Translated from *Uspekhi Khimii*, **43**, 1844 - 1864 (1974) U.D.C. 662.749

Theoretical Generalisation of the Coking of Various Fuels

D.D.Ruschev

The most important ideas on the coking of various types of solid and liquid fuel are examined. Theoretical results are given summarising the thermal degradation of model organic compounds and polymers. Processes involved in the coking of various petroleum products, coal tar, and their mixtures with weakly caking, low-grade coals are analysed. Data are presented on the plastic state and the caking of coals of different degrees of metamorphism. Consideration is given to the caking of lignites and to the effect of the type and origin of brown coal on the physicomechanical parameters of the coke. Formulae are set out for calculating the yield of chemical products in the coking of coals and for predicting the properties of the coke. A list of 94 references is included.

CONTENTS

1. Introduction 875
2. Investigation of coking on model organic compounds and polymers 876
3. Mechanism of the formation of tar coke 877
4. Plastic state, caking, and degree of metamorphism 879
5. Coking of coal—oil mixtures 881
6. Caking of lignites and coking of mixtures of coal and brown coal with oily additives 882
7. Yields of chemical products from coal—properties and structure of coke 884

1. INTRODUCTION

The theoretical problems associated with coking processes are usually considered in connection with either the manufacture of metallurgical coke or the production of coke from heavy petroleum fractions and resinous products of the processing of coal. The former and older scientific approach was concerned mainly with physical and colloidal processes, whereas the latter was directed solely at the chemistry of the processes.

Muck[1] considered that coking took place in several stages. Coal softens when heated and acquires plasticity, which produces various states from slight stickiness to complete fusion. He related the swelling to the extent of melting and the rate of hardening: the gases evolved distended the softened mass and, provided that the pore walls permeating it were sufficiently strong, the latter remained unbroken until solidification occurred. Weding and Rao[2] denied that coal could melt, and explained coking by thermal decomposition of hydrocarbon and resinous components of coal, with the separation of free carbon and high-melting complex carbon-rich compounds, which settle on the carbon particles and consolidate them into monolithic lumps of coke. Simmersbach[3] supported the melting hypothesis, but assumed without justification that coal contained two modifications—"caking" and "lean" coals—which under certain conditions may pass one into the other.

Very unsuccessful attempts were made to relate the coking power of coals with their elementary composition. Interesting considerations were put forward by Simmersbach[4], who regarded the hydrogen and oxygen contents as more important than the carbon content: coal does not coke if it is either very rich (brown coal) or very poor (anthracite) in these elements. It postulated the existence of upper and lower limits to the hydrogen and oxygen contents, beyond which coking was impossible.

Many papers were published during the interwar period[5-10] linking caking and coking with the presence of bitumens in the coal. Berl and Körben[11] concluded that bitumens which distilled off at higher temperatures during coking were responsible for the formation of uncaked coke. If bitumens decompose below their boiling points, they may be converted into substances which cement the remainder of the coal and form strong coke. Several investigators[12-14] were doubtful about the role and significance of bitumens and their components for elucidating coking processes. The polemics on this aspect can be explained by the varied conditions under which bitumens were extracted and the absence of a reliable and unified method for measuring the strength and structural properties of coke.

The use of modern methods yielding fresh experimental information has led during recent decades to other interpretations of caking and coking processes. Illingworth[15] and Mott[16] directed attention to the adsorption and wetting of infusible humic substances by molten bitumens and put forward the "cementation" hypothesis, which was developed by Sapozhnikov[17] as the "adhesion" hypothesis. Yakovlev[18], Onusaitis[19], Aronov[20], and Permitina[21] also discuss caking and coking in physical and physicochemical terms, linking these processes with fusion, disolution, dispersion, wetting, etc. Interesting attempts have been made by Shapiro[22], Kustov[23], and other Soviet authors to explain the formation of coke in terms of colloid chemistry.

All the above hypotheses have the common defect of underrating the role and importance of chemical processes in coking. Audibert[24] regarded the formation of coke as a complicated chemical process yielding several new high-melting compounds. As the temperature is gradually raised, coal is converted into a continuously varying system of liquid, solid, and gaseous phases, and finally passes completely into the solid state. Panchenko and Klopotov[25] consider that chemical processes are responsible for the evolution of water and carbon dioxide, with the formation of new plastic products. In the opinions of Aronov and of Nesterenko[26] caking and coking depend on the relative proportions of hydrocarbon and oxygen compounds in the plastic products and on polycondensation processes. Angelova and Lazarov[27] have established that the plastic state is characterised by an increased content of functional oxygen groups resulting from the thermal destruction of ether and other bonds.

During recent years a broad debate has been conducted in the Soviet Union on the problems of caking and coking processes[28-32]. This has clearly shown that the words of Simmersbach[33]—"The cause of the caking of coal is a problem which, in spite of all the efforts made to solve it, still awaits its final solution"—are valid even today.

2. INVESTIGATION OF COKING ON MODEL ORGANIC COMPOUNDS AND POLYMERS

In a study of the coking of individual organic compounds Tilicheev[34] found that the rate increases with the molecular mass of the aromatic ring system of unsaturated cyclic hydrocarbons. Unsubstituted aromatic hydrocarbons are most rapidly carbonised. In order to study the mechanism of coking, differential thermal and thermogravimetric investigations have been made[35] on model organic compounds, most of which are products of the processing of coal and have been isolated from coal tar (Table 1). The highest coking value was obtained in the pyrolysis of truxene and bifluorenyl, which have the highest molecular mass, melt at a high temperature, and boil above 500°C. Coke is formed comparatively rapidly from chrysene, pyrene, and brazan, whose molecules consist of fused aromatic rings (Table 1). The pyrolysis of n-docosane, naphthalene, 2,6-dimethylnaphthalene, *o*-hydroxybiphenyl, and 2-hydroxy-4-methylquinoline occurs quite differently: their coking values are exceptionally small, and the time required to form 1% of coke varies from 963 min (with naphthalene) to infinity (*o*-hydroxybiphenyl).

Table 1. Physical constants and coking power of model organic compounds.

Compound	Mol. mass	M.p., °C	B.p., °C	Coking value, %	Time for 1% coke, min.
n-Docosane	310.6	44.9	380	0.092	1177
Naphthalene	128.2	80	218	0.110	963
2,6-Dimethylnaphthalene	156.0	111	262	0.031	3419
Fluorene	166.0	116	299	0.192	552
Bifluorenyl	330.4	249	500	17.485	6
Pyrene	202.2	150	394	3.903	27.2
Chrysene	228	255	441	4.025	26.3
Truxene	342	369	550	71.063	1.5
Brazan	218.2	205	395	2.064	51.5
o-Hydroxybiphenyl	170.2	59	286	trace	∞
2-Hydroxy-3-methylquinoline	159.2	240	390	0.038	2790
Carbazole	167.2	245	353	0.985	108

An interesting conclusion can be reached from a comparison of the differential thermal and thermogravimetric curves for n-docosane and naphthalene (*a* and *o* in Fig. 1). The former curves begin with endothermic effects representing their transitions from solid to liquid state. Very characteristic of docosane is the subsequent exothermic effect with its maximum at 245°C, whereas loss in weight due to vaporisation and thermal degradation begins above 280° and is accompanied by an endothermic effect at 309°C. The sublimation of naphthalene, which begins at 150°, is especially intense between 190° and 210°C, and is responsible for an endothermic effect: the weight of a specimen decreases by approximately 90% from 195° to 210°C.

The differential thermal curve for truxene (Fig. 2*c*) exhibits an immense exothermic effect with its maximum at 188°C, whereas changes in weight begin only above 435°C, which confirms the importance in coking of exothermic polymerisation and polycondensation processes occurring between 200° and 430°C. Brazan gives two exothermic effects in the same temperature range (Fig. 2*d*).

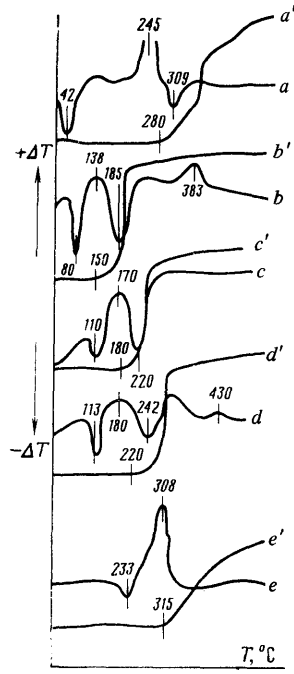


Figure 1. Differential thermal and thermogravimetric curves of: *a*,*a'*) n-docosane; *b*,*b'*) naphthalene; *c*,*c'*) 2,6-dimethylnaphthalene; *d*,*d'*) fluorene; *e*,*e'*) bifluorenyl.

