

COMPARISON OF OIL SHALES FROM DIFFERENT DEPOSITS: OIL SHALE PYROLYSIS AND CO-PYROLYSIS WITH ASH

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This paper studies the effect of alkaline oil shale ash on oil shale thermal decomposition products during oil shale and ash co-retorting. Experiments with and without ash were carried out in a standard laboratory-scale retort (Fischer Assay) to determine relative yields of retorting products and sulfur distribution in them. Oil shales compared in this study were kukersite and Dictyonema shales from Estonia, Jordanian El-Lajjun oil shale and Saveljev oil shale from Russia. Oil shales were primarily selected due their difference in sulfur composition. Ash for co-retorting experiments was prepared from kukersite oil shale. The ash contains about 57.5 wt.% alkaline compounds CaO and MgO.

Introduction

Utilization of oil shales as chemical and energy feedstock is associated with technical and ecological problems related to the chemical composition of fuel and the parameters of the technological process. In Estonia today, there are two types of industrial retorts in use for shale oil production: generators (Kiviter process) and solid heat carrier retorts (Galoter process). The Kiviter process is based on a vertical direct-heated oil shale retort [1, 2] similar in principle to a cross-flow moving bed coal gasifier. The basis of the Galoter process is a rotary kiln-type solid heat carrier reactor heated via contact with hot ash from retorted shale combustion. Description of this process can be found elsewhere [3, 4]. The ash, in addition to being the heat carrier, has chemisorption properties due its alkaline composition that can influence pyrolysis product composition and yields. Although the chemisorption effect of oxides in ash is widely known [5–7], our literature review found no

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reports of a comparative study related to retorting of oil shales. However, some comparison can be obtained when ignoring the dependence of pyrolysis product yield and composition on pyrolysis conditions - there are abundant data on kukersite oil shale pyrolysis from industrial solid heat carrier retorts (feed up to 3000 tons oil shale per day) and there is also a paper describing the use of a bench-scale solid heat carrier retort (0.36 tons oil shale per day) on Jordanian El-Lajjun oil shale [8]. An overview of experimental data on Dictyonema retorting in a solid heat carrier retort (2.5 tons shale per day) will be available soon [9].

This preliminary work was conducted to compare the chemisorption effect of alkaline ash on pyrolysis products during thermal co-processing with different oil shale samples in a Fischer Assay. Oil shales for study were selected mainly based on their different sulfur composition (in total sulfur and sulfur presenting bonding forms) and partly due to the availability of data on solid heat carrier retorts for comparison. The Fischer Assay was chosen as it is a widely accepted method of oil shale quality evaluation for determining oil potential (pyrolysis oil yield) of oil shales as well as yields of pyrolysis water, gas and semicoke.

Oil shale samples studied were Estonian oil shale kukersite (average sample from Estonian Power Plant, Narva, Estonia), concentrated kukersite kerogen obtained via flotation, Estonian Dictyonema shale (often referred as Dictyonema argillite, locality Maardu, Estonia), Saveljev oil shale (Volga district, Russia) and Jordanian oil shale (sample from El-Lajjun deposit, Jordan).

Experimental

Oil shale samples for study were received from known deposits. Only the kukersite with concentrated kerogen content of 88% was prepared to alter sulfur composition via a flotation method [10]. The Fisher Assay standard method (ISO-647-74) was utilized for pyrolysis of selected oil shales with and without ash. Samples of different oil shales were crushed to pass a 900 apertures per cm² sieve. Determination of total sulfur and its bonding forms were carried out according to EVS 664:1995 [11]. Conventional carbon, hydrogen and nitrogen content of organic matter of oil shales were calculated based on CHN analysis and evolved CO₂ amount. The ashes were prepared from kukersite oil shale and for one comparison run from Dictyonema shale at the temperature 850 °C in a muffle furnace.

