CONTRIBUTIONS TO THE GAS PRODUCER THEORY

By Ernest G. Graf

Report No. VI

Contributions To The Gas Producer Theory.

Contents: Based on exact gas analyses and temperature measurements in the bed of a gas producer it is stated that the heterogeneous producer equilibria do not adjust. Ideas are given to papers dealing with the contrary opinion. It is further tried to explain interferences, in gas producer theories by the difficulties of exact measuring, and sampling and also to evaluate model experiments. Finally, measurements and calculations of the homogeneous water gas equilibrium and the heterogeneous Boudouard equilibrium are represented.

In the United States gas producers for complete gasification of solid fuels are not as widely spread as in Europe due to the development of small Diesel engine units and cheap hydroelectric power and due to the use of blast furnace gas and coke oven gas for heating purposes in steel mills. According to Dickermann*, in the United States there were until 1936 installed about 3,800 mechanical and about 1,000 hand-fed producers only. Nevertheless the literature on this subject shows that the industry of the United States is not only interested in investigation and improvement of all types of gas producer apparatus but also in any kind of research work on the physics and chemistry of the gas producer processes.

The fundamental reactions of burning solid fuels on grates and stokers are the same as they occur in gas producers. Each grate firing may be considered as a more or less complete gas producer for we find in the lower layer of the fuel bed the oxidation and in the upper one the reduction reactions of the gas producer. Therefore all research work on the mechanism, the kinetics and thermodynamics of the gasification processes stimulate investigations and improvements to the coal burner and furnace industry.

Our knowledge of the rates of the gas producer reactions and of the order of succession of the fundamental reactions is still very small in spite of the importance of the coal utilization and in spite of the fact, that

*Dickermann, I. C. Trans. World Power Conf., 3rd Conf. Washington, 1936 4(1938) 491-542

the chemistry of the carbon reactions has been investigated from the early days of chemical science.

The aim of the gasification in gas producers is the manufacture of gases, the calorific value of which is used in power engines and industrial furnaces. The principal thermodynamic constants, the molar change in enthalpy and in free energy of the gas producer reactions are known with high accuracy. These reactions are reversible and lead to chemical equilibria, the values of which are depending on the temperature only. The equilibrium constants and their change with the temperature are also well known. The gasification reactions can only proceed until the compositions, given by the equilibrium constants, are reached. The speed of the chemical reactions is very slow at temperatures below about $530^{\circ}C$ the beginning of incandescence, it is measurable by the laboratory methods available at red hot temperatures up to about $850^{\circ}C$. and it becomes practically unmeasurable fast at the highest producer reaction temperatures of 1200 to $1500^{\circ}C$. In practice the gasification and combustion rates consist of the rate of the chemical reactions which are practically infinite at high temperatures, plus the relatively slow rate of the physical processes of the transfer of the oxygen (air) and water vapor to the carbonaceous surface and the transport of the carbon oxides from the carbon surface, plus the heat transfer by radiation, convection and conduction in the fuel bed. These physical factors and the influence of the size and shape of the coal particles and the voids determine therefore practically the combustion and gasification rates at the necessary high temperatures in fuel beds.

The adjustment of the equilibrium of the most important heterogeneous gas producer reactions $C + CO_2 \longrightarrow 2\ CO$ and $C + H_2O \longrightarrow H_2 + CO$ was frequently studied with the result, that these equilibria do not adjust with respect to the temperature of the fuel. It was further stated, that an apparent adjustment takes place when the gasifying agents leave fuel zones of higher

temperatures, at which the adjustment is incomplete, and pass through zones of lower temperatures, so that the adjustment seems to be accomplished at the lower temperatures. This theory is well founded by measurements and calculations and most of the papers and books on this subject share the opinion.

One of the recent measurements of W. Horak* were carried out in the gas works of Vienna and presented in order to become Ph. D. Engr. at the Institute of Technology of Fuels at Vienna, where I was employed as first assistant. Together with W. J. Müller I published** own calculations based on the experimental measurements of Horak, which I am going to present here. The reason of occupying with the theme is, besides of a general interest to the gas industry, that in later published papers, foremost by W. Gumz***, recognized as one of the first specialists on this subject and by S. Traustel****, the opinion is still spread, that the adjustment of heterogeneous producer equilibrium takes place and that just the above mentioned Viennese experimental works are used by W. Gumz to demonstrate the opinion in contradiction to the preceding explained theory. It shall be premised, that the methods of measuring temperatures and sampling gases used by Horak were adequate to modern demands. Each temperature value represents a mean value of numerous measurings at the same point of zone and of the same operating conditions and the gas samples were drawn by means of a narrow sampling tubes, water cooled as far as the top, so that practically no changes of gas compositions have occurred during sampling.