It is very important to investigate the behaviour of cellulose, waxes, resins, and other coal-forming components of vegetable origin, which in more or less changed form play a considerable part in the formation of coke, in order to elucidate the processes involved in caking and coking. The heat-treatment of these coal-forming and other simply constructed natural or synthetic model substances of high molecular weight may yield very interesting information on the course of thermal degradation processes in the caking of coal and its conversion into coke. Krasyukov[36] has established that polyethylene does not form a coke residue, but polypropylene gives 16.2% of coke, which is identical with petroleum coke in texture and mechanical and electrical properties.

In investigations of the mechanism of coking, analogous experiments have been made with coumarone–indene resins, carnauba wax, technical paraffin wax, coal tar, cellulose, rosin, etc.[37,38] The results show (Fig. 3) that the characteristic endothermic effects of coumarone–indene resin and rosin (at 358° and 288°C) arise from thermal degradation associated with the evolution of volatile products. Pyrolytic processes begin in carnauba wax (*c* and *c'*) only above 370°, so that the endothermic effect is observed at 402°C.

Formation of a solid coke residue from technical paraffin wax (Fig. 3*d'*) is largely complete by 495°C. The coking value (6.516%) far exceeds that of n-docosane (0.092%). This means that the pyrolysis of a mixture of paraffin hydrocarbons creates more favourable conditions for accelerating coke formation. Coal tar gives an especially interesting differential thermal curve (*f*), characterised by an immense exothermic effect between 248° and 300°C. Heat-treatment of this mixture of many strongly aromatised compounds, of high molecular weight and high boiling point (above 400°C), leads to appreciable changes in weight only above 325°C, which is connected with the absorption of heat. Truxene and coal tar give closely similar differential thermal and thermogravimetric curves. The presence of a plateau on the differential thermal curve of the tar can be explained by the superposition of several exothermic effects similar to those of truxene with a maximum between 248° and 300°C, as can be seen from the proposed hypothetical scheme (Fig. 4).

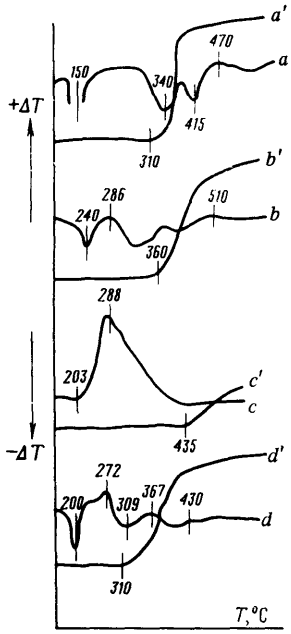


Figure 2. Differential thermal and thermogravimetric curves of: *a*,*a'*) pyrene; *b*,*b'*) chrysene; *c*,*c'*) truxene; *d*,*d'*) brazan.

Paraffin hydrocarbons, like aromatic hydrocarbons which sublime below the degradation temperature, yield a very small quantity of a coke residue consisting of highly fused aromatic compounds. Aromatic heterocyclic compounds containing oxygen and nitrogen usually undergo polymerisation—condensation processes with the formation of solid, non-volatile, strongly aromatised carbon-rich products constituting coke. Even before the start of degradation and vaporisation, the aromatic compounds of high molecular weight, which melt and boil at high temperatures, undergo intense polymerisation and polycondensation processes characterised by exothermic effects with a maximum in the range 250–310°C. They give a large quantity of a solid, non-volatile condensed residue, which forms the main mass of the coke.

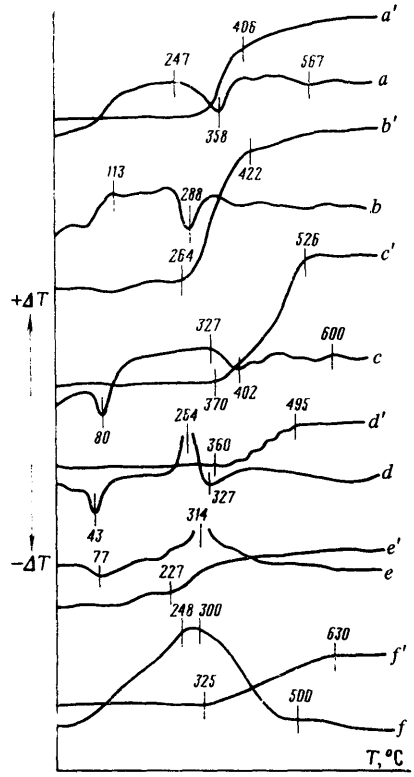


Figure 3. Differential thermal and thermogravimetric curves of: *a*,*a'*) coumarone–indene resin; *b*,*b'*) rosin; *c*,*c'*) carnauba wax; *d*,*d'*) paraffin wax; *e*,*e'*) cellulose; *f*,*f'*) coal tar.

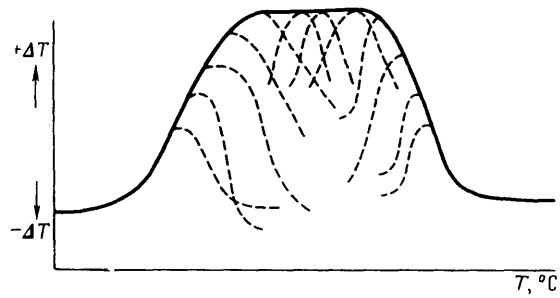


Figure 4. Aggregate differential thermal curve for a mixture of compounds.

3. MECHANISM OF THE FORMATION OF TAR COKE

Investigations of the coking of various tars, resins, and heavy hydrocarbon products and study of the properties of the resulting coke will yield additional information on

coking processes and their mechanism[39-46]. Paper chromatography indicates that silica-gel resins and asphaltenes predominate in vacuum and acid asphalt, kerogens and carbenes in mazut, and asphaltenes in coke-oven tar. Fig. 5 shows diagrammatically the yields of coke, liquid distillate, and gases obtained when these products are coked under laboratory conditions, and Table 2 lists the most important characteristics of the coke residue. Differences in hardness, porosity, and density among the cokes result from the different chemical compositions of the starting materials. Gas-works tar and stearin pitch, which are rich in paraffin hydrocarbons, yield the coke of lowest density, whereas strongly aromatised materials, e.g. coal tar and vacuum asphalt, give a resinous coke of high density. These differences have been confirmed by X-ray examination of the structure.

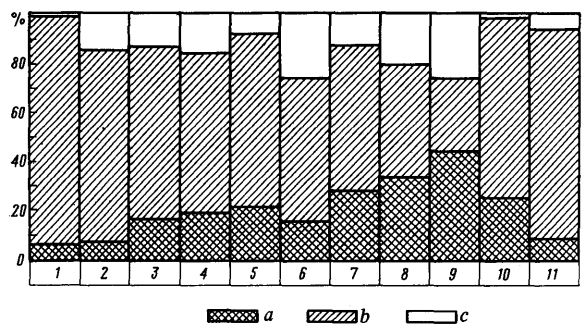


Figure 5. Material balance—(*a*) coke; (*b*) distillate; (*c*) gases—in the coking of: 1) petroleum; 2) mazut; 3) vacuum asphalt; 4) acid asphalt; 5) mazut from bituminous shales; 6) gas-works tar; 7) resin from gas-works tar; 8) coke-oven tar; 9) resin from coal tar; 10) beechwood tar; 11) stearin pitch.

Table 2. Physical constants of resinous coke.

