

## Thermodynamic Analysis of the Gasification of Oil Shale from the Kenderlyk Deposit

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**Abstract**—The temperature dependence of the products of the gasification of oil shale from the Kenderlyk deposit was studied by the methods of chemical thermodynamics. A comparative analysis of gasification products with air and air–steam blasts was carried out. It was found that, in the case of the air–steam blast at temperatures higher than 850°C, carbon entirely reacted and CO and H<sub>2</sub> were the products of gasification.

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In recent years, the application of coal and oil shale to the production of motor fuels and also as raw materials for chemical industry became really promising because of an increasing deficiency in petroleum fuel-energy resources and a constant increase in oil prices.

The development of oil shale has been repeatedly undertaken. However, after a fall in oil prices in the 1980s, interest in oil shale was lost. Today, it grows again. In Russia, OAO Leningradslanets renewed research works on the wide use of oil shale in nonferrous metallurgical processes. The prospects of the use of oil shale in metallurgy are related to its reducing properties and fluxing components in pelletization, agglomeration, and blast smelting processes.

Krichko [1] and Maloletnev et al. [2] substantiated the possibilities of increasing the effectiveness of the use of oil shale by the use of hydrogenation for their processing. Upon the hydrogenation of enriched Baltic shale at 10 MPa, a 96–98% conversion of the organic matter of shale (OMS) into liquid products (76–78%) and gas (18–20%) was reached. Basic diagrams for the production of gasoline, diesel fuel, and jet engine fuel (a total yield of ~ 62% on an OMS basis; a fuel version) were developed, and the yield of motor fuels was 53.8% on the separation of chemical products by liquid solvent extraction methods (a chemical version).

Maloletnev et al. [3] reported the results of studies on the development of a new process for the thermal cracking of tar as a suspension with ground Baltic

shale in order to obtain motor fuel components. The experimental results were indicative of the advantages of this process over industrial thermocontact cracking because the deep destruction of tar (the yield of a gasoline fraction with a boiling point to 180°C was ~12%; the yield of middle distillates with boiling points of 180–360°C was 43–44%; and the yield of raw materials for catalytic cracking with boiling points of 360–520°C was 15–16% on an initial tar basis) was achieved upon the single-stage processing of raw materials under relatively mild conditions (nitrogen, 5 MPa; 425°C; and feed space velocity, 1.0 h<sup>-1</sup>). The resulting coking products and V and Ni, which were present in the raw material, were deposited on the mineral matter of shale and removed from the reaction zone with the liquid products of the process.

In Kazakhstan, research and development works oriented to the production of motor fuels from oil shale from the Kenderlyk deposit have been performed. The total shale reserves of this deposit were estimated at 4075 million tons, including balance reserves of 708 million tons. The analysis of the pyrolysis gas obtained from powdered Kenderlyk shale showed that it differed little from the pyrolysis gases of petroleum products. Polyethylene hydrocarbons, raw materials for the production of high-molecular-weight polymers, can be obtained from it.

It was also found that various tars, a nitrogen–hydrogen mixture, carbon dioxide, and other products necessary for the synthesis of synthetic ammonia,

urea, etc., can be prepared upon the gasification of Kenderlyk shale.

The oil shale of the Kenderlyk deposit belongs to the following three suites: Kenderlyk (medium-late Carboniferous), Karaungur, and Saikan (Taranchin) series of early Permian age. In the upper part of the Kenderlyk series (coal-bearing subseries), two beds (Kalynkara and Luchshii) of industrial importance were recognized. The Luchshii bed with a thickness of 0.9–1.2 m has a relatively simple structure. The interlayers of oil shale with a thickness of 0.1–0.4 m and a shale tar yield of 4.6–6.5% were observed 80 m higher than the Luchshii bed. The yield of tar upon the pyrolysis of shale from the Luchshii bed was higher than 10%, and it reached 27% in some samples. The yields of distillate fractions on a tar basis were the following (wt %): gasoline, 20.7; ligroin, 0.5; and diesel, 28.4.

The studies performed showed that it is most profitable to use shale from the Kenderlyk deposit for the manufacture of pyrolysis gas, which is completely suitable in its characteristics for the production of polymer compounds. The heats of combustion of gas obtained at temperatures of 900, 1000, and 1100°C are 6415, 4500, and 6045 kcal/m<sup>3</sup>, respectively.

Note that the yield of tar on the low-temperature coking of shale was 16–18% on a dry shale basis with an increased hydrocarbon content.

The oil shale from the Kalynkara deposit contained 7.09–7.85% hydrogen; the yields of volatile substances on a dry shale basis at an ash content of 68–73% was 20%, and the yield of shale tar was 5–9%.

Blokhin et al. [4] proposed a promising method for the processing of high-sulfur shale with the production of clean gaseous fuel by gasifying them using steam–air or steam–oxygen blowing under pressure.

