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GENERATION OF PRIMARILY PETROCHEMICAL RAW AND BASIC PRODUCTS BY THE FISCHER-TROPSCH SYNTHESIS

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Interim Report I

Technical Information Center
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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GENERATION OF PRIMARILY PETROCHEMICAL RAW AND BASIC PRODUCTS BY THE FISCHER-TROPSCH SYNTHESIS

Interim Report I

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Union Rheinische Braunkohlen Kraftstoff Aktiengesellschaft

One may make the assumption that within the next decade large amounts of synthetic gas consisting of CO and H_2 may be made available at a reasonable price level when compared with synthetic gas made from crude oil fractions — particularly by the application of nuclear process heat, gasification of coal and especially Rhineland lignite. It is the purpose of this study to consider whether crude and basic products for further petrochemical processing may rationally be obtained by means of the Fischer-Tropsch [F-T] synthesis in its current form or with modifications.

The study, which is carried out by the Union Rheinische Braunkohlen Kraftstoff AG with support of the Federal Ministry for Research and Technology, is subdivided as follows:

Phase 1: Consideration and evaluation of the current state of knowledge of the F-T synthesis and related procedures.

Phase 2: Selection of methods for processing of the synthetic raw products.

Phase 3: Comparative study of economic aspects.

Phase 4: Suggestions for the further development of favorable approaches.

Phase 5: Summary and recommendations for a research program. Report.

This subdivision gives consideration to the factors which influence profitability. Primarily these are the price of the starting gas, the yields and the product distribution.

The price of the starting gas depends chiefly on the price of coal and the amount of coal energy required per unit of starting gas. The above-mentioned combination of lignite and nuclear heat represents a favorable point of departure. We make the assumption in this study that every synthesis can be supplied at the same cost with the hydrogen/carbon ratio in the starting gas which is optimal for the respective method.

The utilization of the starting gas depends primarily on the conversion rate of hydrogen and carbon monoxide. Conversion rates between 50-95% have been reported for different developments. Conversion of the starting gas depends on different variables and is linked to selectivity. The selectivity for a compound (for instance CH_4) is the percentage share of the converted carbon which was consumed in order to synthesize this compound. The selectivity for primary synthetic products limits the distribution of basic and terminal products which can be generated by processing.

Even unconverted synthetic gas may make its contribution to profitability, for instance when it is utilized as residual gas, as heating gas or by way of a reaction cycle with methane cleavage as gas for F-T synthesis or other syntheses.

Selectivity, just as conversion rate, is influenced by different variables. Depending on method, selectivity for a specific class of compounds is also linked in definite ways with the selectivities for other compounds. From the perspective of synthesizing a maximal fraction of C_2-C_4 compounds, this means, for instance, a shift of the yields on iron catalysts by means of higher reaction temperatures and/or a smaller addition of alkali promoters to the catalyst decreases the share of higher hydrocarbon and the desired increase of selectivity for C_2-C_4 compounds. However, it is unavoidable that the selectivity for the initially undesired methane rises at the same time and that for alcohol drops. Therefore, in order to judge the profitability of a method, the F-T synthesis must not be viewed by itself but in conjunction with the preceding generation of starting gas and the subsequent processing and utilization of the product.

The present interim report covers the work of the period 1 June 1974 to early October 1974 – and deals with only the first of the five program points.

TARGETS OF PHASE I

Initially all known synthetic methods had to be reviewed regardless of their state of development. Promising methods of development had to be compared. In this connection the perspective had to be general economic points of view and the special target to produce a large amount of petrochemical crude and basic products, particularly low molecular olefins.

The resulting quantitative balance sheets are to serve as a basis for the selection of methods for processing of the synthetic crude products (Phase 2).

SUMMARY

More than 20 synthetic methods were compared. Industrially untested methods were considered as long as the expectation seemed to be justified that a development toward industrial maturity within 5 to 8 years would be possible.

The methods listed in Table 1 were compared to each other in view of the initially-mentioned factors related to profitability and from the point of view of their stage of technical development.

This comparison led to the selection of 11 methods or procedural groups. For each of these a quantitative balance sheet for 2.5 MMTPY C_2+ was established.

Initially, often from numerous groups of data, we tried to balance those which with acceptable gas conversion are typical for the respective method. The summary of the balances (Table 2) showed that very large differences in the composition of the primary product distribution can be encountered:

Largest C_2 yield	531.000 t/a, Synthol with 30% CH_4 yield
Lowest C_2 yield:	70.000 t/a, Arge synthesis, Sasol "normal case"
Largest yield of oxygen-containing compounds:	1.005.000 t/a, Fluidized-bed iron nitride catalyst
Lowest yield of oxygen-containing compounds.	70-80.000 t/a, Liquid phase synthesis, Rheinpreussen

The following Figure 1* shows the most important connections between selectivity and gas utilization which are discussed in detail in the body of the report.

In the collection and evaluation of the available information few suggestions were found for selectivity shifts which go significantly beyond those which we have evaluated. Among the methods which can be used on a 2.5 MMTPY scale without further development Synthol offers the most advantages.

A final relative evaluation of all methods can only be accomplished by means of the studies planned for the subsequent phases of the program.

Possible points of departure for further development studies, which go beyond what is already being done by Sasol and Lurgi for reactor development, were encountered in a few cases; among these:

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*Of the residual gas only the methane share is shown. ? in the figure means that the methane content could not be determined.

