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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Simulation of Degradation of Coal Organic Matter

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Abstract—The existing procedures for calculating thermodynamic functions of individual compounds of coal organic matter were analyzed, and possible reactions of its degradation were simulated. The possibility of the occurrence of pyrolysis reactions in the forward direction with the formation of methane, propane, and other saturated hydrocarbons as target products was examined by calculation of the Gibbs energies using an additive procedure for determining the thermodynamic functions of structural fragments and data on the composition of coal from Kuznetsk coal fields. The chemical and thermodynamic relationships between the starting compounds and pyrolysis products were examined, and the temperature intervals of the reactions were determined.

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The efficiency of coal utilization in the modern power engineering is about 20%, and in the coming years it is required to increase this parameter to 30–40% [1]. Therefore, it becomes necessary to use combined procedures for thermochemical transformation of coal, along with methods for increasing the efficiency of direct combustion of coal in combustion chambers of boilers.

This complex problem can be solved only by widely introducing procedures for thermochemical processing of coal, with the formation of a wide range of products that can be used in power engineering and industry. Gasification and pyrolysis of coal, performed both separately and in combination with each other, yield producer gas with a calorific value of 4000 to 20000 kJ kg^{-1} depending on the process conditions, and also coal tars and cokes. Producer gas is of the greatest interest for use in power engineering, as it can be used instead of natural gas in combustion chambers of gas turbine units (GTUs) or of steam boilers. However, wide use of coal-chemical processes in power engineering is hindered by the lack of reliable engineering procedures for calculating the pyrolysis and gasification processes.

In this study, the possibility of the occurrence of chemical reactions leading to formation of pyrolysis gas, coal tar, and coke as final products from the initial substances of the organic matter of coal (OMC) is evaluated by simulation of the OMC degradation process. Using the equations of known chemical reactions, it is possible to estimate the power expenditure for performing the process, and also the process parameters: temperature, pressure, and time. It will thus become possible to develop efficient flowsheets for preparing high-energy gas by thermochemical processing of coal.

Pyrolysis is one of procedures for thermochemical processing of coal. It occurs in the temperature range 120–1000°C. Pyrolysis occurs in the course of industrial processes of coal coking and semicoking. The mechanisms of these processes and the actually functioning systems are described in detail in [2]. However, these processes were mainly demanded by metallurgy and chemical technology, and therefore the major goal was improving the quality of coke and semicoke as target products. Today a somewhat different approach is required, aimed at integrated utilization of the solid fuel and generation of thermal and electrical energy.

When coals are gradually heated under anaerobic conditions, first water vapor is released. At 250°C, CO_2 and H_2S can also be detected, and at approximately 300°C condensing liquid products start to evolve and a noticeable amount of water is formed, i.e., the organic matter of coal starts to degrade. The majority of liquid products appear in the range 300–400°C, and this process ends at 550°C with the formation of primary tar [2, 3].

The pyrolysis steps are given in Table 1.

The yield of pyrolysis products depends on the structure of the initial coal. Therefore, it is necessary to consider this process as applied to a specific type of coal.

When choosing compounds simulating the OMC structure, we took data on the composition of coal from Kuznetsk coal fields [4]. According to the studies performed, OMC contains three major types of compounds.

The first group consists of oxygen-containing compounds: phenol, cresol, 4-ethylphenol, propylphenol, tetramethylbenzoic acid, 2-methoxynaphthalene, phenyl benzoate, 2-ethoxynaphthalene, benzophenone, hydroquinone, resorcinol, benzoic acid, dimethylbenzoic acids, diphenyl ether, naphthol, dibenzofuran, methylbenzoic acids, salicylic acid, 1,4-naphthoquinone, 2,3-naphthalenediol, 2,7-naphthalenediol, trimethylbenzoic acid, α-naphthoic acid, β-naphthoic acid, phenyl salicylate, α-acetoxynaphthalene, β-acetoxynaphthalene, 2-naphthyl benzoate, 2-, 3-, and 4-methoxybenzoic acids, 1- and 2-naphthylacetic acids, anthra- and phenanthroquinones, and 3-hydroxy-2-naphthoic acid.

