

APPENDIX 1
CARBON BALANCES

From the official Betriebsbericht, together with certain assumptions, the following balances have been drawn up.

(1) Whole of 1943 (Ref.8)

Synthesis gas made = 330,774,000 m³ (=av. of 12,600 m³/hr.
Producer gas made = 522,633,000 m³ per generator, if 3
Raw coal direct to gas production = 308,593 t always running)
Raw coal to coal drying plant and
ultimately sent to producers = 119,058 t
Purchased coal dust to producers = 7,076 t

Synthesis gas contained CO + H₂ = 74.7% and H₂/CO = 1.98
whence CO = 25.0% and H₂ = 49.7%

assume CO₂ = 18.0%, CH₄ = 3.5%, N₂ = 3.5%, O₂ = 0.3%

∴ carbon in synthesis gas = 0.249 t/1000 m³

Producer gas: assume composition of CO₂ = 12%, CO = 16%, CH₄ = 2%

∴ carbon in producer gas = 0.161 t/1000 m³

∴ carbon appearing in synthesis gas = 0.249 x 330,774 = 82,400 t

" " " producer gas = 0.161 x 522,633 = 84,000 t

∴ total carbon accounted for = 166,400 t

Coal: assume raw brown coal contained 52% H₂O, 29% C (= 60% C
on dry basis) and assume purchased coal dust contained
12% H₂O, 53% C.

∴ carbon entering as raw coal direct = 0.29 x 308,593 = 234,500 t

" " " " " via coal

drying = 0.29 x 119,058 = 34,500 t

" " " purchased coal dust = 0.53 x 7,076 = 3,750 t

total carbon entering system 272,750 t

total carbon accounted for 166,400 t

∴ carbon unaccounted for 106,350 t

i.e. carbon unaccounted for = 39% of carbon used

The relatively low output and air raids no doubt account for the high production of fuel gas compared with April 1944 (see below) and hence to the considerable use of the coal drying plant.

(b) April 1944 (Ref.9)

Synthesis gas made 45,900,000^{m³} (= 21,300 m³/hr. per
Producer gas made 47,950,000^{m³} generator, if 3 always
Raw coal direct to gas production 111,823 t running)

Raw coal to coal drying plant and
ultimately sent to producers 1,012 t
Purchased coal dust to producers 2,454 t
Multicyclone dust sent to boilers 1,800 t
Synthesis gas contained CO + H₂ = 75.2% H₂/CO = 2.0

whence CO = 25.1% H₂ = 50.1%
assume CO₂ = 18% CH₄ = 3.5%, N₂ = 3.0%, O₂ = 0.3%

∴ carbon in synthesis gas = 0.250 t/1000 m³

Producer gas: assume composition of CO₂ = 12%, CO = 16%, CH₄ = 2%

∴ carbon in producer gas = 0.161 t/1000 m³

∴ carbon appearing in synthesis gas = 0.250x45,900 = 11,475 t

" " " producer gas = 0.161x47,950 = 7,720 t

" in cyclone dust sent to boilers = 0.50x1,800 = 900 t

∴ total carbon accounted for = 20,095 t

Coal: assume raw brown coal contained 52% H₂O, 29% C
and assume purchased coal dust contained 12% H₂O, 53% C

∴ carbon entering as raw coal direct = 0.29x111,823 = 32,400 t

" " " " " via coal

drying = 0.29x1,012 = 294 t

" " " purchased coal dust = 0.53x2,454 = 1,300 t

total carbon entering system = 33,994 t

total carbon accounted for 20,095 t

∴ carbon unaccounted for 13,899 t

i.e. carbon unaccounted for = 40.8% of carbon used

Total C losses, counting cyclone dust to boilers

as a loss, = 43.5% of carbon used

APPENDIX 2.

MATERIAL BALANCES

Sufficient information was obtained from the visit to enable a good deal of information on material balances, etc., to be deduced, but the various assumptions made in the following calculations should be borne in mind.

(a) Synthesis Gas

Consider a unit on normal output, and assume a recirculated synthesis gas rate of 35,000 m³/hour for a make of 25,000 m³/hour; about 2,500 m³/hour oxygen would be used and about 60.8 t/hour raw brown coal (based on 1943 data) or 29.1 t/hour of water-free brown coal.

Now raw coal, on a dry basis, contained 60% C, 4% H, 20% O, 3% S, 1% N and 12% ash. The analysis of dry coal dust leaving the drier was given as 60% C and 18% ash, but no figures were given for the other constituents.

