Part I.

Introduction

1. Introduction to the mathematical method of treatment:

Computations have been made for decades to determine the course of the synthesis and the yield from the analysis of gases of the hydrogenation of carbon monoxide. Such computations are carried out daily in many places. This is done today nearly as laboriously as some twenty years ago at the beginning of the work on gasoline synthesis, repeating the general derivations more or less completely for each individual computations. The great advantages derived from changing over to a strictly mathematical form with a simultaneous use of the corresponding abbreviations have not as yet been gained.

An attempt has been made in the following pages to show the basis of a mathematical treatment of the computations of the gas utilization during the hydrogenation of carbon monoxide. We started here from the basic relationships between the amounts of raw materials and of the resulting products. These fundamental relationships lead readily to convenient formulas which can be applied algebraically to any additional computations. This results in a comprehensive collection of formulas which include the whole field.

The application of these formulas eliminates sources of errors in application, shortens considerably the computations and actually permits to evaluate rapidly and accurately the gas analyses and to

test the results. A uniform use of such formulas would facilitate a comparison of synthesis data obtained at the different works.

Moreover, quantitative relationships between the participants of reactions become readily recognizable; such relationships could neither be found nor used without the use of a mathematical method of treatment. Finally the accuracy of such computations can be tested now better than formerly, i.e. finding what are sources of error and to what extent they affect this accuracy.

2. Selection of auxiliary figures and characteristic numbers:

The development accomplished in the course of years has not resulted in the introduction of uniform abbreviations nor in any agreement about the characteristic numbers to be used. We shall therefore give below a detailed explanation of the symbols, with an attempt to limit the use of factors to only a few.

a). The residual volume R

The term "contraction" is a habit acquired in the initial stages of experimental investigations. At that time, contraction was a factor which was particularly readily determined in laboratory tests at a normal pressure, and was capable of leading to numerous conclusions. With cobalt catalysts, conversion is practically directly proportional to the contraction. However, contraction is merely an illustration of the process, but cannot be used directly in computations.

One cannot directly use the numerical value of contraction in calculating the conversion. The numerical value of the residual value is here preferable. The latter is determined experimentally, and the contraction is calculated from it. It will necessitate going backwards in subsequent computations, and have the two values add up to 100, which makes it simpler and more useful to limit one-self to the concept of the residual volume.

We may therefore eliminate the use of the concept "contraction" and its numerical value in judging the course of the synthesis and base our computations on the residual volume only. Substitution of the expression for the actual volume of the residual gas for the concept of contraction as an expression for the change of volume will simplify discussions. We shall use below the abbreviation R for the concept "residual volume". We introduce no symbol for contraction in our list of symbols.

b). The Characteristic Numbers Proper

The expressions for yield are the most important figures to characterize the course of synthesis. To judge the course of the synthesis computations of gas utilization are expected therefore either to show the yield expected or else to permit arriving at conclusions why the maximum yield has not been obtained.

Considerations of causes which might affect the maximum yield brings us the following:

1. Insufficient conversion,

2. Formation of methane instead of higher hydrocarbons,

3. Consumption of CO and H_2 in some other ratio, then expected,

4. Deposition of carbon,

Other stoichiometric transformations which will affect the gas utilization are not known. Deposition of carbon is either unavoidable or else would soon bring an end to the synthesis, and we may therefore leave it out of consideration here. There remain only the processes 1 to 3 which should enable us to find an adequate characterization of the course of synthesis. Such is indeed the case.

The conversion formation of methane and consumption proportions can be always computed for the theoretical calculations of the yield and the exposition below is limited to the computation of the following four values:

Conversion U

Methane formation M

Consumption proportion X

Yield A

c). Relation Between the Factors and the ($CO + H_2$) Conversion.

Synthesis such as with cobalt and nickel, proceeds either

entirely or almost entirely with the formation of water, and the yield of higher hydrocarbons is proportional to the consumption of carbon monoxide in the simple and rigid ratio of 1 CO to 1 CH_2. For this reason, computations of conversion and yield have become commonly based on the consumption of carbon monoxide. As a result attempts have been repeatedly made to prove the excess of the amounts of gas introduced by means of a carbon balance, which is also calculated from the consumption of carbon monoxide.

However, with iron catalysts carbon dioxide is formed in considerable and very variable amounts, and as a result computations of carbon monoxide conversion no longer offer any advantages. It becomes simpler and clearer to judge conditions from the conversion of ($CO + H_2$). This method of computations offers the important advantage over the use of the CO conversion, in that the ($CO + H_2$) conversions can be compared with each other even when syntheris takes place in different consumption proportion.

For this reason, whenever conversion is discussed below, the ($CO + H_2$) conversion will be meant and designated by the abbreviation U. The values of the CO conversion can be dispensed with, as well as of the H_2 conversion. Their values are definitely established from the ratio of consumption of H_2 : CO. In the list of symbols an abbreviation of Uco is used for the CO conversion to be used

only for any possible intermediate computations.

What has been said about conversion applies also to the formation of methane. The methane formation will be given below entirely by the corresponding ($CO+H_2$) consumption, and abbreviated to Mv. These Mv values are comparable for the most varied syntheses and catalysts, while the Mco values are not.

3. Explanation of symbols:

The number of the necessary abbreviations have been found to be so great that a careful selection had to be made to come inside the capacity of the usual typewriter. A total of some ninety different concepts require symbols.

For some of the abbreviations the commonly used symbols may be used, but not for the most of them. We have made the following rule when selecting our symbols:

A). Symbols already in use have been retained as far as possible.

B). As an aid to memory new symbols have been selected to agree with the concept.

C). With many similar symbols, the simplest form has been selected for the most commonly used case.

D). All symbols must be clearly distinguishable, and be capable of being written on the usual typewriter.

E). No abbreviations have been given to concepts which are in use, but may be considered superfluous from the results from this investigation. There are for instance no abbreviations for the degree of liquefaction, for the H_2 conversion, etc.

In cases when for the sake of clarity an addition to a symbol becomes necessary to one already in existence, the writing is facilitated by not placing the index letters below the line, but adding small letters to the existing symbol, e.g. by writing Uco instead of U_{CO}.

A summary of all of the abbreviations used will be found in the explanation of symbols at the end of the article. Abbreviations used in this article are a first attempt in this line. No claims are made to include all of the symbols required in the laboratories and in large scale operations. This is particularly not the case for abbreviation used for yields.

Yields can be expressed in numerous ways depending on the nature of the gas or gas constituent converted, as well as on the nature of conversion, and may be used for expressing the products formed, as well as for the method of computations in use:

1. Kind of gas
   a). Synthesis gas,
   b). Total ($CO + H_2$) content,
   c). The proportion of ($CO + H_2$) which may be consumed from a given consumption proportion,
2. Conversion
   a). Actual conversion,
   b). The practically possible conversion, e.g. 90 percent,
   c). Complete conversion, 100 percent,

3. Products

a). All hydrocarbons formed, including methane,

b). Hydrocarbons formed, without methane,

c). Hydrocarbons formed without methane, ethane, ethylene,

d). a - c, with the addition however of oxygenated products or of oxygen-containing chemical groups.

There may be numerous combinations between the enumerated cases, and there are therefore numerous ways of expressing yields. These different expressions can however be more or less simply converted one into another. Their selection is therefore not a subject of a mathematical derivation, but a convention, and is not therefore the real object of the present work. We will limit ourselves here in all computations of yields to the simplest and most profitable cases, namely to grams of higher hydrocarbons without methane/cbm of synthesis gas, occasionally including also the oxygen-containing groups.