

ABOUT THE GASIFICATION OF KUKERSITE OIL SHALE

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Abstract. *The production of oil shale gas from kukersite oil shale is a successfully implemented industrial process. The above process was urgently introduced in the former Soviet Union due to the energy crisis after World War II. During the second half of the 20th century the oil shale processing technologies and material sciences developed very fast, and with no doubt, whenever the need for the production of oil shale gas emerges today, we have valuable experience in this field. An economic analysis must give the answer to the profitability of this kind of production. The environmental issues are also important, first of all those related to the residue of organic matter in the solid waste from oil shale pyrolysis.*

Keywords: *kukersite oil shale, gasification, solid fuels, thermal decomposition, oil shale gas.*

1. Introduction

In the Estonian State Development Plan of Oil Shale Utilization for 2008–2015, the need for a thorough reform in this field, which should include technical, administrative, economic and environmental measures, has been expressed [1]. Most of the oil shale mined in Estonia today is used as a fuel stock for the production of energy. It is widely recognized that the current carbon-based energy system is unsustainable and costly, both financially and environmentally. It means that we should find for oil shale more profitable fields of use with less environmental impact. Promising areas in the oil shale industry are the production of shale oil and gasification of oil shale [2].

In 1850, wood made almost 90% of the global energy use. However, the significance of wood fell rapidly and already in 1890 half of the energy was produced from coal. By 1910 the share of coal in the energy balance had

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grown to 60%. Coal remained the world's leading fuel to the sixties of the last century when its position was overtaken by oil. By today, the variety of energy carriers has increased considerably. If we take only the production of electricity, for example, the coal, lignite and oil shale power plants give 40%, gas power plants about 19.5%, oil fired power plants 6.5%, nuclear power plants and hydropower plants both 16%, while power plants based on other fuels account for only a minor share – a bit over 2% of the total electricity production in the world.

In spite of the planned energy saving measures, the energy intensity keeps rapidly growing all over the world. According to the prognosis of British Petroleum Company, UK, up to the year 2030 the highest absolute growth is predicted for coal power plants (the annual growth rate 2.8%) and their share will increase to 45%. Even a more rapid growth is predicted for gas power plants (annual growth 3.3%), but their share will still remain half less than that of coal plants. The annual growth of hydropower (1.7%) and oil fired (0.9%) plants will evidently be insignificant. The electricity from all alternative sources (wind, solar, biofuels, geothermal heat, hydrogen energy) will remain marginal and may reach 4% at best.

It follows from the above that the interest in different gas sources has rapidly grown in the world, including the most promising so-called shale gas. However, the perspective of shale gas in Europe due to environmental risks is not clear yet.

2. On the gasification of solid fuels

Gasification of solid fuels (coal, peat, lignite, oil shale, biological waste, etc.) is conversion of fuels into combustible gas at high temperatures and in the presence of an oxidizer or gasification component, which consists mainly of carbon monoxide (CO) and hydrogen (H₂). Since the gas is mainly extracted in generators, the product gas is often called generator gas as well.

The primary product of solid fuel gasification is the so-called coke gas, which contains a certain amount of carbon dioxide (CO₂), water vapor (H₂O), methane (CH₄), sometimes also higher hydrocarbons and, when air is injected, also nitrogen (N₂). If the fuel contains heteroatoms (S, N, etc.), also hydrogen sulphide (H₂S) and nitrogen oxides (NO_x) can be found in the coke gas.

The duration of the gasification process depends essentially on temperature, and as a rule, when no special catalyzers are used, it is higher than 800–900 °C. In the presence of oxygen in the gasification of solid fuels the temperatures would rise too high and therefore the mixture of water vapor/air or water vapor enriched with oxygen was used for this purpose. The methane content in the final product can be increased with raising the pressure of the gasification process.

In Estonia, we could gasify wood, biological waste, oil shale, graptolite argillite, peat and perhaps various polymeric wastes, for example worn-out tires. What matters is the economic side – would it be worthwhile? Neither can the national interest be ruled out. In view of the waste management in Estonia alone, we have several options: to burn the waste directly, use pyrolysis for extracting oil, gasify the waste or produce sugars, bioethanol, etc., by biotechnological processing.

