INVESTIGATIONS IN FISCHER-TROPSCH SYNTHESIS REACTIONS BY C-BALANCE

By P. K. Deshpande, S. S. Ghosh, K. Shivaramaiah,
D. V. Subba Rao and E. Weingaertner
(*Department of Chemical Technology and Chemical Engineering, Indian Institute of Science, Bangalore*-3)

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PART I

A. *Description of C-balance method for obtaining conversion and specific yields of Fischer-Tropsch reactions in the simplest form*

Through the practice of Fischer-Tropsch Synthesis calculations a method has been developed to obtain the reaction conversion, degree of liquefaction and specific yield, by C-balance calculations. The fundamentals of this method have been reported for the first time by W. Grimme[1] and later by O. Roelen.[2] This particular method of calculation is being used at present in different forms according to different needs and localities.[3]

The method is based on the analysis of the inlet and outlet gas passing through the catalyst bed. The main reaction results are obtained from the gas side in the form of a balance of the total process. For this purpose the presence of nitrogen in the gas is being utilised as it does not usually take part in any of the possible reactions and leaves the catalyst bed unaltered, with regard to its absolute value. Very often carbon dioxide content of the gas is used for the same purpose as it is much easier to estimate. This method is sufficiently accurate in all such syntheses where either no or very little carbon dioxide is being formed or the formation of carbon dioxide is constant. Naturally this method cannot be adopted where carbon dioxide is formed in rather large amounts and also for all accurate calculations as carbon dioxide itself is an important product of the total reaction and must be taken into account.

The above mentioned method is described here in short, in the form in which it is used for factory purposes. This description is necessary as our further calculations and investigations in Fischer-Tropsch reactions are based on this method. The complete set of calculations of one synthesis example is given in Table I. As a first step, we arrive with the help of nitrogen contents of inlet and outlet gas, at the so-called apparent contraction, k_{N_2}. We can obtain the residual volume $(1 - k_{N_2})$ by the ratio of nitrogen contents of the inlet and outlet gas. The contraction occurs by the conversion of large amounts of gaseous reaction components CO and H_2 into condensable products like hydrocarbons and water vapours. These are mostly removed from the gas sample and even if present have a much smaller volume compared with the gas volume.

TABLE I

C-Balance Calculations of Co-Catalyst, Medium Pressure Synthesis

No.	Gas volume %	CO_2	C_nH_m	CO	H_2	$C_nH_{2(n+1)}$	N_2	C-No.	H_2+CO	$1-k_{N2}$	H_2/CO
1	Inlet gas	5·60	0·00	39·80	48·60	0·30	5·60	1·0	88·40	..	1·22
2	Outlet gas	13·20	0·80	45·00	25·00	4·50	11·50	1·21	70·00	0·487	0·556
3	Outlet gas composition relative to inlet gas composition	6·428	0·39	21·913	12·174	2·191	5·60	1·21	34·087	..	0·556
4	Disappeared (−) and formed (+) products	+0·828	+0·39	−17·887	−36·426	+1·891	±0·0	1·244	−54·313	..	2·040
5	Calculation of pure Methane $e' = t'\left(\frac{i-\text{C-No.}}{i-1}\right)$ ..				$\therefore\ e' = 1{\cdot}891 \times \frac{(2{\cdot}1-1{\cdot}244)}{(2{\cdot}1-1{\cdot}0)}$				$= 1{\cdot}470$		
6	$CO+H_2$ Total conversion ..								$= \frac{54{\cdot}313}{88{\cdot}40} \times 100 = 61{\cdot}40\%$		
7	$CO+H_2$ Total conversion to $C_1+ <$ products			−17·887 + 0·828 −17·059	−36·426				$= \frac{53{\cdot}488}{88{\cdot}40} \times 100 = 60{\cdot}40\%$		
8	$CO+H_2$ Total conversion to $C_2+ <$ products			−17·059 + 1·470 −15·589	−36·426 + 2·940 −33·486				$= \frac{48{\cdot}683}{88{\cdot}40} \times 100 = 55{\cdot}10\%$		
9	Liquid products formed ..								$= \frac{48{\cdot}683}{54{\cdot}313} \times 100 = 89{\cdot}80\%$		

