Nitrogen Section EB/Op. 462

Oppau, March 9, 1942

METHANE SPLITTING IN THE K PLANT AT HEYDEBRECK

A) Splitting in equipment for gas for distant transmission.

3,500 m^3/h methane per system is to be split.
The temperature in the converter outlet is 850°, methane preheated to 650° C.

Analysis:

	analysis at inlet	CH reaction		water gas reaction	split gas parts	split gas %
CO_2				+ 0.225	0.225	7.0
		+ 0.487 O_2				
CO			0.994	- 0.225	0.769	23.8
H_2			2.008	+ 0.225	2.233	69.0
CH_4	1.000		0.006		0.006	0.2
Dry Gas	1.000				3.233	100.0
m^3 H_2O	1.000	- 0.020	0.980	0.225	0.755	
g H_2O	735				556	

K, theor. = 1.16 at 850°

I.) Calculations of CH_4 converter.

~~a). oxygen required = 0.487 m^3 O_2/m^3 CH_4~~

b). heat balance of the converter

Heat produced:

~~Reaction I: $CH_4 + 1/2\ O_2 = CO + 2\ H_2$~~
Heat of reaction at 650°: 269 h.un/m^3;
0.974 x 269 = 262 h. un.
Reaction II; $CO + H_2O = CO_2 + H_2$
Heat of reaction at 650°: 337 h.un./m^3;
0.225 x 337 = 76 " "
Heat produced 338 " "

Heat consumed:

Reaction III; $CH_4 + H_2O = CO + 3\ H_2$
Heat of reaction at 650°: - 2689 h.un/m^3;
0.02 x 2689 = 54 " "

Heating of split gas from 650° to 850°;
$\Delta T x C_p$ = 200 x 1.322 = 264 " "

True specific heat of the split gas at 800° C

CO_2:	0.225 x 0.563 =	0.127	
CH_4:	0.006 x 1.065 =	0.006	
H_2O:	0.755 x 0.419 -	0.316	
diatomic:	3.002 x 0.330 =	0.992	
		1.441 x 0.917 =	1.322

Heat losses — 20 h.un.

Heat consumed (heat units/m^3 CH_4) = 338 h.un.

II.) Cooling of the split gas.

a) heat content of the split gas at catalyst converter outlet. sensible heat:

$T \times c_p = 850 \times 1.257$ — 1068 " "

Average sp. heat of the split gas between 0 and 850° C

CO_2:	0.225 x 0.503 =	0.114	
CH_4:	0.006 x 0.746 =	0.005	
H_2O:	0.755 x 0.390 =	0.294	
diatomic:	3.002 x 0.319 =	0.958	
		1.371 x 0.917 =	1.257

Heat of condensation of water: 0.556 x 595 = 331 " "

Heat content at outlet of converter (ht.un./m^3 CH_4) 1399 " "

b) Heat exchanger

The standpipe is disconnected. The split gas, immediately upon leaving the catalyst converter, enters the heat exchanger. The inlet gases are heated to 650° in the heat exchanger.

Heat contents of inlet gas at 650° C:

$650\ c_p + W.L_o = 650 \times 1098 + 0.735 \times 595 = 713 + 437 = 1150$ h.un.

Average spec. heat of inlet gases, between 0° and 650°C

CH_4:	1.000 x 0.661 =	0.661	
H_2O:	1.000 x 0.382 =	0.382	
O_2 :	0.487 x 0.316 -	0.154	
		1.197 x 0.917 =	1.098

The oxygen is practically dry when let in, and at a temp. of 15°. Its heat content is 0.487 x 15 x 0.917 x 0.311 — 2 h.un.

Methane may be heated in the evaporator to 67.5° (v. Section III) and saturated with 206 g. H_2O. Its heat content will be 156 h. un. The heat content is raised from 0.529 x 643.8 = 340 h. un. to 496 h.un. by the addition of 529 g. make-up steam at 1.5 atm. = 111° C.

(After the addition of steam the partial pressure of water is 1/2 P, where P = 956 mm, or by 478 mm (notice: text gives 438 mm). The dew point is at 85.3° (notice: for 438 mm; 87.5° for 478 mm; the rest of the calculations not checked. W.M.S.) The heat content at the dew point is 501 ht. un. (v. III, a1). Upon the addition of steam at 1.5 atm., CH_4 is therefore not entirely dry).