Results and discussion

Characteristics of specific oil shale samples investigated in this study are given in Tables 1–4. In these tables the oil shale samples studied were

denoted as follows: K (kukersite), KK (kukersite kerogen), D (Dictyonema), E-L (El-Lajjun), S (Saveljev), KAsh (kukersite ash) and DAsh (dictyonema ash). As the oil shales selected originate from well-studied deposits, characterization results presented in Tables 1–4 for these specific oil shales are briefly described. Similar characterization information for comparison can be found from different literature sources. For example, a general summary on chemical-technical characteristics for 100 oil shales and oil shale like rocks together with 226 references is published by Urov and Sumberg in 1999 [12]. Table 1 shows that the oil shales selected differ significantly in the composition and content of their organic matter, and particularly of interest for this work, in sulfur form (pyrite and organic) and content. Table 2 summarizes yields of pyrolysis products from Fischer Assay retorting under standard conditions. Relative product yields (pyrolysis gas, oil, water and solid residue) and compositions are specific to oil shales. Data are given both in oil shale and organic matter basis. Oil yields from organic matter of the oil shales studied here range from 19.8 wt.% to 67.7 wt.% and increase with increasing hydrogen per carbon in the organic matter of oil shale. For example, kukersite and El-Lajjun oil shales yield relatively high amounts of volatiles, and more than 60 wt.% of the organic mass of oil shale can be collected as a liquid pyrolysis product (oil and water). Both oil shales are characterized by low yields of pyrogenous water in the liquid retorting products: kukersite 13.5 wt.% and Jordanian oil shale 9.4 wt.%. For Saveljev and Dictyonema oil shales the yield of liquid products, on the organic matter basis, is 47.5 wt.% and 38.1 wt.%, and water content 20.4 wt.% and 48.0 wt.%, respectively. Table 3 presents volumetric yields of pyrolysis gases and pyrolysis gas compositions. The volumetric yields of semicoking gas per organic matter varies from 100.1 m³/kg for kukersite kerogen to 189.4 m³/kg for Jordanian oil shale. Table 4 shows the distribution of sulfur in the retorting products. Pyrite sulfur is known to be one of the main sources of hydrogen sulfide in the semicoking gas and for sulfide sulfur in the solid. Although thermal decomposition of pyrite occurs at higher temperatures than used in retorting, the transformation of pyrite sulfur to mono-sulfide bonding forms still occurs as a result of interaction with molecular hydrogen, that is produced during kerogen thermal decomposition. The pyrite fraction of total sulfur for the studied shales is as follows: kukersite $\frac{2}{3}$, Dictyonema $\frac{3}{4}$ and Saveljev shale $\frac{1}{2}$ (see Table 1). Examples of the trends in organic sulfur transfer to retorting products (gas, oil and residue) could be concentrated kukersite (total sulfur 1.3 wt.%, ~85% organic sulfur) and El-Lajjun (total sulfur 3.7 wt.%, ~78% organic sulfur). For kukersite concentrate, 47% of the sulfur is transferred to semicoking gas, 33.5% to oil and 19.5% to semicoke. Similar sulfur transfer can be seen for El-Lajjun oil shale (41% to gas, 33.6% to oil and 25.4% to solid residue) resulting in very high sulfur content in the semicoking oil (~ 8.5 wt.%) for this oil shale.

While Tables 1 to 4 describe the characteristics of oil shale samples studied, Table 5 shows the chemical composition of ashes prepared for

