Power Chemical Processing of Mineral Coals for Sustainable Development of Tyva Republic

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Abstract

The results of the geological, physicochemical, and technological studies of mineral coals of the Tyva region are presented. Directions of high-level comprehensive processing of coals, which ensure the development of economy and raise the living standards of the population of the Tyva Republic, are shown.

INTRODUCTION

The geographical autonomy and orientation for independent development of the Tyva Republic presuppose a change-over from production of raw materials to creation of competitive production technologies from the available raw materials to ensure power independence of the republic.

Tuva's mineral coals and their conversion products are envisioned as the most viable and reliable power supplies in the Republic at present and in the long-term prospect, but we should not rule out other energy sources.

The Republic has large reserves of mineral coals (estimated total supply of, *e. g.*, coking coals is 14.2 billion tons). Their major part is concentrated in the Ulug-Khem coal basin [1] located in the central part of Tyva (Fig. 1). The total area of the basin is of the order of 2700 sq. km. The resources of the other five coal deposits have been studied and estimated. Among these only the Chadan deposit is now being mined; the Changyz-Khadyn deposit is ready to be mined and is treated as promising for mining after the Chadan deposit has been exhausted. Presently, coal is mostly applied as an energy source. Mining is conducted by the open-cut method (Kaa-Khem, Chadan strip mines). Preliminary technological treatment of coal is not performed now. Because of the high volatile matter contents (non-condensable gases, coal tar) and a tendency toward sintering, the fuel-bed combustion of Tuva coals in boiler units is accompanied by significant chemical underfiring. The sharp continental climate and the geographical conditions such as settlements located in intermountain basins (some kind of an "inversion cover") hinder air mixing and cleaning. In winter, low temperatures (-45 °C) and the lack of active circulation in the ground layer lead to atmospheric pollution with coal combustion products. According to [2], pollution of urban districts in winter is primarily caused by emissions from furnaces in the private sector. The danger of such emissions is also aggravated by the fact that many pollutants are generally sorbed on the surface of soot particles, possessing respirable properties. The concentrations of carcinogenic polycyclic aromatic hydrocarbons sorbed on the particle surface may be as high as grams per kilogram.

Abatement of harmful atmospheric emissions, environmental protection, and

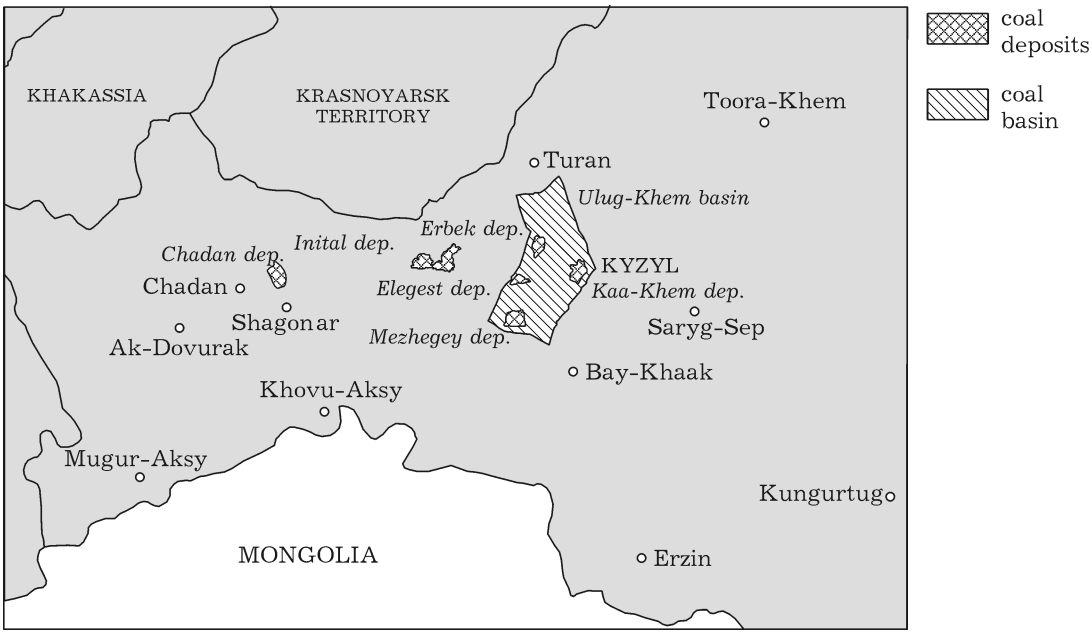

Fig. 1. Map of coal deposits of the Tyva Republic.

rational utilization of power resources are major social and economic challenges. Abatement of damage from coal power industry may be achieved through a transition to ecologically safer kinds of fuel of coal origin. Another important problem now waiting to be solved is promotion of the promising technologies of integrated power chemical processing of Tuva's coals to increase the economic returns from the application of coal raw materials.

CHARACTERISTICS OF THE ULUG-KHEM COAL BASIN

The Ulug-Khem coal basin is a negative structure of superimposed trough type complicated by several lower order anticlines. This allows us to distinguish Sesserlig-Tapsin, Kyzyl-Erbek and Verkhne-Elegest troughs, as well as Ekki-Ottug and Berezovskaya synclines (Fig. 2). The Kyzyl-Erbek trough is the largest structure, whose area is about 1650 km^2. Erbek coal formation is a commercial coal region containing from 1 to 10 coal seams ranging from 0.7 to 20 m in height. The major commercial seam, Ulug, containing about 70 % of the total prospective coal reserves of the basin, can be traced practically over the entire area of the basin and mostly has a simple structure [1].

