ABOUT THERMAL LOW-TEMPERATURE PROCESSING OF OIL SHALE BY SOLID HEAT CARRIER METHOD

J. KANN, A. ELENURM, I. ROHTLA[*]

Chemical Engineering Department
at Tallinn University of Technology
5 Ehitajate Rd., Tallinn 19086, Estonia

N. GOLUBEV, A. KAIDALOV, B. KINDORKIN

Narva Power Plants Inc.
59 Elektrijaama Rd., Narva 21004, Estonia

The method of retorting shale fines bases on the effect of ultrarapid heat transfer between polydispersed fine-grained solid substances – from high-temperature solid heat carrier (ash of the retorted oil shale) to the decomposable oil shale. The solid heat carrier method is also applied for utilization of organic liquid and solid wastes, e.g. waste oil and scrap rubber waste, etc. The process of solid heat carrier (SHC) has been developed at a commercial scale plant with a capacity of 3,000 tonnes shale per day at Oil Factory of Narva Power Plants Inc. in Narva (Estonia).

Description of the Technological Process

The composition of shale organic matter kerogen differs from that of the organic parts of the other solid fuels. As compared with coal, oil shale kerogen contains more hydrogen and may, therefore, be well subjected to thermal conversion into oil and gas, whose yield depends on the hydrogen content of the convertible solid fuel.

Taking this into consideration, the properties of kukersite oil shale are very favorable, as up to two thirds of its organic substance is convertible into oil.

The distribution of organic substance of kukersite at carbonizing in the standard Fischer retort (final temperature 520 °C) occurs as follows, %: oil 64.5, pyrogenous water 5.0, solid residue 16.5 and semicoking gas 14.0.

Thermal destruction of kukersite begins at 170–180 °C, pyrogenous water appears at 270–290 °C. At the temperature 350–400 °C the organic

---

[*] Corresponding author: e-mail *irohtla@staff.ttu.ee*

substance of kukersite is converted into semiliquid state, called thermobitumen. Decomposition of the latter gives oil and gas. Formation of the thermobitumen is one of the peculiarities occurring at thermal destruction of oil shale. It has caused a lot of trouble for engineers working on this process because the semiliquid mixture is apt to clog up the retort.

Thermal processing of oil shale in Estonia has quite a long history, various facilities and technologies having been used for that purpose. In principle, two ways of thermal processing have been used: heating oil shale up to 500 °C – semicoking (retorting) or low-temperature processing, and heating up to 1000–1200 °C – on purpose to produce city gas.

Nowadays only the low-temperature processing is in use in Estonian oil shale industry.

For retorting shale fines (≤25 mm) a process with solid heat carrier has been developed at commercial scale at Oil Factory of Narva Power Plants Inc., having two thermal processing units with the capacity of 3,000 tonnes oil shale per day each. The solid heat carrier process for thermal decomposition is based on the effect of ultrarapid heat transfer from fine-grained heat carrier to fine-grained oil shale at their compounding in rotary drum reactor. This method for oil shale thermal processing was designed and developed in laboratory scale in 1945–1946 at G.M. Krzhizhanovski Power Engineering Institute of the Academy of Sciences of the USSR [1, 2]. The further research was continued in Estonia in semi-industrial and later in industrial scale in co-operation with Estonian organizations (Institute of Chemistry and Institute of Energetics of the Estonian Academy of Sciences, Oil Shale Processing Complex *Kiviõli*, Estonian power plants, and Oil Shale Research Institute).

The solid heat carrier method enables high efficiency in using up the organic substance of oil shale, as the calorific value of the solid residue of retorting (semicoke) is used for realizing the technological process, and merely combusted residual ash with minimum content of organic substance is sent to the ash disposal system.

