

THE THERMO-OXIDIZING PYROLYSIS OF OIL SHALES

Vladimir Kashirsky and Aleksandr Koval

When using high-ash and high-sulfur fuels in thermal electric power plants, we have a lot of problems with steam boilers. These problems are: great deposits on the heating surfaces, corrosion and abrasion of these surfaces, some difficulties in providing the nominal parameters of steam, and production of large quantities of air pollutants, such as sulfur oxides and particulate matter (Epik 1961).

In the future we will have some serious technical problems with burning solid fuels in modern power plants with gas turbines, with combined gas-steam units and magnetohydrodynamic generators. We will not be able to use original high-ash and high-sulfur solid fuels in these units, because all of these plants must be based only on clean fuels.

We will be able to get over these difficulties by using preliminary thermal preparation of solid fuels, and by burning clean fuels, like gas or oil.

For design and construction of large capacity units for thermal decomposition of fuels, a rapid heating rate of pulverized fuel with solid or gaseous or combined heat carrier is suggested (Chukanov 1961). Under these conditions, the process of thermal decomposition may be regulated.

It is known that raising of pyrolysis temperature increases gas yield. As a result, the yield of decomposition liquid products goes down, but concentration of aromatic hydrocarbons in liquid and gaseous products goes up (Chukanov 1961). However, the rise in temperature demands a big increase of solid heat-carrier consumption for processes of thermal decomposition of fuels.

Thermo-oxidizing pyrolysis of solid fuels has been suggested (Kashirsky 1966; Kashirsky, Koval and Sokolova 1969). In one stage the process provides deeper destruction of organic matter and produces large amounts of high heating value gas, olefins and aromatic hydrocarbons.

Vladimir Kashirsky, Professor of Technical Sciences; Aleksandr Koval, Associate Professor of Technical Sciences, Saratov Polytechnical Institute, Saratov, USSR.

It was determined (Kashirsky 1966) that the supply of a small quantity of oxidizer in the pyrolysis zone intensifies the process of organic matter destruction and reduces heat-carrier consumption.

We studied the thermo-oxidizing pyrolysis of the Ukrainian Boltyschiski oil shales (Kashirsky, Koval and Sokolova 1969; Kashirsky, Koval and Igonkina 1969; Kashirsky and Koval 1969; Koval 1969; Koval 1971; Kashirsky and Koval 1972). The focus of our investigation was as follows: to get from oil shale fine fuel for thermal-electric power plants and the most interesting products for the chemical industry; to define influence of temperature, consumption of oxidizer by the gas evolution process, and quality and yields of obtained products.

The Boltyschiski oil shale is representative of high-ash, high-sulfur fuels and has typical characteristics for shales (fig. 1). In laboratory tests we used pulverized oil shale with size particles less than 0.25 mm. The heating rate of particles was 1,000 to 1,500°C/sec.

The principle of the experimental unit is shown on figure 2. The tube-reactor is the main element of this unit. Fine-ground oil shale was carried through a tube-reactor in a stream of air. The tube-reactor was heated in five tube-electro furnaces. Gas samples were removed for analysis at the

(Percentage of Dry Shale, Unless Otherwise Indicated)	
ASH -----	63.7
KEROGEN CONTENT -----	36.3
CARBON -----	68.4
HYDROGEN -----	9.1
NITROGEN -----	1.3
SULFUR -----	1.0
OXYGEN -----	21.2
HEATING VALUE, Kcal/kg -----	2500
<hr/>	
Size of Particles, MM -----	<0.25
Heating Rate of Particles, °C/sec -----	(1000-1500)

FIGURE 1.—Ukrainian oil shale characteristics.