Chemical thermodynamics methods are an effective tool for the theoretical analysis of the gasification and pyrolysis process of oil shale. In this article, we report the results of the thermodynamic analysis of the gasification of oil shale from the Kenderlyk deposit in Kazakhstan with the use of chemical thermodynamics methods.

Table 1 summarizes the characteristics of the oil shale, and Table 2 gives the elemental composition accepted for the calculations.

The equilibrium composition of gasification products was calculated by chemical thermodynamics methods. At the specified values of process temperature  $T$  (K) and pressure  $P$  (MPa) and the amounts of introduced oxidizing agent (atmospheric oxygen) and water vapor (mol per 100 g of the initial mass), the program [5] determined the thermodynamically equilib-

**Table 1.** Characteristics of Kenderlyk oil shale

Characteristic	Value
1. Proximate analysis, wt %:	
Total moisture $W^t$	1–6
Ash content $A^d$	68–73
Yield of volatile substances $V^{daf}$	20
2. Ultimate analysis, wt %:	
$C^{daf}$	74–77
$H^{daf}$	7.3–9.9
$S_i^d$	Traces
$N^{daf}$	0.6–1.3
$O^{daf}$	14.95
Low heat value $Q_i^d$ , MJ/kg	6.0
High heat value $Q_s^{daf}$ , MJ/kg	13.0
3. Chemical composition of the mineral matter, wt %:	
SiO <sub>2</sub>	58.2
Al <sub>2</sub> O <sub>3</sub>	17.2
Fe <sub>2</sub> O <sub>3</sub>	7.3
CaO	2.3
MgO	1.0
K <sub>2</sub> O + Na <sub>2</sub> O	10.5
SO <sub>3</sub>	3.4

**Table 2.** Elemental composition of Kenderlyk oil shale taken for the calculations

Element on a $daf^*$	Atomic weight, g/mol	Concentration, wt %	mol/100 g
C	12	77.1	6.42
H	1	7.3	7.30
N	14	0.6	18.19
O	16	15.0	4.66

\* The concentrations of elements were recalculated on an as-received basis at  $W^r = 3.5\%$  and  $A^r = 70.5\%$  using the formula  $E^r = E^{daf} [100 - (A^r + W^r)] / 100 = 0.26 E^{daf}$ .

rium component composition at which the free Gibbs energy of the test system was minimized [6, 7]:

$$G_{T,\Sigma}^0 = \sum_{i=1}^M m_i G_{T,i}^0 \Rightarrow \min, \quad (1)$$

where  $G_{T,i}^0$  is the free energy of the  $i$ th mixture component, and  $m_i$  is the number of moles of this component in 100 g of the initial organic mass of shale.

**Table 3.** Equilibrium concentrations of the gasification products of Kenderlyk oil shale at  $T = 850^\circ\text{C}$  and  $P = 0.1\text{ MPa}$ 

Compound	Air blast		Steam–air blast	
	$n_o$	$n_r$	$n_o$	$n_r$
Gas phase				
@C( $\Gamma$ ) @	6.42	0	6.42	0
CH <sub>4</sub>	0	0.0227	0	0.0361
C <sub>2</sub> H <sub>2</sub>	0	0	0	0
C <sub>2</sub> H <sub>4</sub>	0	0	0	0
C <sub>2</sub> H <sub>6</sub>	0	0	0	0
CO	0	4.4525	0	6.2435
CO <sub>2</sub>	0	0.0720	0	0.1404
H	7.30	0	7.30	0
H <sub>2</sub>	0	3.5406	0	5.4413
HCOOH	0	0	0	0
HCOOH	0	0	0	0
HCOOH	0	0	0	0
HNCO	0	0	0	0
HNO	0	0	0	0
HNO <sub>2</sub>	0	0	0	0
HNO <sub>2</sub>	0	0	0	0
HNO <sub>2</sub>	0	0	0	0
HNO <sub>3</sub>	0	0	0	0
H <sub>2</sub> O	0	0.0635	2.00	0.1357
H <sub>2</sub> O <sub>2</sub>	0	0	0	0
N	18.19	0	18.19	0
N <sub>2</sub>	0	9.0948	0	9.0947
NH <sub>3</sub>	0	0.0003	0	0.0005
NO	0	0	0	0
NO <sub>2</sub>	0	0	0	0
NO <sub>3</sub>	0	0	0	0
N <sub>2</sub> O	0	0	0	0
N <sub>2</sub> O <sub>2</sub>	0	0	0	0
N <sub>2</sub> O <sub>3</sub>	0	0	0	0
N <sub>2</sub> O <sub>4</sub>	0	0	0	0
N <sub>2</sub> O <sub>5</sub>	0	0	0	0
O	4.66	0	4.66	0
O <sub>2</sub>	0	0	0	0
Condensed phase				
HNO <sub>3</sub>	0	0	0	0
H <sub>2</sub> O	0	0	0	0
NH <sub>4</sub> HCO <sub>3</sub>	0	0	0	0
NH <sub>4</sub> NO <sub>3</sub>	0	0	0	0
NH <sub>4</sub> OH	0	0	0	0
N <sub>2</sub> O <sub>4</sub>	0	0	0	0
N <sub>2</sub> O <sub>5</sub>	0	0	0	0
@C(T)@	0	1.8728	0	0

Table 3 summarizes the compounds considered in the thermodynamic calculations.