The basic data are as follows:-

- (1) O₂ found as CO (25%) and CO₂ (18%) in synthesis gas
= 3,125 + 4,500 = 7,625 m³/hour
- (2) O₂ added as say 96% oxygen = 0.96 x 2500 = 2400 m³/hour
- (3) H₂ found as H₂ (49.5%), CH₄ (3.0%) and H₂S (1.5%) in synthesis gas
= 12,375 + 1,500 + 375 = 14,250
- (4) Carbon found as CO (25%), CO₂ (18%) and CH₄ (3.0%) in synthesis gas = 11,500 m³/hour = 6.15 t/hour
- (5) H₂ present in raw brown coal = 4% x 29.1 = 1.16 t/hr = 13,000 m³/hr
- (6) O₂ " " " " " = 20% x 29.1 = 5.82 t/hr = 4,070 m³/hr

Since about one-third of the coal was completely gasified in the synthesis gas generators at least one-third of the H₂ and O₂ in the raw brown coal would appear in synthesis gas, even if no evolution of H₂ and O₂ occurred in the drier. In practice we should expect from the temperature conditions some evolution of CO₂ & H₂S in the drier. There is insufficient information available to estimate exactly this quantity, but it has been assumed that 40% of the oxygen in raw brown coal, excluding water, appeared as CO₂ in synthesis gas. With this assumption a complete balance can be struck and it will be shown that a reasonable analysis of dry coal dust results.

Thus, by assumption, O_2 obtained from coal = $0.40 \times 5.82 \text{ t/hr}$
 = $2.33 \text{ t/hr.} = 1,630 \text{ lb/hr.}$

Hence, by O_2 balance, O_2 out = $7,625 = O_2$ in = $2400 + 1630 + 1/2(\text{steam decomposed})$

\therefore steam decomposed = $7,190 \text{ lb/hour} = 5.78 \text{ T/hour}$

Hence, by H_2 balance, H_2 out = $14,250 = H_2$ in = $7190 + H_2$ obtained from coal.
 H_2 obtained from coal = $7,060 \text{ lb/hour} = 0.63 \text{ t/hr.}$

Lastly it is assumed that two thirds of the sulphur in raw coal is volatile.

It is now possible, by algebraic methods and without further assumptions, to deduce the following flowsheet, calculated to show the required quantities of C, H, O and S gasified and also to show the same analyses for dry coal dust fed to the generator and leaving the drier respectively.

	C	Ash	H	O	S	N
Raw brown coal to drier)	60%	12%	4%	20%	3%	1%
29.1 t/hr (dry))t	17.47	3.49	1.16	5.82	0.87	0.29
Gases evolved in drier t	0.18		0.36	0.50	0.49	
Dry coal dust to gener-)t	5.97	1.83	0.27	1.83	0.17	0.10
ator 10.20 t/hr						
Gasified in generator	5.97	nil	0.27	1.83	0.05	0.10
Dry coal dust leaving) t	17.29	5.32	0.80	5.32	0.50	0.29
drier 29.5 t/hr.) %	58.6	18.0	2.7	18.0	1.7	1.0
Total gasified in gener-)t	6.15	nil	0.63	2.33	0.54	0.10
ator and drier						

The truth of the assumption, that 40% of the O_2 in raw brown coal appeared as CO_2 in synthesis gas, can be tested only by seeing how the above flowsheet fits other known facts. It will be seen that the analysis of dry coal dust is very close to that given quite independently by Dassow: thus for C, 58.6% compares with 60%, and for ash, 18.0% compares with 18%. It should be noted that the flowsheet assumes complete gasification of C, H and O in the dry coal dust fed to the generator. From the above balance the gases evolved in the drier, apart from water vapour, would consist of

CO_2	334 lb/hr.
H_2S	343 lb/hr.
H_2	3,700 lb/hr.

Since the calculation of these quantities involve the accumulated errors in the whole balance they are subject to considerable error. The amount of H₂ evolved is impossibly high and the amount of CO₂ evolved is low. The real cause of these errors lies either in the over-estimation of H and under estimation of O in the gas or the reverse in the coal. However these errors do not seriously affect any conclusions in this report.

The above flowsheet also confirms that about one-third of the dry coal dust was fed to the generators.