Table 1. Characteristics of investigated oil shale samples

Constituents, wt. %	Kukersite (K)	Kukersite concentrate (KK)	Saveljev (S)	Dictyonema (D)	El-Lajjun (E-L)
A ^d , ash content	51.09	11.45	61.41	81.42	63.10
(CO ₂) _M ^d , mineral	22.02	0.40	10.80	0.52	14.94
S _t ^d , total sulfur	1.55	1.30	3.86	2.94	3.70
S _{SO₄} ^d , sulfate sulfur	0.05	0.03	0.23	0.41	0.15
S _p ^d , pyrite sulfur	1.04	0.17	1.95	2.14	0.67
S _o ^d , organic sulfur	0.46	1.10	1.68	0.39	2.88
Org ^d conventional*	26.89	88.15	27.79	18.06	21.96
Org ^d adjusted**	27.98	88.55	29.47	16.06	23.04
Elemental analysis of organic matter	K	KK	S	D	E-L
C	77.0		62.2	69.3	74.5
H	9.7		7.0	6.6	8.5
S	1.6		5.7	2.5	12.5
O+N+Cl	11.7		25.1	21.6	4.5
Mass%					
C:H	7.9		8.9	10.5	8.8
C:S	48.1		10.9	27.7	6.0
Atomic ratio					
C:H	0.67		0.76	0.87	0.74
C:S	128.4		29.1	74.0	15.9

* Conventional content of organic matter, $Org^d = 100 - [A^d + (CO_2)_M^d]$;

** Adjusted content of organic matter, calculated according to [16].

Table 2. Product yields from Fischer Assay

Dry oil shale basis, wt%	K	KK	S	D	E-L
Oil	16.1	59.7	10.5	3.6	13.6
Pyrogenous water	2.5	6.1	2.7	3.3	1.4
Gas	5.8	12.7	6.3	3.0	4.6
Semicoke	75.6	21.5	80.5	90.1	80.4
Organic matter basis, wt%	K	KK	S	D	E-L
Oil	60.0	67.7	37.8	19.8	61.9
Pyrogenous water	9.4	6.9	9.7	18.3	6.4
Gas	21.5	14.4	22.7	16.5	20.9
Semicoke	9.1	11.0	29.8	45.4	10.8

Table 3. Comparison of compositions of semicoking gas from Fischer Assay

Volumetric yield of gas	K	KK	S	D	E-L
dm ³ /kg oil shale	32.5	88.2	42.0	21.7	41.6
dm ³ /kg organic matter	120.9	100.1	151.1	120.2	189.4
Composition of gas, vol.%	K	KK	S	D	E-L
CO ₂	25.0	25.5	23.1	13.6	14.5
H ₂ S	8.8	5.7	26.9	20.3	25.2
C _m H _n	16.1	15.4	4.5	7.5	9.3
CO	7.9	13.5	6.7	5.7	1.0
H ₂	8.2	6.8	16.1	27.1	21.6
C _n H _{2n+2}	34.0	33.1	22.7	25.8	28.4

Table 4. Sulfur distribution in the retorting products, wt.%

Sulfur distribution	K	KK	S	D	E-L
Semicoking gas	26.4	47.0	41.5	29.3	41.0
Liquid products (oil+pyr. water)	7.3	33.5	14.7	5.6	33.6
Semicoke	66.3	19.5	43.8	65.1	25.4
Sulfur content, wt.%	K	KK	S	D	E-L
Oil	0.70	0.73	2.9	4.0	8.5
Semicoke	1.36	1.18	2.1	2.12	1.17

Table 5. Chemical composition of oil shale ashes – analysis as oxides in wt.% of total ash

Oil shale	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O+K ₂ O	SO ₃
Kukersite	23.61	5.77	3.74	49.10	8.41	4.12	4.97
Dictyonema	63.72	16.43	8.80	0.85	0.50	8.72	0.70
Saveljev	37.53	12.55	8.35	26.27	1.72		8.60
*El-Lajjun	28.86	7.43	3.70	52.79	1.30		1.30

co-pyrolysis from kukersite and Dictyonema shales together with corresponding ash characteristics for Saveljev ash (from this laboratory) and El-Lajjun ash [13]. From the ashes shown the El-Lajjun ash is the closest to and the Dictyonema ash the most different from the kukersite ash. It is to note that kukersite ash contains 57.5 wt.% of the alkaline compounds CaO and MgO, while Dictyonema ash contains only about 1.35 wt.%. The Fe₂O₃ content in Dictyonema ash is 8.8 wt.% in comparison with 3.74 wt.% in kukersite ash. To characterize the effect of Fe₂O₃, co-pyrolysis with Dictyonema shale and its ash was carried out for comparison. Note that iron oxides and waste materials containing iron oxides have been utilized as absorbents for desulfurization of hot coal gas [6, 7, 14].