~~The split gas must therefore give up 1150-(2+486) = 562 ht. un. in the heat exchanger. It leaves the exchanger with a heat~~ content of 1399-652 = 747 ht. un./m^3/CH_4. Its temperature is

$$(747-331) : 1.322 = \frac{416}{1.32} = 315°$$

III. The cooler-vaporizer system.

a). Heat balance of water circuit.

The heat given up to CH_4 in the vaporizer = heat contents of the fresh condensate + the heat taken up in the cooler.

1). Heat given up to CH_4 in the vaporizer:

Heat contents of CH_4 saturated with water = Cp T + WL_T, with P = 1.3 atm = 956 mm Hg, $W = \frac{P}{956-P} \times \frac{18}{24.5} = 0.735 \times \frac{P}{956-P}$

The average specific heat of CH_4 between 0° and 100° is 0.429 x 0.917 = 0.395.

T, °C	P, mm	W	W x L_T	Cp x T	Heat Cont.
15	12.8	0.010	6	6	12
~~30~~	~~32~~	~~0.025~~	~~15~~	~~12~~	~~27~~
45°	72	0.060	37	18	55
57	130	0.116	72	22	94
60°	149	0.136	84	24	108
67	205	0.201	126	27	153
68	214	0.212	133	27	160
85.4	441	0.628	398	34	432
87.5	478	0.735	466	35	501

The heat transferred to CH_4 in the vaporizer depends on the temperature of the water heated in the cooler. The point of equalization of the split gas is 71.5 (v. III a3). The water is heated in the cooler to 69.5°C. CH_4 leaves therefore the saturator with a saturation of abt 67.5°.

Heat contents of CH_4 at outlet from saturator	156 h.u.
" " " dry CH_4 at 15° at the inlet to saturator	6 " "
CH_4 absorbed in the vaporizer a total of	150 " "

2). Heat contents of the fresh condensate

The fresh condensate is brought in at 15° C. Its amount depends on the amount of water condensed from the split gas in the cooler, or else evaporated into the split gas. However, ~~the heat content of the fresh condensate is small, and the condensate requirements can be obtained from an approximation,~~ in which the heat introduced by the fresh condensate is set in the proper order of magnitude. The second computation of the heat balance gives then the above condensation requirements.

CH_4 takes on in the evaporator (v. a1)	206 g. H_2O
Split gas " " " cooler (v. a3)	312 " "
Fresh condensate requirements	518 " "/m³ CH_4

Heat content of fresh condensate 0.518 x 15 = 8 h.un./m³ CH_4

3). Heat removed from split gas in the cooler.

Heat content of split gas saturated with H_2O = C_pT W L_T at 800 mm Hg pressure. The water content is

$$W = \frac{P}{800-P} \times 3.233 \times \frac{18}{24.5} = 2.38 \times \frac{P}{800-P} \ \text{kg/m}^3\ CH_4$$

~~The average sp. ht. of the split gas 0-100°C:~~

CO_2:	0.225 x 0.409 =	0.092	
CH_4:	0.006 x 0.429 =	0.003	
~~diatomic:~~	~~3.002 x 0.308 =~~	~~0.925~~	
		1.020	x 0.917 = 0.936

T	P	W	WxL_T	C_pT	Heat Content
~~20°~~	~~17.5~~	~~0.053~~	~~33~~	~~14~~	~~47~~
56°	124	0.436	271	52	323
57°	130	0.462	287	53	340
60.3	152	0.556	347	56	403
61	156	0.586	360	57	417
67	205	0.820	513	63	576
68°	214	0.868	543	64	607
69	224	0.919	575	65	640
71	244	1.045	654	67	721
72	255	1.112	700	67	767

150-8 = 142 h. un./m^3 CH_4 must be removed from the split gas in the cooler. The split gas enters the cooler with a heat content of 747 h. un./m^3 CH_4 (v. II). Such an amount of heat corresponds to an equalization point of 71.5°. The water can therefore be heated to about 69.5° by the split gas in the cooler.

The heat content at the outlet of the split gas is still 747-142 = 605 h.un. Its temperature is 68°, its water content ~~868 g/m^3 CH_4. The split gas then takes on 868-556 = 312 g~~ additional water.

b). Determination of the amount of water in the cooler-vaporizer.