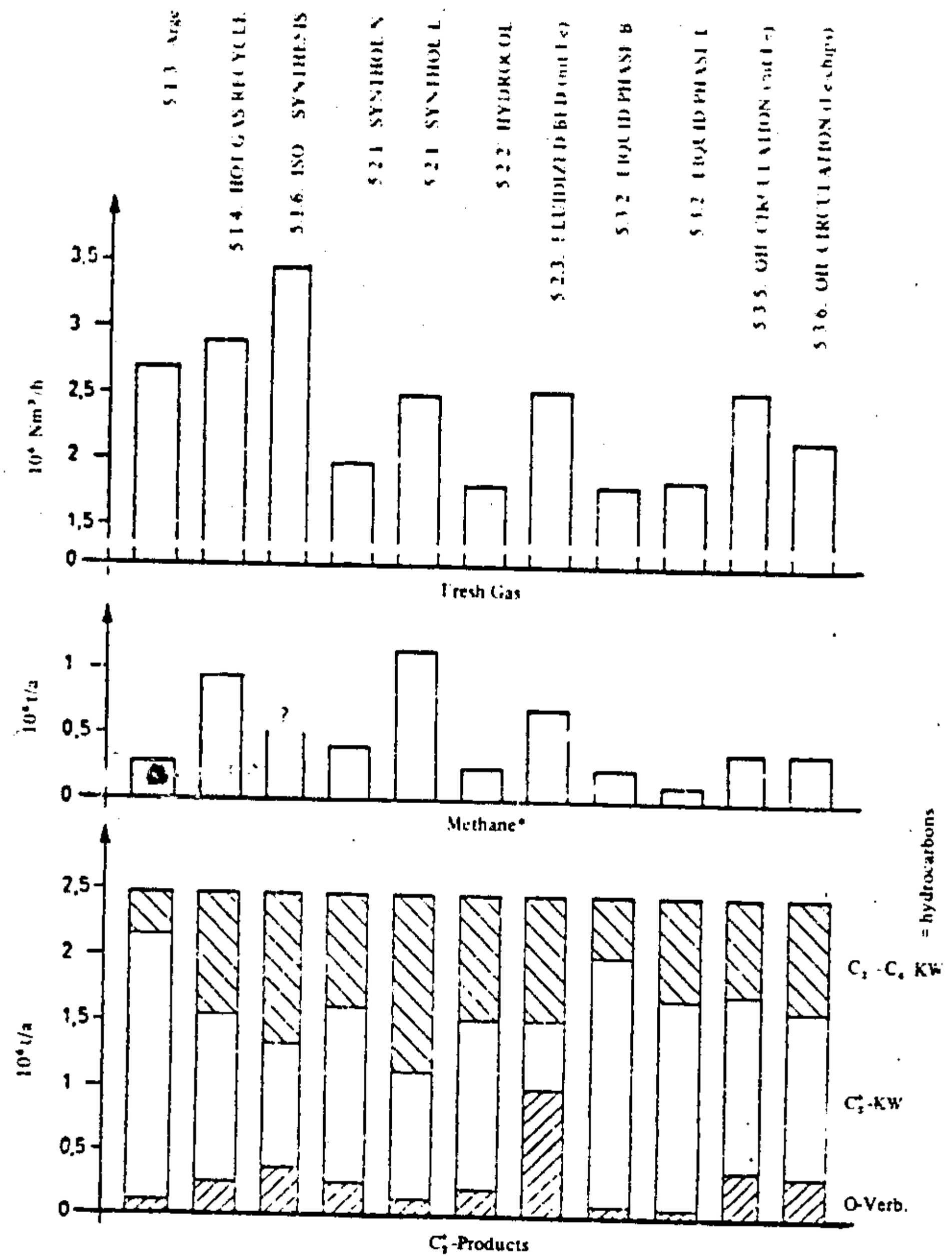

Fig. 1. Dependence of selectivity from gas utilization

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*Of the residual gas only the methane share was represented.

The industrial applicability of nitrided contacts in the tested reactor types should be established by large-scale experiments.

The direct synthesis of ethylene appears so attractive that a further search for details should be pushed, parallel with Phases 2 and 3 of this study, in the hope that genuine promises for development efforts in this direction may yet be found.

From a long term point of view it may be possible to develop the use of cobalt catalysts with longer useful life in modern reactors for the production of hydrocarbons with a very small fraction of oxygen-containing compounds.

Could other synthetic methods be directed in such a manner that a similarly favorable ethylene/ethane ratio may be obtained, as in the stationary liquid phase synthesis?

2. LIMITS OF THE INVESTIGATION

Since our objective differed from the one that led to the construction of the Sasol facilities, the screening of synthetic procedures could not be restricted to those which are in industrial operation. Another reason to include in the initial comparison syntheses which have been tested on a small scale also is the fact that since 1950 some new developments have been published.

However, we have considered only methods for which at least experimental reports were published in the technical literature.

Collection and screening was limited to pure F-T procedures and to related methods, namely the Iso synthesis and the Ethylene Direct Synthesis.

Disregarded were the syntheses from CO_2 and H_2, syntheses from CO and H_2O, and the Oxo synthesis, methanol synthesis and coal liquification methods.

3. SOURCES OF INFORMATION

In addition to the well known text books and standard works, Chemical Abstracts issues from 1952 to 1974 were screened. A card file with more than 2,000 abstracts[1] was created. For the years prior to 1952 the first part of a Bibliography of the F-T synthesis and Related Processes[2] was used.

Evaluation of the literature references to a large extent had to proceed by way of a preselection on the basis of published summaries. A complete evaluation and review of all relevant publications was not possible.

However it is not likely that essential published findings remain undiscovered in this manner.

The reports of individual methods are frequently incomplete. Complete data for a balance sheet were available only for the Sasol method and some other synthetic experiments published by the U. S. Bureau of Mines (BOM). Assumptions and recalculations were partly based on analogies with related processes. Details about calculations and sources which go beyond the examples in the appendix are available.