Raw material	Density		Porosity, %	Hardness, s
	apparent	true		
Petroleum (Tyulenovskii)	0.75	1.23	39.0	180
Mazut from Tyulenovskii petroleum	0.84	1.50	44.6	190
Vacuum asphalt from Tyulenovskii petroleum	0.96	1.67	42.6	200
Acid asphalt	0.75	1.30	40.0	235
Mazut (from oil shales)	0.77	1.40	27.5	165
Gas-works tar	0.63	1.08	41.7	125
Resin from gas-works tar	1.01	1.53	33.4	300
Coal tar	0.99	1.74	43.0	170
Resin from coal tar	1.26	1.46	15.0	240
Beechwood tar	0.39	1.55	75.0	85
Stearin pitch	0.65	1.09	39.5	305

In order to elucidate the chemistry and the mechanism of the formation of coal-tar coke, systematic investigations have been made of the changes in properties and chemical composition of coal tar during its oxidative degradation and coking[47,48] (Figs. 6–8). The microstructure of the coke obtained at 450°C shows no significant changes from the initial material. A sharp change ensues at 500°C, when a bright, light-coloured coke is obtained which has strong anisotropy and a secondary structure. Such coke contains many round and oval pores. The most important physicochemical data on coal-tar coke are given in Table 3. This shows that compounds containing functional carboxyls undergo especially intense decarboxylation between 450° and 500°C, and the coal-tar coke obtained at 550°C no longer contains any carboxy-groups. The hydroxyl content increases, reaches a maximum at 500°, and falls to zero at 550°C. The hydroxy-groups are formed by the rupture of ether bonds and disappear as a result of polycondensation processes, which lead to formation of the coal-tar coke.

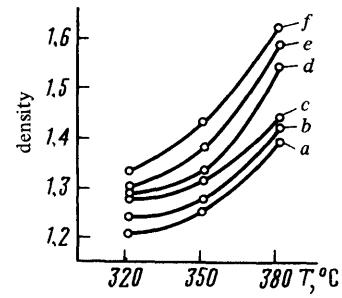


Figure 6. Temperature variation of density of pitch from (air flow, litres kg^{-1} h^{-1}/duration of heating, h): *a*) petroleum (20/3); *b*) vacuum asphalt (50/3); *c*) acid asphalt (80/3); *d*) mazut from oil shales (20/6); *e*) coke-oven tar (50/6); *f*) gas-works tar (80/6); *g*) semicoke tar.

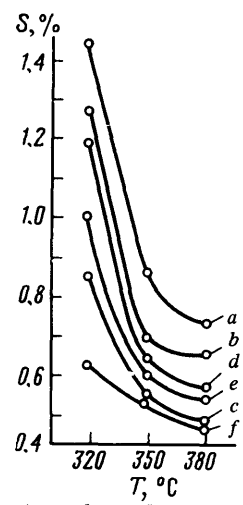


Figure 7. Temperature dependence of mean pitch content (units as in Fig. 6): *a*) 20/3; *b*) 50/3; *c*) 80/3; *d*) 20/6; *e*) 50/6; *f*) 80/6.

The course of such processes has been demonstrated by thermogravimetric examination of individual and high-molecular model compounds. The chemical structure of coal-tar coke is characterised by functional carbonyl groups, whose content steadily increases over the temperature range investigated, whereas they were not

detected at all in the original tar[48]. The infrared spectrum of the coal-tar coke obtained at 450°C shows a considerable weakening of bands in the range 770–960 cm^{-1}, and the maxima at 1450 and 1613 cm^{-1} almost disappear. This confirms that polycondensation of benzene rings has occurred.

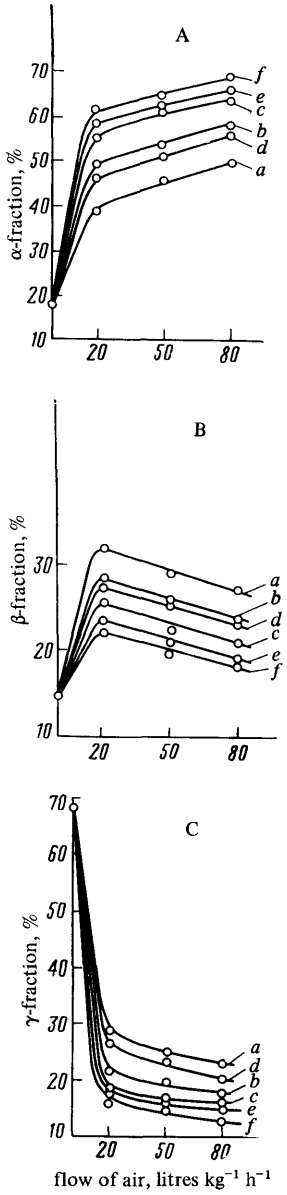


Figure 8. Effect of flow of air on contents of different fractions in the pitch for different temperatures (°C) and durations of heating (h): *a*) 320/3; *o*) 320/6; *c*) 320/9; *d*) 350/3; *e*) 350/6; *f*) 380/3.

The investigations have shown that the yield of coal-tar coke, its apparent and true densities, and its hardness increase with the molecular mass and the proportion of compounds containing a fused aromatic system (asphaltenes, carbenes, etc.) among the products undergoing coking. Pores are formed between 450° and 500°C to give a coal-tar coke varying in porosity from 15 to 75%, also depending on the chemical composition of the products. Formation of a coal-tar coke involves the decarboxylation of existing carboxy-groups with the gradual formation of new hydroxy-groups (with a maximum at 450°C) as a result of rupture of existing ether groups and the polycondensation of hydroxy-groups. Carbonyl groups, whose content increases with rise in temperature, are characteristic of the chemical structure of coal-tar coke.

Table 3. Physicochemical parameters of resinous coke obtained at various temperatures.

Analytic results	Final coking temperature, °C		
	450°	500°	550°
Yield of volatiles, %	18.30	10.40	6.35
Elementary composition, %:			
carbon	86.30	90.40	93.95
hydrogen	3.60	2.95	1.90
oxygen	6.67	2.52	0.26
sulphur	0.94	1.41	1.09
nitrogen	2.49	2.72	2.80
Functional oxygen groups, mg-equiv. g^{-1}			
hydroxy	0.12	0.23	0.00
carboxy	0.17	0.01	0.00
carbonyl	0.18	0.44	0.51

4. PLASTIC STATE, CAKING, AND DEGREE OF METAMORPHISM

Investigations of the plastic state and the caking of coals with different degrees of metamorphism[49-51] have yielded very interesting results contributing to a general theoretical explanation of the processes involved in coking. Several specimens of coal were selected from the Balkan coal-field. Pyrolysis results showed that the yield of volatile substances varied between 40.7% and 13.7% with a plastic layer varying in thickness from 23 mm to zero. Petrological analysis showed[52] that vitrinite predominated (69–76%) in the initial coals, the inertinite content varied from 8% to 12%, and very little exinite (trace to 1%) was present.

The variation in petrogaphic composition observed during the step-by-step coking of gas coal from the Lev mine showed that the vitrinite (the main mass) remained homogeneous and isotropic (up to 400–430°C). A secondary pitted structure was detected in it at 470°C, it acquired a bright greyish-white colour, and above 600°C pleochroism and anisotropy developed. The cuticles began to change even before appearance of the plastic state (400–430°C), gradually becoming thinner and difficult to detect, and they finally disappeared at 470°C. Fusain and semifusain remained unchanged even at 625°C: they played no active part in formation of the plastic phase or in caking of the coal. Between 570° and 625°C the boundaries separating these inert ingredients from the main vitrinised mass began to become obscure.

Single pores already begin to appear at 400°C, but pore formation becomes especially intense from 470° to 500°C, when the plastic phase passes into a semicoke phase.

The percentage content of pores is especially high at 570–625°C, when closely situated, large, and mostly shapeless pores are observed, probably formed by the coalescence of several smaller pores.

The coking of a fat coal releases a considerable quantity of liquid products up to 400°C, and thermal degradation is largely complete by 460°C (Fig. 9*A*). The plastic phase formed is of low viscosity and exerts a great resistance (up to 1320 mmH_2O) to gases passing through it (curve *1* in Fig. 9*A*). Pyrolysis becomes especially intense between 400° and 430°C, with maximum evolution of volatile products (curve *2*). The quantity of gases able to diffuse through the plastic phase is considerably smaller than the total quantity evolved, so that pores already begin to form at 400°C. Larger pores are produced by the union of small pores separated by thin walls of softened plastic material (Fig. 10*a*). Hardening of the plastic phase at 452°C coincides with the maximum of a large endothermic effect (Fig. 9*A*, curve *4*). It is significant that formation of a solid semicoke phase from the softened coal coincides with a maximum increase in carbonyl groups (curve *7*). It had earlier been found that these functional groups are especially characteristic also of the chemical structure of coal-tar coke. When heated above 600°C coal forms a coke possessing clearly defined anisotropic properties (Fig. 10*b*).

