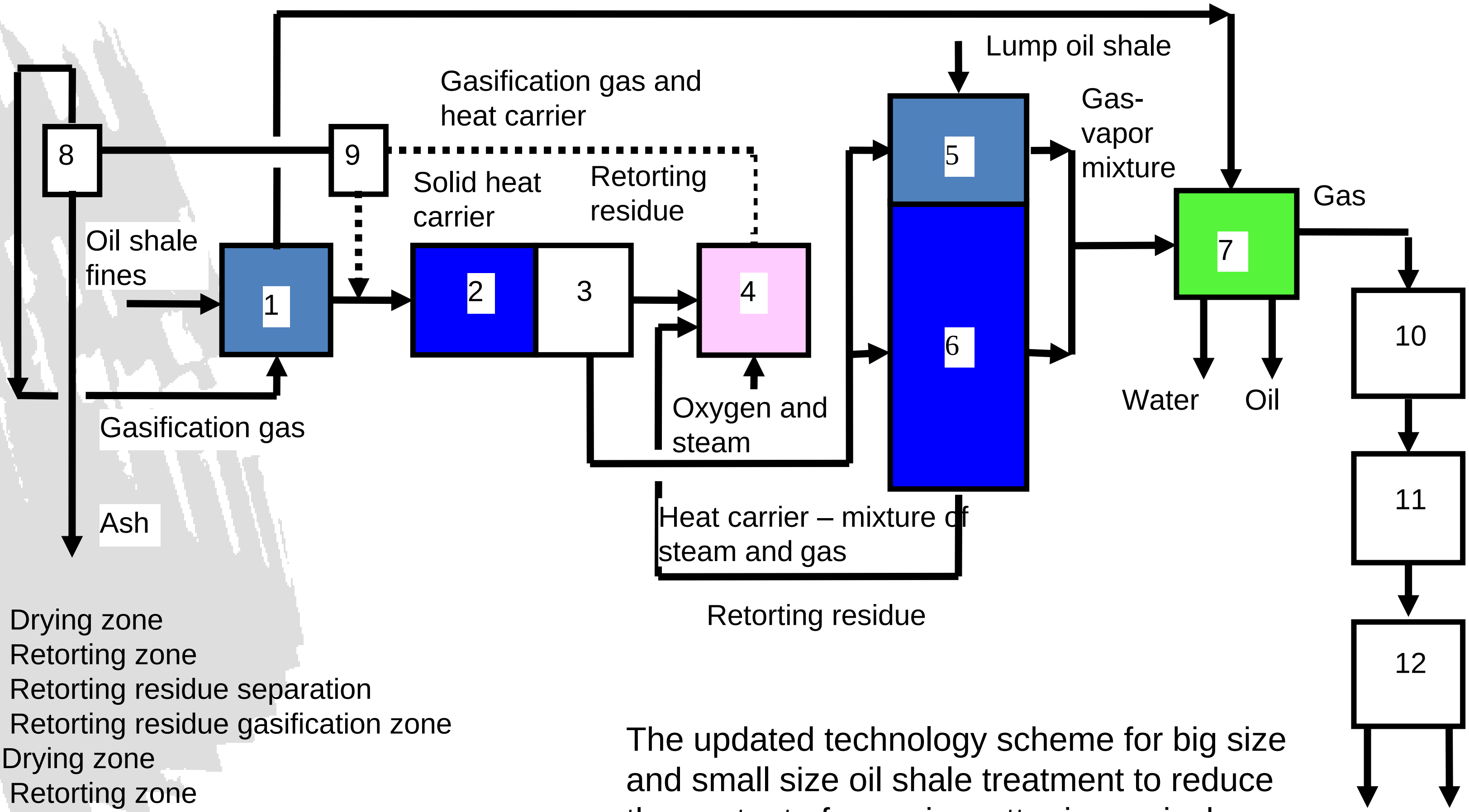
Topics

- Existing semikocing technology
- Solid fuel liqueifaction -   the modern direction for processing of solid fuels
- Laboratory experiments
- Characterization of the products
- Comparison of oil shale thermal treatment processes (semicoking and treatment through bitumen stage)
- Possible development of oil shale processing technology