The principles of biomass gasification have been known from the end of the 18th century when one of them was applied for supplying gas to gas lamps [3]. During World War II wood gas engines were used in the German Army and in Estonia too.

Gasification of fuels with low calorific value and of low quality is used for the following reasons:

- in industry fuels of low quality are used;
- there is a need to produce a clean fuel for special purposes;
- clean gas is produced from otherwise problematic fuels for energy purposes [3].

Biogas production deserves heightened attention. The indicatively estimated applicable potential of Estonian biogas in 2020 will be about 1500 GWh and increase up to 2600 GWh by 2030. Thereby the theoretical potential of Estonian biogas in 2013 will be 6400 GWh. This amount of biogas is considered from the land of semi-natural habitats with an area of 75,000 hectares, total unused agricultural land and about 5% of the biomass potential of agricultural land.

One of Estonian national treasures is its large peat resource, of which almost one million tons is extracted in a year. 22.3% of Estonian territory is covered by mires. The thickness of the peat layer in bigger peat bogs is 4–5 m on average, rarely 7–8 m. A positive factor from the point of view of peat usage is the fact that peat resources are in all counties, being the highest in Pärnu and Ida-Virumaa counties.

3. About the gasification of kukersite oil shale

Estonia has extensive know-how in oil shale gasification. Older people remember well the time when Estonia supplied high-quality household gas to both Leningrad and Tallinn. The peak in gas production was in 1976 when Kohtla-Järve supplied 597.4 million m³ of gas to the consumers. The local oil shale gas was mixed with the Russian natural gas and soon the cheap natural gas wiped the shale gas out of the market. However, this situation might not stay here forever, because the technologies have developed to new levels.

The yield and composition of the gas released during the thermal decomposition of oil shale fluctuates in a very large range, depending on the method used. The coke gas has the highest calorific value of about 50 MJ/m³

(Table 1) followed by the coke oven gas (16.7 MJ/m) [4]. At the same time, the coke oven gas has long been successfully implemented in industry. Continuous feed vertical shaft retort was patented by the engineers V. Zhunko and L. Zaglodin already in 1933, the patent was granted in 1935 [5].

Table 1. Composition (%) and calorific value of oil shale gas [4]

Component	Coke gas	Coke oven gas
CO ₂ + H ₂ S	5.3	17.0
Alkenes	11.6	6.3
O ₂	–	0.8
CO	5.0	10.6
H ₂	5.0	28.6
Alkanes	73.1	17.1
N ₂	–	19.6
Calorific value:		
MJ/m ³	50	16.7
kcal/m ³	12000	4000

In the former Soviet Union, testing of shale gas production started in 1938 and the experiments were successful, but stopped during World War II. Immediately after the war (1945–1946) the improvement of chamber furnace technologies continued in the then Oil Shale Research Institute [6]. In 1947, a 9-chamber test plant was launched at Kohtla-Järve Gas Factory and based on this an industrial 276-chamber gas plant a year later. The thermal treatment of oil shale in chamber furnaces yielded 290–310 m³ of coke oven gas, 50–60 kg of tar (Table 2), 27–29 kg of gasoline and up to 200 kg of pyrolysis water per 1 t of oil shale [6].

Table 2. Characteristic indicators of chamber furnace tar [7]

Indicator and unit	Content*
Density, g/cm ³	1.088
Viscosity, E	1.7
Elements of composition, atomic ratio	
C	86.2
H	7.2
O+N	5.4
S	1.2
C/H	12.0
Up to 200 °C boils over, vol.%	3.0
Up to 377 °C boils over, vol.%	70
Content of neutral O-compounds, vol.%	24.3
Unsaturated compounds, vol.%	13.2
Paraffinic and naphthenic compounds, vol.%	4.8
Naphthalene, vol.%	5.1

* Tar was extracted in an industrial operating mode of chamber furnaces in 1955.

