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CALCULATION OF THE THEORETICAL YIELD FROM ANALYSES OF SYNTHESIS AND RESIDUAL GAS

We are presenting below a method for the calculation of yields from the analyses of synthesis and residual gases.

In the computations, the analysis of the residual gas after activated carbon treatment is used. This means, that the gasol and possibly also gasoline which have failed to be absorbed in the carbon are not included in the yield. The calculated yield represents therefore an amount which should be in agreement with the measured amount, namely the total yield. No separation is possible into gaseous and liquids yield. Computations proper are carried out on the following fundamental assumption:

THE CARBON AND HYDROGEN BALANCE MUST BALANCE

The conversion of CO and H_2 are calculat ed separately. Individual products of reactions, like CO_2, CH_4, wat er of the reaction, must be subtracted from the amounts converted. Certain amounts of CO and H_2 remain. These two amounts must exist in a certain proportion, which is obtained from the CO : H_2 ratio in the h ydrocarbons formed, as like 1 : 1.18 given by Dr. Grimme for the synthesis under atmospheric pressure. Should this proportion not be obtained from the contraction for H_2 or the volume contraction, one will have to conclude that either the analytical results or the contraction are in error. Computations show, that when one arrives at an uncertainty, the results of analysis for CO or H_2 in the residua l gas must be first of all suspected, because changes in the conversion are not important, and when there is a considerable variation of these values, e.g. by 1 point in the residual gas, the proportion of C and H_2 remainin g for the hydrocarbon synthesis will be changed only slightly. Results will be greatly affected however by variations in the formation of CO_2. This may be obtained by continued testing of the contraction until the required C : H_2 ratio in the products is reached. We have another way by raising the CO_2 value in the residual gas analysis with unchanged contraction until we again get the required proportion.

A calculation of the two methods shows that the yields obtained will vary by only 3.4% from each other, and that therefore a suspicion of the source of error here present (in the contraction or the CO_2 value) is relatively unimportant, as long as we are willing to accept either one of the two.

We may say for the computations that regardless of any assumed way of formation of CO_2, and independent ly of the reaction which had taken place, no H_2 i s necessary for the formation of water of reaction of formation of one mol CO_2 from 2 mols CO:

1. $2\ CO + H_2 = CH_2 + CO_2$

2. $2\ CO + H_2O = CO2 + H_2$

$$CO + 2\ H_2 = CH_2 + H_2O$$

$$\underline{CO + H_2O = CO_2 + H_2}$$

$$2\ CO + 2\ H_2 + H_2O = CH_2 + CO_2 + H_2O + H_2$$

$$2\ CO + H_2 = CH_2 + CO_2$$

We will illustrate this method by the theoretical yields computated for the pressure synthesis as well as the atmospheric pressure synthesis during September.

High Pressure Synthesis	CO_2	C_nH_m	CO	H_2	CH_{4+}	N_2	Carbon No.
Theoretical Synthesis gas	13.9	--	16.7	52.3	0.4	6.7	1.00
Residual gas	48.8	0.3	8.7	8.3	11.4	22.5	1.10

H_2 Contraction 70.25 %

Synthesis Gas	13.9	--	26.7	52.3	0.4
	14.52	0.09	2.59	2.47	3.39
	+0.62	0.09	24.11	49.83	
CO_2 Formation			-0.62	+0.62	
			23.49	50.45	
Water of reaction				23.49	
				26.96	
$CH_4 + C_nH_m$			-3.63	-6.62	
			19.86	20.34	

Consumption

		CO	H_2
CH_4 : 3.39 x 1.10	=	3.73	3.59 x 2.10 = 7.12
		-0.40	-0.80
		3.33	6.32
For C_nH_m 0.09 x 3.3	=	0.30	0.30
		3.63	6.62

Changing the contraction to <u>68.3%</u>

	13.9	--	26.7	52.3	0.4	
	15.46	.010	2.76	2.63	3.61	
	+ 1.56			23.94	49.67	
CO_2 Formation				-1.56	+1.56	
				22.38	51.23	
Water of Reaction					22.38	
					28.85	
CH_{4+} + C_nH_m				3.88	7.10	
				18.50	21.75	$C:H_2$ = 1.175

Consumption	CO	H_2
CH_{4+}	3.97	7.59
	-0.40	-0.90
	3.57	6.79
C_nH_m	0.31	0.31
	3.88	7.10