As a means of fleshing out the literature data an information exchange with a number of experts was initiated —which has not been completed in all cases. The following individuals or groups furnished essential information:

Dr. A. P. Ackermann, Moers, was involved in the development of liquid phase synthesis with stationary oil phase and in the experimental operation of a 10 m^3 reactor with the firm Rheinpreussen. Together with Prof. H. Koelbel, he provided several publications about liquid phase synthesis. Dr. Ackermann also furnished comments about the liquid phase synthesis.

Dr. H. Berge, City Works, Stuttgart, participated as an employee of the Koppers firm in the operation and evaluation of the liquid phase synthesis with Rheinpreussen. Dr. Berge supplied information about this subject.

Prof. H. Hammer, Technical University, Aachen, among others, made a detailed investigation of the optimal operation of bubble column reactors — as they are used in the liquid phase synthesis — and took part in the studies about F-T catalysts. The discussions with Prof. Hammer dealt particularly with liquid phase synthesis and with the possibilities of obtaining, with further research in the catalysis area, essential progress in the direction of the goals of the present study.

Dr. E. Sauter, Eislingen, worked with Sasol as manager of the laboratory from 1953 to 1959, and subsequently for three years at the Institute of Prof. Pichler at the Technical University in Karlsruhe. Dr. Sauter supported our efforts with information about the Hydrocol method, with a study about the balancing of syntheses and a thorough analysis of the balances of two liquid phase syntheses.

Prof. H. Schultz, Technical University, Karlsruhe, author of numerous publications on the theme of F-T syntheses, together with Prof. H. Pichler gave essential advice for the general collection of information and the programming of the study.

Dr. K.-H. Ziesecke, Erdoel-Chemie, Dormagen, was responsibly involved in the development of the Iso synthesis and contributed particularly with information to the analysis of this procedure.

U. S. Bureau of Mines worked during the last 30 years (with an interruption of only a few years) on the development of almost all types of F-T synthesis. The information exchange with the BOM led to their making available some of their publications which are difficult to obtain in Germany. It is to be expected that further contact will be useful to the current study.

South Africa Coal, Oil and Gas Corporation (Sasol), since 1954 has operated an Arge (fixed bed) synthesis and a Synthol (entrained catalyst) synthesis with a joint annual production of about 250.000 tons. Contact with the firm Sasol has led to the communication of data regarding their syntheses. Some of these data are used in the present report. A detailed exchange of ideas is being planned for the interpretation of further data for the present report and further development of the study. A secrecy agreement was concluded with Sasol. Within the next few weeks an agreement is to be signed about collaboration during the study and possible further collaboration after its conclusion.

4. SYSTEMATIZATION OF TECHNOLOGIES

In Table 1 we list the most important —even though not always directly comparable— characteristics of individual methods. The composition of the synthetic products of a method as regards boiling range, amount of oxygen-containing compounds and amount of olefins and paraffins can be adjusted within certain limits. Unless mentioned otherwise, the "standard run" of a method was evaluated. A comparison of some available data about possible control of product composition shows that larger differences in yield, as they are seen in Tables 1 and 2, may be significant and characteristic for individual methods or catalysts.

As a means of getting a better picture, a classification of the methods discussed [illegible] desirable. The synthetic procedures could be arranged according to the kind of catalyst used, according to the composition of the starting gas, according to selectivity, according to operational characteristics and other variables. The following classification [illegible] significant relations, and these relations have been discussed in several standard works (3, 4, 5). They may be summarized as follows.

In the application of iron catalysts, particularly from the point of view of [illegible] customary composition and at the same time application of the conditions [illegible] for the principal types, the following is generally accepted.

1. Catalyst Fixed Bed, Gas Phase

Lower temperatures (200-250°C), active catalyst, moderate CH_4 yield, high yield of waxy hydrocarbons, low yield of oxygen-containing compounds.*

2. Moving Catalysts, Gas Phase

Higher temperature (300-340°C), higher conversion, larger methane yields, lower yield of heavy hydrocarbons, higher (ca. 70%) olefin content of the C_3 hydrocarbons and higher content of O-compounds.

3. Liquid Phase

Temperature mostly higher than for the first group. The distribution of the hydrocarbons is more variable, but they are always of higher molecular weight than those of gas phase synthesis with fixed catalyst. Lowest selectivity for CH_4. Olefin content is close to the method listed under 2.

4. Direct Synthesis of Ethylene

These relations can be changed by varying the reaction conditions and particularly by alkali additions or by NH_3 treatment of the catalyst.

The syntheses of the first three types react quantitatively in the same manner to changes of the catalyst, of gas composition, of pressure and of temperature. For instance, in every case increased addition of alkali with otherwise unchanged conditions causes increased gas conversion and a shift of selectivity to higher molecular hydrocarbons. Similarly, in every case an increase of temperature causes higher gas conversion, a shift of selectivities in favor of lower molecular products and an accelerated deactivation of the catalyst. The possibilities of variations are limited differentially for different types of synthesis. The following example is typical for such limitations depending on the method: the syntheses with moving catalyst must be operated at least at 260°C, and better above 300°C. On the abrasion-resistant but sluggish fused catalyst the initial gas conversion would be uneconomically low, while larger amounts of waxlike compounds are formed and interfere with the operation by "gumming". Finally, with further lowering of temperature the reaction would die out.