Co-retorting of lump oil shale and oil shale fines



1. Drying zone
2. Retorting zone
3. Retorting residue separation
4. Retorting residue gasification zone
5 Drying zone
6. Retorting zone
7. Condensation
8. Ash cyclone
9. Doser
10. Gas cleaning
11. Gas conversion
12. Synthesis of liquid fuels

The updated technology scheme for big size and small size oil shale treatment to reduce the content of organic matter in semicoke

Characterization of the oil shale semicoking process

- The final temperature of the process is 520 ^{o}C
- The environment problem of semicoke utilization due to TOC content in semicoke up to 14 %
- The conversion of organic matter to potential liquid products is about 65 %

The solid fuel liqueifaction - the modern direction of processing of solid fuels – CTL 1.

- **(a) thermal solution;**

p= 3,5-5,0 Mpa, t= 380-450°C, H_2 or H_2 – donor(for example – tetralin)
Output of liquid product - 60-90 % on solid fuel

- **(b) hydrogenation;**

Requirements for feed :

Water content 1,0-1,5%
content of mineral part (Ash) 10-12%
Oxygen content 12-13%

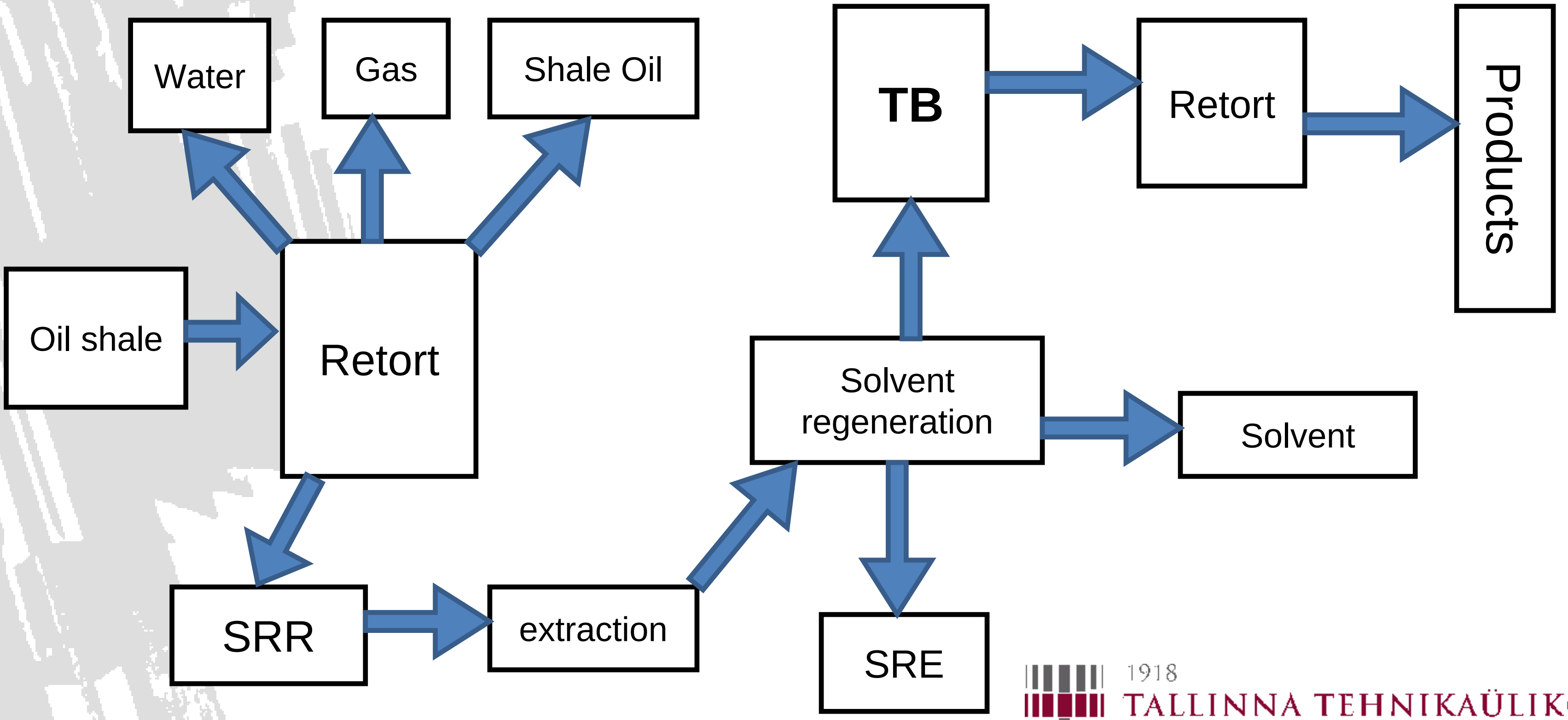
The solid fuel liqueifaction - the modern direction of processing of solid fuels – CTL 2.