Yield * $\frac{18.50 \times 12}{22.4} = 99.0\,g$

$\frac{21.75 \times 2.016}{22.4} = 19.5\ g$

118.5 g/nm^3 synthesis gas =150 g/nm^3 I-Gas

Changes of the values of CO_2 in the Residual Gas:

13.9		26.7	52.3	0.4
52.0	0.3	8.7	8.3	11.4

Contraction 70.25%

	13.9	--	26.7	52.3	0.4
	15.48	0.09	2.59	2.47	3.39
	1.58		24.11	49.83	
CO_2 Formation			-1.58	1.58	
			22.53	51.41	
Water of Reaction				22.53	
				28.88	
CH_{4+} + C_nH_m	3.63			6.62	
	18.90			22.26	$C:H_2$ = 1.178

Carbon Yield $\frac{18.90 \times 12}{22.4} = 101.2\,g$

Hydrogen Yield $\frac{22.26 \times 2.016}{22.4} = 20.0\ g$

121.2 g/nm^3 synthesis gas

= 153.2 n/nm^3 I-gas

Norm. Press. Synth.	CO_2	C_nH_m	CO	H_2	CH_{4+}	N_2	N_2-pure	C Numb.
Synth. Gas	14.7	--	25.2	52.2	0.4	6.5	6.38	1.08
Residual Gas	46.9	0.3	6.8	13.4	12.5	20.1	18.7	1.08

	14.7		26.2	52.2	0.4		
	16.0	0.1	2.39		4.57	4.26	
	1.30		23.88	47.65		Consumption	
						CO	H_2
CO_2 Formation			-1.30	+1.30		4.61	8.87
			22.58	48.93		0.40	0.80
Water of Reaction				22.58		0.34	0.34
				26.35		4.55	8.41
CH_4+ C_nH_m			4.55	-8.41			
			18.03	17.94			

$C:H_2$ = 1 : 0.995

1. Changes in contraction

Contraction = 63.5%

	14.7		26.2	52.2	0.4		
	17.12	0.11	2.48	4.89	4.56		
	2.42		23.72	47.31		Consumption	
CO_2 - Formation			2.42	2.42		CO	H_2
			21.30	49.73		4.93	9.50
Water of Reaction				21.30		0.40	0.80
				28.43		4.53	8.70
CH_{4+} + C_nH_m			4.89	9.06		+0.36	0.36
			16.41	19.37		4.89	9.06

c:H_2 = 1 : 1.18

Yield: Carbon $\frac{164.1 \times 12}{22.4}$ = 87.9 g

H_2 $\frac{193.7 \times 2.016}{22.4}$ = 17.3 g

105.2 g/nm^3 synthesis gas

134.2 g/nm^3 I-gas

2. Changes in CO_2 Values

14.7		26.2	52.2	0.4			
50.0		6.8	13.4	12.5			
14.7		26.2	53.2	0.4			
17.05	0.10	2.32		4.87		4.25	
2.35		23.88	47.63				

	CO	H_2
CO_2 Formation	2.35	2.35
	21.53	49.98
Water of Reaction		21.55
		28.45
CH_{4+} + C_nH_m	4.53	8.41
	16.98	20.04

$C:H_2$ = 1 : 1.18

Yield: C $\frac{169.8 \times 12}{22.4} =$ 90.9 g

H $\frac{200.4 \times 2.016}{22.4} =$ 18.0 g

108.9 g/nm^3 synthesis gas
138.9 g/nm^3 I gas

The following production is obtained by inserting these calculated values:

1. Changing the contraction:

Press. synth.	$\frac{150 \times 23.44 \times 10^6}{10^6}$	=	3,517 te
Atm. Press. synth	$\frac{134.2 \times 13.73 \times 10^6}{10^6}$	=	1,843 te
			5,360 te

and an average yield of 144.2 g/nm^3 I gas

2. Changes in CO_2 Values

Press. synth.	$\frac{153.2 \times 23.44 \times 10^6}{10^6}$	=	3,590 te
Atm. Press. synth.	$\frac{138.9 \times 13.73 \times 10^6}{10^6}$	=	1,968 te
			5,498 te

and an average yield of 147.8 g/nm^3 I gas

The yields calculated from measurements of volumes during September amounted to 140.1 g. It is therefore 4 - 8 g below the calculated yield.

