

# INVESTIGATIONS IN FISCHER-TROPSCH SYNTHESIS REACTIONS BY C-BALANCE

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## PART II

The fundamentals of the C-balance method for control purposes with some improvements have been described in Part I\*. This method was selected as it enables to investigate the fundamentals of catalyst performance and also to ascertain the conditions necessary for obtaining desired products.

In this part a decisive scheme, formulated from the C-balance method, has been described which makes it useful for further findings.

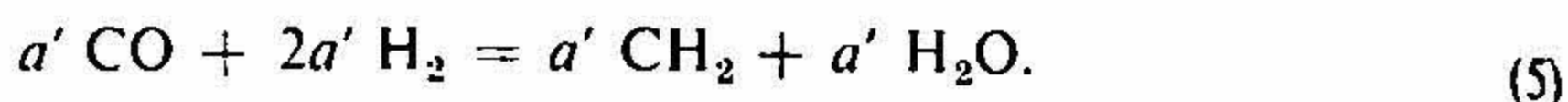
If we go through the C-balance calculations more carefully, we find that the total converted hydrogen has served three different purposes. Accordingly, the hydrogen, utilised for these different purposes, can be distinguished if the different parts can be calculated separately. A larger part of the hydrogen used up has served as reduction hydrogen by reacting with a part of CO to give  $(\text{CH}_2)$ -radicals or similar intermediate compounds with simultaneous formation of water. Another part of hydrogen has been used up for the reduction of carbon that has been formed from CO through  $\text{CO}_2$  reaction into  $(\text{CH}_2)$ -radicals. A third but much smaller part of hydrogen has been utilised for the hydrogenation of such primary olefines as have been formed by the polymerization of  $(\text{CH}_2)$ -radicals. Methane also belongs to this group being the first member of the paraffin series and occupies a significant part in the Fischer Tropsch Synthesis. This division of the converted hydrogen into *Reduction Hydrogen* and *Hydrogenation Hydrogen* and its calculation from C-balance method is a highly important step and will be derived here. It can be best understood by setting up a complete scheme of possible reactions. We will carry out this scheme at present only to such an extent as is necessary for obtaining the hydrogenation hydrogen. We will however not take into account the various reaction mechanisms. It is assumed here that only primary olefines are formed by the polymerization of the  $(\text{CH}_2)$ -radicals or intermediate compounds of similar nature and that a part of these primary olefines are then hydrogenated into paraffins for which purpose a certain amount of hydrogen is utilised. We will not enter into details of the formation of olefines or other intermediary radicals at this stage.

\* *Jour. Indian Inst. Sci.*, 1955, 37, 215-25.

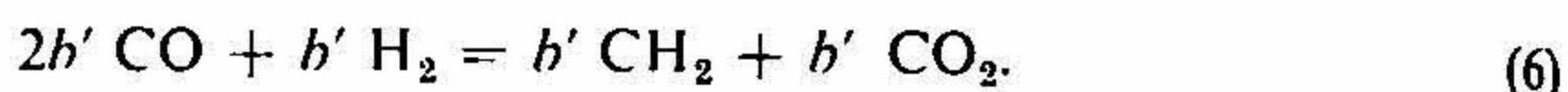


## GENERAL SCHEME OF REACTIONS

The first of the Synthesis Reactions consists of reduction of a part of CO with double its amount of hydrogen to give the so-called "water"-reaction ('*a*'-reaction) by which methylene radicals may be formed according to:



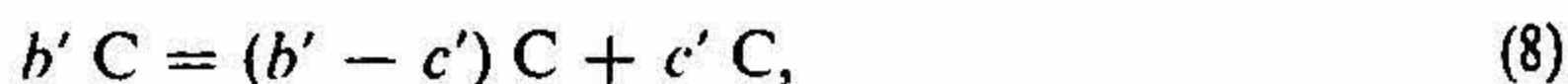
Apart from this highly hydrogen consuming reaction (5), another reduction reaction takes place which uses hydrogen more economically but consumes more CO instead. This is the so-called "CO<sub>2</sub>"-reaction ('*b*'-reaction).