In the pyrolysis of a typical coking coal thermal degradation and the appearance of liquid products ensue at considerably higher temperatures, so that the initial softening is observed at 403°, and hardening of the plastic phase at 470°C (Fig. 9*B*). The maximum resistance offered by this mass to diffusing gases is considerably smaller (curve *1*). Hardening of the plastic phase is in this case accompanied by a well defined endothermic effect (curve *4*). The quantity of carbonyl groups also increases, as is indicated by the well-defined maximum (0.76 mg-equiv. g^{-1}) at 500°C, lying within the range of the newly formed solid semicoke phase (curve *7*).

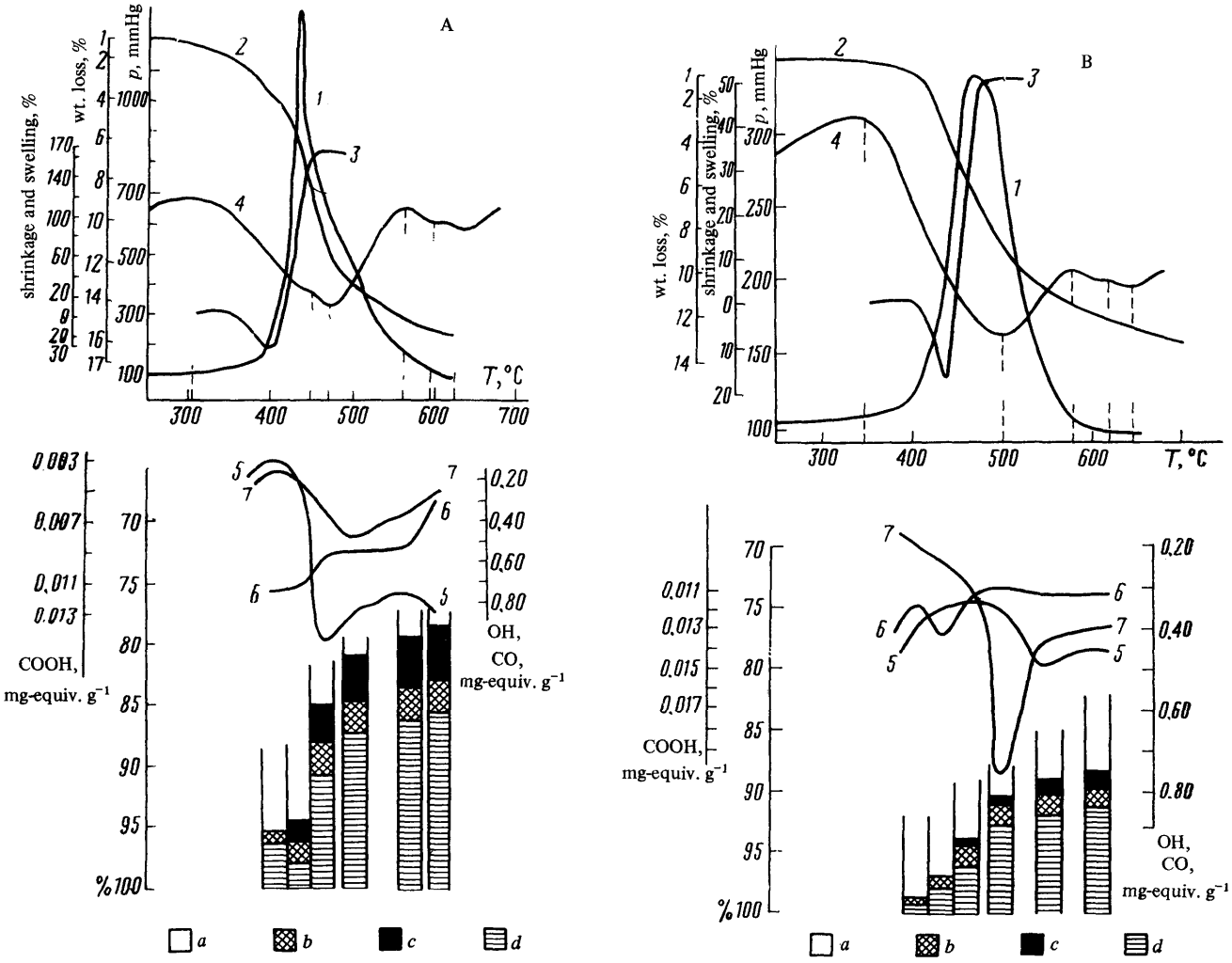


Figure 9. Investigations of plastic state of: A) fat coal from Kachulka mine; B) coking coal from Sheshkingrad mine: 1) Foxwell curve; 2) thermogravimetric curve; 3) dilatometric curve; 4) differential curve; 5) carboxy-groups; 6) hydroxy-groups; 7) carbonyl groups; *a*) semicoke; *b*) pyrogenous water; *c*) coal tar; *d*) gas.

The processes involved in the thermal degradation of, the appearance of a plastic phase in, and the caking of a fat and coking coal are clearly presented in Fig. 11. At every stage the individual phases undergo complicated pyrolytic processes associated with the formation of new products—solid (S), liquid (L), and gaseous (G)—which yield the corresponding phases of the subsequent stage. Fusain and semifusain do not pass into a plastic state, and are occluded directly into the solid coke phase. Hardening of the plastic phase is associated with the appearance of an endothermic effect, whose maximum coincides with the maximum increase in carbonyl groups. Pore formation begins approximately at 400°, and is especially intense between 470° and 500°C. Thermal degradation involves rupture of ether, ester, and other bonds, with the production of exceptionally reactive compounds of low and high molecular weight, which undergo complicated polymerisation and polycondensation processes leading to gradual formation of the continuous three-dimensional structure of high-temperature coke.

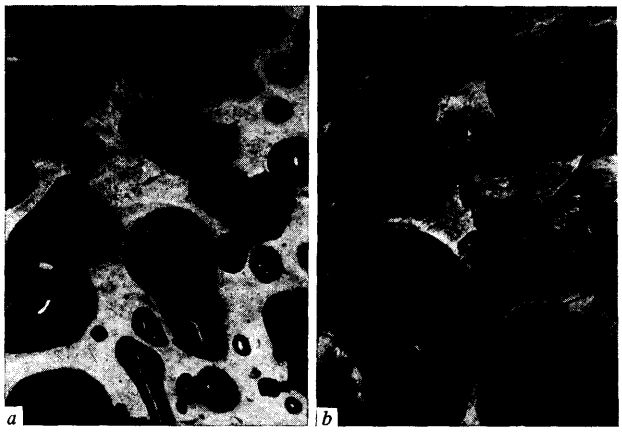
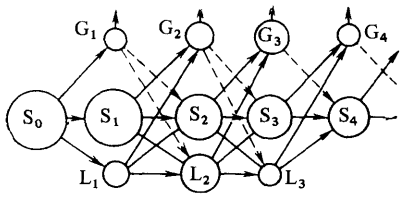


Figure 10. Photomicrographs (× 175) of structure of: *a*) semicoke obtained at 550°C; *b*) coke obtained at 750°C.



S_0	S_1	S_2	S_3	S_4
Initial coal	Start of softening, °C	Plastic state, °C	Max. plasticity, °C	Formation of solid phase, °C.
Fat	350	415	435	500
Coking	403	440	465	550

Figure 11. Thermal degradation, appearance of plastic phase, and caking.

5. COKING OF COAL–OIL MIXTURES

The value and the role of liquid products in the appearance of a plastic phase and the formation of coke were revealed by a study of the coking of mixtures of a weakly caking lean coal with various petroleum, tarry, and resinous products[53–57]. Table 4 gives some of the characteristics of the crucible coke obtained. These investigations show how great an influence the chemical composition and the quantity of liquid additives have on the appearance, density, porosity, hardness, and other properties of coke.

Table 4. Characteristics of crucible coke from weakly caking coal with various additives.