Analysis of the Ulug seam coals suggests that reflection index of vitrinite varies from $R_r = 0.64$ in the northeast of the basin to $R_r = 1.12$ in the southwest. The isoresplends drawn along the boundary values $R_r = 0.65$, 0.75, 0.85, 1.0 % divided the Ulug seam in the Kyzyl-Erbek trough into five zones containing coals of different classes: 06, 07, 08, 09 and 11 (GOST 25543–82, GOST 9477–86) [3].

Class 7 and 8 coals are commonly met on the territory of the Kyzyl-Erbek trough. The least metamorphized coals with R_r of less than 0.65 % (class 6) occur in the northeastern part of the trough. The most highly metamorphized coals are concentrated in the southwestern part of the Kyzyl-Erbek trough. The Krasnogorsk site of the Elegest deposit has class 11 coals characterized by $R_r = 1.0–1.13$ % and distributed over an area of ~80 km^2. Class 9 coals ($R_r = 0.85–1.0$ %) are distributed over the southern dipped flank of the Elegest anticline and over the southern part of the Kyzyl-Erbek trough.

The composition of the organic mass of the Ulug seam coal is constant across the seam section and area over the entire basin.

According to the ratio of microcomponents [4], this coal belongs to the humolite group, helitolite class, helite type with 86–100 % vitrinite (average 94.3 %), 0–6 % semivitrinite (average 1 %), 0–8 % fusinite (average 2.7 %), and 0–7 % liptinite (average 2 %). The initial plant material of the coals was dominated by

brushwood and herbaceous plant residues. Microcomponents from the vitrinite group are represented mainly by parynchite and, to a lesser degree, by phellinite and xylinite. According to its composition, the coal of the entire seam belongs to the first category.

According to volatile matter contents, Ulug seam coals are divided into four types: 42, 37, 32, and 29 (GOST 25543–82 and 9477–86). More than 75 % of coals are classed with type 42, less percent belong to types 37 and 32, and very little to type 29. Given constant and uniform composition of Ulug seam coal, variations in the volatile-matter contents, plastic layer thickness, and combustion heat are caused solely by the metamorphism stage. The thickness