By contrast the fixed bed reactor is charged with more active precipitated catalyst of lower mechanical strength. Operation is at 200-250°C. Temperatures, as they are required for the moving catalyst, would cause high methane yields in the solid bed and finally give rise to deposition of carbon. Among the methods which we are considering here, the only one which could not be assigned to one of the three types of synthesis is the direct synthesis of ethylene. In view of the

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*In subsequent sections oxygen-containing compounds are also briefly termed O-compounds.

great advantages which a synthesis of this type could offer, an evaluation is being attempted even though only patents and a patent based study[6] are available. The uncertainty of the data does not permit direct comparison with other syntheses.

5. DESCRIPTION AND FIRST APPRAISAL OF THE METHODS

5.1. Gas Phase Syntheses in Fixed Catalyst Beds

To this group belong

5.1.1. Normal pressure syntheses
  2. Middle pressure syntheses on Co contacts
  3. Middle pressure syntheses on Fe contacts (Arge, as practiced by Sasol and Lurgi stage oven)
  4. U. S. BOM Hot Gas Recycle method
  5. Synol method
  6. Iso synthesis

(5.1.1. to 5.1.6. are the designations used for these syntheses in the supplements)

5.1.1. 5.1.2. NORMAL PRESSURE SYNTHESES AND MIDDLE PRESSURE SYNTHESES ON COBALT CATALYSTS[4]

Normal pressure syntheses was operated industrially. For instance, in 52 synthesis ovens of the Ruhrchemie AG, 72,000 tons of products per year were generated.

The catalyst was arranged in vertical layers of 7 mm thickness between cooling tubes ("laminar ovens").

The middle pressure syntheses on cobalt catalysts were carried out in double tube ovens. The catalyst was placed in a 10 mm wide annular tube which was surrounded by water and enclosed a water tube. As in the normal pressure method, the temperature was adjusted to 200-210 °C by regulation of the steam pressure. The pressure amounted to 7-12 atm.

This method also has been used industrially, for instance by Krupp Kohlechemie, where 32 ovens were able to produce up to 60,000 tons of product per year.

A comparison shows that most of the syntheses mentioned under 5.1.1. and 5.1.2. were operated at normal pressure and middle pressure on cobalt, and were mostly developed before 1950. From a short range and middle range point of view the similar Arge method appears to rank higher because of its relatively high space time yield, its annual production per reactor and its established industrial record.

From a long term point of view the extremely low selectivity of the cobalt catalyst for the O-compounds may deserve consideration. The syntheses classified under 5.1.1. and 5.1.2. have not been further considered after evaluation of Table 1.

5.1.3. MIDDLE PRESSURE SYNTHESES ON IRON CATALYSTS: THE "ARGE METHOD"

Among the syntheses classified under 5.1.3. complete data are available for the Arge method (Table 3). As the industrially most reliable among the methods which have been operated since 1950, it is compared with the other balances shown in Table 2 and will enter into the subsequent phases of the present study.

As operated today a reactor generates [illegible]0,000 tons of products/year[7,12] from about 20,000 Nm^3 $CO + H_2$/h. The reactors are standing cylinders, each with 2,000 vertically arranged tubes of 50 mm inner diameter which are filled with precipitated iron catalyst[8]. The heat of reaction is carried off by the controlled evaporation of boiler feed water on the jacket side. The gas, consisting of about 2 volumes of recycle gas per volume of fresh gas, passes through the reactor from top to bottom. The pressure is about 20 atm and the temperature 220-250°C -- depending on age of catalyst and reaction control. As shown in the supplement (Table 3), with normal operation relatively large amounts of heavy hydrocarbons are produced which contain a comparatively small olefin fraction, namely 35% in the 190-316°C fraction.

A possible shifting of selectivity from the relatively high yields of hard paraffins boiling above 450°C (which are unmarketable in large amounts) to a larger proportion of light products can be considered later -- if it is of interest. It would seem, however, that in this way at the very best an approximation to the Synthol product distribution may be obtained, with a space/time yield being lower than that permitted by the moving catalyst of the Synthol reactor.

If it should turn out that a development of the Arge synthesis in the direction of the Synthol product distribution offers advantages, the stage oven would probably be more suitable than the Arge reactor as operated in South Africa.

Few data are available about the Lurgi stage oven, which in certain respects may be viewed as an advanced form of the Arge reactor. So far it has been operated only at the pilot level. In its prospective industrial form the stage oven reactor is to have the 4-fold capacity of the Arge reactor operated by Sasol, and with a better turnover it should produce somewhat lighter products, particularly within the boiling range of the Diesel oils. For the objectives of the present study the stage reactor would seem to be economically more attractive than the Arge reactor.

5.1.4. HOT GAS RECYCLE METHOD OF THE BUREAU OF MINES[9]

With the hot gas recycle method of the BOM, which in principle resembles the stage oven, with a very high ratio of circulation gas to fresh gas the heat is carried away from the reactor with the gas (Table 4). With 278°C the reaction temperature is higher than in the Arge synthesis. So far the method has only been tested on a laboratory scale. Like the Lurgi stage oven it may be viewed as a further development of the Michael method. The balance (Table 2) for this process and the data in Table 1 show a relatively high selectivity for methane, but also for C_2 and C_4 hydrocarbons, with yields similar to that of the Synthol method. The balances for the hot gas recycle process will enter into the next program phase also, because this gas phase method, with a high catalyst life, offers relatively large possibilities for variations in the composition of the products boiling below 200°C. At the same time, these advantages would have to be paid for with larger expenditures of energy and equipment.

5.1.5. SYNOL METHOD

So far this synthesis also has only been practiced in the laboratory. Main characteristics are the low temperature of 190-200°C and a low H_2/CO ratio of 0.8:1. With low conversion, high yields of oxygen-containing compounds were obtained.

