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INTERPRETATION OF THE NON-ISOTHERMAL REACTION OF CARBON WITH CARBON DIOXIDE BY MEANS OF KINETIC PARAMETERS

J. MEDEK

Mining Institute of the Czechoslovak Academy of Sciences,
Prague, Czechoslovakia

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The non-isothermal reaction of carbon with CO_2 in a differential reactor with a constant temperature rise was used for simultaneous determination of the reaction order, the effective activation energy, the pre-exponential factor, and the specific maximum reaction rate. The effect of the pyrolytic decomposition products was continuously compensated and the automatically recorded curve of the dependence of the transformation rate on the temperature was evaluated by means of the kinetic equation for a homogeneous reaction, using the relative values of variables. The reaction order $n = 1$ and the values of the activation energy agreed with the results of isothermal experiments.

The kinetics of the reaction $C + CO_2 \rightleftharpoons 2CO$ (1)
have been studied mostly under isothermal conditions and the rate of conversion of CO_2 has been expressed by means of the Langmuir–Hinshelwood scheme for a heterogeneous reaction, or (neglecting the CO concentration on the carbon surface) by the equation for a pseudohomogeneous reaction. The effective reaction order n lies within the range 0 to 1.5, depending on the experimental conditions. When the reaction occurs in a through-flow reactor without overpressure, it is assumed that n is unity.

In technological processes, where reaction (1) is of primary importance, its course is not isothermal; on the contrary, a temperature gradient of several hundred degrees is formed. Romováček and Malínský [1] determined the relative values of the reaction rate for the gasification of lignite in the temperature range from 700 to 1250° and expressed their results by an integral curve of carbon loss. However, the experimental equipment which they developed yields data from which the main kinetic quantities of reaction (1) under non-isothermal conditions can be determined.

Experimental

The method according to [1] is based on the temperature-synchronized operation of two reactors (Fig. 1), in which two identical samples of the same mass are placed. In reactor 1, into which pure CO_2 enters, the pyrolytic decomposition of carbonaceous substance and reaction (1) take place simultaneously, whereas in reactor 2, which is supplied by the same volume flow of pure N_2, only the pyrolytic decomposition occurs. Behind the reactors oxygen is added to both lines and the gas mixtures are fed to combustion cells, where the oxidizable matter is burned on an electrically-heated filament. The filaments of the two cells are connected into a Wheatstone bridge, which remains in balance if the gaseous products produced in the same quality and quantity in both reactors are burned on the filaments and the released heats yield identical changes of their resistance. The unbalanced condition of the bridge is caused be the burning of CO, formed in reactor 1 according to Eq. (1).

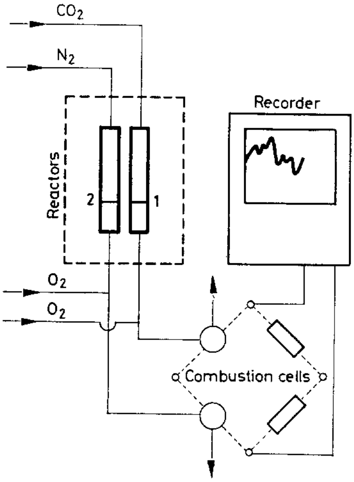

Fig. 1. Temperature-synchronized reactors with compensating connection of combustion cells

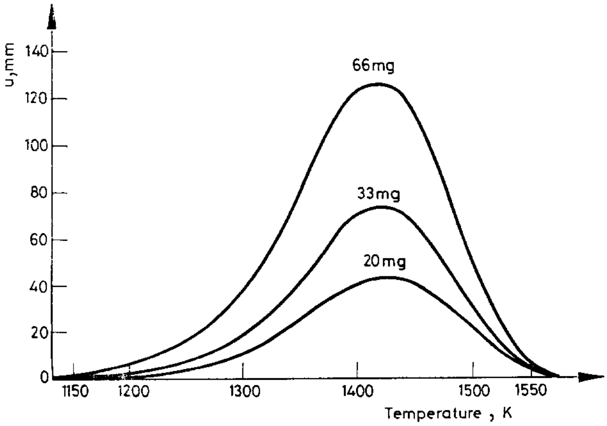

Fig. 2. Measured dependence of relative rate of carbon loss u on temperature T for electrocarbon C 52