The technological process in the solid heat-carrier unit includes three fundamental operations (Fig. 1).
1. Drying and preheating of the fine-grained oil shale in the flow of hot stack gas directed from the heat-regeneration furnace through the drier.
2. Thermal low-temperature decomposition of dry shale during continuous mixing with heat carrier in the rotary drum reactor. As heat carrier the ash of spent shale is used.
3. Combustion of the mixture of semicoke and heat carrier in the heat-regeneration furnace for heating up the ash residue as heat carrier for the next technological cycle.
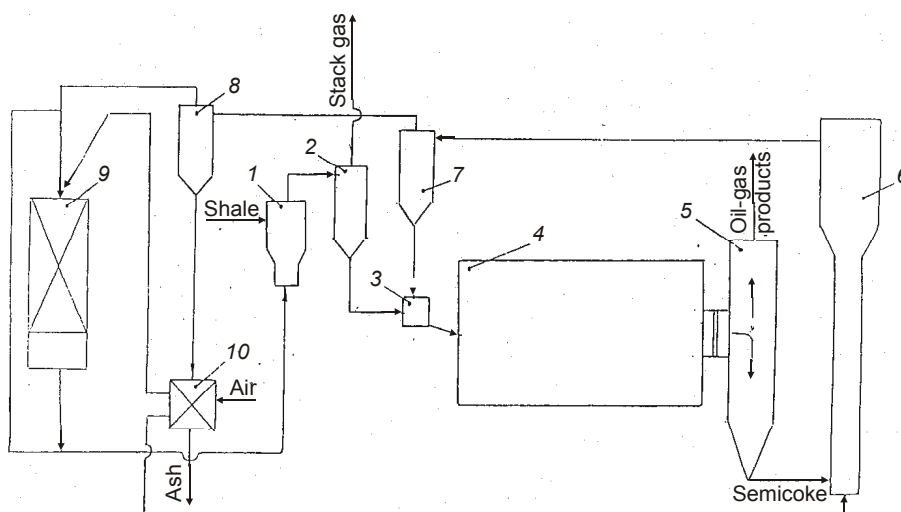
Fig. 1. Layout of the unit for retorting oil shale with solid heat carrier: *1* – drier; *2* – dry shale cyclone; *3* – mixer; *4* – rotary reactor drum; *5* – dust separator; *6* – heat-regeneration furnace; *7* – heat-carrier cyclone; *8* – ash cyclone; *9* – waste heat boiler; *10* – ash heat exchanger

Oil shale crushed to ≤25 mm is fed into drier *1*, where the drying and preheating of oil shale are realized in the flow of hot (750–820 °C) stack gas. Dry, preheated to 150 °C oil shale is separated from the stack gas in dry shale cyclone *2* and directed to mixer *3*, where it is mixed with 1.8–2-fold quantity of hot solid heat carrier. The mixture of oil shale and heat carrier is directed to rotary drum reactor *4*, where in the course of 15–20 min over 80% of shale organic substance is converted into liquid and gaseous products of thermal decomposition. Small grain size and large surface areas of shale and heat-carrier particles ensure their close contact in the mixing process in the reactor and high rate of heat transfer from the heat carrier to the shale, resulting in rapid heating of the latter.

At the same time dispersed distribution of oil shale in the mixture with heat carrier avoids sticking of the thermobitumen (semiliquid phase at kukersite thermal decomposition) on the interior surface of the reactor.

Vapor–gas mixture formed in reactor is directed for condensation through dust separator *5*, where in connected cyclones volatile products are separated from spent shale and heat carrier mixture. In the condensation system the vapor–gas mixture is directed through multistage condensers for obtaining heavy, medium, and gas turbine fuel and gasoline fractions. Spent shale and heat-carrier mixture from the dust separator is fed by screw-conveyor to heat-regeneration furnace *6*. Calorific value (60–85 kJ/kg) of the spent shale and heat-carrier mixture, having a temperature about 430–450 °C, is sufficient for covering the heat consumption of the thermal processing. Ash residue from the heat-regeneration furnace and stack gas are directed together through the cyclone system. In heat-carrier cyclone *7* the relatively

coarse-grained granulometric fraction of ash is separated from the flow of stack gas and directed as solid heat carrier through the mixer *3* together with the feedstock into the reactor. Excess of ash from the retorted oil shale is removed in the ash cyclone *8*. The residual heat of stack gas and excess ash can be utilized in waste heat boiler *9* and in ash heat exchanger *10*. The stack gas is cleaned from flue dust by electrical filter before outlet into the open air.

An average chemical composition of oil shale used for thermal processing in the solid heat-carrier unit SHC-3000 is characterized as follows, % (dry basis): ash content A^d 52.39; carbon dioxide, carbonaceous $(CO_2)^d_M$ 21.10; total sulphur S^d_t 1.60; sulphate sulphur $S^d_{SO_4}$ 0.06; pyrite sulphur S^d_p 1.08; organic sulphur S^d_o 0.46.