- Hydrogenation:

1. Drying of solid fuel
2. Two- stage hydrogenation of the paste of solid fuel with oil fraction
3. Extraction the liquid product
4. Hydrogenation of the liquid product

Principal laboratory scale scheme of the process

SRR – Solid Residue after Retort
SRE – Solid Residue after Extraction
TB – Thermobitumen



Conditions of Experiments

- Oil Shale with OM – 32 %
- Temperature range 360 – 410 ^{o}C
- Isothermal time range 20-60 minutes
- Ethanol-benzen mixutre was used for thermobitumen extraction

Experimental data of Thermobitumen formation

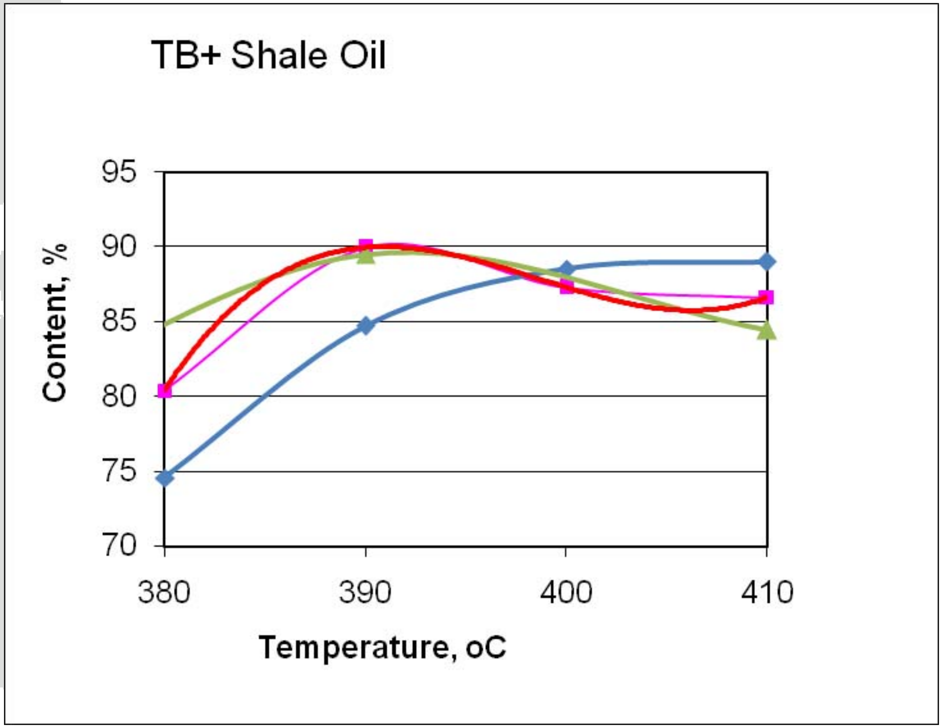
Material Balance of thermobitumen and oil on OM