Although the large amount of these compounds offers economic advantages the procedure is not being investigated further, since in the direction of larger fractions of neutral oxygen-containing compounds the fluidized bed synthesis developed by the BOM (5.2.3.) with iron nitride catalyst offers definite advantages. The method discussed under 5.2.3. is superior, particularly in view of the space/time yield (kgC_2 + products/m^3 catalyst and hour).

5.1.6. ISO SYNTHESIS

The extensive publications[10,11] about this method describe experiments carried out on a laboratory scale exclusively. The particular characteristics of the method are a high synthesis pressure and the primary use of thorium-containing catalysts. In one experimental series also more economical zinc aluminum catalysts were used with success (Table 5). As regards the high proportion of oxygen-containing compounds and C_2-C_4 hydrocarbons of the Iso synthesis, this method also is exceeded by the fluidized bed method of the BOM (5.2.3.) which achieves a much better gas conversion. Despite other disadvantages of the Iso synthesis —work at elevated pressures (about 300 instead of 20-30 at) and the attendant problems of ironcarbonyl formation —the balance of the procedure for the time being enters into the second phase of the study, until it has been shown definitely that even the high Iso C_4 fraction offers no particular incentive.

5.2 Gas Phase Synthesis With Moving Catalysts

We discuss:

5.2.1. The Synthol method: circulating catalyst, as operated by Sasol.
2. The Hydrocol method: Fluidized bed, operated 1951-1957 in Brownsville.
3. The fluidized bed method of U. S. BOM (here with iron nitride-containing catalysts).

5.2.1. THE SYNTHOL METHOD

The Synthol method[4,12] shows the characteristics of the typical fluidized bed procedures, as described in section 4.

Synthesis takes place at 320°C and about 20 atm. The circulating hot entrained dust catalyst is fed continuously in controlled amounts into the entering gas stream. The entering gas consists of fresh gas with an H_2/CO ratio of 2 : 1 and the 2-fold volume of recycle gas.

The reaction starts immediately and the catalyst is carried by the gas stream into a separate chamber through a reactor equipped with internal coolers. The gas leaves this separator with the products of synthesis by way of cyclones, while the catalyst flows back into the entering gas stream through a "standpipe". With good gas conversion small yields of high boiling fractions and about 10% oxygen-containing compounds are produced. The hydrocarbons contain about 70% olefins and, depending on boiling range, 5-15% aromatics. On the basis of a reactor performance of 80,000 t/a, tested through many years of operation, a point of departure exists for any development required over the near term, despite the short catalyst life.

In addition to the detailed balance for the "Normal Sasol" case (Table 6) a quantity balance for a selectivity experimentally obtained by Sasol is to be investigated in the further development of this study (Table 7). While the normal case shows a methane selectivity of 10%, this case which lies within the range of the maximally possible yield of ethylene shows a methane selectivity of 30%.

For the further evaluation of this "light case"—which is typical for the selectivity control on moving non-nitride-containing iron catalysts—Sasol will contribute additional details. Already it is known that with increasing fractions of C_2 to C_4 not only the methane share of the overall product increases but at the same time the ethylene share of the total C_2 drops.

5.2.2. THE HYDROCOL METHOD[4,5,13]

At about 300°C in 20 atm fresh starting gas with an H_2/CO ratio of 2 : 1, together with 3-4-fold volume of recycle gas, streams through a stationary bed of fused iron catalysts. Much of the reaction heat was carried off by a bundle of tubes built into the bed. Steam was generated in the tube bundles. Unreacted starting gas and the vaporous reaction products --as in other procedures of the type --leave the reaction space by way of cyclones.

The Hydrocol method was operated for several years in Brownsville Texas. Yields resemble those of the Synthol method. The greater reactor performance of the deployed units and the better possibilities of additional scaleup are advantages compared with the Synthol method. It seems, however, that the circulation technique is easier to handle than that of the stationary fluidized bed. Publications[14,15] suggest that the operational problems were not solved when the plant was definitely discontinued for economic reasons in 1957/58. We are trying to obtain further details about the Hydrocol method.

Sasol and its associated engineering firms now think that a more than 2.5-fold enlargement of the "Synthol reactor" would not be possible, which makes it necessary to consider a fluidized bed reactor. Primarily it will be Sasol that will supply information about additional developments in the area of enlargement and improvement of the fluidized bed synthesis. We will try also to obtain details from the earlier operators of the Brownsville plant about their erstwhile efforts for the optimation by way of the production of oxygen-containing compounds.

In the meantime the tabulated quantitative balance, 5.2.2. (Table 3), is incorporated into the further program.

5.2.3. FLUIDIZED BED METHOD OF THE BUREAU OF MINES[16]

So far this method has been tested only on a laboratory scale. By using iron nitride-containing sinter catalysts, the advantages of which were described in 1950[17], good yields with high output of O-compounds can be obtained at low temperatures. The method is to be further investigated, particularly as being typical for the developmental trend which became possible through iron nitride catalysts. It was selected since, with higher conversion rates and greater space/time yield, it produces larger yields of O-compounds than the syntheses with iron nitride in an oil circulation reactor and in the stationary oil phase ("slurry reaction")[16,18] (Table 9).

In spite of the essential differences (summarized below) between the synthetic conditions of the BOM method and of the other industrially tested procedures, it is conceivable to operate industrially tested reactors with iron nitride catalysts.