Steam Balance

According to the official monthly report for April 1944 27,375 t steam were charged to the synthesis gas units, (definitely excluding the producers), for a make of 45,900,000 m³ synthesis gas. This is equivalent to 0.6 t. steam/1000 m³ synthesis gas. On the other hand it was stated quite frequently that recirculated synthesis gas was saturated at 82°C when entering the regenerators at 0.15 atms g. i.e. contained 0.62 t water vapour/1000 m³ gas. Since 1.4 volumes of synthesis gas were recirculated for 1 volume made, the quantity of water vapour entering the regenerators was therefore 0.87 t steam/1000 m³ synthesis gas made. The fact that only 0.6 t steam/1000 m³ synthesis gas made was charged against the whole synthesis gas plant means that recirculated synthesis gas leaving the washers must have been saturated at a temperature approaching 75°C and containing about 0.59 t water vapour/1000 m³ synthesis gas made; for undoubtedly some of the 0.6 t steam was used in the form of oxygen saturated at 82°C (about 0.06 t) and an unknown amount of steam was added directly to the second gasifier; there were also no doubt miscellaneous usages of steam on auxiliary equipment. It is concluded that the total quantity of water vapour entering the generators was about 1.0 t steam/1000 m³ synthesis gas made, both in the form of water of saturation and in the form of direct addition of steam. Steam actually reacting with carbon was quite a small proportion of this, viz 0.23 t/1000 m³ synthesis gas made, according to the amount of steam decomposition deduced above.

The steam balance for 25,000 m³/hour synthesis gas made then becomes -

	<u>t/hr</u>	<u>m³/hr</u>
Water vapour and direct steam added	25	31,100
steam decomposed	5.8	7,200
∴ steam entering drier	19.2	23,900
Water added as raw brown coal	31.5	39,200
∴ steam leaving drier	50.7	63,100

And since gas leaving drier = 60,000 m³/hour
 ∴ gas and steam leaving drier = 123,000 m³/hour

This mixture contains more than enough heat and water vapour to permit saturation of recirculated synthesis gas leaving the washer to a temperature of as high as 82°C.

(b) Producer Gas

Insufficient information is available to deduce an accurate flowsheet for the producers, but a rough flowsheet has been deduced as follows.

Consider a producer making 30,000 m³/hour producer gas, of composition 12% CO₂, 0.3% O₂, 16% CO, 16% H₂, 2% CH₄, 53.7% N₂. The equivalent carbon content was 0.161 kg/m³ or 4.83 T/hour. The dry coal dust rate to the producer is not known accurately, but a figure of 0.5 t/1000 m³ producer gas was quoted by Dassow, which agrees with the figure of 15 t/hour also quoted by Dassow in connection with the rates through the pneumatic feed lines. With a carbon content of 58.6%, to be consistent with the analysis deduced above, this corresponds with a carbon feed of 8.79 t/hour. Thus the carbon loss from the system = 8.79 - 4.83 = 3.96t or 45% of the feed; this is high, but later it will be that this was probably the case.

Then with the coal analysis deduced above we have:

H ₂ fed with coal	= 2.7% x 15.0	= 0.405 T	= 4,540 m ³ /hour
O ₂ " " "	= 18.0% x 15.0	= 2.70 T	= 1,890 m ³ /hour
N ₂ " " "	= 1% x 15.0	= 0.15 T	= 120 m ³ /hour
O ₂ found in producer gas	= 12 + 0.3 + 8	= 20.3%	= 6,090 m ³ /hour
H ₂ " " " "	= 16 + 2 x 2	= 20.0%	= 6,000 m ³ /hour
		(= 0.535 t)	
N ₂ " " " "	= 0.537 x 30,000		= 16,110 m ³ /hour

∴ H₂ derived from air = 16,110 - 120 = 15,990 m³/hour

∴ O₂ " " " = 4,235 m³/hour

∴ O₂ burnt to steam = 4,235 + 1,890 - 6,090 = 35 m³/hour

∴ H₂ burnt to steam = 2 x 35 = 70 m³/hour

∴ H₂, by difference, derived from coal = 6,000 + 70 = 6,070 m³/hour
 whereas H₂ derived from coal, by analysis = 4,540 m³/hour

It will be remembered that it was suspected in the calculations on synthesis gas that less H_2 was evolved in the drier than appeared from the calculations; if the H and O contents of dry coal dust were not 2.7% and 18.0% as deduced but 3.5% and 17.0% respectively, the hydrogen balance for the producers would be correct, and there would be a small positive steam decomposition. This could well be so, and tends to confirm the air rate and negligible steam decomposition deduced above. It is noteworthy that the bulk of the hydrogen appearing in producer gas may be regarded as derived from coal rather than from steam; moreover the C/H ratio found in the gas is about 9, which is close the C/H ratio found in brown coal tar. This bears out the contention of Koppers (see p.14), that the Schmalfeldt producers are little more than distillation and cracking units, with practically no gasification of solid carbon.