Temp-re	Time	TB on OM	Oil on OM	TB+Oil on OM
370	20	25,90	8,65	34,55
380	20	55,29	19,27	74,56
390	20	61,61	23,10	84,71
400	20	60,40	28,15	88,55
410	20	58,90	30,12	89,02
370	60	55,11	23,07	78,18
390	60	57,00	32,51	89,51
410	60	47,80	36,66	84,46
380	30	58,00	22,38	80,38
390	30	62,10	27,86	89,96
400	30	56,90	30,39	87,29
410	30	54,90	31,73	86,63

Material Balance of retort

Temp-re	Time	Oil	Solid Residue after Retort	Water	Gas+Loses
370	20	1.4	96.6	0.6	1.4
380	20	2.6	94.4	0.8	2.2
390	20	4.6	92.5	1.0	1.9
400	20	7.8	88.2	1.2	2.8
410	20	11.1	85.2	1.4	2.4
380	30	3.6	93.8	0.7	1.9
390	30	4.4	92.8	0.5	2.2
400	30	10.3	86.3	1.0	2.4
410	30	14.2	81.4	1.2	3.2
370	60	7.2	88.9	0.9	3.0
390	60	10.5	85.3	1.0	3.2
410	60	16.5	79.0	1.6	2.9

The potential liquid compounds yield



Red – Process at 20 min

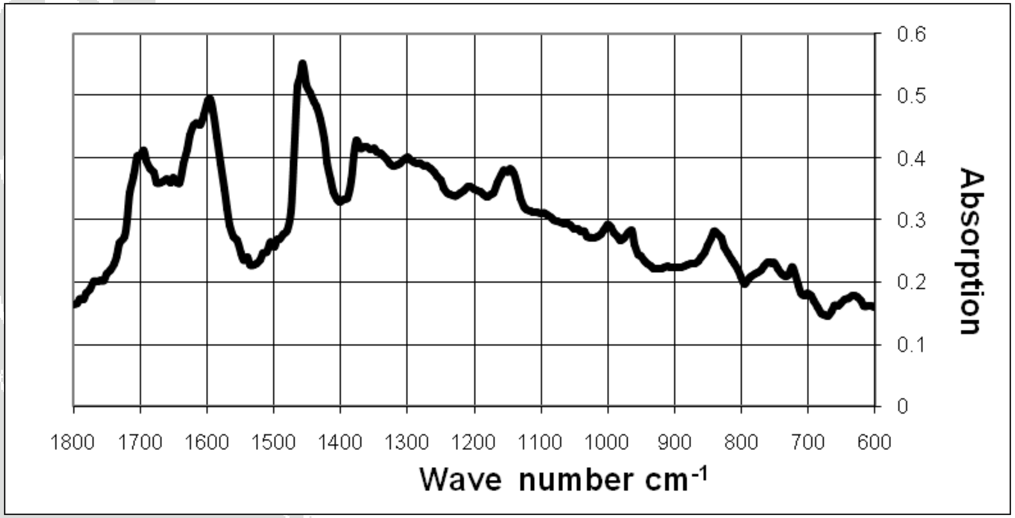
Blue – Process at 30 min

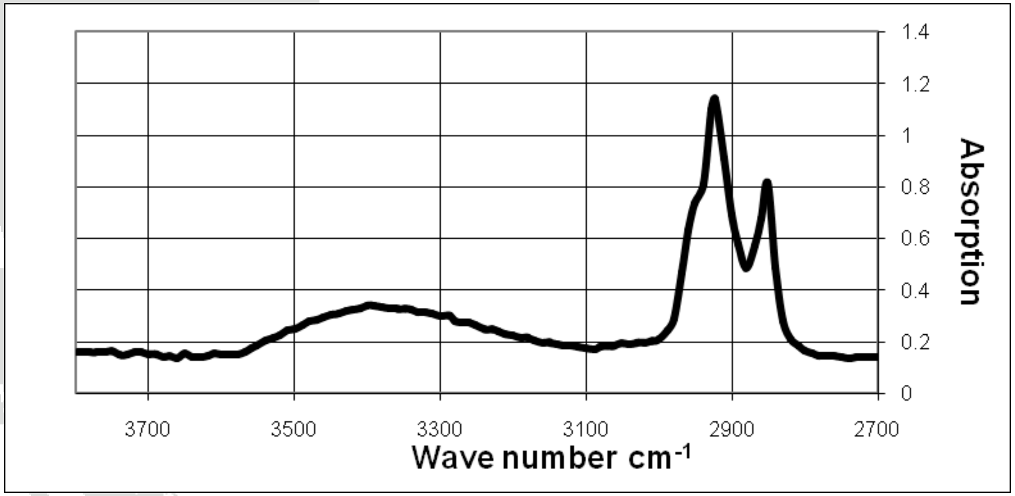
Green – Process at 60 min