Content of organic substance in the dry oil shale calculated according to the formula $Org^d = 100 - (A^d + (CO_2)^d_M)$ is 26.51%. As the mass of ash residue A^d increases due to the formation of SO_4^{-2} ion from combustible sulphur in the process of cineration in the muffle-furnace, the calculated content of organic substance in oil shale according to the above formula is somewhat lower than the factual one [3]. The corrected content of organic substance in the present case makes up $Org^d = 27.66\%$.

Characterization of Thermal Processing Products

Material balance of oil shale thermal processing in the solid heat-carrier unit SHC-3000 can be characterized by the following average data, % (output, on dry oil shale): total oil 14.4; pyrogenous water 2.6; semicoking gas 5.0 (38.3 m^3/t); ash residue 64.9; stack gas (by difference) 13.1.

The total oil yield, on (corrected) organic substance, makes up 52.06%, or 80.7% of the Fischer assay. Total oil characteristics are as follows: density, d_4^{15} 0.9595 g/cm^3; viscosity at 80 °C 6.40 mm^2/s; flash point by open cup 48 °C; pour point −27 °C; calorific value 39570 kJ/kg. Elementary analysis of the total oil: C 82.35%; H 9.98%; S 0.70%; N 0.25%; Cl 0.07%; O (by difference) 6.65%.

The products obtained by thermal decomposition of kukersite oil shale in the retorts with solid heat carrier are notable for their high content of unsaturated hydrocarbons.

The content of lower olefinic hydrocarbons, including ethylene, propylene and homologues in the semicoking (retort) gas, totals to 33–35vol.%. The fraction of paraffinic hydrocarbons, such as methane, ethane, etc., is 35–37vol.%. The calorific value of the gas exceeds 42 MJ/m^3.

One of the outstanding features of the solid heat carrier process is that the semicoking gas and oil vapors are not diluted with combustion gas, a circumstance which simplifies the condensation of oil fractions and ensures getting high-calorific gas.

The light oil fraction (up to 150 °C) rectified from the total oil contains a notable quantity (41–44%) unsaturated hydrocarbons. In the oil fraction 150–200 °C the content of alkenes decreases to the level of 27–28%, at the same time the degree of aromatization increases to 24–29%.

The produced oil serves as raw feedstock, from which, according to the approved Estonian Standard EE10579981, the oil factory produces its marketable product – low-sulphur fuel oil used for heating in boiler plants everywhere in Estonia as well as in Latvia and Lithuania [4].The standard for this liquid oil shale fuel has been worked out on the basis of a long-term practical study of liquid fuel oil consumption market (the Table).

Assortment of Shale Oils produced at Oil Factory

Oil	Standard value according to EE10579981				
	Density, kg/m^3, at 15 °C	Kinematic viscosity, mm^2/s	Flash point open cup method, °C	Ash content, mass%	Water content, mass%
Heavy oil	min. 1040	at 60 °C min. 150	min. 100	max. 2.5	max. 1.0
Middle oil	1035–1050	at 80 °C 20–28	min. 120	max. 0.15	max. 0.30
Summary oil:					
Mark A			min. 25		
Mark B	max. 1000	at 50 °C max. 20	min. 10	max. 0.15	max. 0.30
Mark C			min. –10		
Gas turbine fuel:					
Mark L1	900–930	at 50 °C max. 4.1	min. 61	max. 0.015	
Mark L2	max. 950	at 50 °C max. 8.5	min. 61	max. 0.07	max. 0.30
Mark L3	950–1000	at 50 °C max. 25	min. 70	max. 0.10	

The solid heat carrier method is also applied for utilization of organic liquid and solid wastes and out of use tires in order to get oil and gas for energetics and chemical industry.

Various processes have been tested to select an economically favorable and environmentally safe technology. Incomplete use of the initial substance and due to that thermally unbalanced process are the problems not easy to solve.

