

THERMAL PROCESSING OF DICTYONEMA ARGILLITE AND KUKERSITE OIL SHALE: TRANSFORMATION AND DISTRIBUTION OF SULFUR COMPOUNDS IN PILOT-SCALE GALOTER PROCESS

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Transformation and distribution of sulfur compounds in fossil fuel thermal processing depends on the bonding forms of sulfur in the specific feed-stock, thermal processing conditions and the technology used. This paper is focused on oil shale semicoking in a pilot-scale solid heat carrier retort (Galoter process) where oil shale is heated by means of mixing with ash from retorted shale combustion. The effect of out-burning conditions of the solid semicoking residue in the technological regeneration furnace on transformation and distribution of sulfur in retorting products is shown for two types of Estonian oil shales – dictyonema argillite and kukersite oil shale. These oil shales used differ significantly in their sulfur composition (total sulfur and sulfur bonding forms present) and mineral matter content.

Introduction

Several oil shale *ex situ* or over-ground thermal processes that utilize mixing oil shale with hot solid heat carrier (inert material, oil shale ash) to provide heat for oil shale thermal decomposition have been developed and patented worldwide. Examples of these processes are Alberta Taciuk, Galoter, Lurgi-Ruhrgas or TOSCO II. This study focuses on the Galoter process which has been industrially used in Estonia for over 25 years to produce oil from kukersite oil shale. Descriptions of these industrial units are widely available in literature [1–3].

The principle of the Galoter process is heating fine-grained oil shale in a horizontal rotary kiln-type retort in contact of hot oil shale ash obtained from solid retorting residue combustion. The process causes sulfur from the original oil shale to be distributed between the solid residue, semicoking gas,

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semicoking oil and stack gas, and sulfur distribution to be influenced by ash properties. The previous paper [4] from this laboratory presented a comparison of the chemisorption effect of alkaline ash on sulfur distribution during thermal co-processing of ash and oil shale mixtures in a standard Fischer Assay; i.e. in a laboratory-scale batch process [5, 6]. This paper is concerned on sulfur transformation and distribution in a pilot-scale heat carrier retort, where oil shale and its ash are co-pyrolysed in a continuous pilot-scale process. Estonian oil shale kukersite (locality Kiviõli, Estonia) and Estonian dictyonema argillite (locality Maardu, Estonia) were studied. It is worth noting that while there are abundant data available on kukersite oil shale retorting processes (from laboratory-scale equipment to different types of industrial-scale units used over a century in Estonia), for dictyonema argillite literature reports for conditions other than laboratory-scale data are difficult to find. Therefore the primary aim of this article is to increase availability of experimental data related to dictyonema argillite pyrolysis. Although dictyonema argillite above-ground retorting is far from being an economical process due to its low pyrolysis oil yields, in the future technologies might appear where pyrolysis of dictyonema argillite could be of interest as a preparation step.

Experimental

In solid heat carrier retorting experiments oil shales of particle sizes below 15 mm were pyrolyzed in a continuous pilot-scale unit with a productivity of 100 kg oil shale per hour. A detailed description of the unit can be found elsewhere [7, 8]. Determination of total sulfur and its bonding forms were carried out according to EVS 664:1995 [9]. For general comparison, a standard laboratory retorting technique i.e. Fischer retort (Fischer Assay standard method ISO-647-74) was used to describe technical-chemical characterization of oil shales studied. Conventional carbon, hydrogen and nitrogen content of organic matter of oil shales were calculated based on CHN analysis and evolved CO₂ amount.

Results and discussion

Transformation and distribution of sulfur compounds in thermal processing in pilot Galoter processes is investigated using two types of Estonian oil shales – dictyonema and kukersite. These oil shales contain different amounts of carbonate and clay mineral matter: kukersite is a carbonate-rich oil shale while dictyonema is a carbonate-lean oil shale [10, 11]. Characteristics of oil shale samples are shown in Table 1. Standard Fischer Assay based technical-chemical characteristics for specific oil-shale samples of this study are presented in Tables 2 to 3. Results from the pilot scale continuous

Table 1. Characteristics of investigated dictyonema argillite and kukersite oil shale samples

Constituents, wt. %	Dictyonema	Kukersite
Ash, A^d	79.85	46.69
Carbon dioxide mineral, $(CO_2)_M^d$	0.17	23.34
Sulfur, Total, S_t^d	2.29	2.05
Sulfate, $S_{SO_4}^d$	0.49	0.11
Pyrite, S_p^d	1.38	1.41
Organic, S_o^d	0.42	0.53
Organic matter:		
Conditional Org. ^d = $100-[A^d + (CO_2)_M^d]$	19.98	29.97
*Adjusted Org. ^d _{ad}	18.43	31.46

