

SULPHUR AND FISCHER-TROPSCH DIFFICULTIES

Schmalfeldt gas caused considerable difficulties in the Fischer Tropsch process, which used a cobalt-kieselguhr catalyst, due to the relatively high content of thiophene[#] and other S-ring compounds, as well as gum-forming compounds. This, in the opinion of Dassow, was due to drying and gasification being done in the same apparatus: he reckoned there would be no difficulty if the drying were done first, say in a Büttner drier, separately from gasification. S-ring and gum-forming compounds would tend to be destroyed in passing through the regenerator at 1,350°C and to a lesser extent in passing through the generators at 1,000°C. Since only 60% of the synthesis gas was recirculated and 40% was bled off as make immediately after the drier, therefore 40% of the gaseous products of drying did not pass through either regenerator or generators, and 40% of the carbonisation products did not pass through the regenerator, although all carbonisation products passed through a zone at 1,000°C. It is not certain whether the deleterious impurities were evolved in the drying or in the carbonisation, but in either case we should expect an appreciable fraction of them to escape with the make gas and that such gas would contain more of them than would gas derived from a gasification system, e.g. Winkler generators, where drying and carbonisation were carried out in a separate process.

[#]Schultz said that whereas the organic sulphur in coke water gas was about 90% CS₂ and COS and 5-10% thiophene, organic sulphur in Schmalfeldt gas contained about 20% thiophene.

from 300 to 60 g/l³).

In Ref. 5 Koppers refer to the Schmalfeldt producers as being little more than distillation and cracking units, with practically no gasification of solid carbon; calculations in Appendix 2 confirm that this is no exaggeration. The cause of this is uncertain, but may lie in the fact that all free oxygen has disappeared by the time the coal particles have been stripped of their volatile matter, and the subsequent reactions between H₂O, CO₂ and the coke particles are comparatively slow.

Coal Drying Plant

Three of the boilers installed in the power plant could use only dry coal, and a coal drying plant, fired by coal and producer gas, was installed to provide this dry coal. The plant was also used to a certain extent to supply dry coal to the producers, when for any reason the driers of the synthesis gas units were unable to dry enough coal.

Purchased Coal Dust

A small quantity of dried brown coal dust, containing 12% H₂O and 53% C, was also purchased and used partly on the boilers and partly on the producers.

Labour

Dassow gave the following figures for labour.

<u>Process:</u>	Synthesis gas	180
	Producer gas	80
	Coal transport and preparation	70
	Total	330

<u>Maintenance:</u>	Fitters and labourers	80
	Bricklayers	10
	Electricians	5
	Instruments	5
	Total	100

Split of 180 Process Workers for Synthesis Gas Production

(a) <u>Shift Men</u>	<u>Men/shift/unit</u>	<u>Men/3 shifts/3 units</u>
Chargehand (Vorarbeiter)	1	9
Loading-hand (Schichtsführer)	1	9
Automatic Control (Steuerhaus) and air heating	2	18
Cupola operator	1	9
Recycled gas blowers	1	9
Plant fitter	1	9

The raw synthesis gas contained about 1 to 2% H_2S . The only purification steps originally installed were to remove the bulk of the H_2S in an Alkacid plant, followed by Luxmasse (30% soda, running at 160° to $280^\circ C$). The latter however passed too much organic sulphur, especially ring-compounds, and gum-forming compounds, so in 1940 an oil-scrubber was installed after the Alkacid plant. The oil-scrubber also enabled the 6 to 8 g/m³ benzol in the gas to be recovered. Later when gas outputs were increased the Alkacid plant was backed up by oxide boxes, running cold and using bog ore. At this stage therefore the purification train was: water wash, Alkacid, oxide boxes, oil wash and Luxmasse. The Luxmasse reduced the organic sulphur content from 40-100 g/100 m³ to 0.5 g/100 m³ at best, but usually only to 1.5 to 2.5 g/100 m³. This however was still not good enough and in 1944 an active carbon plant was installed before the Luxmasse; this greatly improved matters and reduced the organic sulphur content after the Luxmasse to 0.3 g/100 m³ or less. The plant was run with this improvement for only two months before bombing stopped operations, but during this period the Fischer-Tropsch plant showed greatly improved performance.

It should be noted however that there was no difficulty in using Schmalfeldt gas for hydrogenation, where sulphur was not a poison. Gas for this purpose was taken from after the oil wash.

RAW MATERIALS AND SERVICES

In Appendix 2 flowsheets are deduced for synthesis gas and producer gas. From this and other data derived from the reports for April 1944 the following have been drawn up, for a generator output of 20-25,000 m³/hour synthesis gas.