Additive	Density		Porosity, %	Hardness, s
	apparent	true		
None	0.56	1.78	68.6	27
Stearin pitch	0.55	1.66	66.8	84
Coke tar	0.32	1.77	81.9	19
Gas-works tar	0.56	1.73	67.6	45
Anthracene oil	0.52	1.71	69.6	37
Petroleum	0.55	1.93	71.5	30
Semicoke tar	0.63	1.74	63.9	35
Acid asphalt	0.51	1.77	71.2	36
Mazut	0.56	1.65	66.1	19
Coke-oven tar (8%)	0.52	1.77	70.8	27
Coke-oven tar (14%)	0.46	1.72	74.6	25
Coke-oven tar (25%)	0.40	1.69	76.4	23
Coke-oven tar (33%)	0.32	1.74	79.9	18
Coke-oven tar (40%)	0.29	1.79	83.8	10
Coke-oven tar (45%)	0.24	1.73	86.1	—

Especially interesting results were obtained in plastometric investigations of mixtures of a weakly caking coal with additions of 5%, 10%, and 15% of petroleum and tar products. Several plastometric curves are shown in Fig. 12, while Table 5 gives the plastometric parameters (x and y) and the strength of the coke obtained from these mixtures. The relation between the quantity x (%) of additives and the thickness y (mm) of the plastic layer can be represented approximately by the equation

$$y = a \cdot x^2 + b \cdot x + c .$$

Such an equation enables us to calculate the quantity of an additive necessary to convert a given weakly caking, lean coal into a coking or fat coal (Fig. 12).

The heavier is an additive and the richer in asphaltic–resinous compounds, the smaller the quantity required to obtain a plastic layer of maximum thickness. Coke-oven tar changes not only the thickness but also the temperature limits within which the plastic layer appears (Fig. 12), which occurs at considerably lower temperatures (360–460°C) on the addition of 10–15% of this material. The addition of gas-works and beechwood tars has no significant effect on the thickness of the plastic layer or on the temperature range of its formation.

Excessive increase of the additives causes intense cracking of the coke, so that its strength diminishes (Table 5). The optimum quantity of additives increases the strength of the coke by factors of 2–4. The strength is diminished by the addition of beechwood tar, which can be attributed to the large quantity of oxygen compounds present in such tar[58].

In order to establish the effect of the chemical and fractional composition of additives on the thickness of the plastic layer and the strength of the coke, coke-oven and gas-works tars were fractionally distilled, and the fractions isolated (10%) were added to a weakly caking coal (Table 6).[59] It was found that the addition of fractions rich in phenols (42–55%) and in naphthalene (80%) caused the plastic layer to break down, and an unstable coke was obtained. The thermogravimetric coking of model compounds has established[35] that naphthalene has escaped almost completely by 210°C (Fig. 1*b*), and cannot influence either formation of the plastic phase or caking. The greatest influence on the increase in the plastic phase and the strength of the coke is exerted by residues of coke-oven and gas-works tars rich in asphthaltic–resinous substances boiling above 350°C.

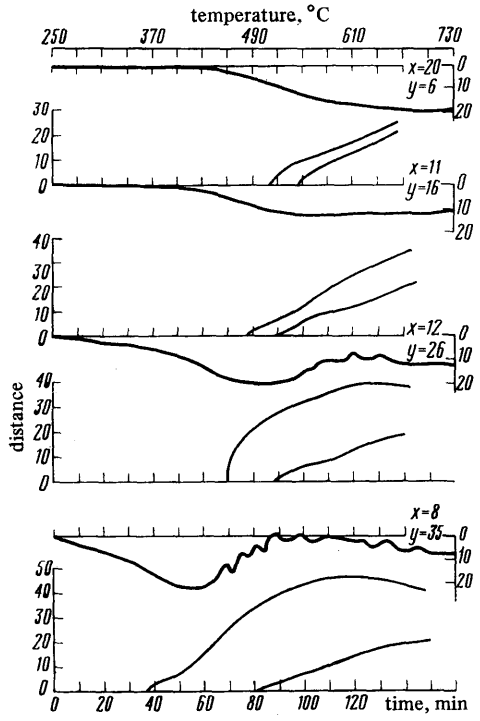


Figure 12. Plastometric curves of coal with various percentages of coke-oven tar: *a*) 0; *b*) 5; *c*) 10; *d*) 15.

Investigations of the coking of model mixtures of a weakly caking coal with various types of tar and fractions thereof revealed the mechanism of caking and coking[60,61]. On the addition of coke-oven tar and its resin the coal is readily dissolved and dispersed in silica-gel resins and asphaltenes, which leads to a great increase in the plastic layer, as a consequence of which the resulting coke is fused, light grey, and lustrous. Gas-works tar and the resin from it hardly affect the thickness of the plastic layer, since coal is insoluble in the petrolenes and kerogens that predominate in its composition. The coke obtained by cementation is grey and dull. Despite the differences in the physical processes accompanying formation of the coke, its strength is almost the same. It has thus been demonstrated that coke formation involves the dissolution and dispersion of coal and the cementation of particles of the resinous coke.

Table 5. Plastometric indices and strength of coke from coal with various additions.

Addition	Plastometric parameters, mm		Strength of coke, kg cm^{-2}	Addition	Plastometric parameters, mm		Strength of coke, kg cm^{-2}
	x	*y*			*x*	*y*	
None	20	6	39	Coke-oven tar (5%)	11	16	49
Mazut (5%)	21	10	44	Coke-oven tar (10%)	12	26	79
Mazut (10%)	19	11	64	Coke-oven tar (15%)	8	35	71
Mazut (15%)	12	12	52	Gas-works tar (5%)	22	7	25
Vacuum asphalt (5%)	20	13	48	Gas-works tar (10%)	17	8	33
Vacuum asphalt (10%)	30	13	55	Gas-works tar (15%)	18	10	35
Vacuum asphalt (15%)	12	12	50	Beechwood tar (5%)	35	5	39
Acid asphalt (5%)	21	12	55	Beechwood tar (10%)	42	7	32
Acid asphalt (10%)	21	17	80	Beechwood tar (15%)	39	7	13
Acid asphalt (15%)	18	12	44				

Table 6. Effect of tar fractions on plastometric parameters and strength of coke.

Type and fractional composition		Plastometric parameters, mm		Strength of coke, kg cm^{-2}
tar	temp. range, °C	*x*	*y*	
Coke-oven	⩽180	31	10	141
Ditto	180—220	51	0	80
»	220—250	25	0	85
»	250—300	32	19	135
»	300—360	18	32	153
»	>360	17	35	203
Gas-works	⩽230	29	0	disintegrates
Ditto	230—300	47	17	186
»	300—350	30	19	196
»	>350	25	20	364

6. CAKING OF LIGNITES AND COKING OF MIXTURES OF COAL AND BROWN COAL WITH OILY ADDITIVES

All brown coals are non-caking, so that they do not form a monolithic coke residue. Karavaev[62] found that Bulgarian lignites showed a slight tendency to cake, which he explained by an increased content of bitumens and sulphur. Investigation of Eastern Maritsa lignitic coal[63–68]

established that only xylite and vitrinised lignite are capable of caking, independently of the sulphur content. The differential thermal curves of these components (Fig. 13) clearly show that thermal degradation processes are closely similar in caking xylite and vitrinised lignite, but differ significantly from processes in which a caked coke residue is not formed.

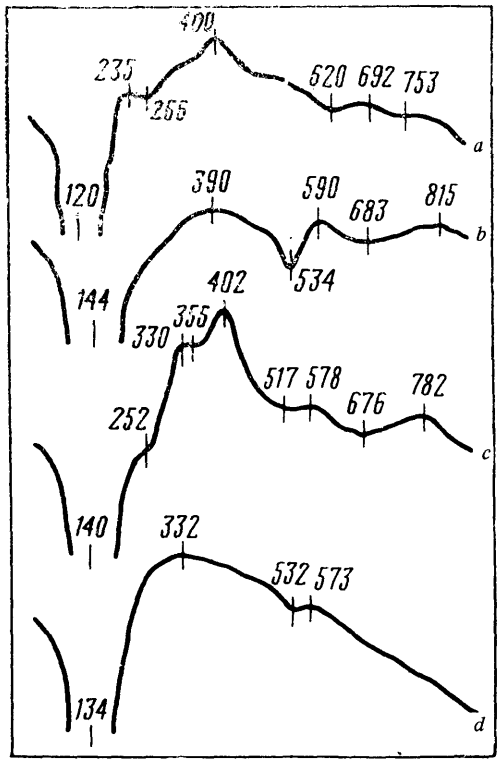


Figure 13. Differential thermal curves of: *a*) xylite; *o*) earthy mass; *c*) vitrinised lignite; *d*) fusinite.

Xylite was subjected to a combined chemical analysis[69,70] to reveal the reason for its caking. Fig. 14 gives differential thermal curves for the debituminised xylite, the residual carbon, and the humic acids liberated. The formation of a caked coke residue from the debituminised xylite (from which 16.2% of bitumens had been isolated) shows that caking is not due to the presence of bitumens. The humic acids yield a well caked crucible coke, whereas the residual coal forms an uncaked coke. This shows that the humic acids are responsible for the tendency of xylite to cake. Extraction of the humic acids leads to fundamental changes in the structure of the organic mass, involving loss of caking power, as is shown by the differential thermal results (*c* and *d* in Fig. 13).