The air blast coefficient was  $\alpha = 0.3$ . Consequently,

$$O_{\text{blast}} = 4.66 \text{ mol};$$

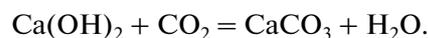
$$N_{\text{blast}} = 0.3 \cdot 3.9 \text{ O} + \text{N} = 18.19 \text{ mol}.$$

Figure 1 shows the equilibrium composition of the products of shale gasification at the air blast coefficient  $\alpha = 0.3$ . Hence, it follows that methane is formed at low temperatures; the maximum yield corresponds to a temperature of  $300^\circ\text{C}$ , and it approaches zero at  $850^\circ\text{C}$ . At temperatures higher than  $850^\circ\text{C}$ , the gasification products contained the following components: CO, H<sub>2</sub>, and solid carbon. In order to decrease the yield of solid carbon, we changed the composition of an oxidizing agent; namely, we used a steam–air blast instead of an air blast. Figure 2 shows the temperature dependence of the equilibrium composition of shale gasification products with a steam–air blast:  $\alpha = 0.3$ ;  $n(\text{H}_2\text{O}) = 2 \text{ mol}$ . Hence, it follows that, in this case, the gasification products consist of the two components CO and H<sub>2</sub> at temperatures higher than  $850^\circ\text{C}$ . For evaluating the calorific value of gasification products at a temperature of  $850^\circ\text{C}$ , Table 1 summarizes the numbers of moles of the initial components and equilibrium components for the cases of air and steam–air blasts.

The total numbers of moles in a gas phase on air and steam–air blasts are  $\Sigma n_i = 17.2564 \text{ mol}/100 \text{ g}$  and  $\Sigma n_i = 21.0922 \text{ mol}/100 \text{ g}$ , respectively.

Taking into account that the gas volume at  $T = 273.16 \text{ K}$  and  $P = 0.1 \text{ MPa}$  is  $V = 0.02241 \text{ m}^3/\text{mol}$ , we found that the gas phase volumes  $V_\Sigma$  are  $0.39$  and  $0.47 \text{ m}^3/100 \text{ g}$ , respectively.

In the case that oxygen is an oxidizing agent for preparing synthesis gas (CO + H<sub>2</sub>), water is condensed by cooling and CO<sub>2</sub> is trapped by passing the process gas through lime:



The number of moles  $n_j$  of combustible gases at equilibrium is

$$\begin{aligned} \Sigma n(j) &= n(\text{CH}_4) + n(\text{CO}) + n(\text{H}_2) \\ &= 11.7214 \text{ mol}/100 \text{ g}. \end{aligned}$$

The gas volume is

$$\begin{aligned} V &= 0.263 \text{ m}^3/100 \text{ g} \text{ (on an organic matter basis)} \\ &= 0.068 \text{ m}^3/100 \text{ g} \text{ (on an as-received basis)}. \end{aligned}$$

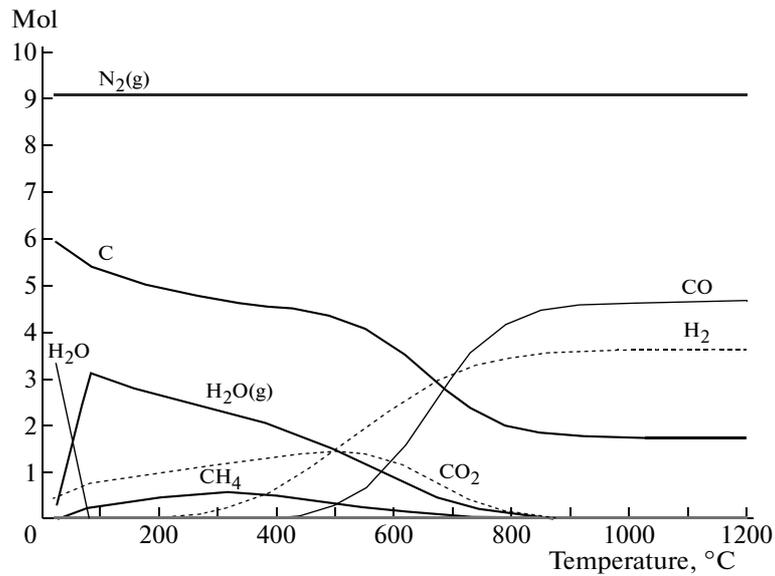


Fig. 1. Equilibrium composition of shale gasification products at the air blast coefficient  $\alpha = 0.3$ .