Comparison of some synthesis conditions of the three described methods (Synthol, Hydrocol, BOM iron nitride) with moving catalysts, are shown in the following chart:

	Synthol	Hydrocol	Bureau of Mines with Iron nitride catalysts
H_2 : CO in Synthesis-gas	2.1 : 1	2.0 : 1	1.0 : 1
Recycle Ratio*	2.1 : 1	3-4 : 1	9-11 : 1
Temperature	320°C	300-340°C	238-253°C
Pressure	20 at	20-30 at	20 at

*Recycle ratio = returned residual gas: fresh synthesis gas (Nm^3/Nm^3)

5.3 Liquid Phase Synthesis

To be discussed:

	Synthesis method	Characteristics of the method
5.3.1.	Foam method of BASF	Oil and catalyst are circulated through the reactor through which the gas flows.
5.3.2.	Rheinpreussen, liquid phase	The gas streams through the suspension of the catalyst in the oil phase. Heat removal takes place primarily through internal structures in the reactor.
5.3.3.	"Slurry synthesis" of BOM	The oil which serves as the liquid medium in the reactor is kept in circulation. The heat of reaction is carried off mainly by way of this circulation, outside of the reactor.
5.3.4.	Duftschmidt method	The catalyst does not take part in the circulation; gas and circulating oil pass through it.
5.3.5.	BOM, expanded catalyst bed with oil circulation	
5.3.6.	BOM, iron chips with oil circulation	

None of the methods of synthesis type 5.3. have so far been tested in an industrial scale.

5.3.1. BASF FOAM METHOD[4,19]

This synthesis was operated on a pilot scale at 20 atm. and 240-250°C. The principle of the foam procedure leads to unmanageable deposits of solid matter in the circulation system, and with good reason has been judged negatively in different studies.

After the BASF experiments, which were carried out before 1945, a system with a circulating catalyst-oil slurry was not investigated again.

In the present study the method will not be further evaluated.

5.3 2. RHEINPREUSSEN LIQUID PHASE[4,20]

Among group 5.3. the liquid phase method of Rheinpreussen-Koppers is the one which so far has been practiced on the largest scale (about 400 kg/h). The main advantages of this synthesis are a low yield of methane and a reaction control which, on a single pass, i.e., without circulating gas, yields good conversion rates and a favorable enthylene:ethane ratio[21].

However, the Rheinpreussen reactor has met with significant problems in the control of the "bubble column reactor". Experts have stated that large carbon deposits and their consequences were chiefly the result of conditions deviating from the ideal state of smooth and uniform gas passage. Theoretical and laboratory-developed improvements for the design and operation of a bubble column reactor remain to be examined on a substantial scale

While the enthylene:enthane ratio is favorable, a comparison of the quantitative balances of Table 2 show that selectivity for C_2 hydrocarbons and C_2-C_4 hydrocarbons is significantly smaller than in other syntheses. Together with the balances listed "gasoline modus operandi", Table 10, generation of the maximum amount of light products, Table 11 the method is being incorporated into the continuation program as representative of the syntheses in the stationary liquid phase (5.3.2. and 5.3.3.).

5.3.3. "SLURRY SYNTHESIS" OF BOM

The slurry method of the BOM[22] is not significantly different from the Rheinpreussen procedure. The BOM also records a high ethylene:ethane ratio. While the Rheinpreussen method was developed up to a 10 m^3 reactor, the BOM experiments were carried out in 15 l reactors.

The same is true for the experimental series of the BOM using the slurry reactor with iron nitride-containing catalyst[18] which for the predominant production of alcohols is exceeded by the fluidized bed method (5.2.3.).

5.3.4.-5.3.6. OIL CIRCULATION METHODS

Compared with the syntheses with a stationary oil column, the liquid phase syntheses with oil circulation have the disadvantage of greater costs in terms of equipment and energy requirements. In this connection, for the greater oil circulation an intermediate depressurization for the removal of CO_2 and H_2O probably would be required.[4,23] (Even with partial vaporization of the circulating oil in the Duftschmidt method 80 l/kg hydrocarbon had to be pumped back; for a 100,000 t/a reactor this would mean an oil circulation of about 1,000 m^3/h.)

The Duftschmidt method can be considered as a precursor of this trend.

For the circulation method, 5.3.5., with a 10-20% expansion of the catalyst bed caused by the upward movement of the oil stream, results are available for work with iron nitride catalysts.[24] This method is being further evaluated as a representative of the trend "liquid phase synthesis on iron nitride" (Table 12). The circulation method in its latest form, with iron chips, 5.3.6.[23], compared with the stationary liquid bed probably has the advantage that the conditions of flow, and thus the gas distribution, can be better controlled. With the balance for the non-nitrided contact this method will be further investigated (Table 13).

5.4. Direct Synthesis from Ethylene

Since 1949 several patents have claimed that ethylene can be prepared directly from CO and H_2 with a high selectivity, although frequently with low yields.

Although most descriptions of such "procedures" demand allocation to group 5.1. "Fixed Catalyst-Gas Phase" it seemed necessary to treat the method separately.

The stimulus for the development of this sort of procedure into industrial maturity has been enhanced since the evaluation of the information of the methods combined under 5.1.-5.3. have shown only limited possibilities for the production of high ethylene and propylene selectivity on the basis of the classic syntheses. On the other hand, the outlook for development of industrial procedures on the basis of the patent literature seems poor. Experiments to reproduce some results described in patents failed[25]; the fact that despite all obvious attractions no interested parties have so far pursued this approach, seems to indicate that serious doubts exist regarding the possibility of an industrial realization of the methods so far suggested.

The most promising patent application was issued in 1967 to Stanford Research Institute (apparently without examination of the result) as a basis for a project study of a 250,000 t/a ethylene plant.

Reports of the Stanford study are to be further evaluated (Table 14), while additional information is to be secured from the patent owners.

6. MATERIAL BALANCES AND FLEXIBILITY LIMITS

6.1. Balances

Quantitative balances were established for the procedures which are typical for specific developmental trends and which show potentially competitive combinations of the most important characteristics, such as gas conversion, space/time yield and selectivity.