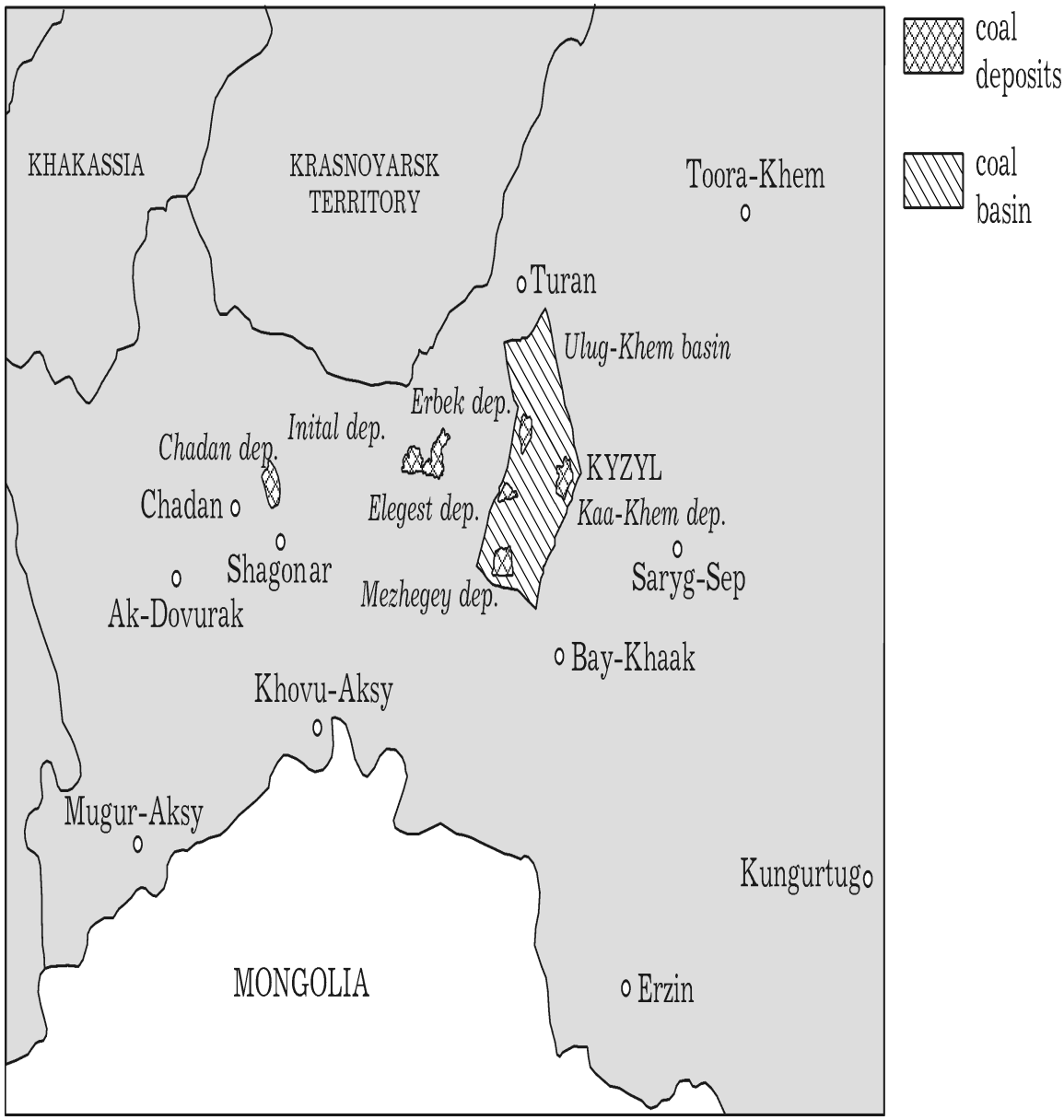

Fig. 2. Grade composition of coals from the Ulug seam, Ulug-Khem basin: *1* – seam outcrop under detrital deposits; *2* – isoheights of the bottom surface, m; *3* – isoresplends (R_r, %); *4* – isovols (V^{daf}, %); *5* – isolines of the plastic yer thickness *V*, mm; *6–9* – coal grades (*6* – gas coal, *7* – gas fat coal, *8* – fat coal, *9* – coking fat coal); *10* – code number of coal (GOST 25543–82); I–V – basin structures: I – Ekki-Ottug syncline, II – Sesserlig-Tapsin trough, III – Kyzyl-Erbek trough, IV – Verkhne-Elegest trough, V – Berezovskaya syncline.

of the y plastic layer of Tuva Jurassic coals has lower resolution than that of coals from other basins. The peculiarities of biomass composition for peat bogs from the Ulug seam and subsequent transformations of the biomass are responsible for higher plastic layer thickness and coal contrtaction. For more than half of all coal resources of the Ulug seam, the plastic layer thickness exceeds the maximum boundary value (26 mm) and is maximum (40–45 mm) in the southwestern direction. The decreased values of y in the zone of fat coals bears witness not only to their increased metamorphism, but also to the start of coal leaning. In their behaviour during processing, these are CF (coking fat) type coals.

According to the classification parameters (R_r, EOK, V^{daf}, y), Ulug seam coals that occur within the limits of the Kyzyl-Erbek trough can be classed as gas (G), gas fat (GF), fat (F), and coking fat (CF) coal types, alternating progressively in the southwestern direction. Gas coals are 21 % of the total prospective reserves; gas fat coals, 34 %; fat coals, 45 %; and coking fat coals, less than 1 %.

The discovered coal reserves (commercial categories A + B + C1 + C2) of F, GF, and G types total 1061.621 million tons [5]. Coal resources and reserves of all types on this territory are estimated at 12,597 million tons [6].

Coals from the Ulug-Khem basin are characterized by low ash and sulphur contents, high caking capacity and volatile-matter content, and relative purity from heavy metals and toxic elements. Analysis of the caking and coking capacities of the coals demonstrated that they differ from fat coals from other basins in some properties and behaviour during pyrolysis. They typically have low temperatures of transition to the plastic state (~290 °C), wide temperature range of plasticity, and high caking capacity. These properties ensure high compatibility of Ulug-Khem coal as a caking basis in mixtures with different types of leaning coals. The Ulug-Khem basin is considered as a potential source of well caking coals to improve the raw material base of coking [8, 12, 13]. Studies on Tuva coals as raw materials for chemical industry and prospects for their use are reported in [7–11].

PHYSICOCHEMICAL PROPERTIES OF COALS

Petrographic analysis of Ulug seam coals defines them as homogeneous vitrinite type coals. However, investigation of coals in transmitted light suggested that vitrinite is not uniform in composition. Three varieties can be distinguished: structured vitrain, cloggy bulk, and unstructured vitrain, the latter being predominant. Structured vitrinite is concentrated in light fractions. The structural features of the organic mass responsible for the unique properties of this coal include structural homogeneity (fragments with short effective conjugation chain prevail) and the lack of strong intermolecular interactions [14].

Variation of composition as a function of density of Ulug-Khem coal (Table 1) has been studied by thermography and IR and EPR spectroscopy methods [15]. Sample separation into narrow fractions in a mixture of benzene

TABLE 1

Composition of Ulug-Khem coals for different densities

Fraction	Density, kg/m^3	Yield, %	R_r, %	Petrographic composition, %		Technical analysis, %			Element composition, %				
				L	Vt	W^a	A^d	V^{daf}	C^0	H^0	N	O^d	S^0
I	<1300	–	0.76	2	98	1.4	2.7	41.9	85.09	5.86	1.49	7.26	0.30
II	1300–1280	10.6	0.75	5	95	1.7	9.5	39.5	85.28	5.56	1.58	7.19	0.39
III	1280–1260	51.9	–	2	98	1.4	2.0	40.1	85.20	5.75	1.49	7.29	0.27
IV	1260–1240	28.0	0.75	3	97	1.0	1.5	41.0	84.01	5.75	1.5	7.56	0.28
V	1240–1225	9.0	–	6	94	0.8	1.3	43.0	85.00	5.85	1.60	7.24	0.31
VI	<1225	0.5	0.73	13	87	0.5	1.4	43.7	85.20	6.13	1.47	7.56	0.28

Note. R_r is the reflection index of vitrinite.