Table 1. Steps of possible pyrolysis mechanisms

Step	*m*, °C	Thermal effect	Possible process
I	Up to 120	Endothermic	Evaporation of moisture present in coal
II	270–280	"	Primary degradation with formation of free radicals; decomposition occurs in side chains and probably in sites of connection of aromatic blocks (long hydrocarbon chains)
III	300–320	"	Accumulation of free radicals (olefins, paraffins)
IV	400–420	"	Formation of volatile components (methane, hydrogen, ammonia)
V	420–700	Exothermic	Condensation (except compounds that cannot initially decompose even at high temperature because the heat is insufficient for decomposition)
VI	above 700	Weak endothermic	

The second group consists of nitrogen-containing compounds: 3-ethyl-2,4,5-trimethyl-1*H*-pyrrole, 1-phenyl-1*H*-pyrrole, 2-phenyl-1*H*-pyrrole, 2,3-dimethyl-1*H*-indole, 9*H*-carbazole, and 9-methyl-9*H*-carbazole.

The third group consists of sulfur-containing compounds: dibenzothiophene and dibenzyl sulfide.

The OMC degradation starts with cleavage of bonds of carbon with heteroatoms (O, S). The process also presumably involves reactions with H_2 formed by the free-radical mechanism. Depending on the location of the heteroatom, the following types of reactions are possible [5]: with heteroatom X at aromatic ring Ar,

$$ArX + H_2 \longrightarrow ArH + HX, \quad (I)$$

with heteroatom X at the methylene group, Ar–CH_2,

$$ArCH_2X + H_2 \longrightarrow A1{-}CH_3 + HX, \quad (II)$$

with heteroatom Y in the bridge Ar–(CH_2)–Y–$(CH_2)_n$–Ar

$$Ar{-}(CH_2){-}Y{-}(CH_2)_n{-}Ar \xrightarrow{H_2} 2Ar(CH_2)_{n-1}{-}CH_3 + YH_2, \quad (III)$$

with heteroatom Y in the five-membered ring,

$$+ 4H_2 \longrightarrow C_2H_{10} + YH_2. \quad (IV)$$

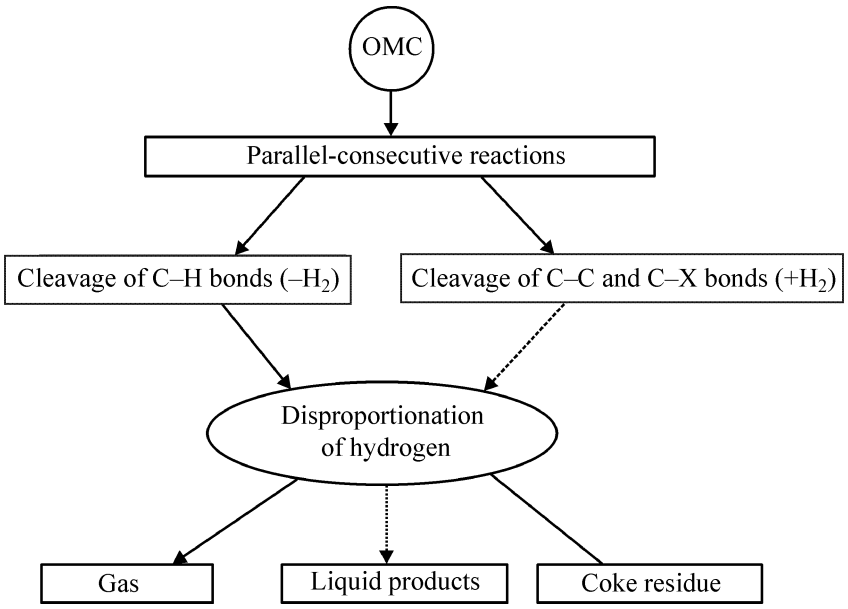
In reactions (I)–(IV) X = OH, SH, COOH, NH_2; Y = O, S, NH; n = 1, 2.

The suggested reaction scheme is presumably true not only for coal distillates as considered in [5], but also for pyrolysis of coal compounds, because the presence of hydrogen formed by the free radical mechanism in consecutive-parallel reactions (see Scheme 1) cannot be ruled out.