The following assumptions were used for all procedures:

Manufacture of 2.5 Million t/a C_2^+ products, inclusive of oxygen-containing compounds.

The starting gas contains 1% CO_2, 1% CH_4 and H_2 and CO in the ratio optimal for the respective method.

The possible separation and return of methane in the residual gas is not yet being considered here.

The readily water soluble oxygen-containing compounds of the oil phase are brought into the water phase by simple washing. 40% of the oxygen-containing compounds of the oil phase go this way, the rest was left in the oil phase.

Tables 3-14 contain the individual conditions which are summarized in Table 2. The synthetic methods are identified in the tables, among others, with the numbers introduced in Chapter 5. The attempt has been made to classify the primary products in the form of the major product streams, residual gas, oil phase and water phase, since these are necessary as starting points for Phase II of the study.

Incomplete literature data are responsible for gaps in some balance tables.

Analogies have been used to obtain certain data wherever this could be done without unpairment of reliability. A typical example for the construction of a balance has been added as a supplement to Table 6 for the Synthol synthesis (5.2.1.).

We shall try to obtain additional information for Phase I and thus for the balances which up to now were not accessible for different reasons, and which are not of major importance for the present report.

Among these are:

Details for the Synthol synthesis: 30% selectivity (Sasol)

Information on recent developments in the Rheinpreussen liquid phase synthesis (Prof. Koelbel) which may not have been published in technical journals

Information from Stanolind about the preparation of the Hydrocol plant in Brownsville

Details about recent studies of the U. S. BOM with nitrided iron catalysts

Details about direct manufacture of ethylene from two patent owners.

6.2 Flexibility Limits

Depending on procedure, economic advantages are to be sought in one or two developmental directions:

Maximization of valuable fractions of the product distribution, such as the lower olefins, olefins and paraffins for the manufacture of washing agents and alcohols (ideal case: direct synthesis of ethylene)

Minimizing of less valuable fractions, like methane, heavy fractions of the Synthol synthesis and ---in most cases---acids.

The Synthol method, with 30% selectivity for methane, and the Hot Gas Recycle method show the greatest possible fractions of light hydrocarbons.

The fluidized bed synthesis with iron nitride catalyst generates a product spectrum with the greatest selectivities for O-compounds and light hydrocarbons.

For further studies, the selectivities for light hydrocarbons and O-compounds were selected which are not accompanied by major disadvantages—such as low gas conversion or rapid deactivation of catalysts.

Tables 2-13 (the "Ethylene Direct Synthesis" is discussed separately) further show:

Ethane yield: only the liquid phase produces ethylene and ethane in a ratio of ethylene/ethane >1. This remarkable exception has not been seen so far in any publication. It may be explained by the diffusion-conditioned, secondary hydrogenation of the primary n-olefins (1). Here may be a starting point for further development.

	10^3 t/a Ethylene		
Synthesis methods	From C_2	From C_3-190°C	Total
5.2.1. Synthol (30% CH_4-Selectivity)	354	?	354
5.1.4. Hot-Gas-Recycle of the Bureau of Mines	278	217	495
5.2.3. Fluidized bed with iron nitride of the U. S. Bureau of Mines	192	?	?
5.2.1. Synthol "Normal"	185	215	400
5.3.6. Oil circulation, iron turnings of the U. S. Bureau of Mines	181	142	323
5.2.2. Hydrocol	160	216	376
5.3.5. U. S. Bureau of Mines, oil circulation, iron nitride	150	158	308
5.3.2. Rheinpreussen (maximum gasoline yield)	63	334	397
5.1.3. Arge	43	97	140

The total yield of ethylene/ethane is always coupled with the production of other low molecular products, like methane or C_3/C_4 hydrocarbons. All investigated methods show the same regularity: the selectivity for C_2 can only be improved if a simultaneous increase — even though not quantitatively equal for all syntheses — of other low molecular hydrocarbons is accepted. This regularity is also relevant for all efforts to minimize higher molecular weight products

Assuming for the following nine balanced procedures an 80% recovery of C_2 from the residual gas and a 75% ethylene yield from primary ethane, one obtains (always for 2.5 Million t/a C_2^+) the figures of column 1. For the second column the assumption was made that after pretreatment 85% of the C_5-190°C fraction could be subjected to pyrolysis and then— including ethane cracking—yield 25% ethylene.

As already mentioned, the ethylene yield of the direct ethylene synthesis is not to be compared and analyzed with the yield of the classical F-T synthesis because of lack of details.

Work with nitrided catalysts[17] —for which long catalyst life and high immunity against sulfur compounds is claimed, in addition to high selectivity for oxygen-containing and low molecular weight compounds, with good yields—is not restricted to specific reactor systems.

7. PROFITABILITY CONSIDERATIONS

7.1. Determining Factors

The most important influences determining economic advantages are:

Operational costs, namely: material, wages and salaries, capital costs and other costs

The average proceeds per ton C_2^+ product which depends on selectivity for different products, combination of processing steps and the market for specific pure products.

7.2 The Most Economic Methods of Today

Among the three syntheses so far practiced with reactor performance adequate for 2.5 Million t/a C_2^+ (Arge, Hydrocol and Synthol) the Hydrocol method because of the reported[14] operational difficulties with the fluidized bed reactor cannot be considered, at least until the receipt of further unpublished information from the Standard Oil of Indiana (Stanolind). Of the other two methods, the advantage of the more valuable high molecular paraffins of the Arge method is lost to a large extent because of the limited world market for these products. As soon as capacities of several 100,000 t/a total product are involved the remaining essential advantage of the Arge method, i.e., the continued great reliability, higher maximum annual reactor time and greater catalyst life, appear as relatively unimportant by comparison with the advantages of the Synthol method:

	Synthol	Arge
$CO + H_2$ conversion	85%	65%
t/a reactor	ca. 80,000	ca. 20,000
Reaction heat is available at	300-330°C	200-240°C

No further calculations are necessary to answer the question about the currently most advantageous method, in view of the large difference of the two syntheses under consideration. The Synthol method is to be preferred. A final evaluation of the index "costs over return" can only be attempted in Phase III of the study.