Many investigators in various countries have worked on the use of brown coals to extend the raw-materials base of the coal-tar chemical industry. Our own researches have established the great importance of the age, origin, and previous heat-treatment of brown coals for the physicomechanical properties of the mixed coke[71-76]. A young lignitic coal, a shiny old brown coal, and a bituminous humic–sapropelic coal were used. The results show that replacing a lignitic coal by its semicoke improves the strength of the mixed coke. The best results were given by a semicoke obtained at 400°C, from which 12% of volatiles were isolated (Table 7).

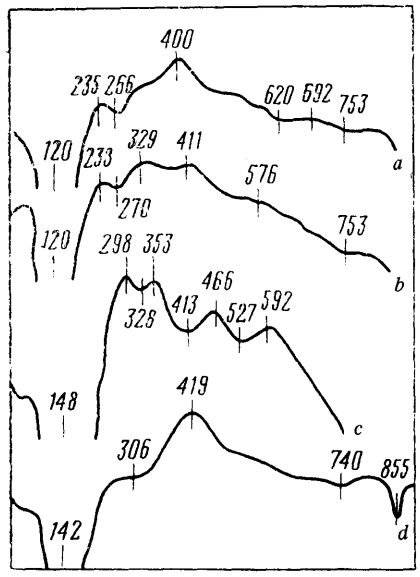


Figure 14. Differential thermal curves of: *a*) initial xylite; *b*) after evolution of bitumens; *c*) humic acids; *d*) isolated humic acids.

Table 7. Effect of semicoking temperature of lignitic coal on plastometric characteristics and strength of coke.

Mixture	Composition, %		Plastometric parameters, mm		Strength of coke, kg cm^{-2}
			x	*y*	
A	Lignites	100	54	0	—
B	Lignites	90	38	0	—
	coke-oven tar	10			
C	Coking coal	100	25	14	107
D	Coking coal	90	12	28	165
	coke-oven tar	10			
E	Coking coal	70			
	coke-oven tar	10	47	10	190
	lignites	20			
F	Coking coal	70			
	coke-oven tar	10	44	16	437
	semicoke from lignite (350°C)	20			
G	Coking coal	70			
	coke-oven tar	10	48	13	473
	semicoke from lignite (400°C)	20			
H	Coking coal	70			
	coke-oven tar	10	44	21	233
	semicoke from lignite (450°C)	20			
I	Coking coal	70			
	coke-oven tar	10			
	semicoke from lignite (510°C)	20	49	12	320

Analogous investigations with other brown coals[77,78] showed that a stronger mixed coke is formed when the older, bright brown coals are used without the addition of coke-oven tar. If the brown coals are replaced by the semicoke from them, a less stable mixed coke is formed.

When 10% of coke-oven tar is added to the charge, replacement of the coal by the semicoke almost doubles the strength of the mixed coke. A similar rule has been established also for a young lignitic coal. Replacing bituminous humous–sapropelic coals by semicoke produces no significant impairment of the strength of the mixed coke, independently of whether or not the charge contained a coke-oven tar.

Table 8. Physicomechanical characteristics of mixed coke.

Composition of mixture, %				Properties			
coking coal	brown coal	semicoke from brown coal	coke-oven tar	gas permeability Γ	total strength π	abrasion resistance π_{ab}	crushing strength π_{cr}
					kg rev. dm^{-2}		
100	—	—	—	277	19.7	114.0	22.4
young lignitic coal							
80	20	—	—	204	7.4	12.5	14.3
70	20	—	10	211	10.9	19.4	25.0
70	—	20	10	250	30.2	58.0	63.0
old bright brown coal							
80	20	—	—	229	25.9	82.5	3.8
70	20	—	10	271	6.0	197.0	6.2
70	—	20	10	263	18.7	95.0	23.3
bituminous humic-sapropelic brown coal							
80	20	—	—	225	8.3	33.4	11.0
70	20	—	10	278	11.6	58.1	1.5
70	—	20	40	234	7.7	3.8	8.1

The coking of ternary mixtures in a Nikolaev laboratory furnace showed (Table 8) that the addition of 20% of young humic lignites to a coking coal sharply impairs the characteristics of the mixed coke (gas permeability $\Gamma = 204$), which cannot be appreciably improved even after the addition of 10% of coke-oven tar ($\Gamma = 211$). If semicoke with the same content of oils in the charge is added instead of the lignitic coal, the gas permeability of the mixed coke is considerably increased, reaching 250, while other strength parameters are improved two- to three-fold. The strength characteristics Π and Π_{cr} even exceed the corresponding values for coke obtained from 100% coking coal. A test on the effect of additions of xylitic coal from the Chukurov mine[79] fully confirmed the rule.

If 20% of an older brown coal is added to a coking coal, a mixed coke of very poor physicomechanical characteristics is obtained. However, the quality of the mixed coke can be considerably improved by adding 10% of coke-oven tar, when the gas permeability is changed from 229 to 271, and both the abrasion resistance and the crushing strength are approximately doubled. Replacement of the brown coal by its semicoke leads to some decrease in gas permeability and to increases in total and crushing strengths. A sharp improvement in all the characteristics of the coke is observed if the young humic lignite is replaced by its semicoke.

The addition of 20% of a bituminous humic–sapropelic coal to a coking coal impairs all the physicomechanical characteristics of the mixed coke, and they cannot be improved by the addition even of 10% of coke-oven tar. It is interesting that replacement of this brown coal by its semicoke produces a sharp deterioration both in the gas permeability coefficient and in the strength characteristics of the mixed coke. This confirms the great value of bitumens of humic–sapropelic brown coal in caking. Coke-oven tar pitch, mazut, and vacuum and acid asphalts were also tested as additives[79]. The results showed that bitumens are as important in caking and coking as are brown coal and its semicoke.

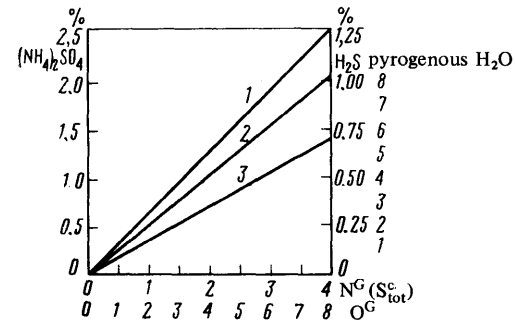


Figure 15. Graph for calculating, from the nitrogen, sulphur, and oxygen contents, the percentage yields of: 1) ammonium sulphate; 2) hydrogen sulphide; 3) "pyrogenous water".

Table 9. Physicochemical and structural properties of coke.

Property characteristic	Soviet coals		Bulgarian coals	
	gas	mixed fat	mixed coking	mixed
I. Chemical composition				
1. Moisture, %	0.30	1.75	1.09	1.70
2. Ash, %	12.90	10.29	12.05	20.45
3. Total sulphur, %	0.79	1.76	1.52	1.65
4. Volatiles, %	1.86	1.94	2.33	3.06
II. Physicomechanical				
1. Gas permeability	239	281	277	—
2. Total strength π, kg rev. dm^{-2}	11.0	10.5	14.1	1.7
3. Abrasion resistance π_{ab}	75.0	75.0	35.8	—
4. Crushing strength π_{cr}	10.8	113.0	24.7	—
5. Class > 40 mm, %				
after 150 rev.	71.0	87.3	88.0	18.0
after 300 rev.	65.0	76.1	81.8	0.0
6. Class < 10 mm, %				
after 150 rev.	9.5	12.7	12.0	80.0
after 300 rev.	11.2	10.9	18.2	100.0
7. Specific surface, m^2 g^{-1}	32	28	38	42
III. Structural				
1. Density	0.809	0.632	0.770	0.841
2. Porosity	86.6	65.5	87.4	96.6
3. Cellularity	83.4	76.0	88.6	90.6
4. Mean pore size, mm	0.258	0.378	0.141	0.074
5. Mean wall thickness, mm	0.078	0.105	0.058	0.054

7. YIELDS OF CHEMICAL PRODUCTS FROM COAL–PROPERTIES AND STRUCTURE OF COKE

The theoretical investigations of caking and coking enabled formulae to be deduced for calculating the yields of chemical products[80–83] and for predicting the qualitative indices and the physical structure of the resulting coke[84–90]. Examination of the coking of individual types of coals and their mixtures has established graphical relations (Fig. 15) and formulae for calculating the yields of ammonium sulphate, hydrogen sulphide, and pyrogenous water as functions of the contents of nitrogen, sulphur, and oxygen in the original coal[90,91]. Table 9 lists the most important physicochemical and structural indices of the coke obtained in these investigations[92].