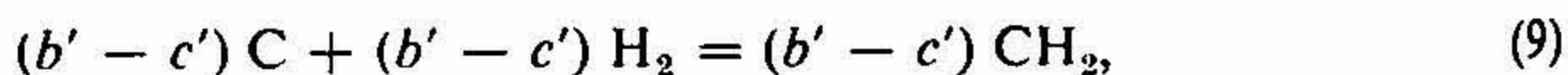
For the completion of the reduction reaction it is necessary to subdivide equation (6) into further steps. The first step is a CO splitting reaction which is identical with the Boudouard reaction. According to this, carbon shall be formed in the form of a labile carbide on the surface of the catalyst or also as somehow otherwise formed intermediary:



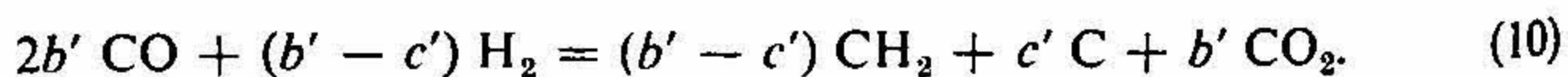
Under normal reaction conditions the so-deposited carbon is then reduced with the respective volume of hydrogen into methylene radicals. Sometimes, under different conditions, there may occur a deposition of free carbon which is no more being reduced. If we represent this part of carbon as *c*', we can write:



and further:

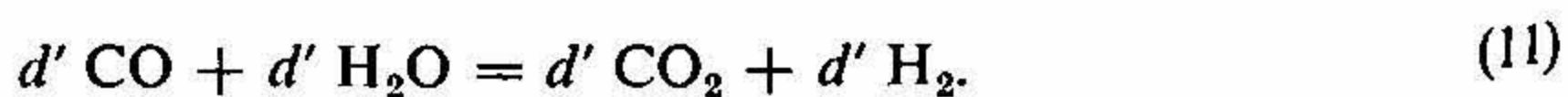


and finally both equations (8) and (9) can be combined with equation (7) as follows:—



Reactions (5) to (10) thus give a complete account of the reduction of CO to form (CH<sub>2</sub>) radicals.

Further, occurrence of the water-gas reaction must be considered, which runs as follows:

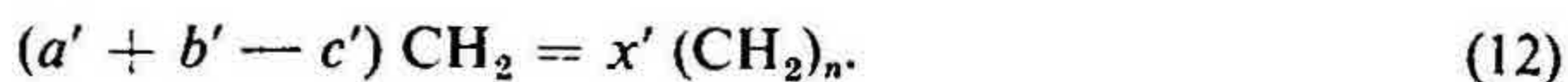


The water, reacted in equation (11) may be a part of water formed according to equation (5) or part of the water already present in the gas. If the water, formed during equation (5), is utilised in equation (11) then the amount of reduction hydrogen equal to *d*' which served for water formation can again be used, but at the same time the equivalent amount of CO will appear as CO<sub>2</sub>. Supposing there is lack of hydrogen activity, a catalyst with sufficient overall activity can save hydrogen at the cost of CO activation, either according to equation (6)



or equation (11) using CO or water of reaction respectively. It has been observed that synthesis catalysts under certain conditions activate both reactions (6) and (11) apart from reaction (5).

The (CH<sub>2</sub>)-radicals or similar compounds formed according to equations (5), (6) and (10) may then polymerize into olefines of all possible chain lengths according to a certain statistical distribution. The formation of products of different chain lengths may be brought about by a mechanism which will be described later. On the basis of the (CH<sub>2</sub>)-radical volume ( $a' + b' - c'$ ) we can say that this volume is then replaced by a vapour volume which consists of the sum of the volumes of olefines of different chain lengths. Let us take this sum of volumes of different chain lengths as  $x'$  and the average of the chain length as  $n$ . Then, this process can be formulated as follows:



From equation (12) we get a function for the polymerization as:

$$(a' + b' - c') = x'n \quad (13)$$

which, if we neglect the irreversible carbon deposition, *i.e.*,  $c' = 0$ , simplifies to:

$$(a' + b') = x' n \quad (14)$$

This equation is valid not only for the sum of all the products as indicated here, but also stands for each single hydrocarbon of specific chain length if appropriate symbols are used. With the help of equation (14) we can calculate the average chain length  $n$ , if  $a'$ ,  $b'$  and  $x'$  are known.