*Zeitschrift der österreichischen Gas – und Wasserfachmanner 73, 170(1933)
**Brennstoffchemie 20, 241-246 (1939)
and
W.J. Müller and E. Graf, Text Book of the Technology of Fuels, Vienna, Edition H. Deuticke 1st Edition, 1939 p. 332-336 II & III Edition 1945 p. 352 – 357
***Handbuch der Brennstoff und Feuerungstechnik
Edition Springer, 1942
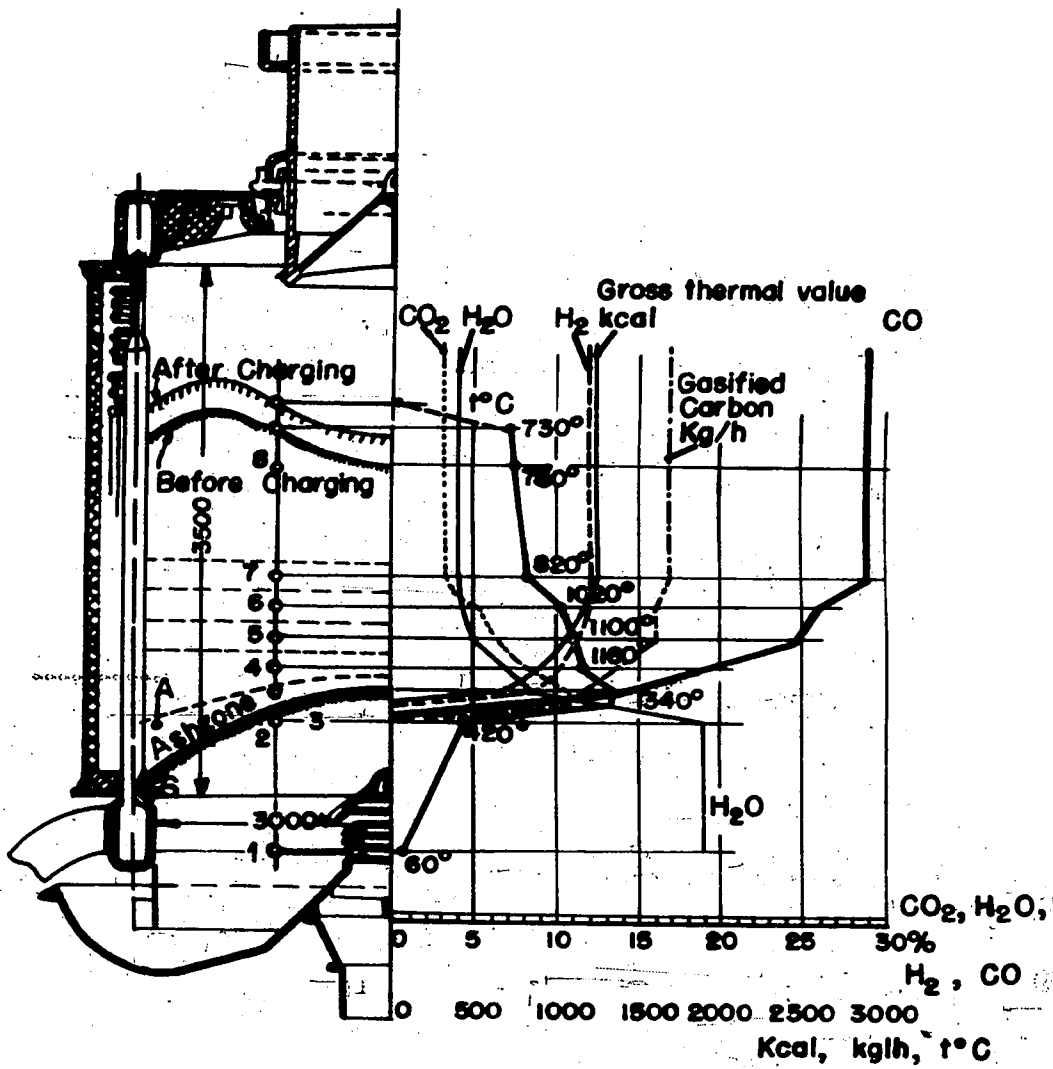****Verbrennung, Vergasung und Verschlackung, Dissertation, 1939

Fig. 1

RESULTS OF MEASUREMENTS ON A GAS PRODUCER

BY TH. MARISCHKA

Number of Zone	Gas Analyses						Gross heat value of gas cal. p. nm^3	Gas volume produced nm^3 p.h.	Ash and water free coke gasified kg. p. h.	Temperature ^{0}C
	CO_2	O_2	CO	H_2	H_2O	N_2				
1, 2	Ash – Zone						–	–	–	–
3	11.2	0.7	12.8	8.8	8.6	58.0	656	7740	1130	1340
4	8.4	0.4	19.0	10.1	6.7	55.4	885	8258	1350	1160
5	6.4	0.1	24.5	11.2	4.9	52.9	1047	8826	1595	1100
6	5.2	0.1	25.7	12.0	4.2	52.9	1145	8890	1596	1020
7	3.3	0.0	28.8	11.9	4.0	52.0	1237	9040	1685	820
8	3.2	0.0	28.6	12.0	4.0	52.2	–	–	–	–

The cross sectional area of the gas producer and the results of measuring are shown in figure 1 and table 1 containsthe analyses and readings according to figure 1.
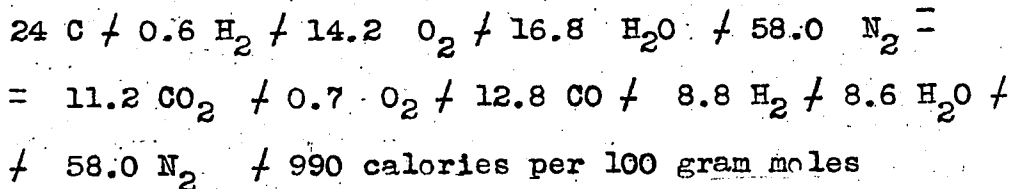
The producer, system Marischka had an inner diameter of 3 m and an inner height of 3.5 m. The producer jacket consisted of high pressure boiling tubes, which were connected to the adjacent tubes by spacers welded to the tubes. The gas coke contained 11.5% of moisture and 9.3% of ash. The water and ash free coke substance consisted of:

$$C = 96.0\% \qquad\qquad S = 0.8\%$$
$$H = 0.4\% \qquad\qquad O / N = 2.8\%$$

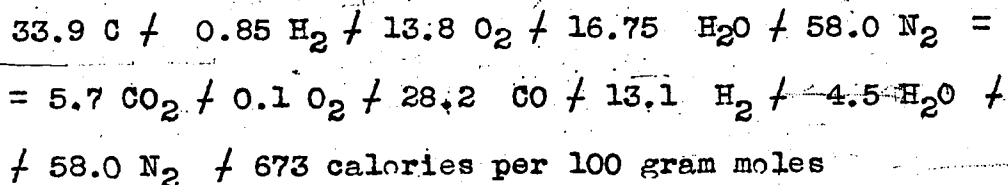with a gross thermal value of 7930 calories per kg.

In order to discuss the measured results it is proposed to put the gas analysis at the right side of an equation and to make the sum of the gas percentages by volume equal to 100 gram moles of gas. The consumed carbon and the introduced gases, oxygen, nitrogen and water steam, are easily to be calculated by means of the stoichiometry. The amount of water steam on the left side of the equation is obtained by adding the hydrogen and water contents of the gas and subtracting the hydrogen content of the coke. Thus, by calculating the oxidation and reduction reactions, the heat evolution and heat consumption pertaining to 100 gram moles of gas is obtained for each of the zones of the coke bed. As the calculations are based on the gas composition of zone 3, the change in volume in the higher zones can be obtained by considering, that the introduced nitrogen volume does not change passing through the fuel bed. Therefore the gas analysis of the zones 4 to 8 of table 1 can be converted into gas compositions with 58.0 moles of nitrogen by multiplying the gas moles with the factor $58.0/N_{2,x}$ wherein $N_{2,x}$ means the nitrogen volume and the nitrogen moles respectively in the equation of the zone X. The obtained equations are the following:
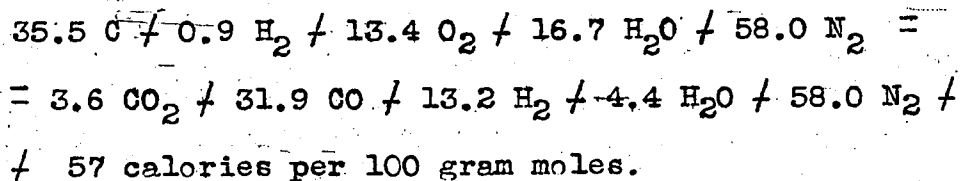
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Zone 3 : distance from the ash zone 20 cm.

$$24 \; C + 0.6 \; H_2 + 14.2 \; O_2 + 16.8 \; H_2O + 58.0 \; N_2 =$$

$$= 11.2 \; CO_2 + 0.7 \; O_2 + 12.8 \; CO + 8.8 \; H_2 + 8.6 \; H_2O +$$

$$+ 58.0 \; N_2 + 990 \text{ calories per 100 gram moles}$$

Zone 6 : distance from the ash zone 70 cm.

$$\text{factor} \; \frac{58.0}{N_{2,6}} = 1.096$$

$$33.9 \; C + 0.85 \; H_2 + 13.8 \; O_2 + 16.75 \; H_2O + 58.0 \; N_2 =$$

$$= 5.7 \; CO_2 + 0.1 \; O_2 + 28.2 \; CO + 13.1 \; H_2 + 4.5 \; H_2O +$$

$$+ 58.0 \; N_2 + 673 \text{ calories per 100 gram moles}$$

Zone 7 (practically equal to Zone 8) : distance from the ash zone

90 and 170 cm respectively, factor 1.112

$$35.5 \; C + 0.9 \; H_2 + 13.4 \; O_2 + 16.7 \; H_2O + 58.0 \; N_2 =$$

$$= 3.6 \; CO_2 + 31.9 \; CO + 13.2 \; H_2 + 4.4 \; H_2O + 58.0 \; N_2 +$$

$$+ 57 \text{ calories per 100 gram moles.}$$

The calculated ratios of the nitrogen volume to the oxygen volume in
these equations is about 4.2, whereas the theoretical ratio is 3.8. This
discrepancy is not surprising as it is well known that the accuracy of the
analytical determination of nitrogen in combustible gases is a relatively
low one because the nitrogen content is determined as the remainder of the
gas sample and the errors of analyzing the soluble and combustible gas com-
ponents go partly into the reading of nitrogen. This discrepancy causes
an inaccuracy of the calculated temperature, heat and chemical equilibrium
adjustment of up to about 10%. However, the conclusions drawn from the
measurements are not influenced substantially.

The heat evolution of the reactions for example in zone 3 is obtained
as follows:

1) $11.2\ C + 11.2\ O_2 = 11.2\ CO_2 +$ $+ 11.2 \times 97$ cal $+ 1087$ cal

2) $4.6\ C + 2.3\ O_2 = 4.6\ CO +$ $+ 2.3 \times 58.6$ " $+ 135$ "

3) $8.2\ C + 8.2\ H_2O = 8.2\ CO + 8.2\ H_2 - 8.2 \times 28.3$ " $- 232$ "

$$\text{Sum} \quad + 990 \text{ "}$$

In table 2 the results of calculations for zone 3, 6, 7/8 are represented. Column 1 contains the number of zone, column 2 the distance in cm from the ash zone, column 3 the gas volume expressed in gram moles, column 4 the gasified carbon related to the gasification state in zones 7/8 as equal 100%. Column 5 shows the water steam decomposition in per cent of the entire steam of 16.8 gram moles per 100 gram moles of gas. Column 6 contains the heat evolution and heat consumption respectively in the zones. Column 7 shows the calculated theoretical maximum temperature whereby the preheating of coke and air in the zones is taken into consideration and column 8 the measured temperatures in $^{\circ}C$.