10	Reaction water formed ..			−17·887 + 1·656 16·231							
11	H_2 for hydrocarbon formation Average mol. weight $C_1+<$			−17·059	−36·426 +16·231 −20·195				$\frac{H_2}{C} = \frac{2\times20{\cdot}195}{17{\cdot}059} \times 2{\cdot}368$		
12	Average molecular weight $C_2+<$			−15·589	−20·195 + 2·940 −17·255				$\frac{H_2}{C} = \frac{2\times17{\cdot}255}{15{\cdot}589} = 2{\cdot}215$		
13	Specific yield 1 g. $C_2+</m^3CO+H_2$					$\frac{(12+2{\cdot}215)\times15{\cdot}589}{22{\cdot}42\times88{\cdot}40\times10^{-3}}$			$=112{\cdot}10$ g. $C_2+</m^3CO+H_2$		
14	Recalculation of step (4) on 100% $(CO+H_2)$ basis ..	1·524	0·718	32·90	67·10	3·480	0·00	..	100·00	..	2·040

By multiplying each component of the outlet gas by $(1 - k_{N_2})$, true exit gas amount and composition in relation to inlet gas composition is obtained. The principle of this method is indicated in Fig. 1. The analysis of both inlet and outlet gas are always referred to 100 per cent. During the reaction the participants like CO and H_2 disappear, but N_2 content remains absolutely unchanged and so a higher nitrogen content is found in the exit gas. With the help of the ratio Nitrogen inlet/Nitrogen outlet we can find directly that amount of exit gas to which the amount of inlet gas has been reduced $(1 - k_{N_2})$ and by which reduction the nitrogen content of the exit gas has been increased. The amount of gas which has disappeared is then the difference between 1 and the former value that is k_{N_2}, the contraction itself. This contraction naturally refers to the state of exit gas as it is given in the gas sample at the time of the analysis at room temperature and normal pressure, whereby all the condensable products have been already condensed. Only very light hydrocarbons remain in the gas depending on their partial pressures at the given conditions. Thus all the components of exit gas like carbon monoxide and hydrogen (which have not been converted), carbon dioxide, methane (originally present and newly formed) are influenced by the contraction, in their ultimate concentrations *vide* Fig. 1.

Thus we get the true composition and amount of the exit gas in relation to the inlet gas, by multiplying each component of the exit gas by $(1 - k_{N_2})$. By these calculations, the influence of the contraction is eliminated and the amount of nitrogen in the exit gas equals to that in the inlet gas, as seen from Table I.

We can obtain the amounts of the disappeared reaction components or the products formed during the reaction, by subtracting the corrected amounts of the exit gas components from the respective inlet gas components. The products, mostly removed by condensation, are equal to the difference between the total products formed in the reaction and the products remaining in the exit gas.

Supposing that the sample taking and gas analysis are correct all the products formed in the reaction must always occur as CO_2, C_nH_{2n} and $C_nH_{2(n+1)}$. The latter fraction contains methane, some ethane, and higher hydrocarbons. Only carbon monoxide and hydrogen should disappear. The water formed during reaction is completely removed by condensation in most of the cases. However, it is possible as shown later, to calculate the amount of reaction-water from the analysis. The amounts and the composition of inlet and exit gases thus calculated, can be utilised in a simple form to calculate C and H balance of the material flow.