Influence of temperature on the thermobitumen elemental composition

Temperature, °C	Isothermal time, min	Element					rate
		C	H	N	S	O	C/H
370	20	76.4	9.7	0.26	0.9	12.74	7.87
380	20	79.5	9.9	0.30	0.8	9.5	8.03
390	20	80.3	9.5	0.27	0.8	9.13	8.45
400	20	81.1	8.9	0.25	0.6	9.15	9.11
410	20	81.2	8.8	0.26	0.7	11	9.22
370	60	80.8	9.2	0.27	0.6	9.16	8.78
390	60	82.5	8.8	0.26	0.7	7.74	9.38
410	60	83.2	8.9	0.28	0.6	7.02	9.35
380	30	79.7	9.6	0.30	0.7	9.7	8.30
390	30	81.3	9.1	0.27	0.8	8.53	8.93
400	30	81.6	9.3	0.23	0.5	8.37	8.77
410	30	82.1	8.9	0.24	0.6	8.16	9.22

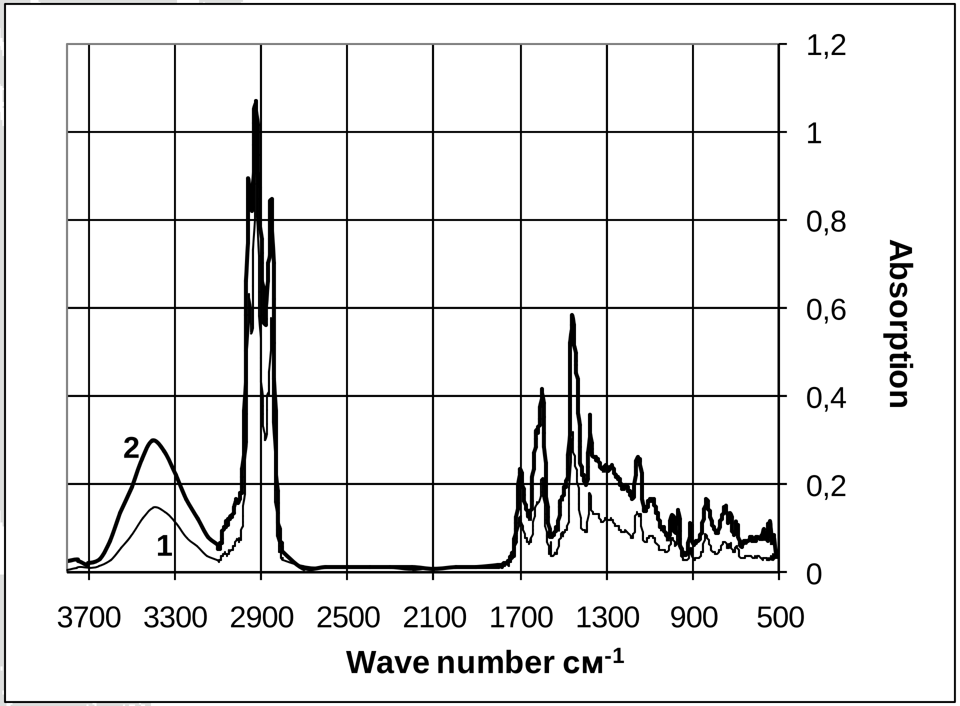
IR spectra of Thermobitumen





- Aromatic compounds: aromatic hydrogen (970-1100 cm^{-1})
- C-O, C-C bonds and oxygen of hydroxyl –OH (1100-1300 cm^{-1})
- Aliphatic compounds (1300-1500 cm^{-1})
- Aromatic ring (1600 cm^{-1})
- Carbonyl compounds: ethers, ketones, aldehydes (1700-1800 cm^{-1})
- Alkanes (2800-3000 cm^{-1})
- Hydroxyl compounds –OH bond (phenols) (3400 cm^{-1})