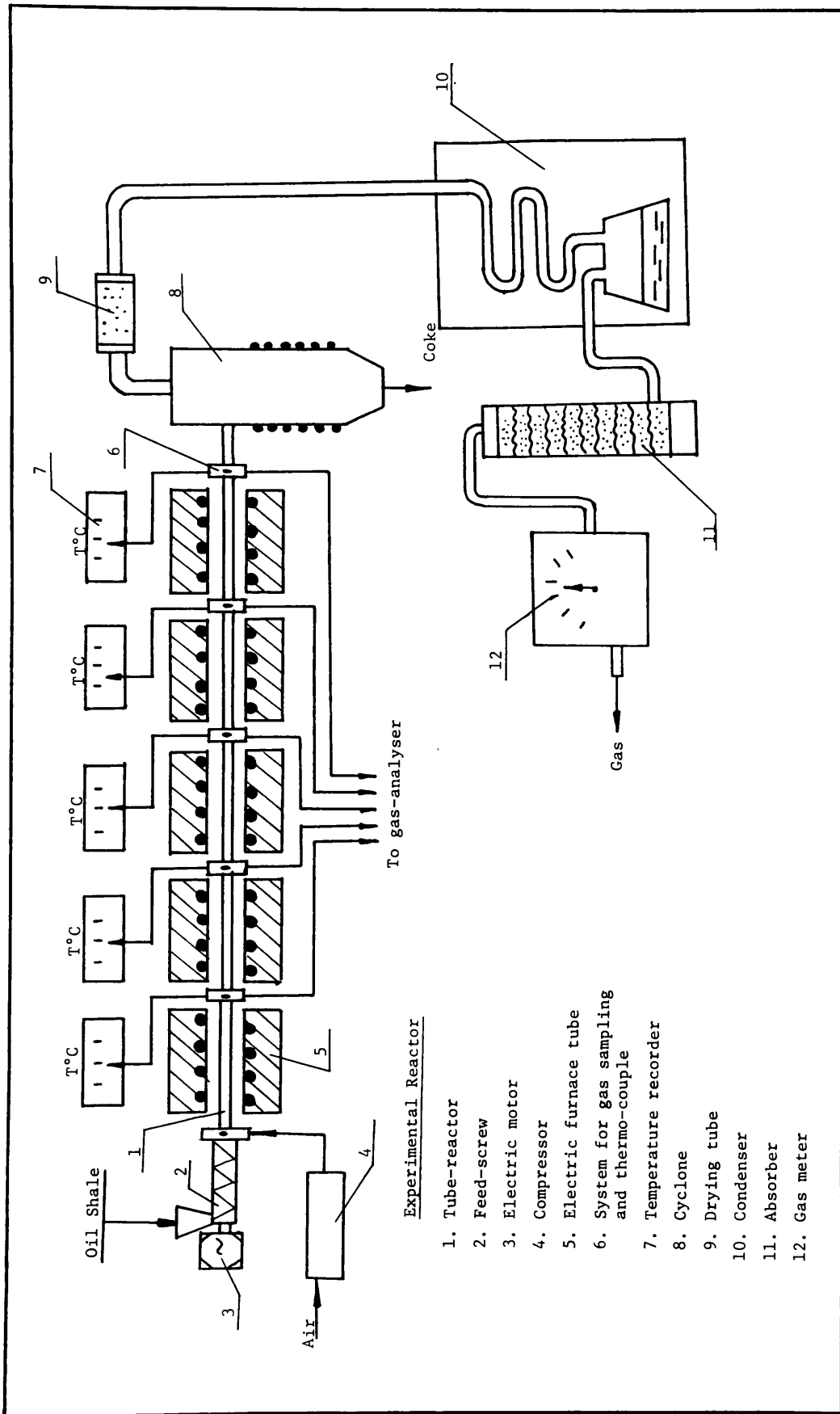


FIGURE 2.—Experimental reactor.

end of each section. The product gas was separated from all solids by a cyclone at the end of the reactor and metered after removal of condensables. Aromatic hydrocarbons were absorbed by special coal char. Since we had precise separation of pyrolysis products, we had an opportunity to investigate all products and to make exact material balances for each test.

Variation of yields of the decomposition products with temperature is shown in figure 3. In these tests the consumption of carrier air was 150 liters/kg of oil shale. Eight to ten percent of theoretical air is required for the combustion of shale. The temperature varied in the range of 700 to 850°C. We can see with raising of the temperature that the rate of the decomposition of the oil (tar) products increases. In fact, at a temperature of 800°C we don't have oil (tar). The high temperature and the feeding in the pyrolysis zone of oxygen result in a deeper decomposition degree of organic matter macromolecules. This process, in combination with catalytic influence of mineral matter, produces conditions for synthesis of aromatic hydrocarbons. Maximum yield of pyrobenzene is at 800°C. Yield of pyro-gas increases with raising of temperature.