Table 2: Reaction processes in a gas producer

1	2	3	4	5	6	7	8
Zone	cm	Gas moles	Gasi- fied C	Decom- posed H_2O	Cal per 100 moles	$^{\circ}C$ Calcu- lated	$^{\circ}C$ Ob- served
3	20	100.0	67.5	49.0	+ 990	1430	1340
6	70	109.6	95.5	73.1	- 317	1020	1030
7/8	90/170	111.2	100.0	73.5	- 97	890	820

The columns 4 and 5 of table 2 show that two thirds of the entire gasification processes of the coke carbon and two thirds of the water steam decomposion (49.0/73.5 = 0.67) take place in a 20 cm wide zone. Above zone 6 with a measured mean temperature of $1020^{\circ}C$, 70 cm from the ash zone, the steam

decomposion is completed as high as 100% and the gasification of carbon by carbon dioxide reduction is also practically finished with about 96%.

In table 3 the constants of the homogeneous watergas equilibrium and the heterogeneous Boudouard equilibrium are calculated for the measured temperatures (columns 4 and 6) and compared with the constants which are practically obtained and measured by gas analysis in the zones of the producer (columns 3 and 5).

The data of table 3 show that the equilibria have not adjusted within the producer zones. In zones 3 and 6 respectively, the watergas equilibrium is approached with 36% and 94% respectively and the Boudouard equilibrium with about 0.01% and 1% respectively. The apparent approaching of the water-gas equilibrium in zones 6 and 7 has to be explained by the relatively rapid reaction at the higher temperatures of the lower zones and, as the equilibrium constants become smaller with lower temperatures, the obtained gas composition accords then to the lower temperatures of the higher zones.

The high carbon monoxide content of 12.8% in zone 3, 20 cm from the ash zone, seem to correspond to the theory of L. Mayer, V. Shivonen and others, concerning the primary carbon reactions maintaining that both carbon monoxide and carbon dioxide must be considered primary reaction products of coal gasification, whereas older theories before about 1920 assumed carbon dioxide as the primary product only, which reacts with the carbon to carbon monoxide in a secondary reaction. The data determining the gasification rate in the investigated fuel bed are the following:

The active coke zones with an overall depth of 80 cm and a cross sectional area of 7.0 square meter had a volume of 5.6 cubic meter. The bulk density of the coke was 0.6 tons per cubic meter and the size distribution of the coke particles:

TABLE 3

The Approaching of Equilibria in a gas producer (system Marischka)

1 Zone Number		2 Measured Temperatures °C	3 Watergas obtained	4 Constants theoretical	5 Boudouard obtained	6 Constants theoretical
3		1340	1.13	3.15	0.146	2150
4		1160	1.50	2.42	0.430	625
5		1100	1.68	2.18	0.938	331
6		1020	1.73	1.83	1.27	143
7		820	2.93	1.07	2.52	11.3

<u>76%</u>   <u>12 to 25 mm</u>

17.5%.   5 to 12 mm

6.5%   below 5 mm

The apparent specific gravity of the particles was 1.38 tons per cubic meter. The coke volume in these zones was 2.45 cubic meter and the weight 3.36 tons. The void volume was about 3.15 cubic meter. 8500 cubic meters of gas were produced per hour, that is 2.36 cubic meters per second. The mean gas velocity in the active zones with the mean temperature of about 1000° C was about 2.8 meter per second and the time of contact 0.28 seconds. As the smallest free void cross section was about 7% of the entire producer cross sectional area, the effective maximum gas velocity was 22 meters per second at an air pressure of 150 mm head of water. This was the optimum gas velocity using the mentioned coke sizes. An increase of gas velocity would have lead to a higher mean temperature of the active zone, causing at the same time a deterioration of the gas quality by the phenomenon that the gases pass more and more through paths of less resistance in the fuel bed.

In the following the procedure of computation by W. Gumz is shown, who applies gas analyses of W. Horak to demonstrate the adjustment of the gas producer equilibria, adopting calculation methods of S. Traustel* who based his derivations on the preceding work of T. Cerasoli**.

According to W. Gumz, the calculation in advance of the nine factors, determining the gasification process is possible, because nine equations are

*Traustel S. Praktische Berechmungen von Vergasungsgleichgewichten (Practical Calculations of Gasification Equilibria) Feuerumgstechnik, 29, 105-114 (1941)
**Cerasoli T. Il calcolo della composizione del gas misto (The Calculation of Gas Mixtures) Ann. di Chim. Applicata 13,257-270 (1923)

available. The unknown factors are the six components of the obtained producer gas CO, CO_2, H_2, CH_4, H_2O, and N_2, the reaction temperature, the amount of gasifying agents per kg of coke and the obtained gas volume. S. Traustel's nine equations are:

1) $V_{CO} + V_{CO_2} + V_{H_2} + V_{CH_4} + V_{H_2O} + V_{N_2} = 1$

2) The carbon balance

3) The hydrogen balance

4) The oxygen balance

5) The nitrogen balance

6) The Boudouard equilibrium

7) The heterogeneous water gas equilibrium

8) The methane equilibrium

9) The heat balance

The following way of solution is given by S. Traustel. The reaction temperature has first to be estimated, later used for the calculation and after finishing the calculation the obtained temperature has to be compared with the assumed one and if necessary must be corrected for an other run. The CO content shall be assumed and the CO_2, H_2 and CH_4 - content of the gas calculated. The control computation furnishes a CO - content, which should coincide with the assumed value. The exact CO value can be eliminated graphically in a relatively short time by means of a diagram. With the obtained factors the H_2O content and the N_2 content and finally the amount of the gasifying agents and the obtained gas volume can be calculated.