The quartz reactors had a cross-section of 2 cm^2, and the carbon bed (grain size < 0.1 mm) was placed on sintered quartz frits. At carbon masses between 25 and 70 mg, no concentration gradient of CO occurred in the direction of flow so that the reactor functioned practically as a differential one. At the constant heating rate $q = 0.128\ \mathrm{K \cdot s^{-1}}$, the temperature increased up to complete gasification of the samples. Within the temperature interval 800 to 1300°, the temperature rise under thyristor control was linear with a precision of 1%. The flow rate of CO_2 and of N_2 was 1 cm$^3 \cdot$ s^{-1}. As a standard source of high purity, electrocarbon C 52 with a 0.15% mineral matter content was used. Comparison measurements were made on 4 coke samples (C 1, C 2, C 3, C 4), prepared directly within the reactors by carbonization of coking coals in a N_2 stream up to 1100°.

The intensity of the bridge output signal depends on the actual concentration of CO and therefore also on its formation rate, d(CO)/dt. According to Eq. (1), the rate of formation of CO is proportional to the carbon loss rate, and thus the recorded curve (Fig. 2) illustrates the dependence of the carbon loss rate on the time t; it therefore holds true for the ordinate u that

$$u = B\frac{\mathrm{d}x}{\mathrm{d}t} \tag{2}$$

where x is the actual quantity of reacted carbon and B the constant of proportionality. If the temperature is raised at the constant rate

$$\frac{\mathrm{d}T}{\mathrm{d}t} = q$$

u will be

$$u = qB\frac{\mathrm{d}x}{\mathrm{d}T} \tag{3}$$

The area A_x bounded by the recorded curve, the abscissa and the ordinate at the point T, can be expressed by means of the integral

$$A_x = qB\int_0^T \frac{\mathrm{d}x}{\mathrm{d}T}\,\mathrm{d}T = qB\int_0^x \mathrm{d}x = qBx \tag{4}$$

from which it follows that the area A_x is proportional to the quantity of reacted carbon x at the temperature T.

When the reaction takes place within the temperature interval from $T = 0$ to $T = \infty$, the integral (4) has the limits $x = 0$ and $x = a$, and the area A_a is proportional to the initial amount of carbon a:

$$A_a = qBa \tag{5}$$

Theoretical

The kinetic equation for a non-isothermal reaction of the n^{th} order has the general form

$$\frac{\mathrm{d}x}{\mathrm{d}T} = \frac{k_0}{q}(a - x)^n \, e^{-E/RT} \tag{6}$$

where E = activation energy, k_0 = pre-exponential factor, R = the gas constant and $q = \frac{\mathrm{d}T}{\mathrm{d}t}$. For the evaluation of the recorded dependence $u = u(T)$, Eq. (6) can be transformed by means of expression (3) and (5) to the form

$$u = k_0 B \left(\frac{A_a}{qB}\right)^n (1 - \alpha)^n e^{-\frac{E}{RT}} \tag{7}$$

where $\alpha = \frac{x}{a} = \frac{A_x}{A_a}$ is the fraction of reacted carbon.

Owing to the fact that the absolute value of $\mathrm{d}x/\mathrm{d}T$ is unknown, it should be substituted by a relative one related to the maximum reaction rate $\left(\frac{\mathrm{d}x}{\mathrm{d}T}\right)_m$, which corresponds to the point where at the temperature T_m, the curve has the ordinate u_{m} and the fraction α is $\alpha_m = x_m/a = A_m/A_a$.

If so, then

$$\frac{u}{u_m} = \frac{(1 - \alpha)^n}{(1 - \alpha_m)^n} \, e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)} \tag{8}$$

or taking lgs

$$\frac{\lg \dfrac{u}{u_m}}{\lg \dfrac{(1 - \alpha)}{(1 - \alpha_m)}} = \frac{-E}{2.303\,R} \; \frac{\left(\dfrac{1}{T} - \dfrac{1}{T_m}\right)}{\lg \dfrac{(1 - \alpha)}{(1 - \alpha_m)}} + n \tag{9}$$

This expression, corresponding to the equation of a straight line of slope $-E/2.303R$ and intercept n, is formally identical with the expression used by Freeman and Carroll [2]. Apart from the temperature it contains only relative quantities, the numerical values of which can easily be determined from the experimental curve.