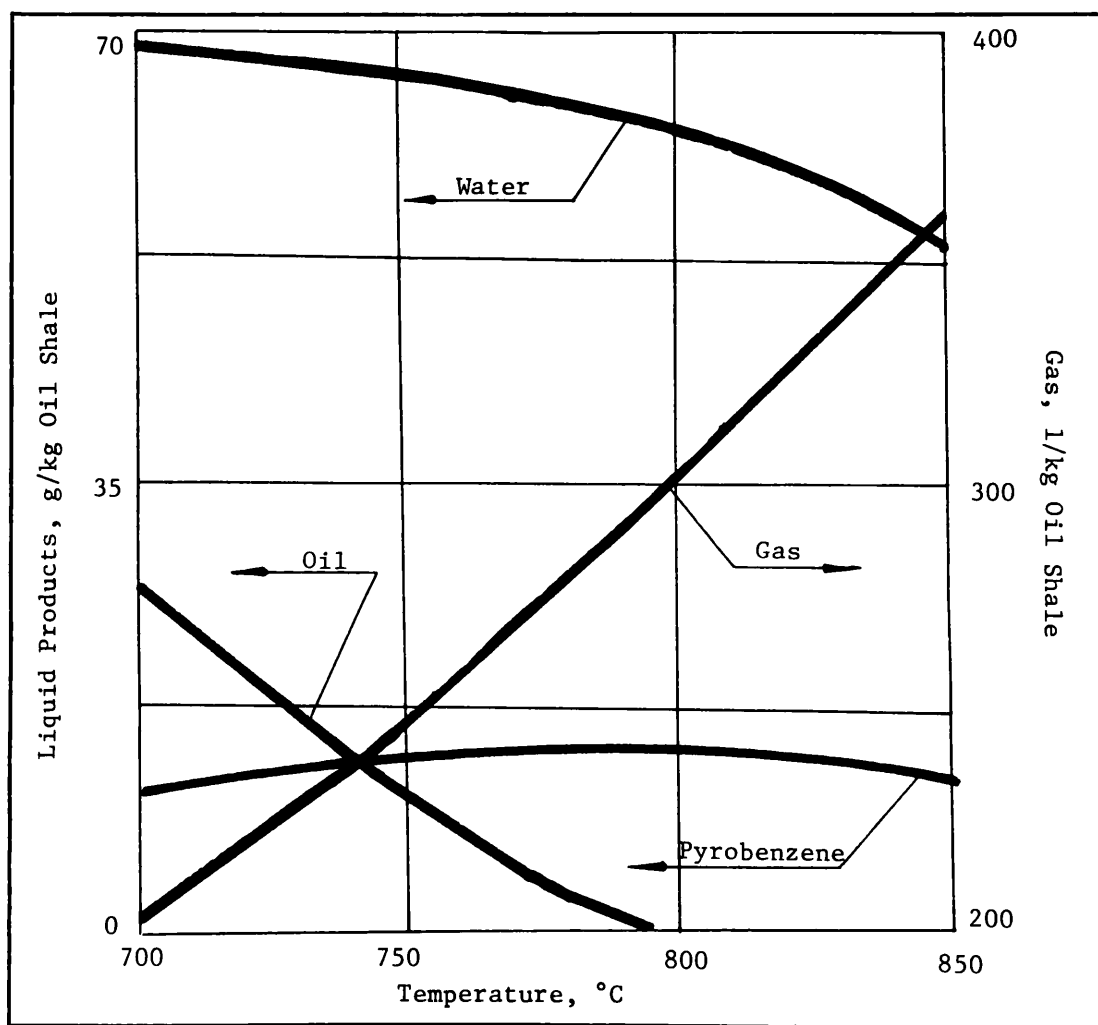


FIGURE 3.—Variation of yields of the decomposition products with temperature.

The influence of pyrolysis temperature on yields and composition of pyrogas is shown in figure 4. Pyrogas is characterized by the large content of ballast component such as CO_2 and N_2 . But the heating value of pyrogas is high, since pyrogas has a large percentage of olefins and methane.

An elementary mass balance of our test permitted us to study a distribution of elements of original oil shale between pyrolysis products. We determined that 55 to 60 percent of the organic carbon and 80 percent of the hydrogen in the original oil shale are contained in the pyrogas. In figure 5, we demonstrate that olefin hydrocarbons contain 50 percent of the total carbon and hydrogen of pyrogas. The maximum of carbon and hydrogen in the olefins is at 800°C and then the content of carbon and hydrogen in olefins is reduced. This means the carbon in olefins takes part in synthesis of high-molecular compounds, which form coke. The hydrogen in the olefins is used in the formation of aromatic hydrocarbons.

In fact, a minimum of carbon in the coke (fig. 6) has been at 800°C and then the percent of carbon, present as coke, increases. With an increase in the temperature we have secondary conversion reactions of volatile products, and high-molecular weight compounds are deposited on the pulverized particles of coke. The temperature of 800°C corresponds to the most complete conversion of oil shale organic matter to volatile products.