W. Gumz chooses the following four reaction temperatures of 700, 750, 800 and 900°C and obtains the gas compositions of table 4.

Table 4

Gas Compositions Depending on

Assumed Reaction Temperatures

	700°C	750°C	800°C	900°C
CO	27.3%	33.3%	35.6%	38.0%
CO_2	6.4%	3.6%	1.7%	0.4%
H_2	12.0%	13.5%	12.7%	12.8%
CH_4	0.2%	0.1%	0.1%	0.0%
H_2O	1.8%	1.1%	0.6%	0.2%
N_2	52.3%	50.4%	49.3%	48.6%

The reaction temperature can be determined using the equation of heat balance.

$$Cg \times Hc \neq Cg \times Ec \neq G \times Eg - H_L - H_p = Ep$$

Cg = carbon gasified per nm^3 of producer gas

Hc = thermal value of carbon

Ec = enthalpy of carbon at the assumed reaction temperature

G = gasifying agents nm^3 per nm^3 of producer gas

Eg = enthalpy of the gasifying agents of the temperature of entering the producer

HL = heat lost by the producer, estimated to 8% of $Cg \times Hc$

H_p = net calorific value of producer gas

Ep = enthalpy of the produced gas in calories per nm^3

The enthalpy Ep and the left side of the heat balance equation, both plotted as curves upon the temperature abscissa intersect at a point which is the reaction temperature in question. The theoretical gas composition pertaining to the obtained reaction temperature of 721°C and to a steam saturation

temperature of 57.5 ^{o}C is compared in Table 5 with the gas analyses of the producer gas obtained by W. Horak and other analyses obtained by F. Plenz[*] and by K. Neumann[**].

Table 5

Comparison of Measurements and Calculations

1	2	3	4	5	6	7
	Values Measured by				Values Calculated by	
	Plenz	Horak		Neumann	Gumz	
Steam Saturation Temperature ^{o}C	57.5	59		58.4	57.5	
	dry	dry	moist	dry	dry	moist
% CO	29.31	30.0	28.6	30.1	29.9	29.5
% CO$_2$	5.17	3.4	3.2	4.1	5.2	5.1
% H$_2$	12.68	12.4	12.0	12.6	12.4	12.2
% CH$_4$	0.41	–	–	0.8	0.2	0.2
% N$_2$	52.43	54.2	52.2	52.4	52.3	51.5
% H$_2$O	–	–	4.0	–	–	1.5

The conclusion of W. Gumz is that the coincidence between calculation and measurement is a very satisfactory one and that this coincidence shows better than it can be done by temperature measurements and gas analysis in the fuel bed and by their comparison with the equilibrium constants, that the producer equilibria were adjusted effectively.

[*]Leistungsversuch an einer (Koksvergasungsanlage) auf dem Gaswerk Berlin-Neukolln (Efficiency run with a coke gasifying plant at the gas works Berlin-Neukolln) Feuerungstechnik 15 232-234 (1926/27).
[**]Die Veränderlichkeit der Gasphase in Gasgenerator, (The changeableness of the gas phase in the gas producer) Z.VDI 58 1481-1484, 1501-1504, (1914)

Indeed, the calculated gas composition in columns 6 and 7 of Table 5 are accurately adequate to the 721°C equilibria constants used by W. Gumz, and a superficial comparison of the CO and H_2 contents with the measured values of Horak seem to support this opinion. Nevertheless the calculation of the equilibrium constants based on the analysis of column 4 gives quite different K values:

Table 6

Comparison of Equilibrium Constants

Heterogeneous Equilibrium	K values of Gumz's analysis Column 7	K values Horak's analysis Column 4
Watergas	$K_{p,W} = \dfrac{(CO)(H_2)}{(H_2O)} = 2.40$	$K_{p,W} = 0.80$
Boudouard	$K_{p,B} = \dfrac{(CO)^2}{CO_2} = 1.80$	$K_{p,B} = 2.60$
Methane	$K_{p,M} = \dfrac{(CH_4)}{(H_2)^2} = 0.10$	$K_{p,M} = 0$

The water steam decomposion measured by Horak was 74%, a plausible value, whereas the theoretical value of W. Gumz is much too high:

$$\frac{1.5}{12.2 + 0.4 + 1.5} \times 100 = 90\%$$

As W. Gumz and S. Traustel do not explain the calculated producer temperature as a mean overall temperature of the fuel bed, so it must be assumed, that the

calculated temperature is the temperature of the top layer of the fuel bed. Indeed, the temperature of $721^{\circ}C$ occurs in the top layer but not constantly at the same location. After feeding the producer the temperature rises from $20^{\circ}C$ to about 400 to $500^{\circ}C$ in 7 min. to about 600 to $700^{\circ}C$ in 15 min. and to 700 to $730^{\circ}C$ in about 22 min., when the producer is fed twice per hour with 2.1 tons of coke per hour.