For the determination of the factor k_0 and the absolute value of $\mathrm{d}x/\mathrm{d}T$, it is necessary to derive the function containing the coordinates of the maximum T_m and $\left(\frac{\mathrm{d}x}{\mathrm{d}T}\right)_m$. The latter quantity, of special significance, should be written as $\left(\frac{\mathrm{d}x}{\mathrm{d}T}\right)_m = v_m$. The integration of Eq. (6)

$$\int_0^x (a-x)^n \, dx = \frac{k_0}{q} \int_0^T e^{-\frac{E}{RT}} \, dt \qquad (10)$$

gives

$$\frac{(d-x)^{-(n-1)} - a^{-(n-1)}}{n-1} = \frac{k_0}{q} \int_0^T e^{-\frac{E}{RT}} \, dT \qquad (11)$$

when $n \neq 1$.

Determining x from (11) and introducing it back into (6), one obtains

$$\frac{dx}{dT} = \frac{k_0}{q} e^{-\frac{E}{RT}} X^{-\frac{n}{n-1}} \qquad (12)$$

where

$$X = \left(a^{-(n-1)} + (n-1) \frac{k_0}{q} \int_0^T e^{-\frac{E}{RT}} \, dT \right)$$

and, analogously, at the maximum

$$v_m = \frac{k_0}{q} e^{-\frac{E}{RT_m}} \cdot X_m^{-\frac{n}{n-1}}$$

$$X_m = \left(a^{-(n-1)} + (n-1) \frac{k_0}{q} \int_0^{T_m} e^{-\frac{E}{RT_m}} \, dT \right) \qquad (13)$$

Putting the second derivative equal to zero

$$\frac{d^2x}{dT^2} = \frac{k_0}{q} e^{-\frac{E}{RT}} \left[\frac{E}{RT^2} X^{-\frac{n}{n-1}} - n \frac{k_0}{q} \cdot e^{-\frac{E}{RT}} {}^{-\frac{2n-1}{n-1}} \right] = 0 \qquad (14)$$

the coordinate T_m at the maximum is defined by the function

$$\frac{E}{nRT_m^2} \left[\frac{k_0}{q} e^{-\frac{E}{RT_m}} \right]^{-1} = X_m^{-1} \qquad (15)$$

By raising Eq. (13) to the exponent $\frac{n-1}{n}$, one obtains

$$v_m^{\frac{n-1}{n}} \left[\frac{k_0}{q} e^{-\frac{E}{RT_m}} \right]^{-\frac{n-1}{n}} = X_m^{-1} \qquad (16)$$

From the identity of the right-hand sides of (15) and (16)

$$v_m^{\frac{n-1}{n}} \left[\frac{k_0}{q} e^{-\frac{E}{RT_m}} \right]^{\frac{1}{n}} = \frac{E}{nRT_m^2} \qquad (17)$$

By raising the fundamental Eq. (6) to the exponent $\frac{1}{n}$

$$\left[\frac{k_0}{q} e^{-\frac{E}{RT_m}}\right]^{\frac{1}{n}} = v_m^{\frac{1}{n}} (a - x_m)^{-1} \tag{18}$$

and by substitution in (17) the characteristic function for v_m can be obtained

$$v_m = \frac{aE}{nRT_m^2}(1 - \alpha_m) \tag{19}$$

Eq. (19) is valid for all n, and therefore also for $n = 1$, when it is in accordance with the expression given by Jüntgen [3]. If related to the unit of matter quantity (mole) or mass (g), v_m has the character of a specific rate. The value of the remaining quantity k_0 can be calculated from Eq. (6) after substitution of v_m, T_m, E and n.

Results and discussion

The dependence $u = u(T)$ is shown in Fig. 2 for the sample of electrocarbon C 52 and in Fig. 3 for cokes. The recorded curves are over-printed on millimetre paper, and the areas A_x and A_a are determined by weighing. The fractions α are calculated from the ratios $\alpha = A_x/A_a$. The necessary data for the construction of the linear dependence according to Eq. (9) are summarized for C 52 in Table 1. These relationships are illustrated graphically for all samples in Figs 4 and 5. Table 2 contains the calculated kinetic quantities; these are only effective values especially for the activation energy. If porous carbon takes part in reaction (1), the course is determined not only by the chemical process, but also by diffusion, the share of which in the total reaction rate depends on the porous structure, rising with increasing temperature. It has been proved [4, 5] that at temperature exceeding 1150° the activation energy decreases by up to 50% of its value at 900–1100°. Even if these results were obtained in an integral reactor, their importance cannot be neglected in evaluating our results. Nevertheless the value of E_{ef} have the significance of constants, because only one slope was found in the