Box coking[93,94] has been based on preliminary experiments on the use of Scheffe's simplex-grid plan for predicting the properties of coke. The scheme of experiments is shown in Fig. 16, and the results are listed in Table 10. Mathematical processing of the data on an electronic computer has given the equations below for calculating the most important chemical and structural characteristics of the coke.

1. For the ash (A^c,%)

$$Y_1 = 13.44X_1 + 20.32X_2 + 10.79X_3 + 22.8X_1X_2 + 0.86X_1X_3 + 0.22X_2X_3 + 2.4X_1X_2 \cdot (X_1 - X_2) + 4.2X_1X_3(X_1 - X_3) - 0.13X_2X_3(X_2 - X_3) - 8.8X_1X_2 \times (X_1 - X_3)^2 - 6.2X_1X_3(X_1 - X_3)^2 + 12.9X_2X_3(X_2 - X_3)^2 + 92.8X_1^2X_2X_3 + 47.1X_2X_3 - 1.7X_2X_3^2.$$

2. For the total sulphur in the coke (A^a, total %)

$$Y_2 = 1.03X_1 + 1.87X_2 + 2.16X_3 - 0.08X_1X_2 - 0.14X_1X_3 - 0.06X_2X_3 - 1.01X_1X_2(X_1 - X_2) + 0.08X_1X_3(X_1 - X_3) - 0.93X_2X_3(X_2 - X_3) + 1.49X_1X_2 \times (X_1 - X_2)^2 - 1.47X_1X_3(X_1 - X_3)^2 + 9.52X_1^2X_2X_3 + 0.88X_2X_3(X_2 - X_3)^2 - 3.92X_1X_2^2X_3 (8; 38X_1X_2X_3^2).$$

3. For M_{40} in micuum drum

$$Y_3 = 67.0X_1 + 50.0X_2 + 77.0X_3 + 8.0X_1X_2 + 12.8X_1X_3 + 48.0X_2X_3 + 34.7X_1X_2 \times (X_1 - X_2) - 12.8X_1X_3(X_1 - X_3) - 1.1X_2X_3(X_2 - X_3) + 10.7X_1X_2(X_1 - X_2)^2 - 49.1X_1X_3(X_1 - X_3)^2 - 13.9X_2X_3(X_2 - X_3)^2 - 462.5X_1^2X_2X_3 + 635X_1X_2^2X_3 + 54.8X_1X_2X_3^2.$$

4. For M_{10} in micuum drum

$$Y_4 = 8.0X_1 + 43.8X_2 + 8.3X_3 - 15.2X_1X_2 + X_1X_3 + 69.0X_2X_3 - 9.6X_1X_2 \times (X_1 - X_2) + 18.9X_1X_3(X_1 - X_3) - 16.2X_2X_3(X_2 - X_3) + 43.2X_1X_2(X_1 - X_2)^2 + 46.1X_1X_3(X_1 - X_3)^2 + 56.3X_2X_3(X_2 - X_3)^2 + 262.1X_1^2X_2X_3 - 320.1X_1X_2^2X_3 + 55.4X_1X_2X_3^2.$$

5. For the structural strength

$$Y_5 = 79.8X_1 + 68.4X_2 + 80.1X_3 + 5.4X_1X_3 - 2.4X_1X_2 + 32.2X_2X_3 + 89.6X_1X_2 \times (X_1 - X_2) - 2.9X_1X_3 - X_3 - 14.1X_2X_3(X_2 - X_3) - 258.1X_1X_2(X_1 - X_2)^2 + 4.0X_1X_3(X_1 - X_3)^2 - 96.8X_2X_3(X_2 - X_3)^2 + 354.3X_1^2X_2X_3 - 66.6X_1X_2^2X_3 - 186.3X_1X_2X_3^2.$$

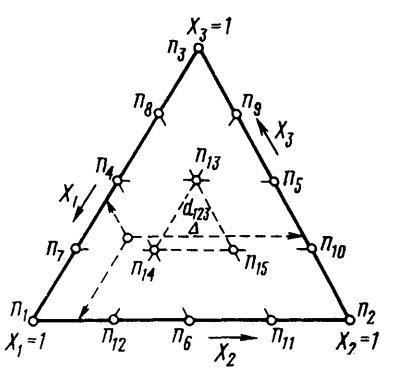


Figure 16. Plan of box experiments used to obtain a fourth-power model.

The equations were checked for five points in Fig. 16: one of the points lies at the centre of the diagram ($X_1 = X_2 = X_3 = 0.333$), while the others correspond to the compositions of the coal charges which are promising for the by-product coke plant at the Kremikovtsy mining complex. Values calculated for M_{40} by means of Eqn. Y_3 differ from the experimental values by ±1.5%, and those for M_{10} (from Eqn. Y_4) by ±1.0% (absolute). Very good agreement was obtained also for the ash, total sulphur, and structural strength.

Table 10. Results of planned experiments.

Ash A^c, %	Total sulphur S_{tot}, %	Micuum drum, %		Structural strength, %	Ash A^c, %	Total sulphur S_{tot}, %	Micuum drum, %		Structural strength, %
		M_{40}	M_{10}				M_{40}	M_{10}	
13.44	1.03	67.0	8.0	79.8	13.75	2.16	78.7	8.4	80.0
20.32	1.87	50.0	43.8	68.4	18.49	1.87	85.0	23.1	71.5
10.79	2.16	77.0	8.3	80.1	18.39	1.81	53.0	36.8	50.3
12.33	1.56	75.2	8.4	81.3	15.40	1.20	68.0	17.1	72.8
15.50	1.97	75.5	8.8	82.3	15.05	1.68	78.0	9.4	80.8
17.45	1.45	60.5	24.6	73.5	16.77	1.50	69.4	15.2	83.7
13.04	1.21	68.4	12.2	80.8	17.93	1.78	74.4	14.8	72.5
10.93	1.75	75.8	8.8	81.5					

REFERENCES

1. F. Muck, "Grundzüge und Ziele der Steinkohlenchemie", Bonn, 1881.
2. O. Rao, Stahl und Eisen, 1910, p. 1240.
3. O. Simmersbach, Stahl und Eisen, 1904, p. 32.
4. O. Simmersbach, "Grundlagen der Kokschemie", Breslau, 1914.
5. F. Fischer, H. Broche, and J. Strauch, Brennstoff-Chem., 5, 299 (1924).
6. J. Massinon, Bull. Soc. belge Ing. ind., 20, 1218 (1935).
7. H. Lefevre, Chimie et Industrie, No. 229, 124 (1932).
8. K. Shishkin, Koks i Khimiya, No. 4, 16 (1934).
9. K. Fujimura, Soc. Chem. Ind. Japan, 35, 201 (1930).
10. H. Landau and R. Asbury, Ind. Eng. Chem., 30, 117 (1938).
11. E. Berl and W. Körben, Ind. Eng. Chem., 32, 1605 (1940).
12. J. van der Valden, Fuel, 6, 252 (1927).
13. E. Kester and F. Schneider, Ind. Eng. Chem. (Anal.), 6, 98 (1934).
14. A. Duparque and J. Massinon, Chimie et Industrie, 42, 36 (1938).
15. S. Illingworth, J. Soc. Chem. Ind., 33, 133 (1920).
16. R. Mott, Fuel, 12, 412 (1933).
17. L. M. Sapozhnikov, "Kamennye Ugli i Metallurgicheskii Koks" (Coals and Metallurgical Coke), Izd. Akad. Nauk SSSR, Moscow, 1941.
18. V. N. Yakovlev, Khim. Tverd. Topliva, 29, 2 (1968).
19. B. A. Onusaitis, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 7 (1947).
20. S. G. Aronov, Zhur. Prikl. Khim., No. 9 (1952).
21. K. S. Permitina, Trudy Lab. Geol. Uglya, 6, 144 (1956).
22. D. M. Shapiro, Koks i Khimiya, No. 6, 16 (1957).
23. V. F. Kustov, Trudy Leningrad. Tekhnol. Inst., No. 51, 5 (1959).
24. E. Audibert, Rev. Ind. min., No. 126, 218 (1926).
25. S. I. Panchenko and I. K. Klopotov, Koks i Khimiya, No. 3, 6 (1959).
26. L. L. Nesterenko, M. G. Sklyar, and Yu. V. Tyutyunikov, Koks i Khimiya, No. 9, 15 (1960).
27. G. Angelova and L. Lazarov, Izv. Inst. Obshch. Neorg. Khim. Bulgarsk. Akad. Nauk, 3, 335 (1965).
28. K. P. Medvedev, Koks i Khimiya, No. 6, 16 (1962).
29. G. K. Petrik, Koks i Khimiya, No. 5, 24 (1964).