* references [17, 18]

Table 2. Fischer assay yields of investigated dictyonema argillite and kukersite oil shale samples, dry oil shale basis. Values on organic matter basis are shown in parentheses

	Dictyonema	Kukersite
Retorting products, wt. %:		
Oil	3.62 (19.64)	19.29 (61.32)
Pyrogenous water	3.41 (18.50)	1.64 (5.21)
Solid residue or semicoke	89.94 (45.42)	73.81 (16.75)
Semicoking gas	3.03 (16.44)	5.26 (16.72)
Volumetric semicoking gas yield dm ³ /kg dry oil shale (dm ³ /kg organic matter)	23.0 (124.8)	34.1 (108.3)

() organic matter basis

solid heat carrier retorting are summarized in Table 4. The composition of oil shale ashes produced in a muffle furnace at 875 °C is shown in Table 5. Comparison of Tables 3 and 4 indicates that oil shales processed in the solid heat carrier unit show different sulfur distribution among pyrolysis products relative to the standard Fisher Assay method [12, 13] due to the impact of the chemical character of the heat carrier (the ash of decomposed shale) and different technological-process conditions. The difference can be especially observed as kukersite and dictyonema differ significantly in their mineral matter composition and therefore in chemical character of ash.

Characterization based on standard Fischer retort conditions together with product analysis obtained for various Estonian oil shale samples are available widely in literature, for example [4, 14–16]. Therefore, only key points related to the present work are emphasized here (from Tables 2–3): dictyonema argillite, compared to kukersite, yields considerably less oil (dictyonema 19.6%, kukersite 61.3%, organic matter basis) and somewhat more semicoking gas (volumetric yield: dictyonema shale 124.8 m³/kg; kukersite

Table 3. Sulfur distribution in the Fischer assay products of investigated dictyonema argillite and kukersite oil shale samples

	Dictyonema	Kukersite
Sulfur content in semicoking products, % from oil shale sulfur content:		
Retorting oil	4.90	6.78
Pyrogenous water	0.74	0.53
Semicoke (total $S_t^d = S_{SO_4}^d + S_p^d + S_s^d + S_o^d$)	65.20	71.29
Sulfate sulfur $S_{SO_4}^d$	6.68	5.04
Pyrite sulfur S_p^d	12.96	33.85
Sulfide sulfur S_s^d	38.49	28.80
Organic sulfur S_o^d	7.07	3.60
Retorting gas	29.16	21.40
H ₂ S in retorting gas, vol.%	19.6	9.0

Table 4. Distribution of sulfur at thermal processing of dictyonema argillite and kukersite oil shale in a solid heat carrier unit under different conditions in the air-fountain technological furnace

	Kukersite				Dictyonema		
	760	830	875	805	765	895	905
Temperature in air-fountain furnace, °C	760	830	875	805	765	895	905
Temperature in reactor, °C	450	480	520	650	430	460	645
Air excess factor, α	1.0	0.8	1.2	1.2	1.2	1.0	1.2
Semicoke : ash (heat carrier)	1.00:2.47	1.00:2.38	1.00:3.12	1.00:6.30	1.00:1.30	1.00:2.34	1.00:4.52
Sulfur content in semicoking products, % from oil shale sulfur content:							
Liquid products	6.39	5.92	4.96	4.56	1.34	1.93	2.30
Semicoking gas	28.62	0.58	0.11	5.47	2.75	3.61	3.54
Ash residue	60.93	87.00	64.83	57.74	12.94	22.46	10.78
Stack gas (by difference)	4.06	6.50	30.10	32.23	82.97	72.00	83.38
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Content of sulfur bonding forms in ash residues, % from oil shale sulfur content							
Sulfate sulfur	37.38	6.91	39.92	47.30	6.73	8.11	8.09
Pyrite sulfur	2.75	1.85	1.21	1.05	2.59	11.74	1.19
Sulfide sulfur	19.61	77.19	22.58	8.69	3.02	0.51	0.54
Organic sulfur (by difference)	1.19	1.05	1.12	0.70	0.60	2.10	0.96
Total	60.93	87.00	64.83	57.74	12.94	22.46	10.78

Table 5. Chemical composition of incinerated kukersite and dictyonema ash (wt.%) prepared in a muffle furnace at 875 °C