The mean temperature of the fuel bed is fluctuating between limits depending on the feeding procedure; and can be calculated as to be approximately $770^{\circ}C$ and $750^{\circ}C$ respectively.

Herbordt* measured the temperatures in the blast furnace coke bed of a water gas producer obtaining results which confirm ours. The produced water gas consisted of 6% CO_2, 42% CO and 52% H_2. The highest temperature was about 50 cm above the top of the grate and could not be measured because the pyrometer was destroyed. 75 cm above the grate top an average temperature over all measurings of $1220^{\circ}C$ at the beginning $1080^{\circ}C$ at the end of the steam run period was measured and the water decomposion found to be very active. 125 cm above the grate top the corresponding average temperatures were $1070^{\circ}C$ and $1045^{\circ}C$ respectively. The little change in temperature at this point demonstrates that the water gas process

$$C + H_2O \longrightarrow CO + H_2$$ is practically finished at $1000^{\circ}C$ and that an adjustment of the heterogeneous gas producer equilibria at temperatures below $1000^{\circ}C$ is out of question. The relatively high CO_2 content of 6% may be explained by a partial adjustment of the homogeneous water-gas equilibrium at $1000^{\circ}C$ to about $800^{\circ}C$. The gas analysis obtained by Herbordt correspond to an approximate adjustment at about $750^{\circ}C$ of the heterogeneous water gas equilibrium.

*Deutsche Licht — und Wasserfachzeitung 31 183 (1937)

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Without regard to the above shown interferences of theories based on one and the same measurement at a commercial plant, the interferences in contemplation experiments can be explained by the difficulties of measuring temperatures, sampling gases and the performance of model experiments under exactly the same conditions as they occur in commercial plants.

When measuring temperatures of gases, fuel particles and fuel surfaces for example by means of thermocouples it must be born in mind that the measuring device causes a disturbance of the temperature field. The difficulties increase when model experiments and micro tests are used because it becomes more and more difficult to maintain the analogous conditions of the geometry of the heat flow and the gas flow. For example it is comparatively easy to obtain the true mean temperature of a given point of high temperature up to $1600^{\circ}C$ of the fuel bed of a gas producer by means of relatively thin and unprotected thermocouples and the true mean gas composition by means of water cooled sampling tubes. However, it becomes more difficult to measure the temperatures and to draw samples using small laboratory apparatus and it becomes practically impossible to draw a micro gas sample from the bounded film of the carbon surface by means of a for example 0.2 mm i.d. quartz capillary sampling tube.

When this capillary tube is not cooled the gas composition is changing more or less in the direction of adjusting chemical equilibria because of the catalytical influence of the inner surface of the tube which is inversely proportional to the tube diameter. Such micro measuring and sampling methods become worthwhile when no changes of the temperature flow and of the gas flow occur as well as of the gas sample during its passage through the sampling device.

Certainly, some of the discrepancies of measured results and interferences in opinions concerning processes of the gas producer are based on the fact that the mentioned difficulties have not been recognized.

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With reference to these difficulties an analogy is offered by the diffi-
culties which exist in an exact sampling of solid fuels.

The value of all conclusions, drawn from chemical or physical analyses
of coal samples, for example from coal piles and coal seams, depends chiefly
upon the exactitude with which the properties found by the analyses correspond
to those of the fuel mass to be analyzed. The divergences and possible errors
caused by inexact sampling are, as a rule, mostly much higher than those made
in analyzing or given by the analytic methods.

It was said at the beginning that the principle thermodynamic constants
are known with high accuracy. Nevertheless, the chemical equilibrium constants
used by different authors differ still considerably and even the specific heat
values of the gases are often doubtful. Before about 1938 in Central Europe
the values of B. Newmann[*] and W. Schüle[**] were preferred and were different
from the English ones published by I. R. Partington and W. G. Shilling[***].
The differences regarding biatomic gases were as high as 5% and even 10 and
more per cent regarding three atomic gases. The doubtfulness especially in
the heat values at the higher temperatures is eliminated by new measurements
using more efficient and unobjectionable methods than the former used calori-
metric and explosion methods, namely foremost by the spectroscopic method,
which gives a high and constant accuracy within the entire range of high
temperatures. Based on the new experimental data of E. Justi[****] and his
coworker, E. Justi[*****] calculated anew the specific heats of the technical
gases, using the so-called "distribution function" (= Verteilungsfunktion)
a refined calculation method, which takes into consideration the statistic

[*]Stahl und Eisen, 39 746-748, 772-775 (1919)
[**] Neue Tabellen und Diagramme für technische Gase von 0bis 4000 C°
    Springer, Berlin (1929)
[***]The specific heat of gases, London 1924
[****] Forschung 2 117-124 (1931)
    "   5 130-137 (1934)
    "   6 209-216 (1935)
[*****]Spezifische Wärme Enthalpie, Entropie und Dissoziation technischer
    Gase, Berlin, Springer 1938,

weights and the energy values of the different possible states of the quanta of the individual atoms and molecules respectively. The so calculated and 1938 published specific heat values of technical gases are of high accuracy and will presumably not be changed in the near future by the progress of the physics.