Because of enormous number of possible compounds, in particular, hydrocarbons and their derivatives, the most widely used are such universal procedures for calculating ΔH°_{vol}, S°, C°_p, and ΔG°_0 as methods of replacement of hydrogen atoms by CH_3 groups and functional groups (Andersen–Bayer–Watson method) and method of group contributions (Benson). The latter method, as noted previously [6], is the most accurate, as it also allows calculation of the thermodynamic functions of radicals.

Approximate methods for calculating thermodynamic quantities were developed by many researchers from Russia and other countries, and each made a certain

Scheme 1.



contribution to studies of specific groups of compounds. The accuracy of one or another method was evaluated by the extent of agreement with the available experimental data. However, even methods for rough estimation of thermodynamic quantities can be useful, as they allow restriction of the number of possible compounds and, in some cases, simplification of further calculations [7].

It was also noted previously [6] that calculation of thermodynamic properties of organic compounds by the additivity rule is based on the fact that, in disproportionation of two molecules ABA and CBC (where A, B, C are atoms or groups)

$$ABA + CBC \longrightarrow 2ABC.$$

The change in a thermodynamic function Φ of the system is associated only with a change in the symmetry. This conclusion is also valid for unsymmetrical molecules ABB'A and CBB'C reacting as follows:

$$ABB'A + CBB'C \longrightarrow ABB'C+CBB'A$$

It is assumed that a thermodynamic function Φ of a molecule can be calculated from the Φ values for fragments of this molecule [6].

The thermodynamic functions of model compounds were calculated in accordance with the scheme [5] that combined the above-mentioned procedures for determination of thermodynamic functions into a generalized additive method consisting in the following.

To calculate the temperature dependence of thermodynamic functions of hydrocarbons of arbitrary structure, a set of parameters is determined, depending on the hybrid states of carbon atoms and on the number of hydrogen atoms chemically bonded to them. Hydrocarbons of arbitrary structure consist of nine types of structural groups:

at C^1_{sp} $-C\equiv(C^0_1)$, $-C\equiv(C^1_1)$;

at C^2_{sp} $\begin{matrix}H\\H\end{matrix}\!\!>\!C=(C^2_2)$, $\begin{matrix}\\H\end{matrix}\!\!>\!C=(C^1_2)$, $=C=(C^0_2)$,

at C^3_{sp} $\begin{matrix}H\\H\\H\end{matrix}\!\!>\!C-(C^3_3)$, $\begin{matrix}H\\\\H\end{matrix}\!\!>\!C-(C^2_3)$,

$\begin{matrix}\\\\H\end{matrix}\!\!>\!C-(C^1_3)$, $>C-(C^0_3)$.

where C is a carbon atom occurring in ith hybrid state ($i = 1, 2, 3$); j is the number of hydrogen atoms chemically bonded to it ($j = 0, 1, 2, 3$).

In this case, heteroatoms are considered as components of functional groups.

Based on this procedure, we calculated the thermodynamic functions of individual compounds and obtain-

ed on their basis the Gibbs energies of pyrolysis in the temperature range 300–550°C, characterizing the probability of the occurrence of the forward reaction.

Changes in the enthalpy ΔH_M and entropy ΔS_M of a molecule with temperature were calculated by the well-known relationships

$$C_p(C_i^j) = a + bT + cT^2, \quad (1)$$

$$\left.\begin{aligned} \Delta H_M(T) &= \Delta H_{298} + \int_{298}^{T} \Delta C_p(T)\, dT, \\ \Delta S_M(T) &= \Delta S_{298} + \Delta T_{298} + \int_{298}^{T} \Delta C_{pM}(T)\, d(\ln T), \end{aligned}\right\} \quad (2)$$

where a, b, and c are the coefficients of the regression equation; T, reaction temperature (K); ΔH_{298}, enthalpy of the substance under standard conditions (298 K, 1 atm); ΔC_{pM}, heat capacity; ΔS^{298}, entropy of the substance under standard conditions.