We will now divide the polymerization hydrocarbons, formed according to equation (12), into three groups namely paraffins, olefines and oxygenated compounds, which are mostly found in all such syntheses. For this purpose we subdivide the total polymerization volume  $x'$  into one part  $f'$  of unchanged olefines, a second part  $g'$ , consisting of oxygenated compounds, and finally into a third part ( $x' - f' - g'$ ) which has been hydrogenated into paraffins. As the different parts of the primary products will have different average chain lengths, we can formulate this subdivision in the following manner:

$$x' (\text{CH}_2)_n = f' (\text{CH}_2)_q + g' (\text{CH}_2)_r + (x' - f' - g') (\text{CH}_2)_p \quad (15)$$

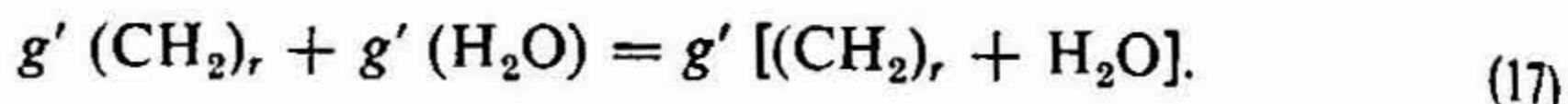
Here we are mainly interested in the part which has been converted to paraffins and which has required its special volume of hydrogenation hydrogen equal to its vapour volume. Hence we obtain the volume of hydrogenation hydrogen according to the equation:

$$(x' - f' - g') (\text{CH}_2)_p + (x' - f' - g') (\text{H}_2) = (x' - f' - g') [(\text{CH}_2)_p + \text{H}_2] \quad (16)$$

The thus defined volume of hydrogenation hydrogen must be a part of the total amount of converted hydrogen and is computable from the C-balance as will be shown later.

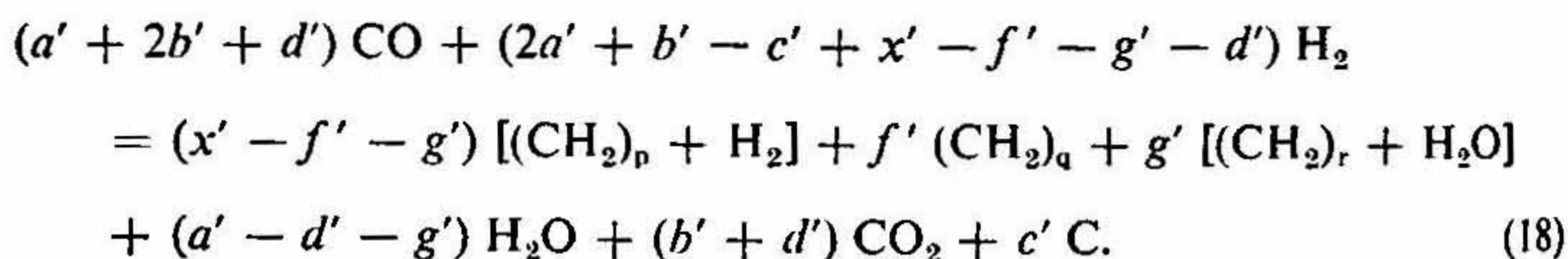


As a simplifying measure, the oxygenated compounds shall be looked upon as consisting mostly of alcohols. They are assumed to have been formed by the addition of water to the respective olefines according to the equation:



With this, all the possible steps of the total reaction shall be considered as being complete, as this will suffice for our present needs. It is possible to scrutinise reactions for other specific mechanisms for formation of branched hydrocarbons. It is as well possible, for instance, that oxygen containing compounds have been formed simultaneously with the olefines, by incomplete reduction. However, such an assumption does not basically change our formulation as given above. The amount of hydrogenation hydrogen, or water, which can be activated by the catalyst for the purpose of hydrogenation, therefore, fundamentally governs the degree of polymerization and the degree, character and composition of the products.

Summing up the partial equations (5), (10), (11), (12), (15), (16) and (17) we get the equation:



The left hand side of the equation (18) represents the overall consumption of CO and H<sub>2</sub> in all the possible synthesis reactions including the different reaction paths. It also includes the amount of hydrogenation hydrogen. Whatever the catalyst chosen may be and whatever be the reaction conditions, the total consumption as well as the distribution between the different paths of the reactions will be different. As all possible reactions are covered by equation (18), it is thus generally valid for all kinds of Fischer Tropsch Syntheses. In order to be able to compare the different catalyst performances and the influence of the reaction conditions on them and quality of the products, it is essential, as already explained in Part I, to recalculate the absolute conversion figures to the uniform hundred parts (CO + H<sub>2</sub>)-conversion figures. This is permissible since all possible reactions are either disturbed equilibrium reactions or chain reactions. These chain reactions consume reactants in a linear proportionality as long as reaction components are available and if sufficient time is given.