IR spectra comparison of shale oil of standard process (2) and shale oil obtained at bitumen process (1)



- In shale oil of bitumen stage the content of oxygen compound is less
- Content of paraffin compounds higher in shale oil of bitumen stage
- Content of aromatic compounds is also less in shale oil of bitumen stage process

Properties of shale oils obtained by standard method, at thermobitumen stage and thermobitumen thermal treatment

Element Composition of shale oil produced in Fisher assay, %				
C	H	S	O+N	C/H
81.2	10.1	0.6	8.0	8

Shale oil element composition of thermobitumen decomposition, %				
C	H	S	O+N	C/H
80.2	9.6	0.3	9.9	8.3

Shale oil element composition of thermobitumen formation stage, %				
C	H	S	O+N	C/H
82.52	12.04	1.31	4.13	6.9

Comparison of shale oils by group composition

Sample	Group content of hydrocarbons and oxygen compounds, %		
	Paraffin and olefin compounds	Aromatic hydrocarbons	Oxygen compounds
Shale Oil of std. process in Fisher assay	44	30	26
Shale Oil of thermobitumen treatment	29	38	33

The process of thermobitumen semicoking is not suitable to produce liquid products due to aromatic carbons formation

Characterization of Solid Residue after Extraction

Fisher assay	C	H	N	S	C/H	TOC
370/20	35.2	4.0	0.1	1.1	8.8	20.1
390/20	26.5	2.7	0.1	1.4	9.8	6.7
400/20	20.9	1.9	0.1	0.7	11.0	5.9
410/20	11.3	0.7	0.1	0.4	16.1	4.8

Gas composition of different processes

Standard Fisher assay

Group	Content, %
H_2	5.3
O_2	-
N_2	6.4
CO	8.9
CH_4	12.5
CO_2	23.4
C_nH_{2n+2}	19.2
C_nH_{2n}	9.7
H_2S	14.6

Thermobitumen stage

Group	Content, %
H_2	5.43
O_2	-
N_2	-
CO	16.43
CH_4	13.55
CO_2	26.90
C_nH_{2n+2}	12.36
C_nH_{2n}	4.69
H_2S	17.98

Thermobitumen decomposition

Group	Content, %
H_2	-
O_2	0
N_2	0
CO	25.14
CH_4	25.45
CO_2	19.6
C_nH_{2n+2}	20.2
C_nH_{2n}	9.61
H_2S	-