(a) Synthesis gas, including producer gas. It is assumed that all the fuel gas to the regenerators was producer gas; if this were actually the case then with the achieved dust losses the synthesis gas units could not dry enough coal, so that separate coal drying plants would have to be used. However in any process using synthesis gas there will be a certain amount of by-product gases, which could be used as fuel gas; at least 300 T.cals/1,000 m³ synthesis gas would be available because of the 3.5% CH_4 in synthesis gas. If such fuel gas is valued at producer gas value then it is permissible to calculate as though all the fuel gas to the regenerators was producer gas.

	<u>Per 1,000 m³ made</u>	
	<u>Synthesis gas</u>	<u>H₂ + CO</u>
Raw brown coal (52% H ₂ O), kgs.	2920	3900
Carbon, kgs, including all losses	845	1130
Steam used, kgs.	765	1020
Steam raised, kgs.	825	1100
Oxygen, m ³	100	134
Nitrogen, m ³	160	214
*Electricity for production only, kwh.	133	177
Cooling water, m ³	88	118

(b) Synthesis gas only, i.e. plant between regenerators and second generator (inclusive)

	<u>1,000 m³ synthesis gas made</u>
Carbon, kgs.	250 (about 100 kgs losses excluded)
Steam used, kgs.	600
Oxygen, m ³	100
Fuel gas, T.cals.	1,750
Electricity for production only, kwh.	67
Cooling water m ³	55
Recirculated synthesis gas, m ³	1,400-2,000
Synthesis gas for conveying dust, m ³	100

(c) Producer gas only

	<u>1,000 m³ producer gas</u>
Carbon, kgs.	300 (losses included)
Steam used, kgs.	100
Steam raised, kgs.	500
Air, m ³	670
Electricity for production only, kwh.	40
Cooling water, m ³	20

(d) Without use of Oxygen When not using oxygen it was said that the producer gas requirements were much the same in total quantity, but amounted to about 2,300 T.cals/1000 m³ synthesis gas made, because they were spread over a smaller quantity of gas; the complete combustion of 100 m³ C₂ to CO₂ would be the equivalent of about 500 T.cals producer gas.

*In addition about 44 kwh/1,000 m³ synthesis gas was used for boosting synthesis gas to the purification plants and for boosting producer gas from the producers to the various points of usage.

Hydrogen Manufacture

Synthesis gas, produced in the manner described above, was used directly for the Fischer-Tropsch plant, after suitable purification. Hydrogen for the hydrogenation plant was produced from the same gas but taken off as a separate stream after the oil scrubbing. It was compressed to 8 ats. and the CO converted with steam to H_2 and CO_2 . CO_2 was removed by water washing at 8 ats. and CO removed by copper liquor scrubbing at 200 ats. The final pressure was 700 ats and the final gas composition 91-92% H_2 , 4% N_2 , 3.5% CH_4 .

COMPARISON OF SCHMALFELDT PROCESS WITH WINKLER GENERATORS

It is of interest to compare the Schmalfeldt process with Winkler generators, since they are to a large extent alternative processes for manufacturing synthesis gas from brown coal.

In a Winkler generator all the heat of reaction for gasification is developed in situ by the combustion of oxygen, apart from a little introduced as superheat in steam. In the Schmalfeldt process, as originally designed and run, no oxygen was used but all the heat of reaction for gasification was introduced by combustion of air, via the formation and subsequent combustion of producer gas; however in the Schmalfeldt process as more recently run some of the heat of reaction was also added by the direct combustion of oxygen.

To simplify the comparison it is assumed that Winkler generators are gasifying dry brown coal, instead of the more usual grude or brown coal coke. Then in both processes no tar is recovered but is cracked during the gasification process.

In the following table performance figures for Winklers are derived from Ref.7, based on Leuna experience. Unit costs are typical of those met with in the neighbourhood of brown coal mines, and items marked thus (x) include their own capital charges. Both types of plants are assumed to be on reasonably high output.

Item	Unit Cost	Schmalfeldt		Winkler	
		Per 1000 ^m H ₂ +CO		Per 1000 ^m H ₂ +CO	
		Units	RM	Units	RM
Raw brown coal, incl. fuel to drier	2.0 RM/t	3.90t	7.80	2.26t	4.52
Drying, excl. fuel	RM5.0 RM/t dry coal	Nil	Nil	0.905t	4.53
Dry brown coal	RM10.0 RM/t	Nil	Nil	0.905t	9.05
L.P. steam	RM 1.6 RM/t	1.02t	1.63	0.44 t	0.70
H.P. steam	RM 2.4 RM/t cr.	1.10t cr.	2.64	cr.0.65 t	cr.1.56
Power	RM 2.0 Pfg/kwh	177 kwh	3.54	52kwh	1.04
Cooling water	RM 2.0 Pfg/ ^m	118 ^m	2.36	27 ^m	0.54
Oxygen	RM 2.3 Pfg/ ^m	134 ^m	3.08	360 ^m	8.28
Process labour	1.2 RM/man hour	2.0	2.40	0.4	0.48
Maintenance labour	1.2 RM/man hour	0.6	0.72		} 1.40
Maintenance materials			2.5?		
Miscellaneous			3.0?		2.0?
Total, excl. capital (approx)			24.4 ^{RM}		21.9
Capital charge @ 10% p.a.			3.0 ^{RM}		1.0
Full cost			27.4		22.9