TABLE 2

Effect of the density of Ulug-Khem coals on the technological and spectral characteristics

Fraction No.	Density, kg/m^3	TG analysis			EPR spectrum			IR spectrum				
		T_{max}, °C	R, °C/min	ΔT, °C	$N\cdot10^{-19}$, g^{-1}	ΔH, G	g factor	D_{3600}	D_{2920}	D_{1260}	D_{3040}/D_{2920}	D_{3600}/D_{3100}
I	<1300	488.3	8.01	99.0	2.34	7.7	2.00312	0.034	0.508	0.426	0.138	0.309
II	1300–1280	488.9	7.02	101.2	2.43	7.3	2.00310	0.047	0.380	0.364	0.158	0.398
III	1280–1260	489.3	7.24	101.8	2.30	7.6	2.00310	0.043	0.445	0.371	0.150	0.401
IV	1260–1240	487.6	7.54	101.3	2.16	7.6	2.00312	0.030	0.457	0.405	0.125	0.309
V	1240–1225	487.3	8.11	96.6	1.94	7.7	2.00312	0.026	0.496	0.403	0.105	0.252
VI	1225	487.8	8.60	95.4	2.07	7.6	2.00213	0.029	0.590	0.382	0.100	0.302

Note. T_{max} is the temperature of the maximum rate of mass loss; ΔT is the temperature range of mass loss.

with carbon tetrachloride in a centrifugal field using the procedure of [16] was employed to demonstrate fractional distribution of vitrinized species.

Heavy fractions have an appreciable degree of mineralization, which explains their increased ash content. The hydrogen and volatile-matter contents increase with the decreasing density of fractions. This is associated not only with the increased content of liptinite, but also with differences in material composition of vitrinite of light fractions.

Differences in the composition were determined by analyzing the EPR and IR spectral parameters (Table 2). Thus fraction VI characterized by the higher content of liptinite microcomponents differs from other fractions in the highest content of C–H groups (2920 cm^{-1}) and accordingly in the smallest value of the D_{3040}/D_{2920} parameter defining the degree of saturation in coals. This fraction also contains smaller amounts of oxygen-containing groups: O–H, C=O, C–O (3660, 1690, 1260 cm^{-1}). Light fractions V and IV differ from fractions III and II in the higher content of C–H groups; they contain more ether groups, but fewer free and hydrogen-bonded hydroxyl groups.

Ulug-Khem coal samples investigated by EPR are characterized by the low content of odd electrons; there is a distinct tendency for the paramagnetic centre (PMCs) concentration to decrease with the density of fractions. The signal width and the g factor are virtually invariable. The structural features of these coals also affect the dynamics of their decomposition.

For fractions of varying density, the temperature of the maximum rate of mass loss T_{max} remains practically constant, as does the reflection index of vitrinite. As the fraction density decreases, the rate R increases and the temperature range of mass loss ΔT narrows. More active decomposition of light fractions is due to the increasing number of aliphatic fragments and weaker oxygen-containing groups in the organic mass.

A spectroscopic study of coal fractions with densities of 1220–1250 kg/m^3 and less than 1400 kg/m^3 from the top and bottom layers of the Ulug seam (Table 3) is reported elsewhere [15]. The coal samples had decreased oxygen contents and lower absorption intensity in the region of carbonyl (1690 cm^{-1}) and hydroxyl group (3100 cm^{-1}) vibrations. They typically showed higher intensity of the absorption bands of the aliphatic groups (2920 cm^{-1}).

The short-wave peak the electronic absorption band λ_m, the small contribution of the long-wave absorption F_{1700}/F_{λ_m}, and the smaller value of ΔV (half-width of the spectral line of Ulug-Khem coal) suggest that homogeneous polyconjugate structures with small lengths of effective conjugation dominate in the coal. The low concentration of PMCs in Ulug-Khem coal was attributed to the relatively small length of the ordered carbon fragments and to the absence of strong intermolecular interactions, leading to decoupling of electrons delocalized over the polyconjugation chain.

Distinction between coals from different layers of the Ulug seam was insignificant. There were some differences in oxygen distribution

TABLE 3

Composition and spectral data for the top and bottom layers of Ulug seam coal

Layer	Fraction density, kg/m^3	Technical analysis, %		Element composition, % daf					Diffuse reflection spectrum			Optical densities of IR absorption bands, см$^{-1}$				
		V^{daf}	A^d	C	H	N	O	S	λ_m, nm	F_{1700}/F_{λ_m}	$V\cdot10^3$, cm^{-1}	3520	3100	2920	1690	1040
Top	1220–1250	37.3	2.1	87.05	5.86	1.70	3.96	0.44	–	–	–	0.084	0.072	0.451	0.157	0.097
	<1400	36.8	2.8	87.70	5.84	1.60	4.22	0.64	520	0.07	18.1	0.091	0.070	0.518	0.123	0.161
Bottom	1220–1250	37.0	2.4	87.42	6.16	1.65	4.09	0.45	2	–	–	0.089	0.062	0.477	0.140	0.072
	<1400	36.3	2.4	87.65	5.80	1.53	4.37	0.72	–	–	–	0.097	0.060	0.516	0.131	0.109

over the functional groups. Coals of the light fraction show more intense absorption in the region of the vibrations of the carbonyl and hydroxyl groups involved in strong hydrogen bonding. Coals of the fraction lighter than 1400 kg/m^3 are characterized by the higher intensity of the absorption bands of ether (1040 cm^{-1}) and hydroxyl groups (3520 cm^{-1}).

The specified coal fractions were subjected to reductive alkylation by the procedure described in [17]. This treatment increases the solubility of coals. The solubility of initial and alkylated coals in pyridine and after successive extraction with hexane, ethanol, chloroform, and pyridine has been studied (Table 4).