The tar from chamber furnaces was used for the production of antiseptic wood impregnation oil [7]. The light oil vapors were extracted from chamber furnaces by absorption and sent forward to the rectification column for desorption. The product is known as gasoline (Table 3) which is used as a component of motor fuels [7].

Table 3. Most important physical and chemical characteristics of gasoline [7]

Indicator and unit	Content
Density, g/cm ³	0.750
Olefins, vol. %	56
Aromatic compounds, vol. %	10
Oxygen and sulphur compounds, vol. %	11
Initial boiling point, C	40
Boiling over 143 °C, %	95

The retort water from the high-temperature degradation of oil shale in a chamber furnace has a relatively high content of organic compounds, the majority of which are phenols (20–40 g/l). These were extracted with butyl acetate and then used for the production of synthetic tanning agents [7].

4. Chemism of oil shale gasification

Gasification in a broader sense means conversion of organic matter to gas during which a gaseous fuel containing carbon and hydrogen is formed when a solid or liquid fuel reacts with the air or oxygen or water vapor. The temperature range applied here is 650–1000 °C. The degradation of kukersite oil shale begins at 170–180 °C while water evaporates at temperatures over 100 °C. At 170–180 °C structurally related gaseous components are released, at 270–290 °C the formation of retort water from kerogen oxygen and hydrogen begins, part of CO₂ and H₂S is released, at 325–350 °C the generation of oil and hydrocarbon gases starts. At 450–500 °C a solid residue or semicoke is formed and at temperatures over 500 °C an intensive decomposition of primary oil begins.

The chemism of kerogen degradation is complicated. Already at 250 °C an intensive dissolution of kerogen in the forming oil begins. At a temperature of about 300 °C 70% of kerogen has already dissolved and the product formed is thermobitumen. Being liquid and viscous, thermobitumen may cause clogging of the retort equipment, which may result in serious breakdowns. At temperatures over 350 °C the decomposition of thermobitumen continues, giving oil, gas and semicoke.

Based on the work of his school, Prof. Agu Aarna presented the following flowchart of thermal decomposition of kukersite kerogen (Fig. 1) [4]:

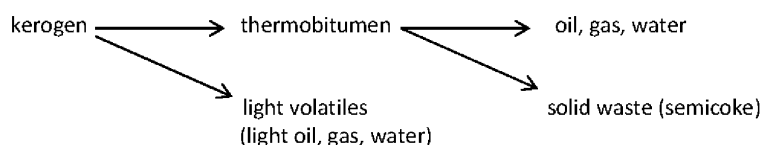


Fig. 1. Thermal decomposition of oil shale [4].

From the point of view of thermal decomposition of oil shale two technological processes for its treatment can be distinguished [4]:

- low-temperature processing, also retorting or semicoking in the temperature range of 500–550 °C;
- high-temperature treatment or coking at temperatures over 550 °C.

According to [8], A. Shamarin started with studies on the decomposition of kukersite oil shale in 1870. More extensive investigations of the issue began in the first quarter of the 20th century. In 1929, the results of A. Puskov's studies on heating kukersite in a quartz tube were presented in the album of the Estonian Society of Chemistry. The author did not indicate the gasification temperature, but assessment of the gas composition showed that this must have been well below 1000 °C.

J. Hisin investigated the composition of gas from coking the oil shale semicoke of Gdov deposit [8]. According to his data, at 1000 °C the gas comprises mainly CO (56.7%), H₂ (18.8%), CO₂ (16.5%) and saturated hydrocarbons (8.0%). The gas yield was 122 m³/t.

The research work by J. Hisin, M. Popov, V. Tshebassov and J. Nihhamov showed changes in the oil shale gas composition relative to depth or temperature of thermal treatment. As expected, with increasing temperature the gas yield increased, but that of oil decreased. In the gas composition the content of CO₂, H₂S, and unsaturated and saturated hydrocarbons decreased and simultaneously, the content of CO and H₂ increased. In the temperature range of 1000–1100 °C the gas was obtained which consisted mainly of CO and H₂ only. The investigation also demonstrated that by high-temperature decomposition temperature is a crucial component, but not the only factor, because the reaction time, semicoke activity and presence of water vapor also played a certain role [8].