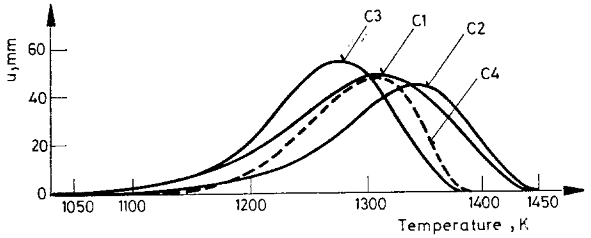

Fig. 3. Measured dependences of relative rate of carbon loss u on temperature T for cokes C 1, C 2, C 3 and C 4

linear dependence according to Eq. (9), as evident from Figs 4 and 5. Compared with the reaction under isothermal conditions, the individual values of E_{ef} for cokes lie within the characteristic interval [6], and for electrocarbon C 52 they agree very well with the values for other carbonaceous model substance [5, 7, 8].

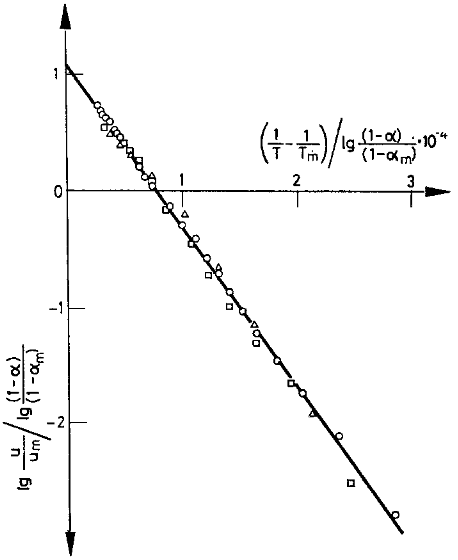

Fig. 4. Linearized dependence of carbon loss on temperature according to Eq. (9) for various sample weights of electrocarbon C 52

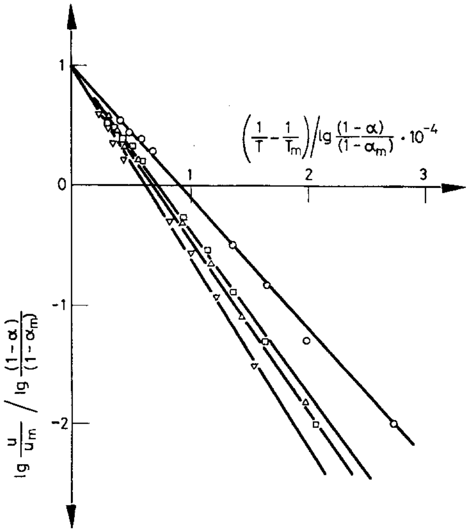

Fig. 5. Linearized dependences of carbon loss on temperature according to Eq. (9) for cokes C 1, C 2, C 3 and C 4

Table 1

Selected experimental values (electrocarbon C 52) for testing of Eq. (9)

T, K	u, mm	A, g	T, K	u, mm	A, g
m = 66 mg;	A_a = 0.8566 g		m = 33 mg;	A_a = 0.4796 g	
1228	10	0.0242	1271	10	0.0335
1263	20	0.0530	1306	20	0.0446
1288	30	0.0833	1330	30	0.0698
1307	40	0.1104	1350	40	0.0977
1321	50	0.1351	1367	50	0.1291
1332	60	0.1594	1382	60	0.1638
1343	70	0.1889	1405	70	0.2257
1352	80	0.2150	1419	72	0.2684
1362	90	0.2470	1436	70	0.3172
1372	100	0.2793	1458	60	0.3740
1383	110	0.3245	1471	50	0.4043
1400	120	0.4088	1485	40	0.4291
1421	124	0.5132	1499	30	0.4482
1437	120	0.5909	1514	20	0.4636
1452	110	0.6564	1532	10	0.4734
1461	100	0.6942	m = 20 mg;	A_a = 0.2837 g	
1470	90	0.7255	1298	10	0.0242
1478	80	0.7505	1337	20	0.0475
1483	70	0.7672	1366	30	0.0762
1491	60	0.7878	1401	40	0.1247
1498	50	0.8017	1423	42	0.1596
1507	40	0.8185	1446	40	0.1959
1516	30	0.8306	1479	30	0.2415
1528	20	0.8428	1502	20	0.2636
1543	10	0.8517	1526	10	0.2774