The only figure available for steam usage is 4,622 t for 47,950,000 m^3 producer gas, charged in the monthly report for April 1944; this corresponds with 96.5 kg/1000 m^3 producer gas or 2.9 t/hour for 30,000 m^3 /hour. Although small this is ample to permit the calculated very small steam decompositions.

Thus the steam content of wet producer gas was about 2.8 t/hour = 3,500 m^3 /hour, so that the wet producer gas rate was 33,500 m^3 /hour

Summarizing then we have for 30,000 m^3 /hour producer gas:

Dry coal dust	=	15.0 t/hour
Air	=	20,225 m^3 /hour
Steam decomposed, say 125 m^3 /hour	=	0.1 t/hour
Total steam added	=	2.9 t/hour

The final dust would then contain :

Carbon	=	8.79 - 4.83	=	3.96 t	=	60%
Ash	=	0.180 x 15	=	2.70 t	=	40%
				<u>6.66 t</u>		

No reliable analyses of final dust were given us, but there is reason to believe that the figures given in Ref.4, of 50% C and 50% ash, were too optimistic and too low in carbon.

(c) Combined Material Balance

As a check on the above calculations it is interesting to use them to calculate the combined material balance for synthesis and producer gas and hence derive a figure for the dust losses on the synthesis gas units.

It will be remembered that the 1943 figures were used to deduce the quantity of raw brown coal fed to the synthesis gas driers. Thus for 330,774,000 m³ synthesis gas and 522,633,000 m³ producer gas, we have from Appendix 1,

Carbon entering as raw coal direct	=	234,500 t
" " " " " via coal drying	=	34,500 t
" " " purchased dust	=	3,750 t
Total carbon entering system	=	<u>272,750 t</u>
Carbon appearing in synthesis gas		82,400 t
" " " producer gas		84,000 t

Then from Appendix 2,

Carbon lost from producers at 3.96 t/30,000 m ³	69,000 t
∴ by difference carbon lost from synthesis gas units	<u>37,350 t</u>
Total carbon	<u>272,750 t</u>

The above of course assumes no carbon losses in the coal drying plant, or any form of gaseous losses, of which there are several potential sources.

Pictorially the above may be shown as follows:

Carbon entering as raw brown coal direct 234,500 t	Lost as dust from synthesis gas units		37,350 t 13.7%
	Found in 330,774,000 m ³ synthesis gas		82,400 t 30.2%
	Found in 522,633,000 m ³ producer gas		84,000 t 30.8%
Carbon entering as raw coal via coal drying plant 34,500 t	Lost as dust from producer gas units	Lost in water from washers	69,000t 25.3%
Carbon as purchased dust 3,750t		Cyclone dust to boilers	
Total carbon losses			<u>39.0%</u>

(d) Fuel Gas Requirements

In the whole of 1943 the synthesis gas units required 1,780 T.cals fuel gas/1,000 ³ synthesis gas, and in April 1944 1,715 T.cals/1,000 ³; in each case the fuel gas consisted of a mixture of producer gas and tail gases from the Fischer-Tropsch and hydrogenation plants.

APPENDIX 3
DUST LOSSES

Ref.4 is a note written at Iditzkendorf in early 1942 when a project requiring larger gas quantities was being considered; the note was intended to show what alterations would be necessary to the washer water system and for this purpose gave figures for the dust emission from the synthesis and producer gas plants. Dassow said these figures were rather optimistic and calculations based on other data confirm this.

An output of 90,000 ³/hour synthesis gas on 3 units and of 120,000 ³/hour producer gas was considered.

(a) Synthesis Gas

Each unit was taken as losing 3.5 t/hour dust containing 60% C, when making 30,000 ³/hour synthesis gas, i.e. 70 kg. carbon lost/1,000 ³ dry synthesis gas.

Synthesis gas composition was taken as 25% CO, 20% CO₂ and 3.5% CH₄, corresponding to 260 kg carbon/1,000 ³ synthesis gas.

(b) Producer Gas

The composition of dust in the final gas was stated to vary considerably, the ash from 45 to 55% and carbon from 50 to 70%; these figures are difficult to believe, since 50 + 55 = 105% and 45 + 70 = 115%! However the average composition was taken as 50% carbon and 50% ash.