Whilst the figures in the above table must be treated with a certain amount of reserve, owing to uncertainties inherent in estimates of this nature, certain features become clear. Even with fuel as cheap as 2 RM/t the Schmalfeldt process is somewhat more expensive in running cost and appreciably more in capital cost. Despite its poor carbon efficiency direct fuel costs are no more in the Schmalfeldt process, even after allowing for costs on that part of the plant used for drying; this is because inefficiency costs so little with coal at this price, whilst drying costs in special driers are not low. Oxygen is a formidable item in the cost of Winkler gas. The costs of power and cooling water in the Schmalfeldt process are high, mainly because about four times as much gas has to be boosted, cooled and dedusted. Labour and maintenance costs are high in the Schmalfeldt process, because of the large and scattered plant, varied operations and many points of control. This is also reflected in the capital costs, which are probably three times that of the Winkler plant proper, i.e. excluding coal drying and oxygen manufacture. This can readily be appreciated from the comparison given in the following table.

^{RM}Ref.2 gives the cost of raw water gas in 1943 as 20.4 RM/1000 ^m, to which has to be added 6.6 RM/1000 ^m for boosting and purification: the former figure is equivalent to 27.4 RM/1000 ^m H₂+CO, although it is not clear whether capital charges are included.

^{RM}Ref.1 gives the capital cost as 22,600,000 RM, specifically excluding railways, water supply & power plant; it probably excludes roads, drains, etc. but may include the oxygen plant.

Plant for Schmalfeldt Process and Winkler Process

	<u>Schmalfeldt Unit</u> <u>at Lützkendorf</u>	<u>Winkler Unit</u> <u>at Böhlen</u>
Max. Output, m ³ /hr. water gas	25,000	25,000
Fuel handled, t/hr: raw brown coal	65	-
dry brown coal	-	17*
Major brick-lined chambers, about 4.5 to 5.5 m.I.D. by 20-25 m. high.		
Producer	1	0
Regenerators	2	0
Generators	2	1
Gas drier	1	0
	<hr/>	<hr/>
Total	6	1
Gas to be cooled and dedusted, m ³ /hr. dry		
Producer gas	25,000	Nil
Recycled synthesis gas	50,000	Nil
Synthesis gas made	25,000	25,000
	<hr/>	<hr/>
Total	100,000	25,000
Major washers, about 5 m.I.D. by 20m. high	3	1
Waste heat boiler capacity, t/hr. steam	12.5	12

Additional costs, which should be debited to the Schmalfeldt process, but are not included above, have to cover (a) the cost of disposal of the large quantities of muddy effluent, (b) the cost of the higher inert content of water gas ($CH_4 + N_2 = 6\%$, as against 3% in Winkler gas) and (c) the expensive purification treatment if the gas is to be used for Fischer Tropsch synthesis.

As coal becomes more expensive so does the difference between the costs of the two processes widen. Thus with raw brown coal at 4 RM/t the difference would be increased by about 4 RM/1000 m³ H₂ + CO, allowing for the coal used in making steam, power, oxygen, etc.

Nevertheless remembering what was said on p.3, that the process has been developed at Lützkendorf in very disadvantageous circumstances, it is yet possible that the Schmalfeldt process could equal the Winkler process in cost whatever the cost of brown coal. Obvious improvements could be brought about (a) by making fuel gas by Winkler generators, running on air and the coarser fraction of the dried dust, replacing the Schmalfeldt producers, which are very inefficient, and (b) by installing multicyclones on the synthesis gas units to reduce dust losses. The Schmalfeldt synthesis gas process could then be imagined as saving the cost of coal drying and much of the cost of oxygen manufacture in the Winkler process, by a process involving a high capital cost of the gasification plant proper and higher costs for labour, maintenance and cooling water.

*actually 14 t/hr. of brown coal coke or grude is used at Böhlen.

It cannot safely be argued that because the Schmalfeldt plant at Lützkendorf was never repeated that therefore, in German opinion, there are more economic processes. Reasonable operating results were not obtained at Lützkendorf until 1942, thus doing something to eradicate earlier bad impressions, due to initial disadvantageous circumstances. After that time new factories, requiring gasification of brown coal, ceased to be built. Moreover German economy was such as to put a premium on tar, so this would give a preference to a Winkler process, using brown coal coke after tar recovery.

It is clear however that the Schmalfeldt process can find no application under British conditions. We have no suitable fuels which are cheap enough to permit large dust losses or which cannot be gasified more economically in conventional ways.