The calculations are used in most cases to find out the total conversion of CO and H_2. They are further used to obtain the conversion into gaseous products like CO_2 and CH_4 separately. As CO_2 and CH_4 conversions are of less practical importance for the plant practice, they are deducted from the total conversion. The remaining conversion figure covers all higher hydrocarbons excluding methane but including oxygenated compounds, if formed. The figures thus arrived are

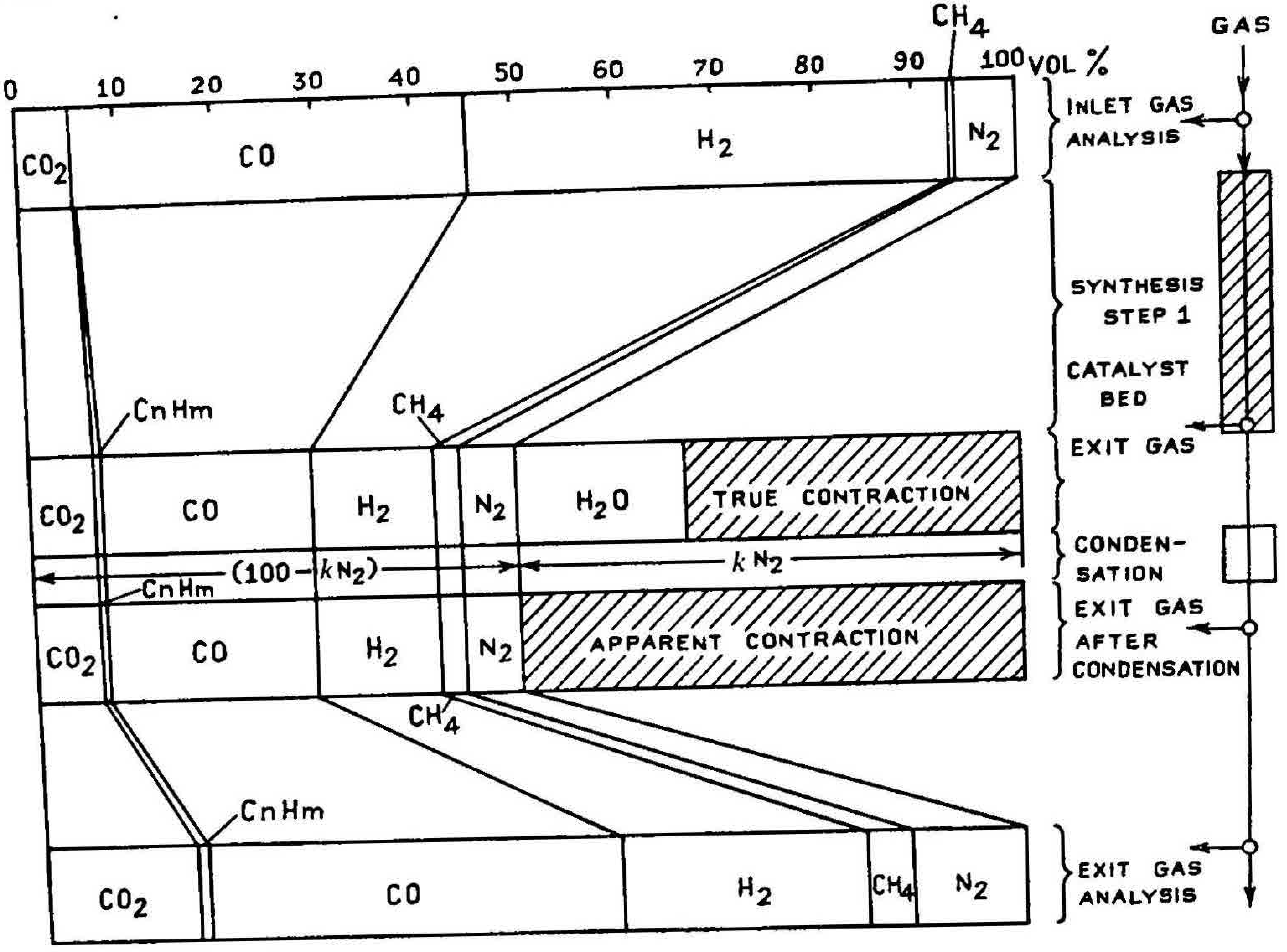

FIG.1 ANALYSIS OF INLET & EXIT GAS & CONTRACTION (Co—CATALYST)