Underlined values relate to the maximum of the curve

Table 2

Constants of the kinetic equation and correlation coefficients

Sample	a, mmol	n,	E_{ef}, kJ·mmol^{-1}	πk_0, mmol$^{(1-n)}$· s^{-1}	v_m, mmol · mol^{-1} ·K^{-1}	r
C 52	5.495	1.08	267.5	$10^{10.32235}$	0.641	−0.999
C 52	2.750	1.08	267.5	$10^{10.35784}$	0.651	−0.997
C 52	1.667	1.08	267.5	$10^{10.33655}$	0.630	−0.997
C 1	1.601	1.00	208.5	$10^{8.58243}$	0.600	−0.999
C 2	1.196	1.00	275.0	$10^{11.06417}$	0.744	−0.999
C 3	1.342	1.00	270.8	$10^{11.47409}$	0.800	−0.996
C 4	1.145	1.00	305.6	$10^{12.59319}$	0.700	−0.999

The effective reaction order n for cokes corresponded exactly with the assumed value $n = 1$; for carbon C 52 the value $n = 1.08$ was found. This small deviation was confirmed in all three measurements.

The possibility of interpretation of the nonisothermal course of reaction (1) by means of the special form (9) of kinetic equation (6) is verifed by the values of the correlation coefficients r, approaching $r = 1$ in all cases.

Should the values of the factor k_0 be constant according to Eq. (6), it would hold true that

$$\frac{u_m}{A_a} = \frac{v_m}{a} = \text{constant} \tag{20}$$

and

$$(1 - \alpha_m) = \left(1 - \frac{A_m}{A_a}\right) = \text{constant} \tag{21}$$

Measurements at various initial amounts a of carbon therefore simplify the verification of Eqs (2) and (5) as well as of Eq. (19). For electrocarbon C 52, the values of a (in mg) were in proportions

$$a_{(1)} : a_{(2)} : a_{(3)} = 66 : 33 : 20 = 1.00 : 0.50 : 0.30$$

and the areas A_a

$$A_{a(1)} : A_{a(2)} : A_{a(3)} = 0.8566 : 0.4796 : 0.2837 = 1.00 : 0.56 : 0.33$$

which confirms the assumption in formula (5).

The directly measured values of maximum relative rates u_m in mm exhibited the following proportions:

$$u_{m(1)} : u_{m(2)} : u_{m(3)} = 124 : 72 : 42 = 1.00 : 0.58 : 0.33$$

and the absolute values v_m, calculated according to (19), the proportions:

$$v_{(m1)} : v_{m(2)} : v_{m(3)} = 0.0325 : 0.0179 : 0.0105 = 1.00 : 0.55 : 0.32$$

which agrees with the assumption in Eq. (2).

Therefore, it was possible to apply, as most accurate, the method of area calibration for determination of the total amount of carbon $a_{(c)}$ in cokes by means of the relation

$$a_{(c)} : A_{a(c)} = a_{52} : A_{a52} \tag{22}$$

where the indices c and *52* relate to coke and electrocarbon, respectively. This can be confirmed by the relations (with the exception of the last one, perhaps) between the measured and calculated maximum rates:

$$u_{m(1)} : u_{m(2)} : u_{m(3)} : u_{m(4)} = 0.897 : 0.831 : 1.000 : 0.748$$

and

$$v_{m(1)} : v_{m(2)} : v_{m(3)} : v_{m(4)} = 0.909 : 0.818 : 1.000 : 0.873$$

The small differences are caused by the fact that Eq. (6) does not take into account, as a kinetic parameter, the surface area $\sum (\mathrm{m^2 g^{-1}})$ on which the heterogeneous reaction takes place. The absolute value of $\sum$ cannot be determined, but it can be assumed that it is equal to a fraction Θ of the total specific surface area $S\,(\mathrm{m^2 g^{-1}})$, so that $\sum = \Theta S$, where $\Theta \leqq 1$. If the area S_a, measured on the carbon before the reaction, remains constant during this reaction, then

$$\frac{\mathrm{d}x}{\mathrm{d}T} = k_0' \, [\Theta S_a(a-x)]^n \, e^{-\frac{E}{RT}} \tag{23}$$