Potential organic matter transforms to gas phase of hydrocarbons

Comparison of technologies

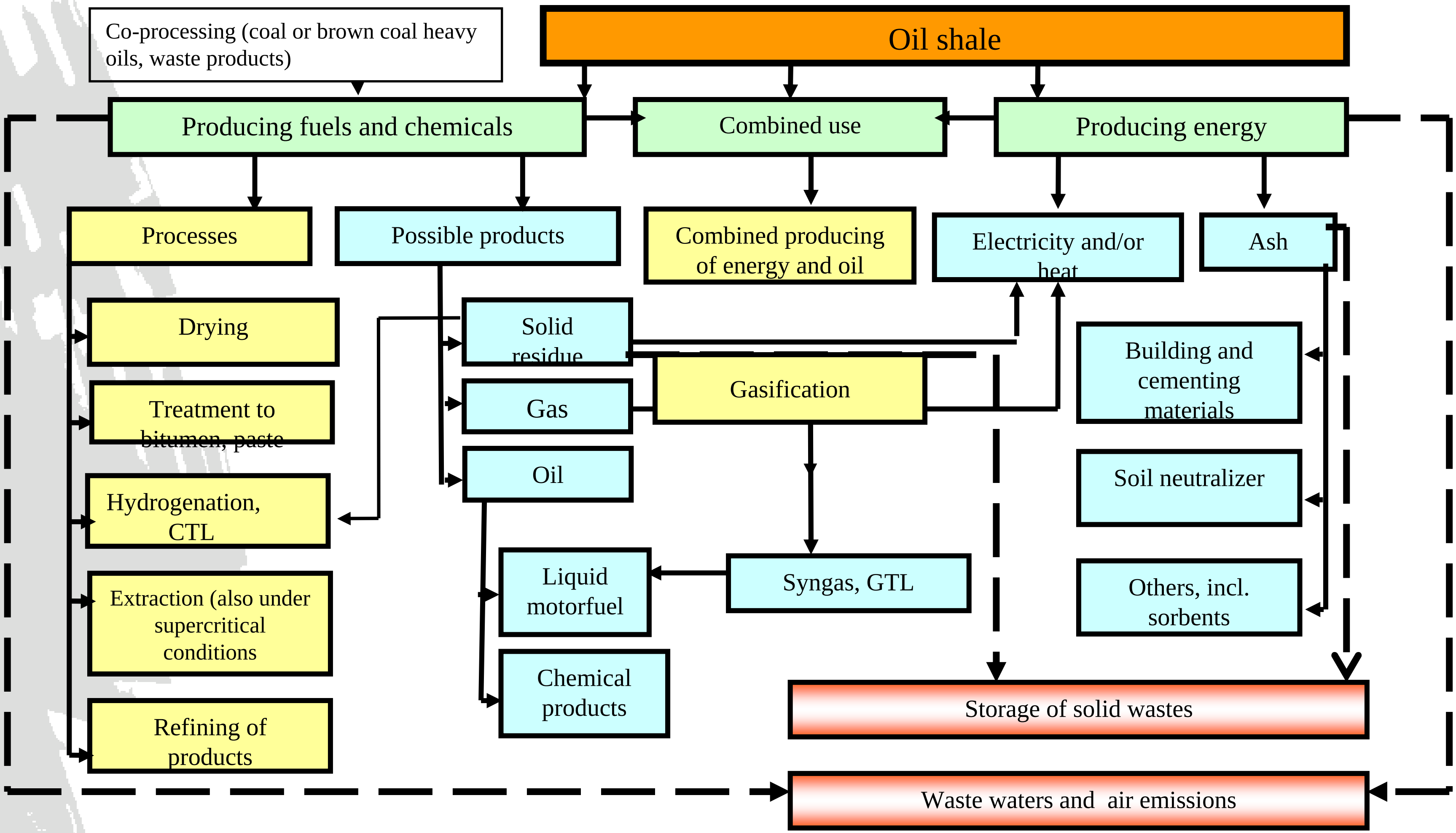
Oil Shale thermal treatment

- The final temperature of the process is 520 ^{o}C
- The environment problem of semicoke utilization due to TOC content in semicoke up to 14 %
- The conversion of organic matter to potential liquid products is about 65 %

Oil Shale thermal treatment through bitumen stage

- The relatively low temperature of the process 330-420 ^{o}C
- Organic matter is transferred to plastic condition
- TOC content in Solid Residue produced during the process is about 3-6 %
- Potential liquid products yield is approx. ~ 90 %

Possibilities of combined use of oil shale for energy and chemical products as Best Available Techniques (BAT)



Conclusions

- Liquid products yield potentially could be obtained up to ~ 90 % on OM in termal treatment processing Estonian oil shale through bitumen stage
- Content of Total Organic Carbon in solid residue obtained at the process with bituminization stage comparing to retorting is decreasing on 10 %
- Oil Shale decomposition through the bitumen stage could be precede the liquefaction of organic matter for hydrogenation process for extraction of mineral part.
- Thermobitumen obtained at oil shale decomposition under thermal conditions could be a good raw material for hydrogenation process to produce a liquid products.

Thank You !