~~The amount of water in the cooler is not definitely fixed,~~ and may be selected between two values. The least amount of water is fixed at 5.4 Kg/m^3 CH_4 by the requirement that the water in the vaporizer be always warmer than the gas to be heated (v. fig. 1). The maximum is given by the requirement that the water be always colder than the split gas, or

$$\frac{142}{71.5-68} = \frac{142}{3.5} = 40.8 \text{ Kg } H_2O/m^3\ CH_4.$$

c). Final cooling.

The split gas leaves the cooler with a heat content of 605 h.un/m^3 CH_4. It must be cooled to 20° in the final cooler. 605-47 = 558 h.un. must therefore be removed from it. The cooling water must then become heated from 15° to 50°.

The requirements in cooling water are therefore

$$\frac{558}{35} = 16 \text{ Kg/m}^3\ CH_4.$$

Summary:

Oxygen requirements:	0.487 m^3/m^3	CH_4
Steam requirements	0.529 kg/m^3	CH_4
~~Condensate~~	~~0.518 "/"~~	~~"~~
Cooling Water	16 "/"	"

B). CH_4 splitting in equipment for long distance gas with additional indirect cooling.

I.) CH_4 converters computed as in A).

II.) Cooling of split gas.

a). Heat contents of split gas at outlet from catalyst converter as in A.

b) Heat exchanger.

The heat exchanger for O_2 remains unchanged.

Methane may be heated in the vaporizer to 85.4° (v.III) and saturated with 628 g. H_2O. Its heat content then is 432 h. un. The heat content will be increased by 0.107 x 643.8 = 69 h.un. to 501 h.un by the addition of 107 g. fresh steam at 1.5 atm - 111°. CH_4 will therefore be exactly at the dew point after the steam was added.

The split gas has therefore given up in the heat exchangers 1150 - (2 + 501) = 647 h. un. It leaves the heat exchanger with a heat content of 1399-647 = 752 h.un./m³ CH_4. Its temperature is about 319°.

III. The Cooler-Vaporizer System.

a). Heat balance of the water circuit.

In the cooler-vaporizer circuit an indirect cooler must be installed, which cools the split gas to within 10° above its dew point, i.e. to 70° C.

The heat balance is then:

The sum of the heat taken away from the split gas in the indirect cooler, the direct cooler and the heat content of the fresh condensate equals the heat given up to CH_4 in the vaporizer.

1). Indirect Cooler

The split gas enters with 752 h. un. from the heat exchanger. The sensible heat of the dry split gas at 70° is 70 x 0.936 = 66 h. un. The heat content of the split gas at the cooler outlet is then 348 + 66 = 414 h. un.

752-414 = 338 h.un. can then be transferred to the water in the cooler.

2). Fresh condensate.

The amount of fresh condensate depends on the amount of water condensed in the direct cooler from the split gas. The amount of heat in the fresh condensate is, however, small, and the condensate requirements may be obtained from an approximate estimate of the heat introduced with the fresh condensate. A second computation will then produce an accurate value of the requirements of the condensate.

CH_4 takes on in the evaporator (Section a 3)	628 g.
The split gas gives up in the cooler (Sec. a4) 556-453 =	103 "
Condensate required.	525 g/m³ CH_4

The fresh condensate will give up 0.525 x 15 = 8 h. un. to the circuit.

3. Vaporizer

The heat transferred to CH_4 in the vaporizer depends essentially on the temperature of the water heated in the direct cooler. The split gas enters the direct cooler with 414 h. un. The dew point with this heat content is 60.9°. The water may then be heated in this cooler to about 57°. The heat content of CH_4 at 57° is 94 h. un. The 338 h. un. of CH_4 transferred in the indirect cooler correspond to a dew point of 85.4°, and to a water content of 628 g/m³ CH_4.

4. Direct cooler

The amount of heat removed from the split gas in the direct cooler must be sufficient to produce 94 heat un. in CH_4 saturated at 57° from the heat content of dry CH_4 at 15° and the heat content of the fresh condensate. The split gas, when leaving the cooler, still has 414-80 = 334 h. un. The dew point corresponding to this heat content is 56.7° with a water content of 453 g. The amount of water given up in the cooler by split gas is therefore 556-453 = 103 g.

C). Determination of the amount of water in cooler-vaporizer circuit.