absolute conversion figures valid only for the particular gas composition and conversion which will differ in different plants and stages. In order to compare in a general way the working of different plants, it is usual to relate the conversion figures to the CO- and H_2-contents of the inlet gas to the so-called ideal gas. From these figures, the man at the spot already gets the first survey of the overall performance of the plant or its test runs. The calculations are given in Table I for an example of a Co-catalyst medium pressure synthesis.

If we divide the conversion figures for C_2- and higher hydrocarbons by the total conversion figure, another conversion figure is obtained which indicates the degree of liquefaction. That is, it gives percentage of conversion of CO and H_2 into useful products like higher hydrocarbons excluding CO_2 and CH_4. These are the valuable Fischer-Tropsch Synthesis products.

The next step in C-balance calculations is to find out specific yields of hydrocarbons, expressed as $g/m^3 CO + H_2$. This specific yield is always related to the synthesis gas unit or the ideal gas unit. Specific yields can be easily calculated from the amount of CO which is converted to C_2- and higher hydrocarbons by assuming C: H ratio of the product as approximately $1:2 \cdot 3$. Thus we can obtain the average molecular weight of the hydrocarbons which are formed by 1 mol. of converted CO. The value of it will be $12 + 2 \cdot 3 = 14 \cdot 3$. The specific yield in terms of g/m^3 can then be obtained by multiplying the CO volume (converted to C_2- and higher hydrocarbons) by 14·3 and 10 (in order to get m^3-unit) and dividing by molecular volume 22·4 litres. If we want this figure to be related to the $(CO + H_2)$-volume the above obtained specific yield must be further divided by $(CO + H_2)$-concentration of the inlet gas. The assumption of C: H ratio as $1:2 \cdot 3$ in this case is merely empirical.

However, it is possible to calculate the C: H-ratio of the products formed, directly from the analysis data. For this it is necessary to get the hydrogen balance. After deducting the amount of hydrogen, used for water formation, from the total converted hydrogen, we obtain the amount of hydrogen, utilised for hydrocarbon formation. In those cases, where methane formation should be excluded, we can further subtract the amount of hydrogen, used for its formation, and amount of carbon monoxide from the total converted carbon monoxide.

In carrying out these calculations for water formation, we should take into account only that amount of converted carbon monoxide which is used for water formation, but not that amount of carbon monoxide which has served for CO_2 formation. To obtain one volume of CO_2, two volumes of CO are required. Therefore, we can obtain the reaction-water by subtracting double the amount of formed CO_2 from the total amount of CO converted, *vide* Table I, Column 10.

All the volume figures can also be expressed in mols, but usually, the original volume computation is followed, in order to be in accordance with technical plant performance and relative data.

It is shown in Column 7, Table I, how we can obtain by simple subtraction, CO- and H_2-volumes, which are converted into hydrocarbons. The ratio of twice the hydrogen volume and that of carbon monoxide give the average molecular weight of $CH_{2\cdot368}$, *i.e.*, in our case 14·368 for each CH-element, that is obtained. Further if we deduct the hydrogen and carbon monoxide volumes required for methane formation from their respective converted amounts, we can also obtain the average molecular weight of C_2- and higher hydrocarbons as shown in Column 12 of Table I. This is $CH_{2\cdot215}$, *i.e.*, 14·215 for the CH-element in our example. The further calculations for specific yields are shown in Column 13 of Table I, the value of which for our example is 112·1 g. $C_2 + L/m^3 (CO + H_2)$.

Thus by this relatively simple method we can calculate the production state of a complete large-scale plant, its different stages, single catalyst unit, or pilot plant, etc. The only requirement for these calculations are the properly taken gas samples and their complete and accurate analyses.