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	SO ₃
Kukersite	28.25	9.84	5.44	41.02	5.05	3.60	6.07
Dictyonema	63.72	16.43	8.80	0.85	0.50	8.72	0.70

108.3 m³/kg); the sulfur content of semicoking gas of dictyonema is higher than that of kukersite (29.16% and 21.40%, respectively), however, there is more than two-fold amount of hydrogen sulfide in the semicoking gas of dictyonema argillite compared to kukersite; the content of sulfur in the retorting oil of dictyonema argillite exceeds 4.4 times this index for kukersite oil; in the semicoke of kukersite the content of sulfur (71.29% from total sulfur of the feed-stock), mainly on account of pyrite bonding form, is somewhat higher than in the semicoke of dictyonema argillite (65.20%).

Table 4 shows preliminary experimental information obtained from a pilot-scale solid heat carrier retort. The table was configured to indicate the influence of mineral matter and two major technological parameters that affect sulfur transformation during the Galoter process relative to pyrolysis without oil shale ash. The technological parameters are the temperature conditions and air excess factor (to be denoted as α) at burning of solid residue (semicoke) in the technological heat-regeneration furnace. Although from practical viewpoint these parameters are not independent from each other, in this work these are separated.

The influence of original mineral matter on chemical character of ash can be observed by comparing data on dictyonema and kukersite shales. During thermal processing of dictyonema argillite in the solid heat carrier unit most of feed-stock sulfur (more than 70%) is transferred to the stack gas, and the content of total sulfur in the solid ash residue of dictyonema argillite is low (containing 10–20% of total sulfur). Table 5 shows that dictyonema ash (heat carrier) practically does not contain alkali compounds such as CaO or MgO.

Carbonate-rich kukersite oil shale residue from the Galoter process contains, depending on process conditions, up to 87% of total sulfur. Thermal processing of kukersite oil shale under high-temperature regimes in the technological furnace with the combustion temperatures over 790 °C causes partial decomposition of calcium carbonate in the thermal processing solid residue resulting the residue to be activated to acid compounds, for instance to hydrogen sulfide. Calcium oxide binds hydrogen sulfide in a wide temperature interval, from the room temperature to 950 °C.

Under the low-temperature regime (below 790 °C) in the technological furnace carbonates practically do not decompose, free calcium oxide is not generated. The solid residue of thermal processing contains in this case less sulfide sulfur, and the sulfur originates mainly from pyrite sulfur-formed ferrous sulfide, as it occurs also at thermal processing of dictyonema argillite. The binding of hydrogen sulfide by calcium carbonate begins only at the temperature over 500 °C.

Deficiency or excess of air is also an important parameter for out-burning sulfides from the solid residue and in transforming them to sulfate form. In the case of deficiency of burning air (for example $\alpha = 0.8$ in Table 4) the out-burning of sulfides in the technological furnace is incomplete: about 75–77% of the sulfur from kukersite oil shale remains in the ash residue as sulfide sulfur and only 7–8% is transferred to stack gas. Furthermore, due to the deficiency of air required for complete combustion, the stack gas contains beside sulfur dioxide also hydrogen sulfide. In the case of high air excess factor ($\alpha = 1.2$) up to 30% from oil shale kukersite sulfur is transferred into the composition of stack gas. In the ash residue, there remain 22–23% as sulfide sulfur and 38–40% as sulfate sulfur. It can also be seen that sulfide sulfur in the high-temperature (650 °C) semicoke with air excess factor $\alpha = 1.2$ is greatly oxidized to sulfate bonding form.

In the case of dictyonema argillite, 72–83% from the sulfur present, depending on air excess factor in the technological furnace, is transferred as sulfur dioxide into the stack gas, indicating also that a higher air excess factor increases sulfur amount in stack gas and lowers it in ash residue.

Conclusions

This paper presents experimental data together with indicative trends for sulfur transformation and distribution in the solid heat carrier process. The data indicate that air excess factor in the heat regeneration furnace plays an important role at out-burning of sulfides in the solid residue, semicoke, also in the process of transforming them to the sulfate form.

Transformation and distribution of sulfur compounds in thermal processing of oil shales by solid carrier method depends, in addition to the temperature conditions and air excess factor in the technological heat regeneration furnace, also on chemical composition of ash residue, which performs in the process as solid heat carrier.

Acknowledgements

Support of the Estonian Science Foundation Grant 7222 is acknowledged. The authors are very grateful to Dr D. S. Kellog from PMUSA for her helpful advice and editorial comments. The authors gratefully acknowledge the assistance of I. Rohtla from Tallinn University of Technology.

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