The amount of water in the circuit is not definitely fixed, but can be selected at will between two values. The maximum and the minimum amounts are found from the requirements, that the cooling water still possess a finite amount of ΔT at the hot end of the direct cooler with respect to the equalization point of the split gas, and that the water in the evaporator be always warmer than the saturated CH_4. The maximum and minimum amounts are shown in fig. 2, as obtained when the cooling water at the end of the direct cooler, is 2° cooler than the entering split gas. The maximum and the minimum amounts are so small, that some of the water vaporizes at the hot end of the cooler in the form of steam.

c).- Final cooler.

The split gas leaves the circuit cooler with 334 h. un.

It must be cooled to 20° in the final cooler.

334-47 = 287 h. un./m^3 CH_4 are therefore to be removed from it. The cooling water must be heated from 15° to 50°.

The required amount of cooling water is therefore

$$\frac{334}{35} = 9.6 \text{ kg/m}^3 \ CH_4$$

Summary:

Oxygen requirements	0.487	m^3/m^3 CH_4
Steam requirements	0.107	kg/m^3 CH_4
~~Condensate requirements~~	~~0.525~~	~~" " "~~
Cooling water	9.6	" " "

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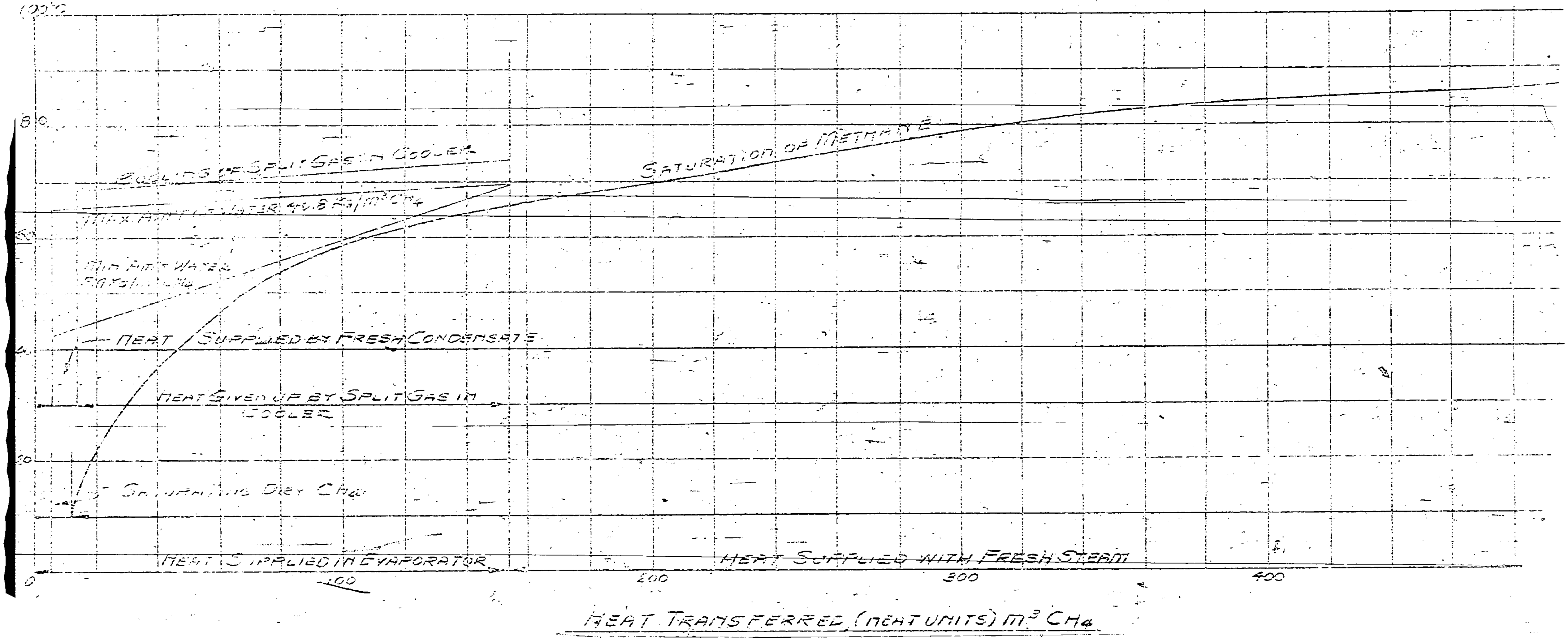
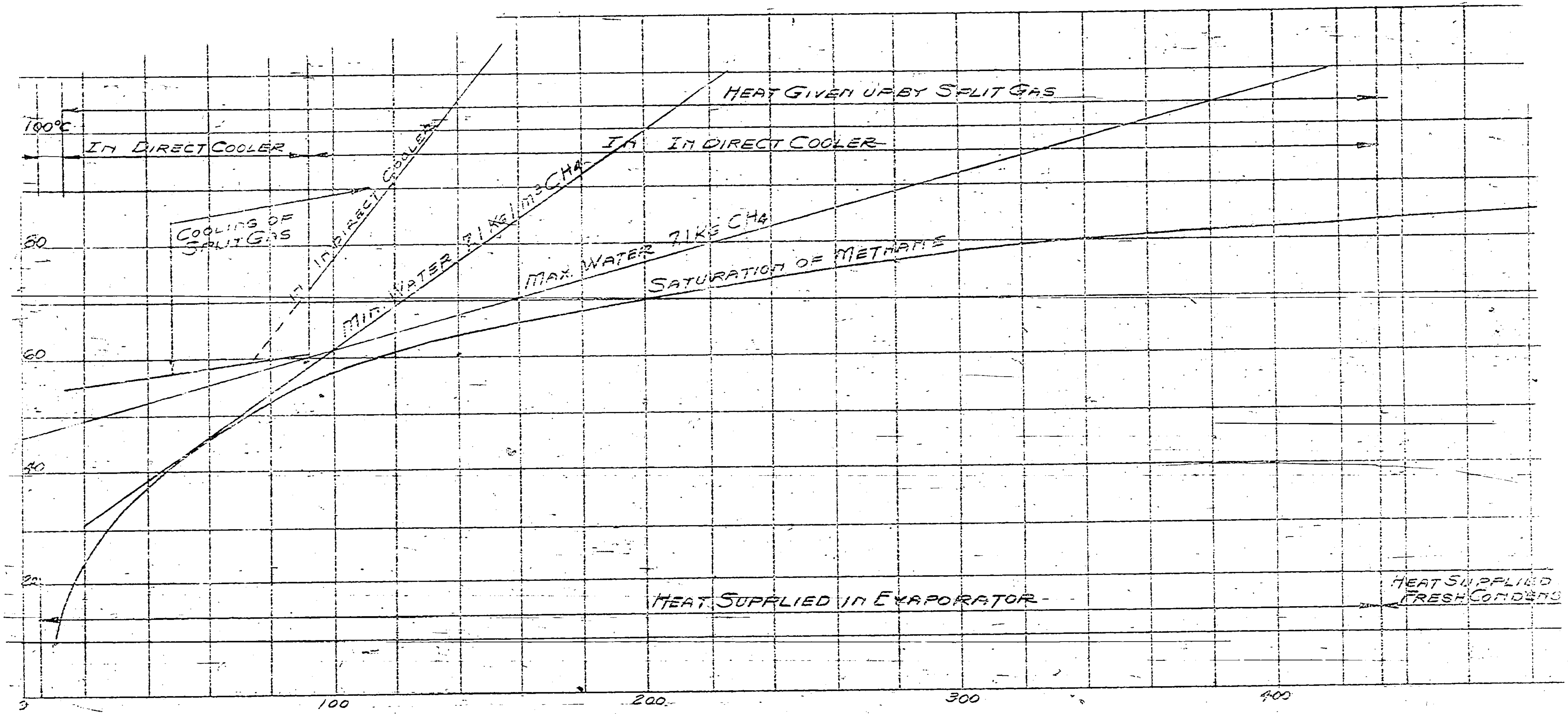
12/13/46