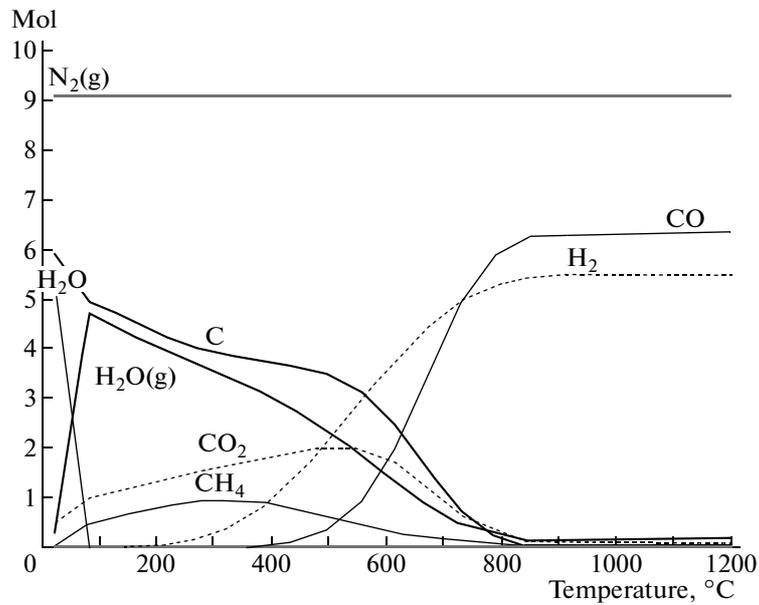
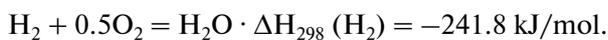
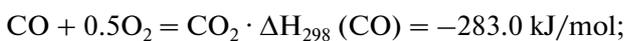
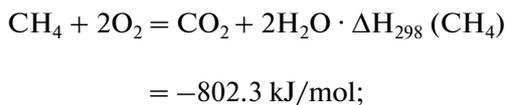


Fig. 2. Equilibrium composition of shale gasification products with a steam–air blast:  $\alpha = 0.3$ ;  $n(\text{H}_2\text{O}) = 2$  mol.

The heat effects of their combustion reactions are as follows [8]:



Hence, for the heat of combustion of gasification products, we obtain

$$\begin{aligned} Q &= - [0.0361 \cdot \Delta H_{298}(\text{CH}_4) + 6.2435 \cdot \Delta H_{298}(\text{CO}) \\ &\quad + 5.4413 \cdot \Delta H_{298}(\text{H}_2)] = 2812 \text{ kJ/100 g} \\ &= 28120 \text{ kJ/kg (on an organic matter basis)} \end{aligned}$$

or

$$Q = 28.12 \text{ MJ/kg (on an organic matter basis)}$$

= 7.31 MJ/kg (on an as-received basis).

The analysis performed showed that, on the gasification of shale with a steam–air blast, the equilibrium composition of the products above 850°C consists of high-calorific CO and H<sub>2</sub> gases, which can be used as fuel or a source material (synthesis gas) for organic syntheses.

#### REFERENCES

1. Krichko, A.A., *Oil Shale*, 2000, vol. 17, no. 3, p. 278.
2. Maloletnev, A.S., Naumov, K.I., Shvedov, I.M., et al., *Khim. Tverd. Topl.* (Moscow), 2011, no. 5, p. 29.
3. Maloletnev, A.S. Yulin, M.K., et al., *Khim. Tverd. Topl.* (Moscow), 2011, no. 4, p. 20.
4. Blokhin, A.I., Zaretskii, M.I., Stel'makh, G.P., and Eivazov, T.S., *Novye tekhnologii pererabotki vysokosernistykh slantsev* (New Technologies for the Processing of High-Sulfur Shale), Moscow: Svetlyi STAN, 2001.
5. HSC Chemistry 6. [http://www.hsc\\_chemistry.net/](http://www.hsc_chemistry.net/).
6. Gyul'maliev, A.M., Krylova, A.Yu., and Lyadov, A.S., *Khim. Tverd. Topl.* (Moscow), 2012, no. 1, p. 37.
7. Stull, D., Westrum, E., and Sinke, G., *The Chemical Thermodynamics of Organic Compounds*, New York: Wiley, 1969.
8. Gyul'maliev, A.M., Golovin, G.S., and Gladun, T.G., *Teoreticheskie osnovy khimii uglia* (Theoretical Fundamentals of Coal Chemistry), Moscow: Izd. MGGU, 2003.

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