Solution of the organic part of coals in solvents with hydrogen-donor properties combined with thermochemical and catalytic reactions is one of the key stages of the preparation of synthetic liquid fuels from coals. It was demonstrated [14] that the yield of extracts from the coal fraction with a density of 1200–1250 kg/m^3 is somewhat higher than from the fraction with a density of less than 1400 kg/m^3 after extraction with pyridine and after successive extraction with hexane, ethanol, chloroform, and pyridine.

Increased total yields of soluble products in successive extraction is achieved by using the chloroform and pyridine extracts. Coals from

TABLE 4

Solubility characteristics of Ulug seam coal

Coals	Fraction density, kg/m^3	Yield of extracts, %					
		Extraction with pyridine	Successive extraction				
			Hexane	Ethanol	Chloro-form	Pyridine	Total
Initial coals:							
top layer	1220–1250	43.8	5.0	1.6	11.6	40.6	58.8
	<1400	41.6	4.2	1.4	15.3	31.9	52.8
bottom layer	1220–1250	42.2	5.0	1.9	14.0	40.1	60.9
	<1400	38.1	4.3	2.1	16.7	30.6	53.7
Alkylated coals:							
top layer	1220–1250	54.0	5.8	–	–	–	–
	<1400	62.9	4.8	3.8	3.7	43.6	55.9
bottom layer	1220–1250	51.3	5.4	6.5	–	43.1	55.0
	<1400	58.6	4.1	3.6	–	48.0	55.7

different layers of the Ulug seam differ slightly from each other in solubility.

Numerous structure and composition studies of fat coal extracts demonstrated that long-chain n-paraffins dominate in the hexane extract; the ethanolic extract is a mixture of aliphatic alcohols, acids, and other acid-containing compounds; the chloroform extract has a larger proportion of olefinic structures, including those with conjugated bonds and carbonyl groups; and the pyridine extract has unsaturated structures with conjugated bonds containing carbonyl and nitrogen-bearing groups [17, 18]. It was found [19] that after successive treatment of fat coal with hexane, ethanol, chloroform, and pyridine, the extraction products have higher hydrogen and oxygen contents, conceivably as a result of interaction with hydrogen and oxygen donors during extraction. The coals subjected to reductive alkylation add more hydrogen and oxygen probably as a consequence of more significant violation of intermolecular interactions as a result of polyalkylation and extraction.

According to [14], the solubility of coal fractions with a density of less than 1400 kg/m^3 in pyridine increases by 20 % after alkylation and exceeds the solubility of the light fraction alkylated under the same conditions. This difference in reactivity can be related to the larger content of ether groups, which are the first to be alkylated, in fractions with a density of less than 1400 kg/m^3.

Analysis of the element composition of coals from the above fractions and extraction products suggested that pyridine extracts of initial and alkylated coals are enriched with hydrogen compared to coal (Table 5).

Extraction is accompanied by oxidation of extracts and residual coals, this process being especially pronounced during successive extraction.

EPR spectral analysis of the extraction products of the coal indicated that the PMC concentration decreases in the series: residual coal > initial coal > pyridine extract. The total concentration of PMCs in the extraction products as calculated from the additive scheme is close to the concentration found in the initial coal. This confirms that the structure of the coal in question has no odd electrons, which exist due to intermolecular interactions.

The properties of coals, in particular, their caking capacity can be modified by changing the intermolecular interactions. The low caking capacity is explained by different factors. For example, for low metamorphized coals, these are condensation reactions initiated by highly reactive hydrogen-bonded oxygen-containing groups, which are present in significant amounts. For highly metamorphized coals, this is the presence of extended and relatively ordered polyconjugate systems that form associates, generating 3D nonplastic substances on heating [20]. In the case of low metamorphized coals, hydrogen bonds should be destroyed by heating coals in reductive media to prevent structure destabilization after violation of intermolecular interactions. For highly metamorphized coals, one might expect that substances capable of destroying the associates of coal fragments would enter electron donor-acceptor interactions with these associates, and that the presence of hydrogen donors in additives must stabilise the labile system after the associates have been destroyed. Studies of intermolecular interactions and their effects on the processing behaviour of coals will make it possible to obtain new data on coal reactivity and to justify the approaches to coal processing.

PROMISING DIRECTIONS OF COAL PROCESSING

Integrated power chemical processing of Tyva coals is an ecologically clean and socially acceptable technology immune to energy crises.

Gasification

High-temperature treatment of solid fuel in oxygen and air, steam, carbon dioxide and hydrogen leads to conversion of the organic components of fuel into gaseous products. Tyva coals of G and GF types are gasified with high yields of gaseous products. Fuel gasification was studied in 1987. According to the prospective technical and economic characteristics obtained during that period, the production cost of coal gasification was up to 20 rub. per 1000 m^3 of converted coal. Complete coal gasification was not a solution to the problem of ecologically

TABLE 5

Characteristics of extraction products of Ulug-Khem coal (fraction <1400 kg/m^3, top layer)