In fact, this method is rendering valuable help in the evaluation of plants and experimental results, in addition to the product analysis control. Unfortunately, many data about gas analysis from the literature cannot be used for such calculations as they are often found to be either incorrect or not suitable. Most of the reasons for the unsuitability of such analyses are as follows: (i) The gas samples might not have been taken simultaneously, though the analysis is correct. In such cases they do not cover the same production period and thus cannot be used. (ii) The inlet gas sample might have been taken as an instantaneous sample while the exit gas sample might have been taken as an accumulated sample for larger periods or *vice-versa*. (iii) Very often the analyses are not complete or not coming up to 100, or nitrogen values are not sufficiently reliable. (iv) The evaluation is also not possible in such cases, where CO_2 consumption is found instead of its formation, or where the ratio for a CH-element is less than two, which is also not correct.

B. *Further Improvements in the Calculations*

A number of improvements of the calculations has been worked out by us, which will be explained here. These are necessary for the ultimate use for further calculations in reaction investigations.

(*a*) *Inclusion of C-number.*—The $C_nH_{2(n+1)}$-fraction of the exit gas and sometimes of the inlet gas usually consists of, not only methane but also ethane, propane and higher paraffins in an unknown distribution. The presence of such hydrocarbons is usually indicated by the increase in the original volume of the fraction during combustion. It is due to the fact that the higher hydrocarbons give CO_2 *n*-times its original volume. The ratio of volumes after and before the combustion expresses the C-number and, therefore, is a summarised expression for the presence of higher paraffins apart from the methane. However, C-number does not give any indication as to the distribution and the absolute amount of higher hydrocarbons.

This means that for C-balance calculations, in all cases, where the C-number is higher than one, the derived figure for methane formation is higher by an unknown volume of higher hydrocarbons. In order to find the true methane value it is therefore necessary to reduce the methane value obtained from C-balance calculations with the help of a factor which takes into account the distribution and amounts of higher hydrocarbons. As will be shown later, it is important to obtain pure methane value and so the evaluation of the C-number accurately is of essential interest. Therefore, this aspect is dealt in detail here.

O. Roelen[3] has introduced a correction factor β which varies with the value of C-number and which gives approximate methane formation. This factor is purely empirical and is as follows:—

C-number	β
1·00 – 1·05	1·00
1·05 – 1·15	0·90
> 1·15	0·85

This factor does not take into account C-numbers of values 1·2 and greater. For our further calculations we cannot rely on this factor, and therefore, we have proposed a new method of calculation. Theoretically we can arrive at pure methane content of the mixture of paraffins by the equation:—

$$t' = e' + z' + q' + r' + \ldots\ldots \text{ etc.} \tag{1}$$

Where t' is the total volume of $C_nH_{2(n+1)}$, obtained from the C-balance, and e', z', q', r', etc., are volumes of different individuals of the paraffins series with increasing C-number. It can then be further developed as

$$t' \times \text{C-No.} = e' \times 1 + z' \times 2 + q' \times 3 + r' \times 4 + \ldots, \text{ etc.} \tag{2}$$

as the parts of original CO volume, which have served for the formation of the hydrocarbons. The further treatment of this equation, for obtaining the equation for e' leads to a solution with as many unknowns as the number of higher terms introduced. The solution is not possible as long as the volumes of higher hydrocarbons are not known directly. Under these circumstances, the only solution possible is to simplify the calculations by assuming that hydrocarbons higher than C_2 are negligible. Thus we get an equation

$$e' - z' \quad \frac{\text{C-No.}}{1} = t' \times (2 - \text{C-No.}) \tag{3}$$

This equation is absolutely correct if only methane and ethane are present in the gas. It can be further corrected, if an allowance is made for still higher hydrocarbons by choosing a value slightly higher than 2, *i.e.*, 2·1. Strictly, this value is also an empirical one, and for this we will introduce the term i. Then we can write