Table 6 presents the effect of alkaline kukersite ash on thermal processing of oil shales performed by the standard Fischer Assay method. In addition to

product yields and sulfur distribution in Table 6, pyrolysis oils are characterized also by densities and concentration of phenolic compounds (refractometric method [15]). Due to the different content of organic matter and sulfur of the oil shale samples investigated here, the oil shale/ash ratios were chosen considering experimental convenience. Only in the case of co-pyrolysis of kukersite and its ash, the selection was based on industrial solid heat carrier retorting units, where the kukersite/ash ratio ~1:2 is a common practice. Table 6 shows that at co-pyrolysis of ash and oil-shale, as compared to oil shale pyrolysis, the following trends were observed: total oil yield, organic matter basis, is slightly decreased (by 8–10%); total gas yield either increases or decreases slightly; sulfur concentration in the oil shows a slight decrease (generally few percents, in the case of Dictyonema up to 12.5%), while H₂S concentration in semicoking gas shows a significant decrease (e.g. from 8.8 vol.% to 0.4 vol.% for kukersite; 25.2 vol.% to 10.5 vol.% in the case of El-Lajjun oil shale). It can be also seen from Table 6 that the ability of Dictyonema ash to reduce H₂S from semicoking gas is similar to that of kukersite ash (from 20.3 vol.% to 11.2 vol.% for kukersite ash and to 10.8 vol.% for Dictyonema ash), however, it has little effect on phenol removal from oil due to its very low CaO and MgO content. Finally it should be pointed out that in industrial solid heat carrier systems [2, 3] put into practice in Estonia, solid residue (semicoke and heat carrier ash) from retorting is combusted to prepare the heat carrier for the retorting process. This in turn can release chemisorbed sulfur (for example in the form of CaS) to stack gas as SO₂.

Table 6. Comparative results – effect of alkaline ash on constituents at thermal processing of oil shales

	KK		K		D			E-L	
	Without ash	KK:KAsH 1:2	Without ash	K:KAsH 1:2	Without ash	D:KAsH 3:1	D:DAsH 3:1	Without ash	E-L:KAsH 1:1
Yield accounted on organic matter, wt.%									
Oil	67.4	55.0	60.0	50.0	19.8	17.0	17.3	61.9	57.8
Gas	14.3	16.8	21.5	14.8	16.5	18.0	17.9	20.9	24.2
Density of oil, d_4^{20} g/cm ³	0.964	0.902	0.959	0.938	0.996	0.919	0.926	0.962	0.966
* Content of phenolic compounds in oil, wt%	32.1	3.0	26.5	7.1	9.6	3.6	8.8		
** Sulfur content in oil, wt%	0.73	0.68	0.70	0.65	4.0	3.7	3.5	8.5	7.9
H ₂ S in semicoking gas, vol.%	5.7	0.5	8.8	0.4	20.3	11.2	10.8	25.2	10.5

* refractometric method [15]; ** standard DIN 51400.

Conclusions

In summary, this paper presents a preliminary comparative characterisation of oil shales basing on co-pyrolysis of ash and oil shale as it could occur in industrial solid heat carrier retorts. The results presented in this paper indicate that under standard Fischer Assay conditions co-pyrolysis of oil shale and ash influences the yield and composition of products as compared to oil shale pyrolysis in the absence of ash. Authors of this paper would like to recommend the use of the Fischer Assay as a simple preliminary technique for describing oil shale and ash co-retorting.

The results also confirm that, although the co-pyrolysis effect of ash on product yields and oil sulfur concentration is slight, the concentration of H₂S in semicoking gas and phenolic compounds in oil can be reduced significantly depending on ash composition. It is to emphasize that heat carrier ash used in solid heat carrier retorts does not affect practically sulfur concentration in oils, and therefore solid heat carrier retorts do not possess any corresponding advantage of processing high organic sulfur oil shales.

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