Sample	Extraction	Elemental composition, % daf					EPR spectrum			Electronic absorption spectrum			
		C^0	H^0	N	O_2	S^0	N, arb. un.	ΔH, G	g factor	λ_m	F_{λ_m}	F_{340}/F_{λ_m}	F_{1700}/F_{λ_m}
Initial coal	–	87.70	5.84	1.60	4.22	0.64	51	7.3	2.00296	520	5.87	0.56	0.07
Extract	With pyridine	84.79	6.80	2.02	6.12	0.29	25	5.4	2.00315	460	7.44	0.69	0.10
Residue	»	83.89	5.21	2.06	7.94	0.90	60	6.6	2.00308	580	7.30	0.53	0.20
Pyridine extract	Successive	86.27	5.10	1.73	6.60	0.30	25	5.4	2.00315	–	–	–	–
Residue	»	82.50	6.37	1.64	8.65	0.84	68	6.8	2.00315	–	–	–	–
Alkylated coal	–	87.17	6.72	1.37	4.32	0.42	53	7.6	2.00306	620	3.07	0.40	0.11
Extract	With pyridine	86.98	7.95	1.34	3.51	0.22	34	5.5	2.00316	620	3.93	0.48	0.04
Residue	»	86.11	5.93	1.51	5.89	0.56	56	7.0	2.00306	620	4.01	0.41	0.17
Pyridine extract	Successive	85.75	6.44	1.61	6.20	–	22	5.3	2.00312	620	4.04	0.44	0.12
Residue	»	86.29	5.49	1.61	6.18	0.43	58	6.8	2.00310	620	4.57	0.39	0.28

clean solid fuel supplies at that moment. Partial gasification at temperatures of up to 800 °C was a potential solution to the problem. According to gas balance, the yield was 1000 m^3 of gas and more than 0.4 t of semicoke (per ton of coal); the production cost of processing was up to 30 rub. per ton of coal. This choice of coal processing method could satisfy the demand of the population for solid fuel and create prospects for developing synthetic procedures using the gas obtained from coals, including procedures for the preparation of liquid synthetic fuels. The net cost of production of 1 t of crude methanol during synthesis of this gas was up to 80 rub. in 1987. According to prospective technical and economic estimations, methanol production from coal of the Kaa-Khem deposit was economically beneficial. The composition of gases as basic components for the synthesis of hydrocarbon raw materials was as follows, kg/l: CO_2 26.2, CO 22.1, CH_4 138.4, H_2 57.2, C_nH_m 9.5. Combustion heat of gas was Q ~ 32 000 kJ/kg, gas density was p ~ 0.9 kg/l.

Hydrogenation

Hydrogenation is high-pressure thermochemical treatment of coal in the presence of catalysts and hydrogen. The organic mass of coal is completely converted into a mixture of liquid synthetic fuels and gaseous products. The best results were obtained in the presence of catalysts capable of activating molecular hydrogen and using organic solvents readily donating hydrogen atoms (tetralin, cresol, *etc.*). Coals of the Kaa-Khem deposit were investigated as raw materials for pyrolysis and liquefaction, and the results of these studies were reported in [21, 22]. Coal was liquefied in a flow of hydrogen and tetralin (8 : 1, 400 °C, 4 MPa) in a laboratory apparatus involving a reactor with a stationary layer of coal. Coal was extracted with benzene for complete extraction of the products. Experimental data on hydrogenation indicated that the coals possess high reactivity and low gas generating capacity (less than 10 %). Gases are represented by saturated hydrocarbons C_1–C_3 (more than 60 %) and carbon oxides (more than 20 %) and may be utilized (after washing from CO_2) in further processing. Liquid products are characterized by low contents of asphaltenes and heteroatomic compounds.

Hydrogenation of F, GF, and G coals was investigated at the Institute of Combustible Minerals (Moscow). Hydrogenation of coals of the Ulug-Khem basin showed high process selectivity. Data on hydrogenation are presented in Table 6.

Despite the high yields of liquid products, hydrogenation of Tyva coals was not recommended (in 1987) because of the high production cost of the process. In stationary power industry, coal is economically preferable to synthetic liquid fuel. Setup of engine fuel production could not compete with highway supplies of engine fuel (with allowance for capital and current expenses for hydrocracking, reforming, and compounding to yield high-quality petrols, propellents, and diesel fuels). Recent price rises for engine fuels and fuel deliveries within the Republic and from external sources, as well as anticipated price rises, make it reasonable to discuss the economic prospects for obtaining liquid synthetic fuels from the Ulug-Khem basin by the hydrogenation method. This calls for further studies under independent project and in the context of other flow charts for Tyva coal processing.

Pyrolysis

Coal semicoking and gasification in a fluid bed has distinct advantages. In contrast to

TABLE 6

Hydrogenation characteristics of Ulug-Khem coals

Coal grade	Consumption of H_2, m^3	Yield of products, %			
		Gas	Total liquid	Fraction below 300 °C	Fraction above 300 °C
F	5.00	9.80	94.77	27.30	57.47
GF	1.81	11.70	82.45	25.33	57.12
G	1.74	10.60	79.81	28.05	50.83

hydrogenation and gasification processes, coal processing technologies aimed at obtaining power semicokes, cokes, coal tar, and process gas are quite profitable. Semicoking and pyrolysis of Kaa-Khem coals are considered in [23, 24, 30].

Semicoking was reported to give gas with increased contents of hydrogen and methane; it was stated that pre-treatment of coals is necessary to reduce their caking capacity. It was demonstrated that the coal in question has a high caking capacity and can serve as a raw material for coking.

Pilot trials (2.6–3.0 t) aimed at testing the coal cleaning ability are reported in [1]. It was recommended that F and GF coals be used for coking after preliminary cleaning. The yield of the concentrate was 89.4–97.8 %, the ash content amounted to 3.8–7.8 % and the yield of waste was 2.2–10.6 %. Coking of Tyva coals was performed in VUKHIN coke ovens. F type coals formed a high-quality cake for batch mixtures intended for use in blast-furnace coke production by laminar coking technology; GFF coals had a high coking capacity.