Jialin Qian and Liang Yin (chief editors) [9] briefly dealt with the gasification of oil shale semicoke in their extensive monograph. As samples the semicoke formed as a product of pyrolysis of Chinese Fushun oil shale served. In the selected temperature range of 650–750 °C, wherein the semicoke was treated with the air/water vapor mixture, two different reaction types were considered.

- In the first stage, additional amounts of CO, CO₂ and H₂ were formed. In essence it was the water gas reaction.
- In the second stage, the produced CO reacted with water vapor forming CO₂ and H₂.

The authors concluded that the mineral matter in semicoke could act as a catalyst. They also found that the reacting surface played an important role in the process. The finer grained the sample of the treated semicoke was, the more intensive was the gasification process [9].

In the early 1980s some US scientists (Thomson, Nuttall et al.) studied the gasification of Colorado oil shale coke in the environment of oxygen, as well as CO₂ and water vapor. The reaction of CO₂ with coke is endothermic producing CO that reacts with O₂, thus giving additional heat. A similar research was carried out in the New Mexico University by Mallon and Brau already in 1976 [9].

The technical and economic considerations have been a guiding force in the research on gasification of solid fuels and liquid fuels. However, the situation has changed due to the wider use of energy from renewable sources and expansion of Estonian oil shale researchers' activities abroad, for example, to Jordan where the gasification of oil shale may prove to be economically viable [10]. Unfortunately up to now the efforts of Estonian researchers have not got attention wider abroad, first of all due to the language barrier. For example, the PhD theses by E. Rikk [6] and K. Help [7] have been written in Estonian and thus it is understandable that the new monograph published in China includes no references to their work [10]. This is a reason why we considered it necessary to publish this paper.

5. About the industrial production of oil shale gas

The first plant tests on oil shale were carried out in coal gasification retorts [7]. In those days there was no knowledge about the specific nature of oil shale decomposition and therefore only 38–40 % of kerogen could be gasified.

The chamber furnace for oil shale gasification designed by V. Zhunko and L. Zaglodin [8] opened a new way to designing and testing different chamber furnace types. The cross-sections of some chamber furnaces used in practice are given in Figures 2 and 3.

As can be seen in these figures, the design of a furnace chamber is quite complicated. In many cases it was developed in the course of practical use in industry. The chamber furnaces were constructed from both firebricks and regular bricks. A 9.3 m high chamber battery was divided into 23 chambers by vertical partitions. The smooth downward flow of oil shale was provided with the design of the chamber – a vertical downward widening flue-type structure.

In order to reduce the content of organic matter in the solid residue, air was injected into the bottom section of chambers (70–90 m³/t oil shale). Tar, gasoline and retort water were separated from the gas produced in the chamber furnaces. The gas was cleaned of sulphur compounds. The gas yielded additionally naphthalene, ammonia and other compounds. Accordingly, the calorific value of gas from industrial processing was 3752 kcal/m³ (Table 4).