Consumption of oxygen, which has been fed to the pyrolysis zone, is a significant parameter for thermo-oxidizing pyrolysis. To determine the influence of oxygen consumption, we investigated the pyrolysis of oil shale in a stream of inert nitrogen and in an air stream. The consumption of oxygen has been changed from 16 to 138 gram/kg of oil shale.

We can see (fig. 7) that the process of gas evolution for pyrolysis in the nitrogen stream goes with less intensity than in the case of thermo-oxidizing pyrolysis. The supply, in the decomposition zone, of a small quantity of oxygen assists in the destruction and weakening of the most stable chemical structure in the organic molecules and increases the rate of decomposition.

The influence of oxygen consumption on the yields and composition of pyrogas is shown in figure 8. Upon raising oxygen consumption, the yield of pyrogas increases, but the heating value goes down as the content of inert components, such as N_2 and CO_2 , goes up.

As is well known, the quality of gas as a raw material for the organic synthesis industry is dependent on the contents of olefins in gas. In choosing optimal pyrolysis conditions it is necessary to know the total weight yield of olefins and hydrocarbons in relation to oxygen consumption. The data of figure 9 shows that the maximum yield of olefins is at a consumption of 80 g oxygen/kg of oil shale. The total olefins yield is equal to 82 kg/ton of oil shale.

The fairly high yield of pyrobenzene is a great advantage for the in-

Temperature °C	Yield of Pyrogas M ³ /kg Oil Shale	Gas Constituents (% by Vol)								Heating Value Kcal/M ³	Heating Value Btu/cu ft	
		H ₂ S	CO ₂	C ₄ H ₈	C ₃ H ₆	C ₂ H ₄	CO	H ₂	CH ₄			N ₂
700	0.203	0.7	11.6	0.8	7.4	6.4	7.8	4.1	9.1	52.1	3,708	416
750	0.288	0.7	11.1	0.6	6.7	10.9	8.1	9.6	13.5	38.8	4,665	524
800	0.300	0.6	10.4	0.3	5.1	12.1	9.9	11.9	13.8	35.9	4,600	510
850	0.373	0.6	9.7	0.4	2.9	11.4	9.1	13.4	12.8	39.7	4,019	451

FIGURE 4.—Influence of temperature on yield and composition of pyrogas.