The same assumptions were made for the first ten days of October.

	CO_2	C_nH_m	CO	H_2	CH_{4+}	N_2	C Numb.	
Synth. Gas	14.4	--	26.1	52.7	0.4	6.40		
Residual Gas		47.9	0.09	3.7	8.5	10.6	23.00	1.10

Assumed contraction 68.2%

	CO_2	C_nH_m	CO	H_2	CH_{4+}
	14.4	--	25.1	52.7	0.4
	15.18	0.09	3.07	2.7	3.36
	+0.78		23.03	50.00	
CO_2 Formation			0.78	0.78	
			22.25	50.78	
Water of Reaction				22.25	
				28.53	
CH_{4+} + C_nH_m			3.61	6.57	
			18.64	21.96	

Consumption

CO	H_2
3.70	7.06
0.40	0.80
3.30	6.26
0.31	0.31
3.61	6.57

$C:H_2$ = 1.178

Yield: C $\frac{18.64 \times 12}{22.4} =$ 99.8 g

H_2 $\frac{21.96 \times 2.016}{22.4} =$ 19.8 g

119.6 g/nm³ synthesis gas
151.8 g/nm³ I Gas

Atm. Press. Synth.	CO_2	C_nH_m	CO	H_2	CH_{4+}	N_2	C Numb.
Synth. Gas.	14.5	--	26.3	52.6	0.4	6.18	
Residual Gas	47.8	0.9	6.8	14.5	11.8	17.70	1.14

Pure H_2 Contraction = 65.1%
Calculated = 64.8%

	CO_2	CO	H_2	CH_{4+}
	14.5	26.3	52.6	0.4
	16.83	2.39	5.10	4.12
	+ 2.33		23.91	47.50
CO_2 Formation		2.38	2.33	
		21.58	49.83	
Water of Reaction			21.58	
			28.25	
CH_{4+} + C_nH_m		5.12	8.88	
		16.46	19.37	

Consumption

CO	H_2
4.73	8.89
0.40	0.80
4.33	8.09
0.79	0.79
5.12	8.88

$C:H_2$ = 1.177

Yield: C $\frac{164.6 \times 12}{22.4} =$ 88.2 g

H_2 $\frac{193.7 \times 2.016}{22.4} =$ 17.4 g

105.6 g/nm³ synthesis gas
133.9 g/nm³ I gas

Theoretical Production:	133.9 x 4,541,700 =	608 te
	151.8 x 8,310,550 =	1,262 te
	12,852,250 =	1,870 te
Actual Production		1,874 te
Average yield	145.5 g/nm^3 I Gas	
Actual yield	146.1 g/nm^3 I Gas	

A computation by this method results therefore in a good agreement with the values obtained from actual measurement. We must mention however that our residual gas analyses in the activated carbon installations do no represent accurately the residual gas composition. CO_2, CH_4, and C_4H_6 removed from activated carbon treatment II appear in the circulation in the residual gas after activated carbon treatment I. The breather gases from tower III are also present in the normal pressure synthesis. Both amounts of gases displace the theoretical yield away from the atmospheric pressure synthesis, and, conversely, in favor of the pressure synthesis. In addition, the partial recirculation of the C_2H_6 gas, causes the residual gas analysis after activated carbon treatment I, to become incorrect, which makes the computations of yields of the normal pressure synthesis uncertain.

Basically, the method of computation appears to me to be useful, primarily for a rapid evaluation of the yield without awaiting the results of the time-consuming low temperature analysis. The actual production during synthesis against that actually measured can be readily calculated when taking the final gas sample over the cooler and activated carbon, which is sure to remove all the hydrocarbons above the C_9 which have fo rmed. This method permits also finding the production of the individual reactors or stages.

To make the method described more exact, the following additional determinations would be necessary.

1) The determination of the $C:H_2$ ratio i n the total pressure and atmospheric synthesis (liquid and gaseous).

2) The determination of the C number of the unabsorbed unsaturated hydrocarbons, which has been assumed in the sample calculation above to be 3.3, in agreement with the Hoesch method. This value is surely too high. During the first ten day of October the value used for atmospheric pressure synthesis was 2.5, because the C_nH_m in this case were certainly produced in the Dubbs unit ethylene. No large errors could have been introduced in this way, because the C_nH_m values have no great affect upon the results.