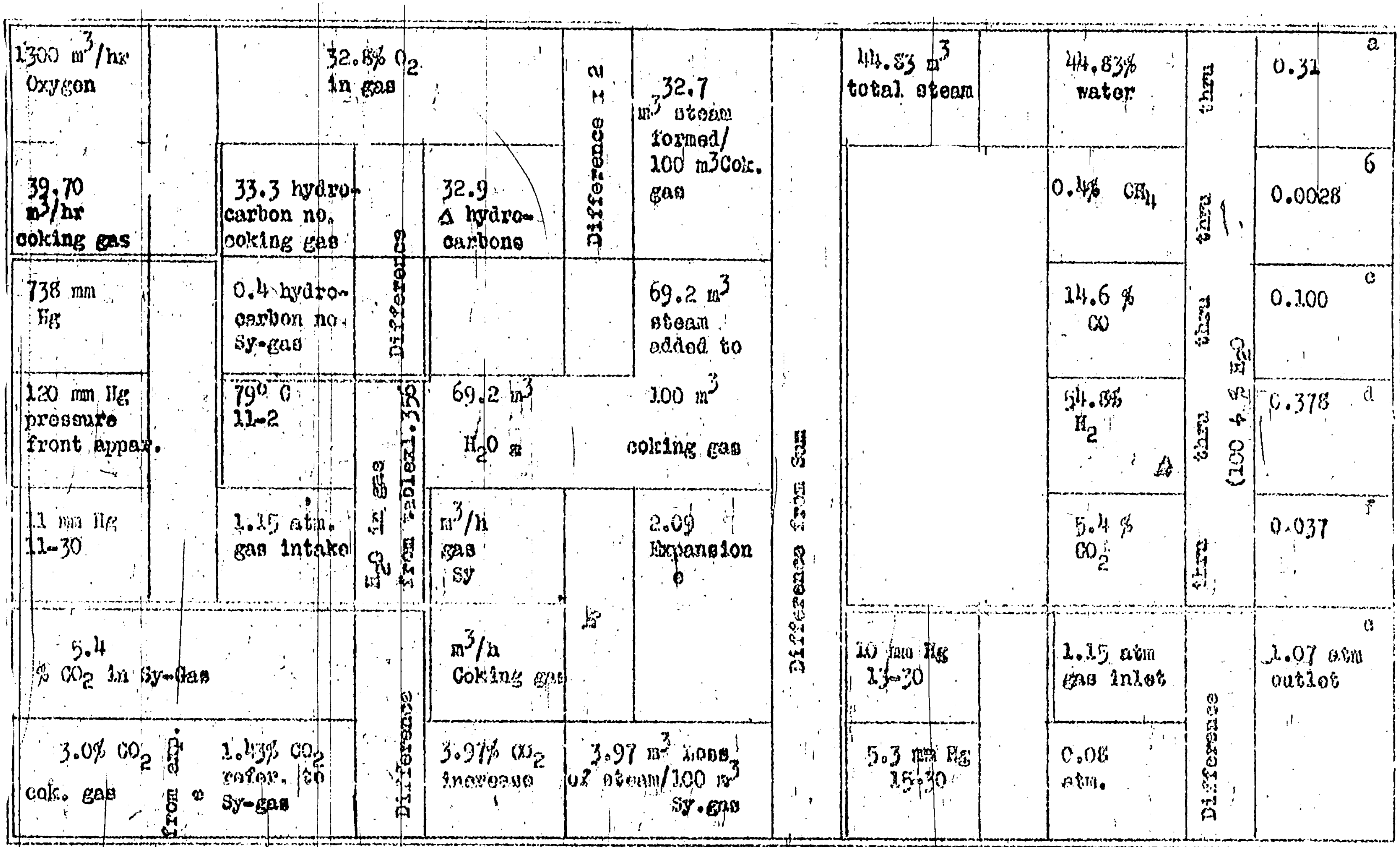
100°C
80
40
20
0
100
200
300
400
COOLING OF SPLIT GAS IN COOLER
SATURATION OF METHANE
HEAT SUPPLIED BY FRESH CONDENSATE
HEAT GIVEN UP BY SPLIT GAS IN COOLER
SATURATING DRY CH4
HEAT SUPPLIED IN EVAPORATOR
HEAT SUPPLIED WITH FRESH STEAM
HEAT TRANSFERRED (HEAT UNITS) m³ CH4

FIG. 1



HEAT TRANSFERRED (HEAT UNITS) m^3 CH_4

FIG. 2



$K_p = \frac{0.31 \times 0.0028}{0.1 \times 0.0543_x\ 1.15_2} = 0.14$ 0.146-1

(methane 0.378 1.07

c d e

Watergas $K_p = \frac{0.31 \times 0.1}{0.378 \times 0.037} = 2.21$

d f

Temp. = 1124° C.

T-186, Figure 3.