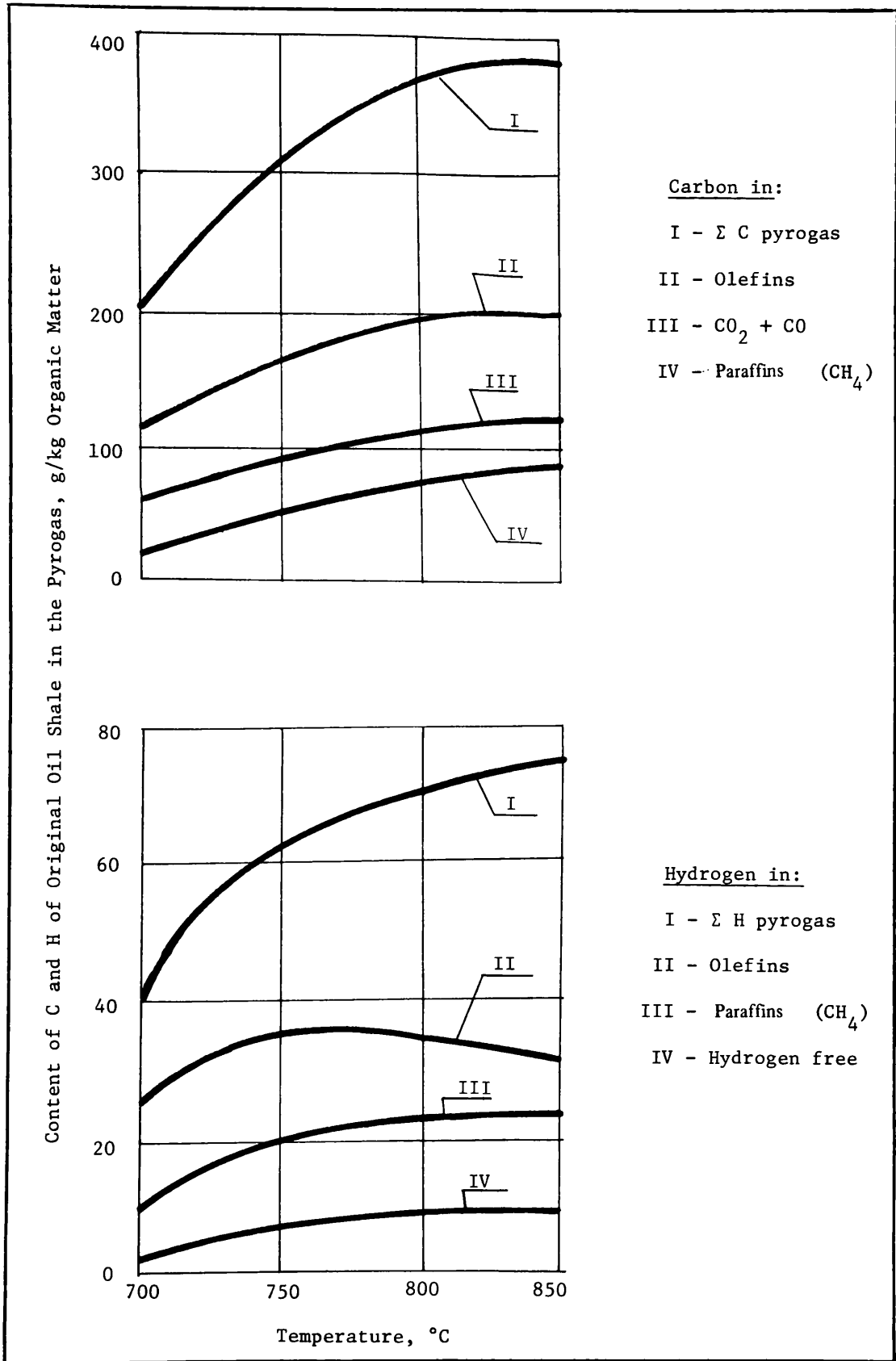


FIGURE 5.—Content of C and H of original oil shale in the components of pyrogas with temperature.