Taking into account (1), from formulas (2) we obtain

$$\left.\begin{aligned} \Delta H(T) &= \Delta H_{298} + \alpha(T - 298) + \frac{\beta}{2}(T^2 - 298^2) \\ &\quad + \frac{\chi}{3}(T^3 - 298^3) \\ \Delta S(T) &= \Delta S_{298} + \alpha \ln\frac{T}{298} + \beta(T - 298) \\ &\quad + \frac{\chi}{2}(T^2 - 298^2), \end{aligned}\right\} \quad (3)$$

where $\alpha = \sum_{\mu} a_{\mu}$, $\beta = \sum_{\mu} b_{\mu}$ and $\chi = \sum_{\mu} c_{\mu}$ are the coefficients that can be determined from data given in [5] for each structural fragment in compounds simulating OMC.

The Gibbs free energy ΔG was calculated by the formula

$$\Delta G(T) = \Delta H(T) + T\Delta S(T)$$

Theoretically, the pyrolysis in the temperature range 300–550°C occurs in two steps.

Primary degradation is characterized by decomposition of benzoic and other aromatic acids into aromatic hydrocarbons and formic acid. Calculations show that direct decomposition of the chosen oxygen-containing compounds into aromatic hydrocarbons and carbon dioxide is thermodynamically impossible (the calculated Gibbs energy in the examined temperature range is from 200 to 460 kJ mol^{-1}). Hence, formic acid is an intermediate which, being unstable [8], decomposes into CO and H_2O with the subsequent formation of CO_2 whose evolution is observed in the course of coal degradation.

Possible reactions characterizing primary degradation of the organic matter of coal are as follows:

$C_7H_6O_2 + H_2 \rightarrow C_6H_6 + HCOOH$
(ΔH =1.52 kJ mol^{-1}),

$C_8H_8O_2 + H_2 \rightarrow C_7H_8 + HCOOH$
(ΔH =1.53 kJ mol^{-1}),

$C_9H_{10}O_2 + H_2 \rightarrow C_8H_{10} + HCOOH$
(ΔH =1.52 kJ mol^{-1}),

$C_{10}H_{12}O_2 + H_2 \rightarrow C_9H_{12} + HCOOH$
(ΔH =1.52 kJ mol^{-1}),

$C_{11}H_{14}O_2 + H_2 \rightarrow C_{10}H_{14} + HCOOH$
(ΔH =1.53 kJ mol^{-1}),

$C_{11}H_8O_2 + H_2 \rightarrow C_{10}H_8 + HCOOH$
(ΔH =1.53 kJ mol^{-1}),

$C_7H_6O_3 + H_2 \rightarrow C_6H_6O + HCOOH$
(ΔH =1.52 kJ mol^{-1}),

$C_{12}H_{10}O_2 + H_2 \rightarrow C_{11}H_{10} + HCOOH$
(ΔH = 19.30 kJ mol^{-1}),

$C_9H_{12}O + H_2 \rightarrow C_6H_6O + C_3H_8\uparrow$
(ΔH = 106.69 kJ mol^{-1}),

$C_7H_8O + H_2 \rightarrow C_6H_6O + CH_4\uparrow$
(ΔH =82.82 kJ mol^{-1}),

$C_6H_6O + H_2 \rightarrow C_6H_6 + H_2O$
(ΔH =221.87 kJ mol^{-1}),

$C_{14}H_{14}S + H_2 \rightarrow C_{14}H_{14} + H_2S\uparrow$
(ΔH =58.94 kJ mol^{-1}).

In the course of secondary degradation, some aromatic hydrocarbons decompose with the formation of benzene and methane:

$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4\uparrow$
(ΔH =1.52 kJ mol^{-1}),

$C_8H_{10} + H_2 \rightarrow C_6H_6 + 2CH_4\uparrow$
(ΔH =1.52 kJ mol^{-1}),

$C_9H_{12} + H_2 \rightarrow C_6H_6 + 3CH_4\uparrow$
(ΔH =1.52 kJ mol^{-1}),

$C_{10}H_{14} + H_2 \rightarrow C_6H_6 + 4CH_4\uparrow$
(ΔH =1.53 kJ mol^{-1}),

$C_6H_6O + H_2 \rightarrow C_6H_6 + H_2O$
(ΔH =221.87 kJ mol^{-1}),

$C_{11}H_{10} + H_2 \rightarrow C_{10}H_8 + CH_4\uparrow$
(ΔH =1.53 kJ mol^{-1}).