$$e' = t' \times \frac{i - \text{C-No.}}{i - 1} \tag{4}$$

Unfortunately this simplification also is not ultimately sufficient for our purpose, as shown in Fig. 2. The figure represents the plot of different i-values against e' and t' values. It indicates that the change of e' is rather rapid or large in the region of small i-values while it is not marked in the region of high i-values. Generally high i-values do not occur in normal gas samples. A further improvement can therefore only be expected by estimating at least the actual ethane and propane values. This is possible by carrying out a fractional distillation by an apparatus like Podbielniak Column. We are about to carry out such an investigation.

Equation (4) can be used at present as the closest possible approach to the pure methane value, being always aware of its limitations. While doing so, a change in C-number itself should be taken into account which is due to the subtraction of the almost pure methane fraction of the inlet gas from the methane fraction of the outlet gas. In case the methane fraction of the inlet gas consists of methane only, the C-number must be higher, as originally the amount of pure methane is contained in respective fraction of the exit gas also and so the C-number is related to higher methane value. And if this amount is deducted, the C-number must increase as it is then related to the smaller amount of methane actually formed.

In case the paraffin fraction of the inlet gas has itself a C-number greater than 1·0, one can proceed in two ways. One is to multiply each paraffin fraction with its respective C-number, and after recalculation $(1 - k_{N_2})$, one can subtract both fractions from each other and calculate the new C-number by using equation (4). Or, one can calculate each paraffin fraction according to equation (4), and obtain pure methane from them and then carry out the contraction calculation and get directly the pure methane formed.

(*b*) *Recalculation of C-balance figures on Uniform Overall Conversion Basis.*— The absolute C-balance values provide a means for calculating plant performances with respect to their overall conversions, yields of products and total production of the plant for certain catalysts under investigation. These values are technically very important.

When the fundamental differences of different catalyst performances in the reactions as such are to be compared, we should eliminate the differences in overall conversions by recalculating the C-balance figures on a uniform basis. Such a comparison can then give a further insight in the conditions which lead to the variations in the composition of the products.

It is found suitable to derive all figures on a uniform overall conversion basis, in order to be able to compare and investigate different catalyst performances.