Based on the specific heat values of E. Justi and the reaction heat of 10,110 Calories per Kilomole, an equation for the homogeneous watergas equilibrium was calculated and published*. The dependence of the reaction heat on the temperature was first calculated by means of the interpolation method of the least squares and the following row functions of the specific heats were found:

$$c_{p, CO_2} = 5.6944 + 12.2762 \times 10^{-3} \times T - 4.8485 \times 10^{-6} \times T^2$$

$$c_{p, H_2O} = 7.4353 + 1.6414 \times 10^{-3} \times T + 0.69117 \times 10^{-6} \times T^2$$

$$c_{p, CO} = 6.4986 + 1.3463 \times 10^{-3} \times T + 0.02187 \times 10^{-6} \times T^2$$

$$c_{p, H_2} = 7.0695 - 0.5644 \times 10^{-3} \times T + 6.6250 \times 10^{-6} \times T^2$$

The reaction heat becomes:

$$Q_{p, T} = Q_{p, 0} + 1.17 \times T - 4.3591 \times 10^{-3} \times T^2 + 1.6455 \times 10^{-6} \times T^2$$

For $T = 273°K$, the value of $Q_{p,0}$ becomes 10,082 calories per mole and the final equation becomes, after being brought in a suitable form by means of the method of the least squares:

$$Q_{p, T} = 10,082 + 4.162 \times 10^{-4} \times T^2 - 4.3733 \times 10^{-6} \times T^3 + 2.3875 \times 10^{-9} \times T^4$$

The expression for log Kp is finally obtained as:

$$\log Kp = -\frac{2205.6}{T} + 0.9105 \times 10^{-4} \times T - 0.4784 \times 10^{-6} \times T^2 + 0.1741 \times 10^{-9} \times T^3 + 2.3.$$

The following table 7 contains the calculated Kp-values.

*W. I. Müller and E. Graf, Short Textbook of the Technology of Fuels, Vienna, 1945 (in German) (Pg. 76).

TABLE 7

K_p - Values of the Homogeneous Watergas Reaction, 0 to $1000^{\circ}C$

t	Kp	t	Kp	t	Kp
350	0.0471	500	0.205	700	0.674
400	0.0832	550	0.294	800	1.002
450	0.135	600	0.403	900	1.407
				1000	1.846

The values given in table 6 correspond with an accuracy of 0 to 5% at temperatures of 450 to $800^{\circ}C$ and 6 to 10% at the higher and lower temperature with the most exact experimental determinations and calculations of Neuman and Kohler*. At the temperature range of $1000^{\circ}C$ to $2000^{\circ}C$ the following Kp-values given by E. Maurer and E. Bischof suit better the practical conditions.

TABLE 8

Kp - Values for the Homogeneous Watergas Equilibrium 1000 to $2000^{\circ}C$

1000	1.76	1600	4.22
1100	2.18	1800	5.04
1200	2.60	2000	5.97
1400	3.42		

The coincidence of the Kp values of Table 7 with the results of catalytical CO conversion into $H_2 \neq CO_2$ used for detoxication of illuminating gases by E. Graf** and W. J. Müller and E. Graf*** at 350 to $600^{\circ}C$ was satisfactory too.

*Zeitschr. Elektrochem. Angew. physik. Chemie 34 218 (1928)
**Das Gas- und Wasserfach 28 (1936) 209
***" " " " 26 (1934) 122
and Chem. Ztg. 38 (1935) 81-86
and Report E. Graf to Fuels and Lubricants Branch, OQMG, "Research Experiments to Detoxicate Illuminating Gases" Sept 1946.

In connection with the research work at my laboratory at the Technical University of Vienna the development of methods* and apparatus for testing the combustibility, the reactivity, the ignition and decomposition points of coals and cokes and the heterogeneous CO_2 - CO equilibrium were subject of investigations. The following equations of Bodmer** was found most reliable for the temperature range 400 to $1200^\circ C$

$$\log Kp = \frac{-8274}{T} + 2.6024 \log T - 0.001829 \times T + 0.2625\ T^2\ 10^{-6} + 2.3933$$

The representation of the dependence of the CO and CO_2 content on the pressure and temperature given in fig 2 was found new*** and advantageous for our research work on gas reactions under elevated pressure for the purposes of teaching students.

In fig. 2 the CO and CO_2 content according to the Boudourd equilibrium is represented by isotherms whereby the pressure is plotted upon the percentage of gas by volume.

Combining the equation of the equilibrium constant $Kp = p^2_{CO}/p_{CO_2}$ and the equation that the total pressure P is the sum of the partial pressures -

$P = p_{CO} + p_{CO_2}$, the following quadratic equation of isotherms is obtained.

$$p^2_{CO} + Kp \cdot p_{CO} - Kp \cdot P = 0$$

The seven isotherms of fig 2 are calculated with the Kp values of table 9 and show sufficiently the dependence of the gas composition on the pressure, whereby total pressure values of 0, 0.1, 0.3, 0.5, 0.8, 1, 3, 5, 8, 10, 10^2, 10^3 and 10^4 were used and the isotherms for the higher pressures plotted upon logarithm of the pressure.