Table 2. Gibbs energies of decomposition of compounds at various temperatures

Starting compound	ΔG, kJ mol^{-1}, at indicated T, °C						Process
	300	350	400	450	500	550	
Primary degradation							
Benzoic acid	–204.92	–225.90	–247.00	–268.19	–289.47	–310.83	Decomposition is possible at 300–500°C
Methylbenzoic acids	–204.92	–225.90	–246.99	–268.19	–289.47	–310.82	"
Dimethylbenzoic acids	–204.92	–225.90	–246.99	–268.19	–289.47	–310.83	"
Trimethylbenzoic acid	–204.92	–225.91	–246.99	–268.19	–289.47	–310.82	"
Tetramethylbenzoic acid	–204.92	–225.91	246.99	–268.20	–289.47	–310.82	"
α- and β-Naphthoic acids	–204.93	–225.90	–247.00	–268.19	–289.47	–310.82	"
Salicylic acid	–204.92	–225.90	–247.00	–268.19	–289.48	–310.82	"
1- and 2-Naphthylacetic acids	–265.77	–290.01	–314.32	–338.72	–363.17	–387.66	"
i-Propylphenol	42.86	28.96	13.62	– 3.13	–21.28	–40.78	at 350–400°C Decomposition at 350–400°C is impossible, can participate in condensation with formation of tar
Cresol	23.04	3.27	4.60	–12.84	–21.38	–30.26	Decomposition at 300–350°C is impossible, can participate in condensation with formation of tar
Phenol	111.30	100.43	89.37	78.14	66.72	55.15	Decomposition at 300–500°C is impossible, can participate in formation of tar
Dibenzyl sulfide	–200.41	–214.02	–227.65	–241.30	–254.96	–268.62	Decomposition is possible
Secondary degradation							
Toluene	23.03	3.27	4.62	12.84	–21.38	–30.26	Decomposition at 300–350°C is impossible
2–Methyltoluene							
2,4–Dimethyltoluene	46.06	6.55	–9.22	–25.67	–42.76	–60.51	"
2,3,6–Trimethyltoluene	69.10	9.82	–13.83	–38.51	–64.14	–90.76	"
Phenol	92.14	13.10	–18.43	–51.34	–85.52	–121.02	"
Methylnaphthalene	111.30	100.43	89.37	78.14	66.72	55.15	"
	23.03	3.27	–4.61	12.84	–21.38	–30.26	"

The Gibbs energies obtained for the model reactions (Table 2) indicate that benzoic acids (methyl-, dimethyl-, trimethyl-) decompose into benzene, xylenes (dimethylbenzenes), and trimethylbenzenes and formic acid in the temperature range 300–550°C. The benzene derivatives formed decompose into benzene and hydrocarbons (methane, propane) in the temperature range 400–550°C or can participate in formation of base compounds of tar.

Hence, it is impossible to obtain hydrocarbons from these compounds by simple heating, because, in so doing, they can participate in such processes as decomposition or condensation with other compounds.

The overall thermal effect in the temperature range 300–350°C for the primary degradation is endothermic, ΔH = 340.7503 kJ mol^{-1}, and for the secondary degradation, ΔH = 1132.8 kJ mol^{-1}.

CONCLUSIONS

(1) A study of the degradation of coal organic matter showed that, starting from 300°C, aliphatic side chains are cleaved. Above 500°C, there is a tendency toward occurrence of parallel reactions with the formation of tarry semicoking products, which is unfavorable for the production of pyrolysis gas as one of the target products.

(2) *i*-Propylphenol and cresol starts to decompose only at 400–550°C. Phenol does not decompose in the temperature range 300–550°C and can participate in the formation of primary tar.

(3) Pathways and sources of formation of gaseous degradation products (methane, propane, carbon monoxide, carbon dioxide) have been determined.

(4) Restrictions imposed by the Gibbs energies in the temperature range 300–550°C have been revealed.

(5) A sequence of operations for estimating the power consumption for degradation of the organic matter of coal in the course of pyrolysis is suggested.

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