A pilot plant for coal semicoking and gasification in a fluid bed of solid fuels has been created at the Tuva Institute of Complex Exploitation of Natural Resources, SB RAS (TuvIKOPR) [23–25]. The flow chart is presented in Fig. 3.

The coal semicoking apparatus operated as follows. Coal with particles of d = 0.2–2.0 mm was loaded into the semicoking reactor and heated in a flow of nitrogen or argon. Evaporator (steam generator) *2* was previously warmed to 500–600 °C, and volatile components gasification reactor *3* was heated to 800 °C. After the semicoking reactor was heated with overheated steam to 140–160 °C, coal was heated (while feeding oxygen) with a heating rate of 8–10 °C/min to a temperature of 600 °C; then isothermal storage followed. Then feeding of overheated steam and oxygen in the reactor stopped, and the reactor was cooled to 200 °C in a flow of air. The setup was switched

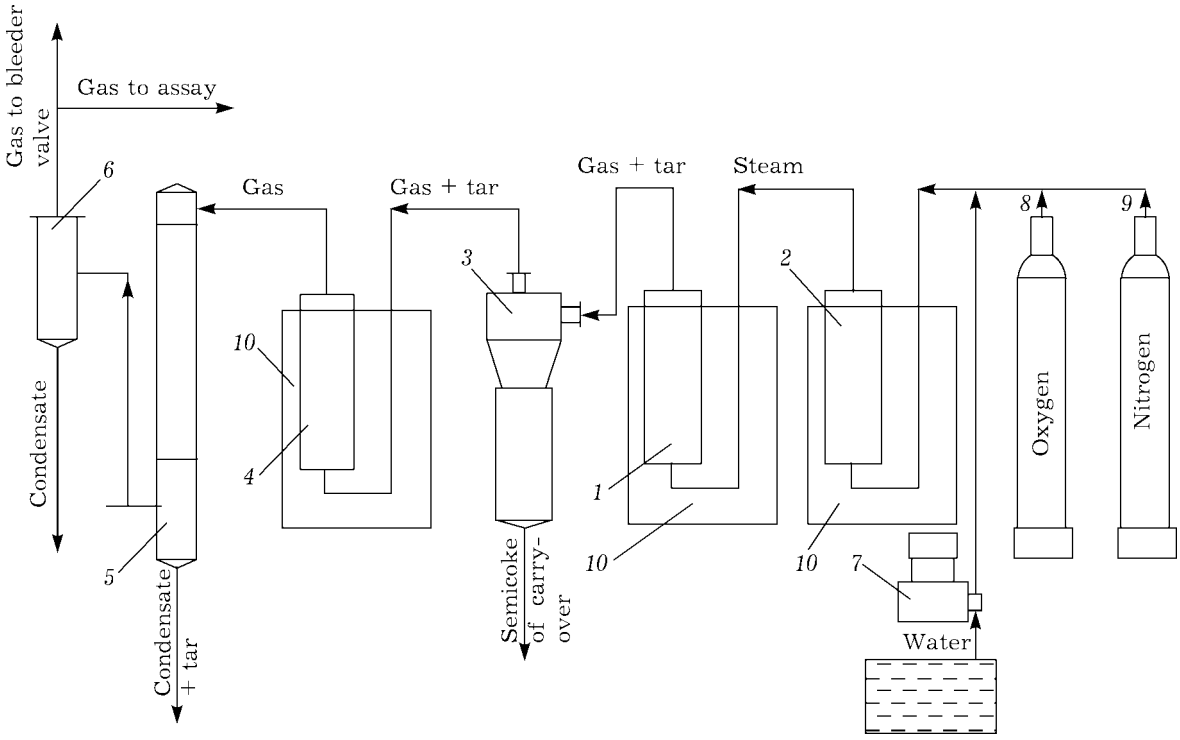

Fig. 3. Flow chart of a pilot setup for coal distillation and gasification in a fluid bed: *1* – coal semicoking and gasification reactor; *2* – steam and gas generator; *3* – cyclone collector (centrifugal separator for removing semicoke particles from the steam-and-gas stream); *4* – reactor for gasification of volatiles and resins; *5* – condenser; *6* – filter; *7* – batching pump; *8*, *9* – cylinders for pressure gas (oxygen, nitrogen, or argon); *10* – chamber electric furnaces; *11* – tank for distilled water.

off, and semicoke was discharged from the reactor.

A complete cycle of heat treatment of coals to obtain semicoke, *i. e.*, heating, isothermal storage, activation with steam for 30 min at 800 °C, and cooling to 400 °C in an inert gas, took 120 min. The carbon material (semicoke) obtained during thermochemical treatment has been analyzed; the element composition, specific surface, sorptive capacity based on phenol, and sorption activity based on iodine have been determined.

The basic characteristics of coal pyrolysis in a fluid bed are T = 600 °C, v = 10 °C/min; product yields, % based on dry coal: semicoke 66.3, tar 7.2, water 4.1, gas 22.4; gas density 0.9 10^{-3} kg/m^3, gas yield 0.2534 kg/m^3.

The semicoking gas yields were rather high, and the gases had a high calorific efficiency. During industrial semicoking (generally conducted in an autothermal mode) oxygen-steam blast should be employed to yield fuel gas with a high calorific efficiency; using wet blast demands dilution of semicoking gases with ballast (nitrogen) [25–32].