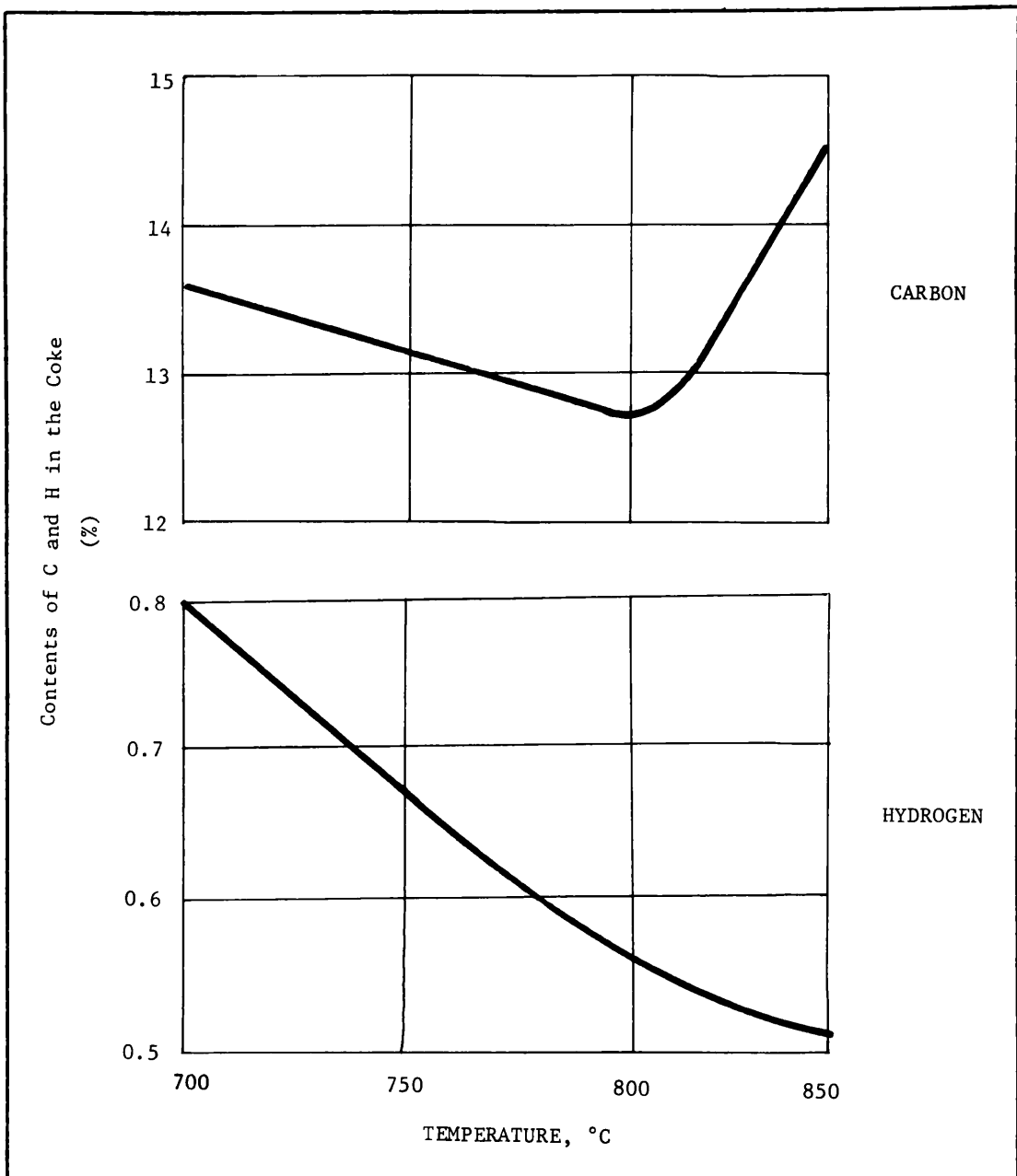


FIGURE 6.—Variation of C and H contents in coke with temperature.

vestigated conditions of pyrolysis (fig. 10). Obtained pyrobenzene is a mixture of benzene hydrocarbons with a mixture of sulfur compounds. With an increase in temperature, percentage of benzene in the pyrobenzene goes up also. At 800 to 850°C we have in pyrobenzene 95 percent aromatic hydrocarbons. The use of pyrobenzene for extraction of individual chemical compounds such as benzene, thiophen, and toluene will improve the economical efficiency of combined power-chemical plants.

We propose that combined power-chemical plants with preliminary thermal treatment of high-ash and high-sulfur fuels, such as oil shale, will extend fuel resources for industry and power technology, and provide the chemical industry with fine raw materials.