30. L. L. Nesterenko, M. G. Sklyar, and V. I. Shubnikov, Koks i Khimiya, No. 1, 4 (1965).
31. S. I. Panchenko, Koks i Khimiya, No. 6, 1 (1965).
32. A. G. Rembashevskii and A. M. Kisina, Khim. Tverd. Topliva, No. 4, 26 (1967).
33. O. Simmersbach, "La Chimie du Coke", Paris, 1924.
34. M. D. Tilicheev, "Khimiya Krekinga" (Chemistry of Cracking), GTTI, 1942.
35. D. Rustschev, J. Thermal Analysis, **2**, 337 (1970).
36. A. F. Krasyukov, "Neftyanoi Koks" (Petroleum Coke), Moscow, 1966.
37. Kh. Pikhler, V. Riperger, and D. Ruschev, Khim. i Ind., No. 6, 264 (1970).
38. D. Rustschev, "Proceedings of the Third International Thermal Conference", Davos, 1971.
39. D. Ruschev, Khim. i Ind., No. 1, (1958), p. 11.
40. D. Ruschev, Tekhnika, No. 6, 26 (1956).
41. D. Ruschev, Tekh. Prom., No. 12 (1956), p. 33.
42. D. Ruschev, Tekh. Prom., No. 2 (1958), p. 31.
43. M. Gerasimov, G. Pankov, D. Ruschev, and Zh. Kalinov, Godishnik KhTI (Sofia), **4**, No. 2, 125 (1957).
44. M. Gerasimov, D. Ruschev, and K. Slavomirov, Erdöl u. Kohle, **13**, 32 (1960).
45. M. Gerasimov and D. Ruschev, Khim. i Ind., No. 5, 140 (1959).
46. D. Ruschev, Erdöl u. Kohle, **14**, 542 (1961).
47. D. Ruschev, G. Shopov, P. Dragostinov, V. Konstantinova, and P. Nankova, Erdöl u. Kohle, **20**, 19 (1967).
48. D. Ruschev, P. Dragostinov, V. Konstantinova, and G. Shopov, Khim. i Ind., No. 3, 91 (1965).
49. D. Ruschev, P. Dragostinov, V. Konstantinova, and G. Shopov, Brennstoff-Chem., **46**, 11 (1965).
50. D. Ruschev, G. Shopov, P. Dragostinov, V. Konstantinova, and D. Minkov, Brennstoff-Chem., **48**, 235 (1967).
51. D. Ruschev, G. Shopov, V. Konstantinova, P. Dragostinov, and D. Minkov, Brennstoff-Chem., **50**, 310 (1969).
52. M. T. Makovska, V. Pikardt, and D. Ruschev, Khim. i Ind., No. 1, 5 (1968).
53. D. Mirev and D. Ruschev, Godishnik KhTI (Sofia), **4**, No. 1, 25 (1957).
54. D. Mirev and D. Ruschev, Godishnik KhTI (Sofia), **5**, No. 1, 1 (1958).
55. D. Mirev and D. Ruschev, Godishnik KhTI (Sofia), **5**, No. 1, 19 (1958).
56. D. Ruschev, Erdöl u. Kohle, **14**, 542 (1961).
57. D. Mirev and D. Ruschev, Brennstoff-Chem., **40**, 289 (1959).
58. D. Ruschev, Koks i Khimiya, No. 5, 11 (1959).
59. Z. Dubinina and D. Ruschev, Izv. Akad. Nauk SSSR, Metallurgiya i Toplivo, No. 6, 168 (1959).
60. D. Ruschev, "VIII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Sektsiya Khimii i Khimicheskoi Tekhnologii Topliva. Referaty Dokladov" (Eighth Mendeleev Congress on General and Applied Chemistry, Fuel Chemistry and Chemical Technology Section—Abstracts of Papers), 1959, No. 9, p. 65.
61. D. Ruschev, Compt. rend. Acad. bulg. Sci., **12**, 57 (1959).
62. N. Karavaev, Khim. Tekhnol. Topliva Masel, No. 1, 13 (1957).
63. D. Ruschev, Paliva, **45**, 193 (1965).
64. D. Ruschev and V. Konstantinova, Godishnik KhTI (Sofia), **9**, No. 1, 143 (1962).
65. D. Ruschev and V. Konstantinova, Compt. rend. Acad. bulg. Sci., **16**, 281 (1963).
66. D. Ruschev and P. Dragostinov, Erdöl u. Kohle, **18**, 372 (1965).
67. D. Ruschev, Brennstoff-Chem., **47**, 22 (1966).
68. D. Ruschev, Chim. analyt., **45**, 572 (1963).
69. D. Ruschev and St. Mikhailov, Zhur. Prikl. Khim., **38**, 925 (1965).
70. D. Ruschev, "IX Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Referaty Dokladov i Soobshchenii" (Ninth Mendeleev Congress on General and Applied Chemistry—Abstracts of Lectures and Communications), 1965, No. 8, p. 113.
71. D. Mirev and D. Ruschev, Brennstoff-Chem., **43**, 46 (1962).
72. D. Mirev and D. Ruschev, Brennstoff-Chem., **43**, 324 (1962).
73. D. Mirev and D. Ruschev, Brennstoff-Chem., **44**, 139 (1963).
74. D. Ruschev, "Fifth International Conference on Coal Science", Cheltenham, 1963.
75. D. Ruschev, Godishnik KhTI (Sofia), **9**, No. 3, 9 (1962).
76. D. Mirev, D. Ruschev, and E. Vasileva, Izv. Inst. Obshch. Neorg. Khim. Bulgarsk. Akad. Nauk, **7**, 9 (1961).
77. D. Ruschev and V. Benev, Tekhnika, No. 2, 7 (1961).
78. D. Ruschev and V. Benev, Khim. i Ind., No. 5, 163 (1962).
79. D. Ruschev, M. Kurchatov, E. Bekyarova, and G. Shopov, Godishnik KhTI (Sofia), **4**, No. 3, 93 (1964).
80. R. Mott and C. Spooner, Fuel, **4**, 106 (1945).
81. S. G. Aronov, "Ispol'zovanie Gazovykh Uglei dlya Koksovaniya" (Use of Gas Coals for Coking), 1949.
82. W. Mantel, Brennstoff-Chem., **31**, 275 (1950).
83. H. Lawry, Chem. and Ind., 619 (1950).
84. V. Barskii, S. Gryaznov, and E. Zaitsev, Khim. Tverd. Topliva, No. 5, 149 (1968).
85. H. Scheffe, J. Roy, Statist. Soc., **13**, 344 (1958).
86. J. W. Corman and J. E. Hinman, Technometrics, **4**, 463 (1962).
87. N. Mikeshina, in "Novye Idei v Planirovanii Eksperimenta" (New Ideas in the Planning of Experiments), Nauka, Moscow, 1969.
88. W. Simmonis and G. Gnuschke, Glückauf-Forschungshefte, **27**, 181 (1966).
89. M.-T. Mackowsky and W. Simmonis, Glückauf-Forschungshefte, **30**, 25 (1969).
90. D. Ruschev, Godishnik VKhTI Sofia, **14**, No. 4, 449 (1971).
91. D. Ruschev, Godishnik VKhTI Sofia, **14**, No. 4, 469 (1971).
92. D. Ruschev and G. Shopov, Godishnik VKhTI Sofia, **16**, No. 2, 45 (1969); **17**, No. 1, 19 (1970); **19**, No. 1, 27 (1972).
93. G. Shopov, Candidate's Thesis, Sofia, 1973.
94. D. Ruschev, G. Shopov, and St. Stoyanov, Khim. Tverd. Topliva, No. 3, 9 (1973).

Department of Fuel Technology,
Institute of Chemical Technology,
Sofia, Bulgaria