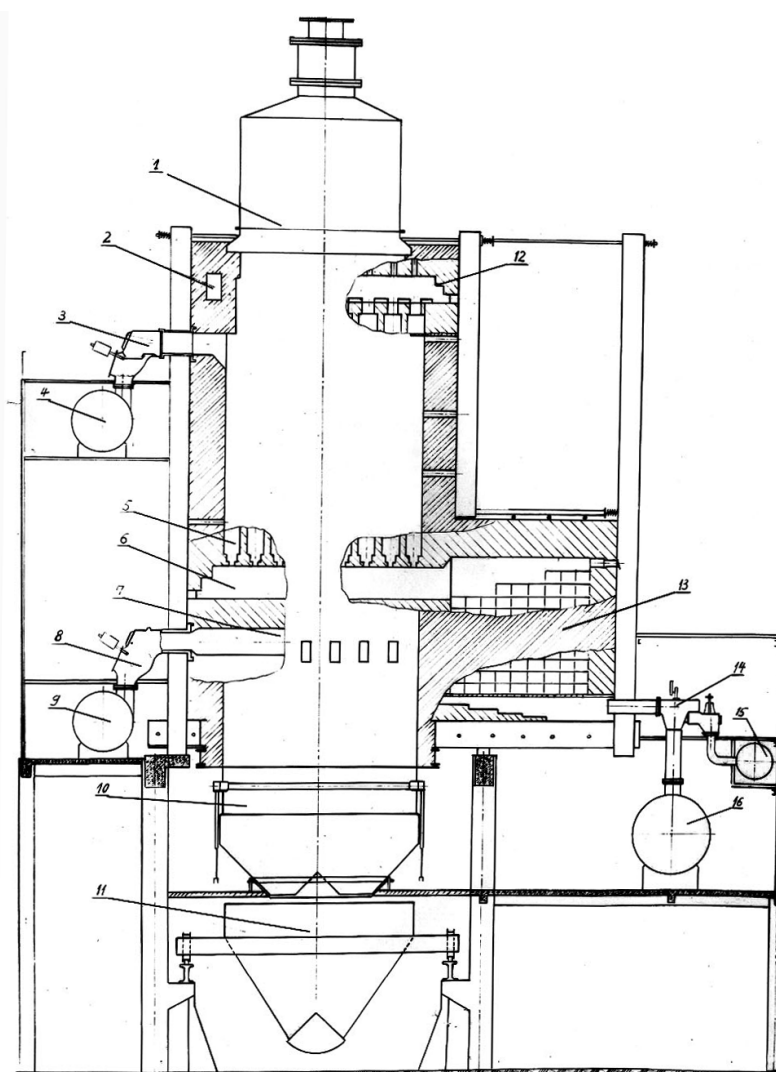


Fig. 2. Longitudinal cross-section of chamber furnace [7].

1 – fuel loader; 2 – air passage; 3 – middle gas knee bed; 4 – middle foul main; 5 – vertical chamber; 6 – bottom channel of vertical chambers; 7 – passage of the foul main; 8 – lower gas knee bed; 9 – lower foul main; 10 – extractor; 11 – bogie; 12 – upper main; 13 – regenerator; 14 – air and gas valve; 15 – flue gas collector; 16 – coke oven gas collector.

The coke oven gas contains much hydrogen (27.4%) and carbon monoxide (12.3%), but also the content of N_2 (21.6%) and H_2S (14.9 g/m) is relatively high. The content of N_2 in industrially processed raw gas depended on the amount of air injected by post-treatment of the solid residue. Ethylene (C_2H_2) made up to 75.0% in the fraction of unsaturated hydrocarbons, and