where $S_a(a-x)$ is the actual value of the surface area. Including the product $k_0' \cdot \Theta^n S_a^n$ into the constant k_0, Eq. (23) leads to relation(6). However, it has been found [4, 9] that during gasification the specific surface area first rises, passes through a maximum, and finally decreases. Of course, it cannot be precluded that not only $S = S(x)$, but also $\Theta = \Theta(x)$. For electrocarbon C 52 a possible change of S and Θ does not affect any of the compared kinetic quantities. On the other hand, $S(x)$ and $\Theta(x)$ will be different for different samples of cokes, so that the coordinates of the maximum will be a function not only of the basic kinetic parameters, but also of the product $(a\Theta S)^n$. In the case of the studied samples, however, it can be deduced from a sufficiently precise characterization of the reaction course by means of Eq. (6) that during the reaction the product ΘS remains constant.

Conclusions

The non-isothermal course of the reaction of carbon with CO_2 in the differential reactor can be adequately described by means of the kinetic equation for a homogeneous reaction. Using the relative experimental values, the effective activation energy E_{ef} and the effective reaction order n were calculated; the total quantity of reacted carbon was used to calculate the pre-exponential factor k_0 and the specific maximum reaction rate v_m. The correlation coefficient for the linearized relation of the variables was in all instances higher than 0.995, so that the kinetic quantities are valid within a wide temperature range. For the electrocarbon and cokes used, $n = 1$. However, owing to the effect of transport phenomena, especially in carbonaceous materials with non-typical porous structure, the reaction order can be somewhat different from this value.

References

1. J. Romováček and J. Malínský, Brennst.-Chem., 47 (1966) 114.
2. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
3. H. Jüntgen, Erdöl und Kohle, 17 (1964) 180.
4. E. Wicke and K. Hedden, Z. Elektrochem., 57 (1953) 636.
5. W. Peters and G. W. Lask, Brennst.-Chem., 42 (1961) 84.
6. A. Dahme and H. J. Junker, Brennst.-Chem., 36 (1955) 193.
7. I. A. Javorsky and M. D. Malanov, Carbon, 7 (1969) 287.
8. E. T. Turkdogan and J. V. Vinters, Carbon, 8 (1970) 39.
9. A. Wittkowsky, Dissertation, Technische Universität, Berlin, 1970.

Résumé — Utilisation d'un réacteur différentiel avec élévation régulière de la température pour déterminer l'ordre de réaction, l'énergie d'activation, le facteur préexponentiel et la vitesse de réaction spécifique maximale de la réaction non-isotherme du carbone avec CO_2. L'effet des produits de la décomposition thermique a été compensé en continu. La courbe donnant la vitesse de transformation en fonction de la température a été enregistrée automatiquement et traitée à l'aide de l'équation cinétique pour la réaction homogène, en utilisant les valeurs relatives des variables. L'ordre de réaction n est égal à 1 et les valeurs de l'énergie d'activation sont en accord avec les résultats des expériences effectuées en isotherme.

Zusammenfassung — Die nicht-isotherme Reaktion von Kohle mit CO_2 in einem Differentialreaktor mit konstantem Temperaturanstieg wurde zur simultanen Bestimmung der Reaktionsordnung, der effektiven Aktivierungsenergie, des präexponentiellen Faktors und der spezifischen maximalen Reaktionsgeschwindigkeit herangezogen. Der Effekt der pyrolytischen Zersetzungsprodukte wurde kontinuierlich kompensiert und die automatisch aufgezeichnete Kurve der Abhängigkeit zwischen Umsetzungsgeschwindigkeit und Temperatur wurde mit Hilfe der kinetischen Gleichung für die homogene Reaktion unter Anwendung der relativen Werte der Variablen ausgewertet. Die Reaktionsordnung $n = 1$ sowie die Werte der Aktivierungsenergie waren mit den Ergebnissen der isothermen Versuche in Übereinstimmung.

Резюме — Неизотермическая реакция углерода с углекислым газом в дифференциальном реакторе с постоянным увеличением температуры была использована для одновременного определения порядка реакции, эффективной энергии активации, предэкспоненциального фактора и удельного максимума скорости реакции. Влияние продуктов пиролитического разложения непрерывно компенсировалось и автоматически снимаемая кривая зависимости между скоростью превращения и температурой, была вычислена с помощью кинетического уравнения для гомогенной реакции, используя относительные значения переменных. Порядок реакции $n = 1$, также как и значение энергии активации, хорошо согласуются с результетами изотермических экспериментов.