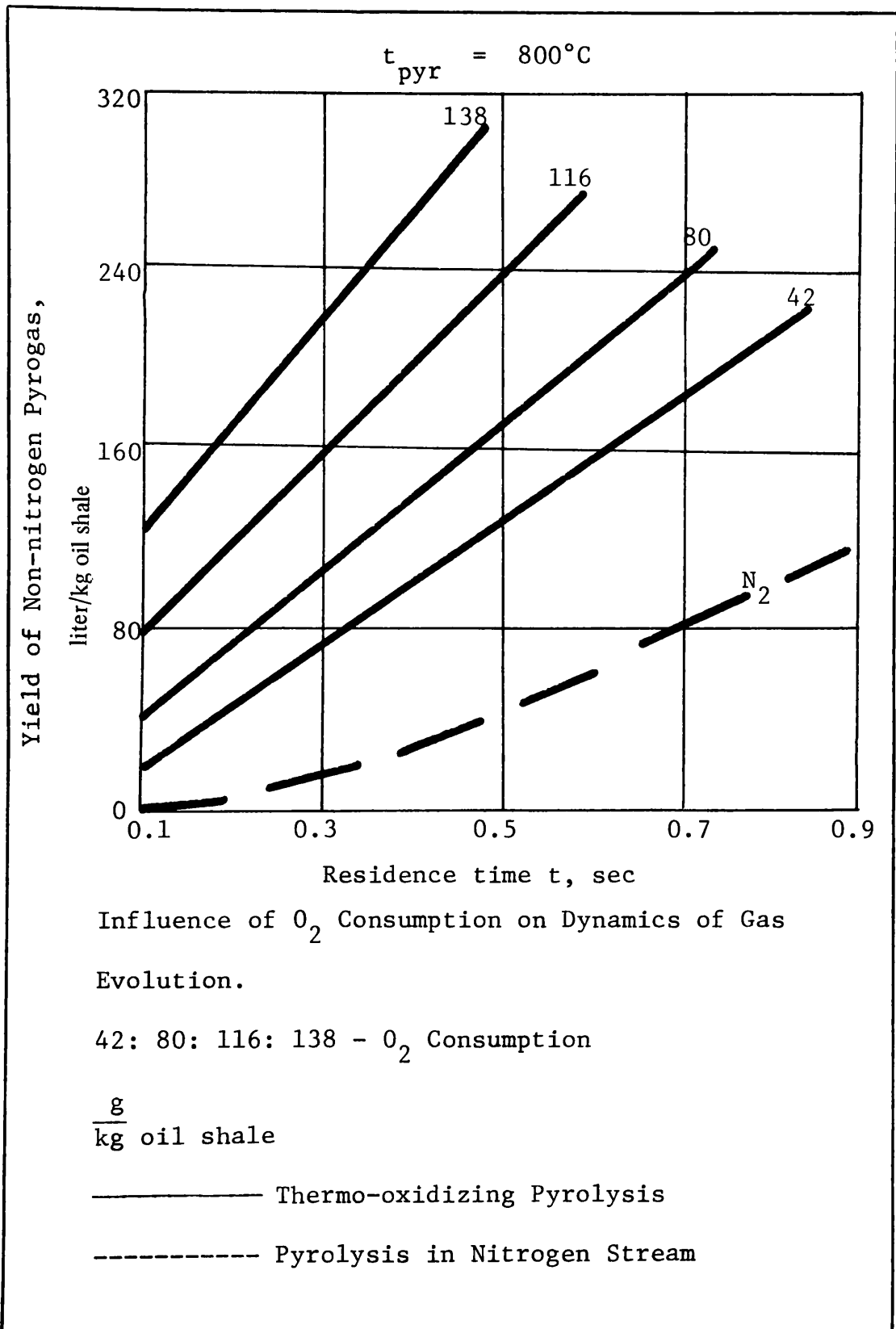
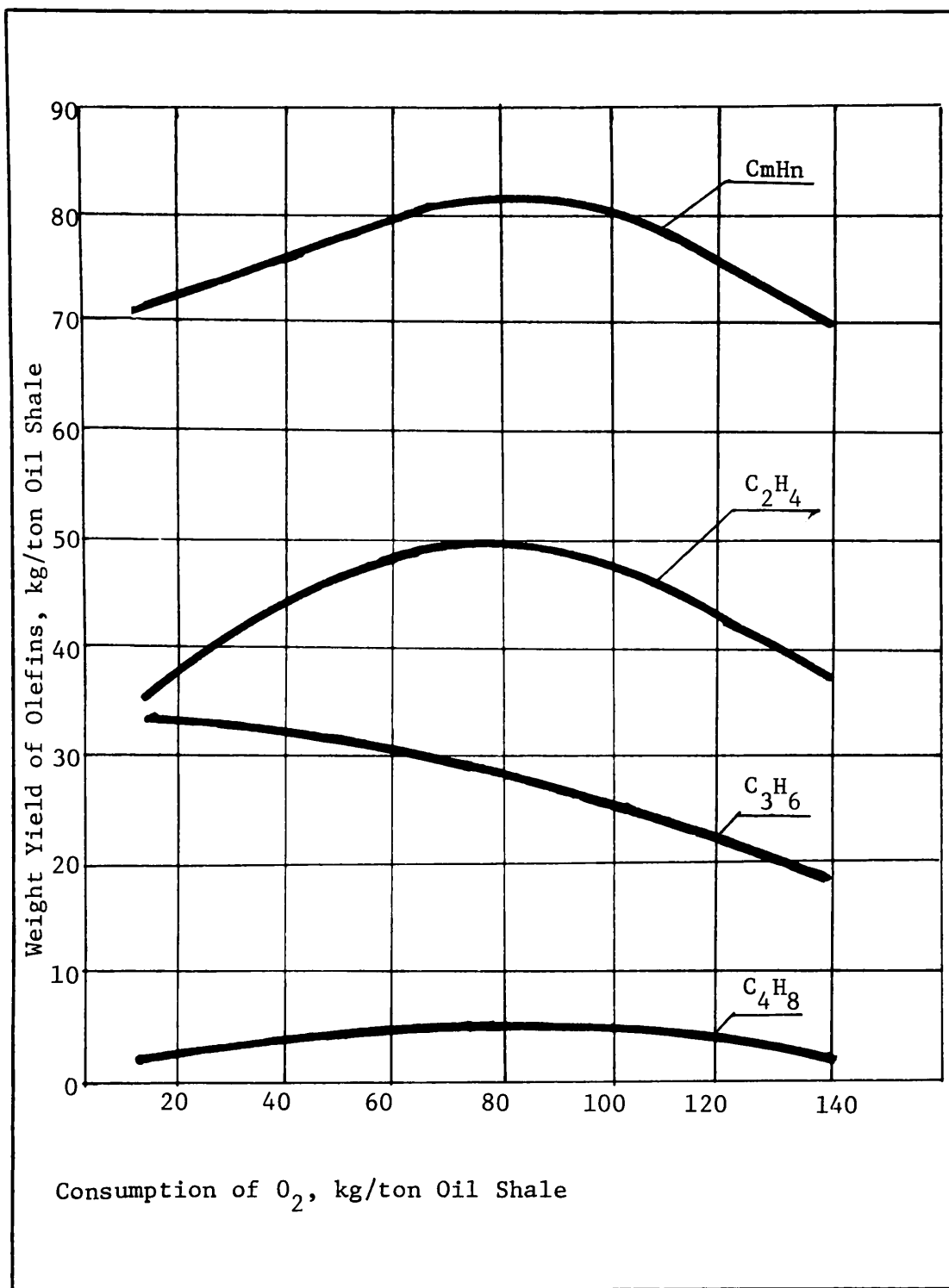