It is theoretically enticing to put to use the high energy content of worn tires for producing electricity and high-pressure steam. However, direct burning of rubber residues requires expensive environmental measures. In burning process, an intensive liberation of light constituents takes place depending on the chemicals present in rubber. It results in the emission of much soat and unburned components to the open air. Emission problems have hindered the acceptance of burning as a viable waste treatment method, particularly due to the release of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans. It is also established that the flue dust and especially the unburned soat in the stack gas contain much carcinogenic polyaromatic hydrocarbons as indicated by the presence of benzo(a)pyrene.

Utilization of rubber scraps and crushed plastic residues together with oil shale by the heat carrier method is in this sense more perspective.

Due to its alkaline properties, oil shale ash used as heat carrier binds a most part of deleterious sulphur compounds – hydrogen sulphide in the retort gas and sulphur dioxide in the stack gas.

On the other side, bituminous fuels like oil shale are able to transfer chemically bound hydrogen to desired substances. This ability was proposed to be used to improve the product quality at pyrolysis of rubber and plastic waste to get higher yield of stable oil products [5].

Thermal processing experiments with the mixtures of oil shale and polymer waste, mainly rubber scraps, on the industrial plant SHC-3000 have demonstrated the scope and limitations of the method.

As rubber component a mixture of scraps from inner tubes (79%) and tires (21%) was used.

The rubber component contains 3.33% ash A^d and 1.02% total sulphur S^d_t.

Its chemical composition is as follows, mass%:

SiO_2	0.31
Al_2O_3	0.15
Fe_2O_3	0.11
CaO	0.13
MgO	1.05
Na_2O	0.08
TiO_2	0.03
K_2O	0.03
ZnO	1.44
Combustible matter (by difference)	96.67
	100.00

Fischer assay, % of rubber mass: oil 33.02, pyrogenous water 0.26, solid residue (semicoke) 37.14, gas 29.58; oil density d_4^{15} 0.9475 g/cm^3; content of phenolic compounds in the oil 0.90%; total sulphur in the semicoke 2.48%.

Industrial experiment of low-temperature processing of rubber scraps together with fine-grained oil shale in the plant SHC-3000 was carried out with the mixture containing 90% oil shale and 10% rubber scraps.

Temperature conditions in the main units of the plant: drum reactor 460–470 °C, drier 180–190 °C, and heat-regeneration furnace 740–760 °C.

The yield of the condensed oil fractions reached 16.48% of the dry mass of oil shale and rubber mixture. The oil was condensed as heavy oil 43.24, middle oil 28.97, gas turbine fuel 5.98, and gasoline fraction 21.81% of the total oil.

In 1996 under the guidance of the Executive Secretary of the Basel Convention a case study on the recovery of hazardous wastes (HW) at solid

heat carrier was organized by a Canadian-Estonian research group of specialists.

The report of the case study was presented to the technical working group to prepare draft technical guidelines for an environmentally sound management of HW subject to the Basel Convention. It was noted that "… the use of this pyrolysis unit with which is capable of recycling HW is a unique case in the world. As this unit of oil shale pyrolysis process above all carries out a recovery of some HW, it is in Estonia's interest to continue, to support, to develop, to correct and to utilize such a unit" [6].

Some primary aspects were advised to be developed and improved: establishing extended monitoring for air emissions of fly ashes, ash disposal site, and the water used for transporting ashes; improving combustion efficiency, reducing the emissions of CO or total hydrocarbons, and fine dust particles.

Environmental Aspects of Oil Shale Thermal Processing

Thermal processing of solid fuels in different retorting units is inevitably related to some environmental problems.

As for the solid heat carrier method, the problems of sulphur transformation and distribution between the products of thermal processing, and probable cumulation of noxious sulphide sulphur in the water body of the hydraulic ash disposal system have been studied. The content of carcinogenic polycyclic aromatic hydrocarbons, benzo(a)pyrene being their generally approved indicator, in the liquid and solid products of thermal processing deserved our special interest.