The amount of dust was then calculated from the analysis of the dry coal fed to the producer (18% ash, 60% C) and of the final dust.

$$\text{Thus } \frac{\text{C lost in dust}}{\text{C fed to producer}} = \frac{50 \times 0.18}{60 \times 0.50} = 0.30$$

i.e. 30% of the carbon fed to the producer was lost as dust.

Producer gas composition was taken as $\text{CO} + \text{CO}_2 + \text{CH}_4 = 32\%$ (figures given on p.8 indicate only 30%), corresponding to 172 kg. carbon/1000 m^3 producer gas. Hence the carbon lost as dust = $\frac{3}{7} \times 172 = 74$ kg. carbon/1000 m^3 dry producer gas and the dust lost = $2 \times 74 = 148$ kg/1000 m^3 dry producer gas, or 17.8 t/hour for a producer gas production of 120,000 m^3 /hour.

(c) Overall Carbon Balance

From the above figures and assuming no other carbon losses the following balance can be deduced, showing carbon in t/hour.

	Lost as dust from synthesis gas units	6.3 t	10.6%	
Carbon in 59.2 t	Found in 90,000 m^3 /hour Synthesis gas	23.4 t	39.5%	Total carbon losses = <u>25.7%</u>
	Found in 120,000 m^3 /hour Producer gas	20.6 t	34.8%	
	Lost as dust from producer gas units	8.9 t	15.1%	

It should be noted that the total carbon loss of 25.7% calculated above is considerably less than the figures of 39 and 43.5% calculated in Appendix 1 from official reports of achieved data. Taking into account Dassow's statement that the figures in Ref.1 were too optimistic and the fact that some carbon losses could have occurred other than as dust, e.g. as leakage of synthesis gas into a regenerator, coal and gas used during starting operations, it is considered that at least one-third of the carbon was lost as dust.

Allocation of achieved dust losses between synthesis gas and producer gas is very difficult. From the material balances in Appendix 2 however we can deduce the following:

(a) Synthesis Gas

Carbon loss = 37,350 t for 330,774,000 m^3 synthesis gas
of 113 kg/1,000 m^3 dry synthesis gas made

This agrees with the figure of 70 kg/1,000 m^3 , deduced from Ref.4, allowing for the much greater overall losses achieved in 1943.

(b) Producer Gas

Carbon loss = 3.96 t/30,000 ³ producer gas
= 132 kg/1000 ³ dry producer gas

This is greater than the figure of 74 kg/1000 ³, deduced from Ref.4. It is however in line with dust concentrations given by Dassow (see below) and with the amount of dust fed to the producers. The achieved 1943 efficiencies cannot be accounted for by lower losses on the producers, without allowing higher losses on synthesis gas.

Dust Concentrations

In Appendix 2 it is deduced that with a synthesis gas unit on normal output the wet gas rate at the exit of the drier and cyclone was 123,000 ³/hour and the dry dust leaving the drier was 29.5 t/hour.

Using the above figure of carbon loss of 113 kg/1000 ³ dry synthesis gas made, the carbon loss for 25,000 ³/hour would be 2.82 t/hour and so the dust loss, with 60% C, would be 4.70 t/hr.

Hence the dust concentrations of wet synthesis gas become:

leaving the drier 250 g/³ wet gas ($\approx 29.5 \times 1000/123$)
after the cyclone 38 g/³ wet gas ($\approx 4.70 \times 1000/123$)

∴ combined separator & cyclone efficiency 85%

The figure of 160 g/³ quoted by Dassow may have referred to the dust content before the cyclone and after the separator, the difference being due to large material removed in the separator.

Also in Appendix 2 it is deduced that with a producer unit on full output the wet gas rate was 33,500 ³/hour and dust leaving the Multiklon was 6.66 t. Thus the dust content after the Multiklon was 199 g/³ wet gas. This is to be compared with Dassow's very rough figure of 200 g/³ for gas before the boilers and Multiklon and it should be noted that even the optimistic figures of Ref.1 lead to a dust concentration of about 135 g/³ wet gas after the Multiklon.

Conclusion

We conclude from a consideration of all the evidence that the following figures are probably near the truth:

dust in synthesis gas before cyclone	150 to 200 g/ ³ wet gas
" " " " after "	30 to 40 g/ ³ wet gas
" " producer gas before Multiklon	200 to 250 g/ ³ wet gas
" " " " after "	150 to 200 g/ ³ wet gas
carbon loss in synthesis gas	80 to 110 kg/1000 ³ dry gas made
" " " producer gas	100 to 130 kg/1000 ³ dry gas