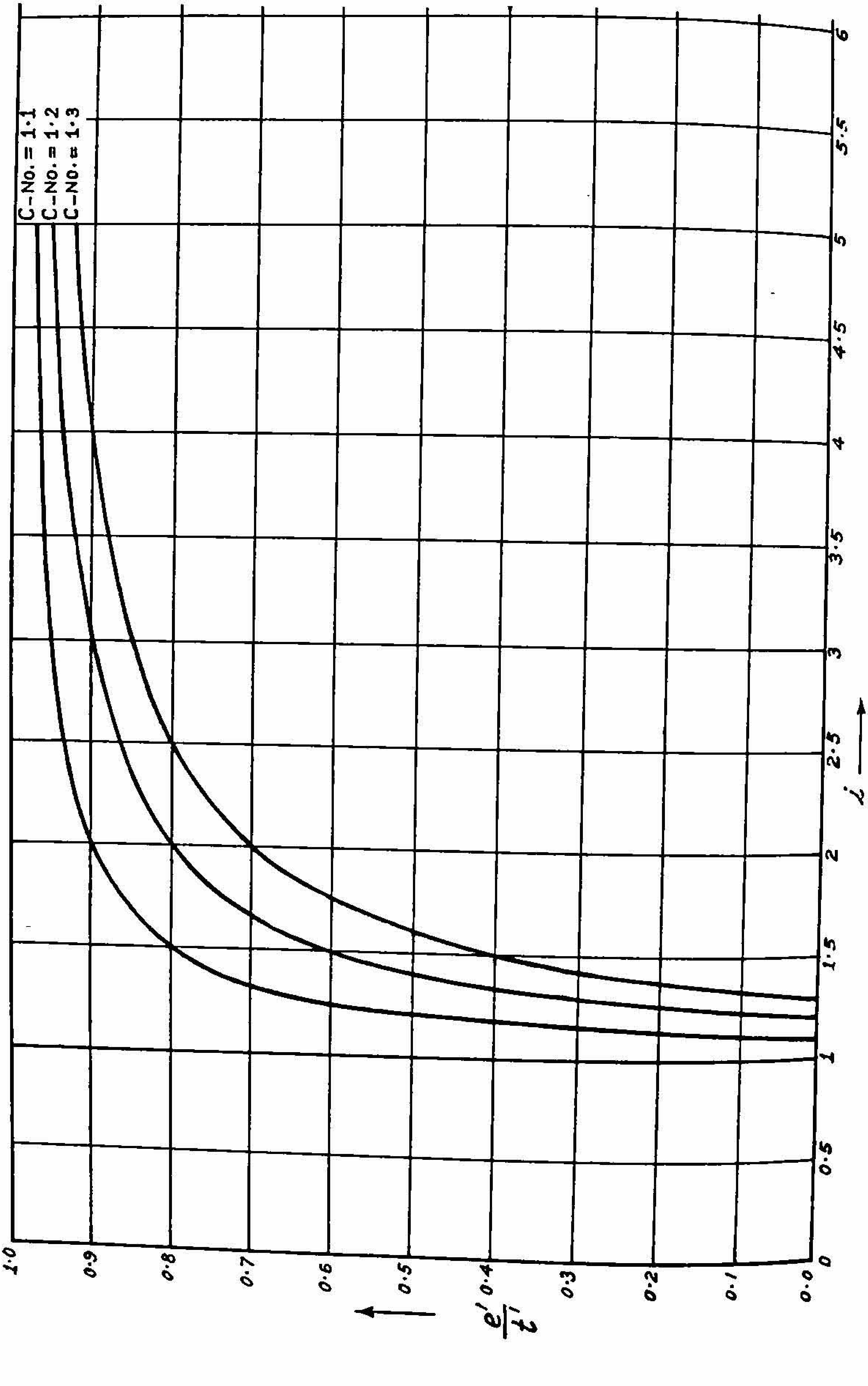

FIG. 2. Relation between *e'* and *l* at fixed C-numbers.

Therefore, it is proposed to calculate all figures on 100% ($CO + H_2$)-conversions. All such recalculated values will be indicated in our nomenclature, as simple letters. As all the reactions in the synthesis are either not equilibrium reactions, or are equilibrium reactions, which are continually disturbed, 100% conversion is in fact always possible whenever sufficient contact time is allowed. Therefore, when 100% conversion is not obtained (as it happens in most of the cases) the overall performance of the reaction would remain unaltered, also if 100% conversion is used. This fact gives us the possibility to introduce 100% conversion calculations. Such recalculations are given in Column 14 of Table I.

In Table II are given a number of examples of different syntheses (Co-catalysts normal pressure, Co-catalysts medium pressure and Fe-catalysts medium pressure), calculated according to the C-balance method. These figures indicate the practical performances of different syntheses plants or catalysts test runs.

(*c*) *H_2: CO Ratio.*—It can also be observed from Tables I and II that whatever may be the ratio of H_2: CO supplied in the inlet gas, every catalyst converts H_2 and CO, in a ratio characteristic of its own type and composition. Thus Co-catalysts take H_2 and CO in ratio of about 2·0 only, even when the ratio in the inlet gas is different as 1·22 (*vide* Table I) the same is the case with iron catalysts which usually have a lower ratio. Thus we notice that the best performance of a catalyst can be expected only when the ratio H_2: CO offered in the inlet gas is equal to the ratio, the catalyst prefers. This is a very important factor, as it gives an indication of the requirements of the quality of the synthesis gas.

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