The ash residue of low-temperature (720–760 °C) incineration in the heat-regeneration furnace contains less sulphide and, respectively, less total sulphur. At the same time sulphide sulphur in the ash residue occurs mainly as ferrous sulphide FeS, which is practically insoluble in water.
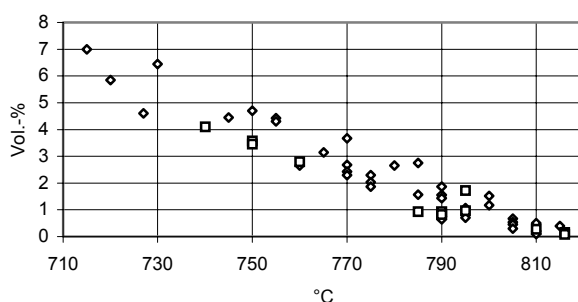

Fig. 2. Hydrocarbon sulphide content of the retort gas of solid heat-carrier unit depending on the thermal treatment of solid heat carrier in the heat-regeneration unit: $\diamond$ H_2S in the gas from oil shale, $\square$ H_2S in the gas from mixture of oil shale and rubber

As a result of high-temperature (>800 °) incineration in the same furnace, the decomposition of carbonates increases resulting in chemical activation of heat carrier due to the formation of free CaO. In this case chemisorption of hydrogen sulphide from the vapor-and-gas mixture in the reactor takes place, and sulphide sulphur in the ash residue occurs mainly as calcium sulphide CaS (Fig. 2).

Essential factor influencing the outburning of sulphides in the heat-regeneration furnace is the air excess ratio. At the lack of combustion air ($\alpha<1$) the perfect outburning of sulphides is hindered, and a noticeable part of total sulphur in the form of hydrogen sulphide will be present in the stack gas in addition to sulphur dioxide.

Under low-temperature conditions in the heat-regeneration furnace, when the activation of heat carrier is prevented, about 28-29% of the total sulphur remains in semicoking (retort) gas.

Carcinogenic polyaromatic hydrocarbon – benzo(a)pyrene – forms unavoidably at thermal processing of fuels. It has been established that about 90–95% of formed benzo(a)pyrene concentrates in oil products. Less than 2.0% remains in ash residue, which is separated from stack gas by cyclones. Highest concentration of benzo(a)pyrene is in flue ash present in stack gas after ash cyclones. In spite of the fact that the quantity of flue ash makes up only 5% of the total amount of ash residue, the content of benzo(a)pyrene in flue ash (0.81 mg/kg) considerably exceeds the content of that noxious compound in the whole rest of ash residue (0.03 μg/kg). For that reason the precipitation of flue ash from stack gas by electrical filter before its escape into the open air is unavoidable.

Ash residue, separated from the technological cycle of oil factory, is directed by the hydrodisposal system to the ash dump common with Estonian Power Plant. The chemical composition of the ash dump water body has formed during repeated contacts with ash residues from power plant and heat-carrier unit. High pH value (12.5) and high concentration of potassium ion (6,100 mg/dm^3) are characteristic for circulating water.

Considerable changes take place in the chemical composition of sulphur compounds in the ash residue when contacting circulating water. Sulphide sulphur concentration measured immediately after contacting water with fresh ash is high. In the circulating water returned from ash dump only traces of sulphides can be detected. Sulphide sulphur is oxidized by the atmospheric oxygen to thiosulphate and sulphate. The presence of thiosulphate sulphur is characteristic of the water of the ash disposal system. During long-time exploitation of the solid heat-carrier unit at the oil factory the content of sulphide sulphur in the circulating water has not exceeded 1.5 mg/dm^3.

REFERENCES

1. *Kõll, A.* Thermal decomposition of oil shale kukersite in the conditions of processing with solid heat carrier // Chemistry and Technology. Moscow–Tallinn, 1951. P. 7–18 and 246–251 [in Russian].

2. *Volkov, E., Stelmakh, G.* The stages of research on creating commercial units for processing oil shale fines. Development of the *Galoter* process in 1944–1999 // Oil Shale. 1999. Vol. 16, No. 2. P. 161–185.

3. *Raudsepp, H.* About the method for determination of organic mass in Baltic oil shale // Proc. Tallinn Polytech. Inst.1953. No. 46 [in Russian].

4. Shale Oils Produced in Oil Plant : Estonian standard EE10579981 [in Estonian].

5. *Hodek, V., Fürtjes, T., van Heek, K.-H.* Chemische Grundlagen zur Co-Pyrolyse von Kohlen und Kunststoffen // Erdöl, Erdgas, Kohle. 1995. Vol. 9. P. 376–378 .

6. United Nations Environment Programme. 11th session, Manchester, 9–13 September 1996. Case study on the recovery of hazardous wastes in Estonia at an oil shale distillation unit in Narva.