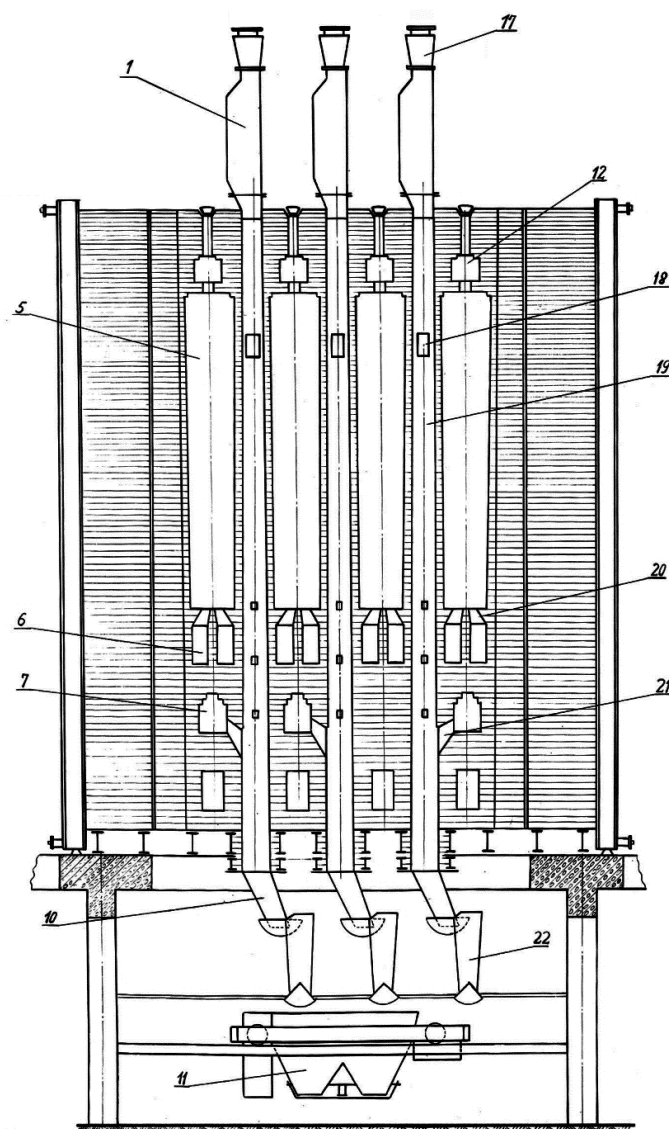


Fig. 3. Cross-section of chamber furnace [7].

1 – fuel loader; 5 – heating wall; 6 – bottom channel of vertical chambers; 7 – passage of the foul main; 10 – extractor; 11 – bogie; 12 – upper main; 17 – loading hopper; 18 – peephole in the gas pipe; 19 – combustion chamber; 20 and 21 – sloping offtake; 22 – extractor.

methane (CH_4) up to 83% in the saturated hydrocarbons. The tar of the chamber furnace is characterised by a high content of crystallized organic compounds. It should be noted that in 1962 K. Help [7] gained a 30% increase of coke oven gas yield when co-gasifying oil shale and milled peat (10%), while the amount of liquid fuels did not decrease.

Table 4. Characteristics of the coke oven gas from Kohtla-Järve Gas Factory [7]

Component	Project based	Industrial
CO ₂ + H ₂ S, vol. %	15.2	15.6
Alkenes, vol. %	5.5	6.0
O ₂ , vol. %	0.7	0.7
CO, vol. %	18.4	12.3
H ₂ , vol. %	30.4	27.4
Alkanes, vol. %	19.5	16.4
N ₂ , vol. %	10.3	21.6
H ₂ S, g/m ³	8.0	14.9
Values calculated by composition of gas, kcal/m ³	4330	3752

6. Conclusions

Now in Estonia, a new State Development Plan of Oil Shale Utilization for 2016–2030 is in preparation, foreseeing a wider use of oil shale and its processing at the highest technological level. All this calls for cardinal rearrangements of mining technology and environmentally safe treatment of the obtained raw material. Up to now oil shale as a cheap raw material was primarily used in power engineering. To date, the production of oil shale oil can successfully compete with oil products, to our mind the gasification of oil shale is also a promising branch.

Based on the researches carried out already half a century ago [6, 7], we can state [10] the following:

- Production of oil shale gas has proved to be an industrially successful process while the production capacity of chamber furnaces (the actual oil shale throughput) was 16–17 t/d. The calorific value of coke gas was 4700–4800 kcal/m³.
- Depending on the parameters of a technological process, the yield of products may vary significantly:
 - coke oven gas 257–361 m³/t,
 - tar 2.8–7.0%,
 - gasoline 1.57–2.1%.
- Introduction of 80 nm³/t of air and 90 kg/t of water vapor into the central section of the chamber increased the productivity of chamber furnaces essentially [7]. The gas yield increased 27% and that of liquid products 2.2%.
- Industrial processing of the heavier fractions of generator oil in the chamber furnace into high-calorific gas enabled the production of gasoline in greater volumes, containing 90% aromatic compounds.
- The need for gasifying kukersite oil shale is determined by the cost, but nevertheless, the respective research work and technological testing should be continued, because the Estonian experience can be applied in other countries.

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