FIGURE 7.—Influence of O_2 consumption on dynamics of gas evolution.

ITEM	O ₂ Consumption, g/kg Oil Shale				
	16	42	80	116	138
Yield of Gas, M ³ /kg Oil Shale	0.203	0.300	0.420	0.527	0.602
Constituents of Gas (%) by Vol)					
H ₂ S	0.5	0.6	0.6	0.4	0.2
CO ₂	10.4	10.4	10.3	10.5	3.0
C ₄ H ₈	0.9	0.3	0.2	0.4	0.1
C ₃ H ₆	9.7	5.1	4.1	3.1	3.0
C ₂ H ₄	13.9	12.1	9.6	6.7	5.2
CO	9.0	9.9	10.0	8.7	10.3
H ₂	15.4	11.9	3.9	6.4	6.8
CH ₄	19.3	13.8	12.4	6.6	5.3
N ₂	20.9	35.0	48.9	57.2	60.1
Heating Value Kcal/M ³	6,507	4,617	2,966	2,703	2,320
Heating Value Btu/cu ft	730	520	330	304	260

FIGURE 8.—Influence of O₂ consumption on yields and constituents of pyrogas ($t_{\text{pyr}} = 800^{\circ}\text{C}$).

FIGURE 9.—Yields of olefins with O₂ consumption.

Temperature or Pyrolysis Process, °C	Yield of Pyrobenzene g/kg Oil Shale	S Content in Pyrobenzene %	Components of Pyrobenzene			
			Low Boiling Hydrocarbons	Benzene	Toluene	Thiophen
700	14.6	1.47	42.1	56.5		1.4
750	15.2	1.63	6.6	70.5	21.2	1.7
800	15.6	1.77	1.0	88.0	7.5	3.5
850	15.3	1.85	1.1	94.3	0.7	3.9

FIGURE 10.—Pyrobenzene characteristics for thermo-oxidizing pyrolysis.

REFERENCES

- Chukanov, Z. F., 1961, Some problems for fuel and power industry: AN SSSR, Moskva.
- Epik, J. P., 1961, The influence of mineral part of oil shales on conditions to operating of steam boilers: Tallin.
- Kashirsky, B. T., 1966, Journal Prikladnoi Himic Vipusk 4.
- Kashirsky, V. G., and Koval, A. A., 1969, Chemical potential of Boltshiski oil shale: Goruchie Slantze N2.
- 1972, The intensifying action of oxygen in the thermal treatment process of oil shale: Issledovania V Oblasti Kompleksnogo Ispolzovania Topliva, Nauchnii Trudi. Vipusk 1, S.G.U., Saratov.
- Kashirsky, V. G., Koval, A. A., and Igonkina, G. S., 1969, The obtaining of benzene hydrocarbons by the rapid rate pyrolysis of Boltshiski oil shale: Himia Tverdogo Topliva, N2.
- Kashirsky, V. G., Koval, A. A., and Sokolova, E. J., 1969, Thermo-oxidizing pyrolysis of Boltshiski oil shale: Ivestia VUZov. Energetika, Ng.
- Koval, A. A., 1969, The effective method of combined utilization of oil shales: Optimizatsia Parametrov I Ratsionalnoe Ispolzovanie Topliva V Energoustanovkakh S.G.U., Saratov.
- 1971, The research of thermal preparation processes of high-ash fuel for use in modern power technology: Dissertation for Candidate of Technical Sciences, Saratov Polytechnical Inst., Saratov.