The possibility of cold shaping to produce coke and fuel briquettes from a fusion mixture containing semicoke and G and GF coals [27, 29] was studied at TuvIKOPR. Molding a fusion mixture of semicoke and coal in a ratio of 1 : 2.5–3 and subsequent heat treatment of the mixture in a mine type reactor (argon and nitrogen as a gas phase; treatment time 90–120 min, temperature 600 °C) gave a briquette whose initial shape preserved well; the briquette layer did not cake. Unlike ordinary coke shaped as irregular pieces from which small crumbs and large lumps are inevitably sieved away, formcoke pieces have strictly definite dimensions, increasing its gas permeability considerably. Mechanical strength of formcoke is much higher than that of ordinary coke.

The element composition of coke based on dry analytical mass (%): C 85.62, H 1.41, N 1.41, S 0.67.

The results of investigations demonstrated that porous powder carbon materials with specifications fitting the level of AG and KAD commercial coals can be produced from coals of the Kaa-Khem deposit by treatment of a coal fraction sized 0.2–2.0 mm with an oxygen-steam mixture in a fluid bed at temperatures of up to 800 °C.

Table 7 lists the comparative characteristics of adsorbents obtained by semicoking of coals from the Kaa-Khem deposit and of AG-3, AR-2, and KAD commercial coals in a fluid bed.

Production technologies for the preparation of semicokes, coal adsorbents, and household fuel briquettes have been refined at a laboratory level at TuvIKOPR; a film type apparatus for treatment of wastewaters using coal adsorbents from coal of the Kaa-Khem deposit [30–32] has been created.

Coal tar is a valuable raw material for the production of aromatic hydrocarbons, carbon fibres, needle adsorbents, and electrode coke. Coal tar pitch is one of the most valuable products of tar processing. It serves as a basic

TABLE 7

Comparative characteristics of adsorbents

Parameter	Coals of Kaa-Khem deposit	Comparable coal grades
Specific surface S_{BET}, m^2/g	600	AG-3, AR-2: 800–1000
Surface area of meso- and macropores, m^2	200	AG-3, AR-2: 30–50
Limiting sorption volume V, cm^3/g	0.2–0.3	AG-3, AR-2: 0.6–0.7
Sorption activity based on iodine, mg/g	40–70	AG-3, KAD-2: 50–80
Sorptive capacity based on phenol, mg/g	120–150	AG-3–70, KAD-160
Particle size distribution of powder adsorbent d, mm	0.2–2.0	
True density, g/cm^3	1.4–1.8	
Apparent density, g/cm^3	0.9	
Packed density, g/cm^3	0.36	

binder and impregnating material in production of general-purpose carbon-graphite products of any type. The production process for the preparation of carbon fibres and needle adsorbents from coal tar pitch is currently being developed at a laboratory level.

In addition, the possibilities for ash recovery and creation of optimum technological processes for ash processing have been examined at TuvIKOPR. Fly ash is a fine powder with a high specific surface; the phase composition of ash is extremely complicated. Variations of chemical composition (%): SiO_2 38–49, Al_2O_3 14–16, Fe_2O_3 9–15, CaO 15–23, MgO 3–5, K_2O 1–7, Na_2O 0.5–0.8, P_2O_5 0.2–0.6. Ash treatment in a classifying activator designed at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, gave fractions of ash enriched with hollow microspheres. Fly ash of Tyva coals can be considered a material containing hollow microspheres, which can be used for some special purposes.

A combined technology for the production of power semicokes and cokes and setup of environmentally sound productions based on the products of thermal degradation of coals are the most promising directions of high-level processing of Tuva's mineral coals. The advantage of this process is the possibility of selecting technological concepts based on the module principle using all of the above schemes of transformation of the starting coal to solid, liquid, and gaseous products. Three directions of coal processing can be distinguished [26, 29].

The first direction is the development of ecologically clean, energy-efficient technologies of solid fuel combustion. Problems of small-scale power generation in Tyva could be solved through modernization of current technologies of coal combustion in low-power boiler houses; also, this could be useful in solving the problem of supplying the population of the Republic with ecologically clean household fuel.

The second direction is setup of science-intensive, environmentally sound productions for making competitive products based on Tyva's mineral coals. This will create the scientific foundation and basic technologies for manufacturing different highly competitive articles (liquid synthetic fuels, cokes, fuel gas, microbiological synthesis products, *etc.*) in Tyva.

The third direction – ash and slag waste disposal – is designed to solve problems of waste disposal at thermal power stations, and primarily in the construction industry sector of economy.

CONCLUSIONS

The above data on the quantity of known reserves and on the quality of coking coals and Tyva's power mineral coals bear witness to the unlimited potentials of large-scale production of coals by shaft mining. Currently we have no ecologically clean energy-efficient innovation technologies of solid fuel combustion based on Tuva's coals. Unfortunately, development of explored deposits is ineffective today because of the high production cost of extractive coal, complicated transportation scheme for its sale, lagging of developments and strippings in the opencasts under operation, and the lack of demand in the foreign market.

Power chemical processing of Tyva's coals will make it possible to turn to ecologically clean technologies and to reduce raw materials and energy consumption due to improved production processes. It will drastically reduce the toxicity and amount of harmful emissions and wastes to ensure clean urban-industrial environment in the Republic. A comprehensive and high-level processing of mineral coals can provide a basis for economic development to raise the living standards of Tyva's population. Full-scale introduction of suggested technologies will accelerate the resolution of the acute economic and social problems of the Tyva Republic.

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