CO and H<sub>2</sub> being of the same volume and using the respective volume factors (letters without dashes) we arrive at the following equation as a condition for recalculation of equation (18):

$$(a + 2b + d) + [(2a + b - c) + (x - f - g) - d] = 100. \quad (19)$$



If we use the above equation to get the hydrogenation hydrogen value,  $(x - f - g)$ , we get:

$$(x - f - g) = 100 - 3(a + b) + c. \quad (20)$$

It is interesting to note that the 'd' reaction is no more represented in this equation, as it cancels out on both sides of the equation. This indicates that if sufficient hydrogen is present, the catalyst need not activate the water gas reaction.

Equation (20) is the final equation for the hydrogenation hydrogen value relating it to the other reaction figures  $a$  and  $b$ . Equation (20) can further be formed into:

$$(x - f - g) = 3 [33.333 - (a + b)] + c, \quad (21)$$

and in this form, it represents, in a general form the hydrogenation hydrogen figure including the permanent carbon deposition  $c$  and simultaneous formation of oxygenated compounds besides olefines and paraffins. For further discussion of this function, for reasons of simplification of the resulting representations it is better to leave aside the exceptional case of permanent carbon deposition. Further, it is better to investigate initially only such cases in which no marked formation of oxygenated compounds is observed, as is mostly the case with Co- and Ru-catalysts, and with special Fe-catalysts. This means that  $c$  and  $g$  have to be taken as Zero in our equations (20) and (21). Then we arrive at the simplified equation:

$$(x - f) = 100 - 3(a + b) = 3 [33.333 - (a + b)]. \quad (22)$$

The values for 'a' and 'b' are easily obtainable from each C-balance calculation after recalculation of the same on 100% CO + H<sub>2</sub> conversion basis, only if proper and complete analyses of inlet and exit gas are available. Since the values,  $-b$ , for CO<sub>2</sub>-formation,  $a + 2b$ , for the total CO conversion, and  $[2a + b + (x - f)]$  for the total H<sub>2</sub> consumption, —are directly obtainable from C-balance calculations, the  $(x - f)$  value can be more directly obtained with the help of these values after writing the equation (22) in the following form:

$$(x - f) = 1 [(2a + b) + (x - f)] - 2(a + 2b) + 3b. \quad (23)$$

In the equations (22) and (23), the hydrogenation hydrogen value represents a differential term within the complete conversion balance of CO and H<sub>2</sub> at all possible H<sub>2</sub>/CO conversion ratios. According to equation (5) as well as equation (6), always three equal volumes are reacting with each other, the sum of which after being deducted from 100, leaves over the residual hydrogen which has been used for hydrogenation. If a catalyst is not in a position to activate hydrogenation hydrogen (a case which has not occurred so far) which means that  $(x - f) = 0$ , then such a catalyst would form only olefines and/or oxygenated compounds or it would deposit carbon. In this case the value of  $3(a + b)$

must become equal to 100 whereby the ratio between  $a$  and  $b$  will remain absolutely unaffected and can have any value. If only oxygenated compounds are formed under such conditions, water would replace the hydrogenation hydrogen. As the ' $a$ '-reaction is a highly  $H_2$  consuming one, this reaction will occur with more  $H_2$  activating catalysts and the ' $b$ '-reaction with less  $H_2$  activating catalysts. Since the additional activation of hydrogenation hydrogen is drawing more on the  $H_2$  activity of the catalyst, it can thus, in the case of the catalyst with poor  $H_2$  activity, come about by an additional preference of the ' $b$ '-reaction. On the other hand, in the case of highly  $H_2$  activating catalysts, the hydrogenation hydrogen can be made available either directly, that is, in any unknown relation to the ' $a$ '-reaction or by lesser use of the ' $b$ '-reaction. In the latter case absolutely higher  $(x - f)$  values are generally to be expected also.