*W. J. Müller and coworkers (Courad, Jandl, Graf, Gruber)
Brennstoffchemie 11 125-128 (1930), ibid., 12 187-191 (1931)
ibid., 14 340-341, 343-347, 421-424 (1933)
ibid., 15 347-351 (1934), ibid., 16 305-309 (1935) ibid., 19 45-48 (1938),
Krafstoff 1 62-64 (1939)
**Monatsbull. schweiz. Ver. Gas-U. Wasserfachm 6 181 (1926)
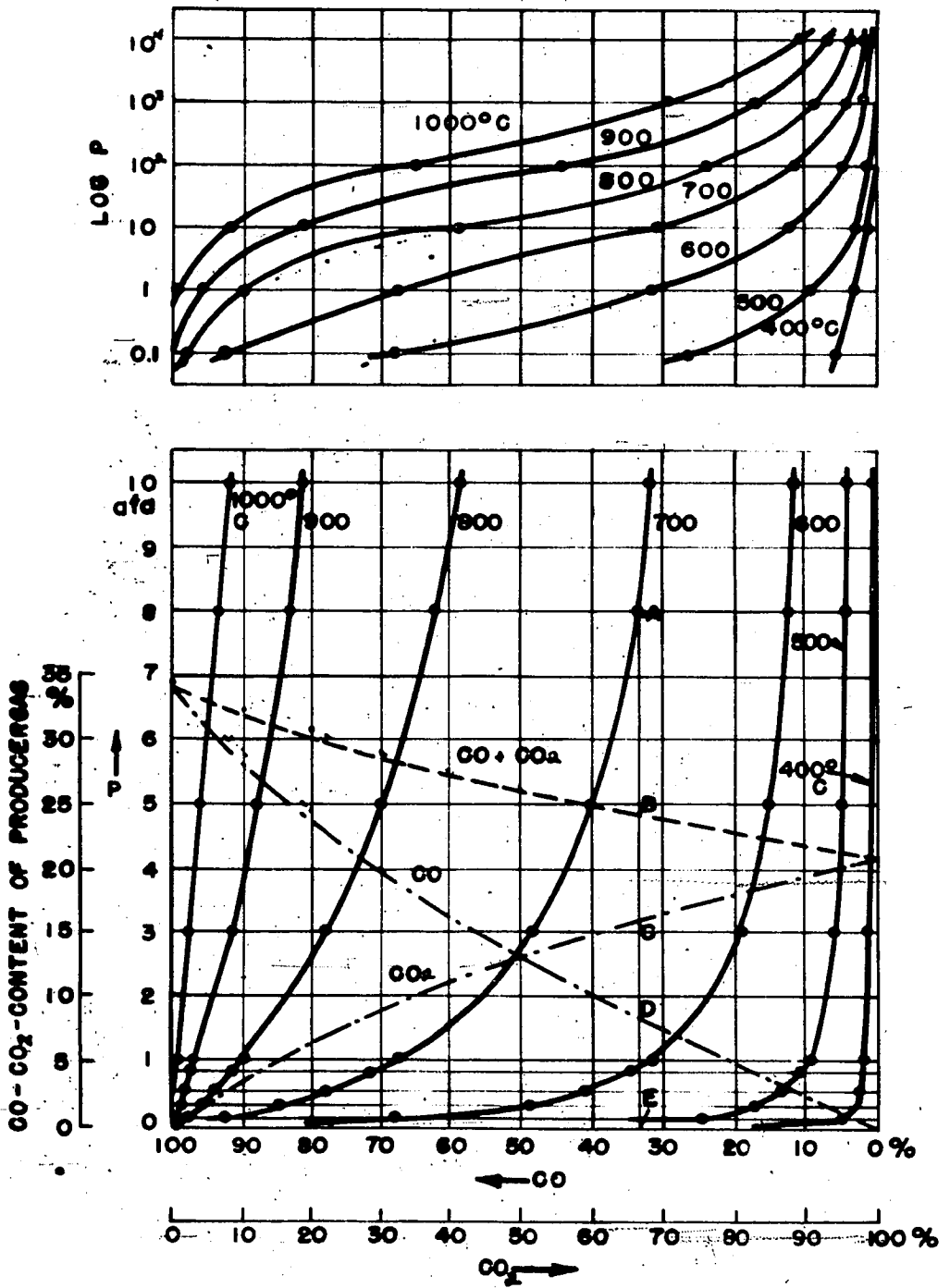*** W. J. Müller and E. Graf, Feuerungstechnik 25 42-44 (1937)

Fig. 2

TABLE 9

Kp – Values of the Boudouard Equilibrium

t $^\circ$C	Kp	t $^\circ$C	Kp
400	0.00022	800	8.150
500	0.00890	900	34.52
600	0.1444	1000	115.66
700	1.366		

The representations given in fig 2 show better than the usual representations by isobars plotted on the temperature abscissa that the equilibrium composition for all temperatures is practically CO only for the lowest absolute pressures and CO_2 only for the highest absolute pressures respectively. The quadratic isothermal equation must be corrected for pressures above about 20 atm. because of the divergences to the law of the ideal gases. The influence of the pressure on the equilibrium composition between 1 and 10 atmospheres is important at the mean temperatures 600 and 700°C and decreases vigorously with the higher and lower temperatures. The curves show that at normal pressure the gas composition is with sufficient accuracy

about 10% CO at 500°C   about 30% CO_2 at 700°C

about 30% CO at 600°C   about 10% CO_2 at 800°C

Extending the CO – CO_2 system to the theoretical producer gas composition, using the relation between CO and CO_2 content in the presence of nitrogen of the air

$$CO = 34.55 - 1.66\ CO_2 \qquad CO = f.\ (CO_2)$$

and the exact composition of the air:

$$CO_2 = 0.035 \quad O_2 = 20.871 \quad N_2\ (+\ A) = 79.094\%$$

the dash dotted lines for the CO_2 and CO constants and the broken line for the sum of CO $\neq$ CO_2 are obtained.

The representations here shown have served on other places too to deepen the knowledge about the processes in gas producers and fuel beds on firing grates.