7.3 Determination of Profitability of the 12 Primarily Selected Syntheses

Although we do not here wish to anticipate later parts of this study, it must be pointed out that the repeatedly calculated[26,27] relation "starting gas costs: synthesis plus processing costs = about 2.2:1" means that a lowering of the cost of synthesis has a rather limited effect upon overall costs and that optimum utilization of the expensive starting gas is of great importance.

Table 2 and Figure 1 show that the smallest consumptions for 2.5 t/a C_3^+ appear with 1.8-1.9 Million Nm^3 $CO + H_2$/h in the liquid phase method and with 1.9-2.0 Million Nm^3 $CO + H_2$/h in the Synthol method. Credits for the methane in the residual gas may change the relative positions of the procedures.

As is known, conversion and selectivity are interlinked and even our comparisons of the "normal cases" can give only hints.

First estimates have shown that the average price for a ton C_3^+ differ markedly for the different calculated product distributions discussed in Chapter 6.

8. TARGETS AND IMPLEMENTATION OF FURTHER WORK

8.1. On the Continuation of the Present Study

The marked difference in gas utilization and selectivity of the balanced syntheses confirms the necessity for the execution of the next phases of the proposed work program. Only the results of Phases II and III (processing and profitability) can show how different factors are to be weighted in regard to profitability and which procedural combination is most favorable.

The support of engineering firms is now sought for the program Phase II "Processing of Synthetic Products." The broad spectrum of the F-T synthesis products requires consideration of a substantial number of procedures and procedural combinations. The engineering firms are to advise in the selection of methods, determine investment costs and – as far as possible – help to estimate yields and costs of operation. The cost of starting gas is to be determined largely on the basis of information available at URBK. The investment costs of syntheses are primarily to be determined with the help of Sasol.

The normal progress of the study was delayed chiefly by a temporary interruption of the contact with Sasol. This interruption did not permit us to approach the engineering firms in August 1974 – as planned in the program.

8.2. Targets Which Go Beyond the Framework of the Present Study

Points of departure for further synthesis developments which, according to our knowledge, have not already been investigated by Sasol or others, are the following topics:

The industrial applicability of nitrided contacts in the tested reactor types should be proved by large scale experiments.

The direct synthesis of ethylene appears so attractive that the further search for details should be pushed in parallel with Phases 2 and 3 of the study, in the hope that genuine starting points for developmental efforts in this direction may be found.

From a long term perspective the development of cobalt catalysts with higher operational life in modern reactors could be developed for the generation of hydrocarbons with a very small fraction of oxygen-containing compounds.

Can other synthetic methods be controlled in such a manner that a similarly favorable ethylene/ethane ratio (as in the stationary liquid phase synthesis) can be obtained?

It is to be expected that in the further course of the study changes or additions to this enumeration of developmental directions may be made.

Supplements

Table 2 Comparison of Methods – Hydrocarbon Syntheses Which Are of Greatest Importance for the Present Study

Method and conditions and results of method	Catalyst	Pressure range atm	Temperature range °C	Synthesis gas (fresh gas)	Circulation (cycle : fresh gas)	CO + H₂ conversion related to fresh gas	Yield of products (g/Nm³ of converted CO + H₂)	Space-time yield	Average product composition	Average olefin content of the fractions	Content of oxygen compounds	Technical realization
5.1 Solid bed, gas phase												
5.1.1 Normal pressure synthesis on cobalt contacts	precipitation catalyst	[illegible]	170–200	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
on cobalt contacts	[illegible] catalyst	[illegible]	180–230	[illegible]		[illegible]	[illegible]		[illegible]	[illegible]		
5.1.2 Middle pressure synthesis on cobalt contacts												
Lurgi [illegible]	standard catalyst	[illegible]	195	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]
[illegible]	standard catalyst	10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
Middle pressure synthesis	standard catalyst	[illegible]	170–200	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
5.1.3 Middle pressure syntheses on iron contacts												
Ruhrchemie–Lurgi synthesis (Arge)	precipitated iron contact	25	220–240	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Michael method	[illegible]	25	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Lurgi stage oven	precipitated contact	20	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
5.1.4 U.S. BOM "Hot Gas Recycle"	[illegible] contact	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5.1.5 Synol	fused iron contact	20	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	
5.1.6 Isosynthesis	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5.2 Moving catalyst, gas phase												
5.2.1 Synthol	fused iron catalyst	20	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.2.2 Hydrocol	fused iron catalyst	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.2.3 [illegible] method of BOM	[illegible] fused iron catalyst	21	250	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5.3 Syntheses in liquid phases												
5.3.1 BASF foam method	iron catalyst suspension	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.3.2 Koppers–Rheinpreussen method	precipitated iron catalyst	12	268	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5.3.3 "Slurry synthesis" of BOM	alkalized fused iron catalyst	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	
5.3.4 Duftschmid method	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.3.5 U.S. BOM Oil circulation "expanded bed"	[illegible] fused iron [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.3.6 U.S. BOM Oil circulation [illegible]	[illegible]	[illegible]	250	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5.4 [illegible] Direct synthesis	[illegible] catalyst	[illegible]	250	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]

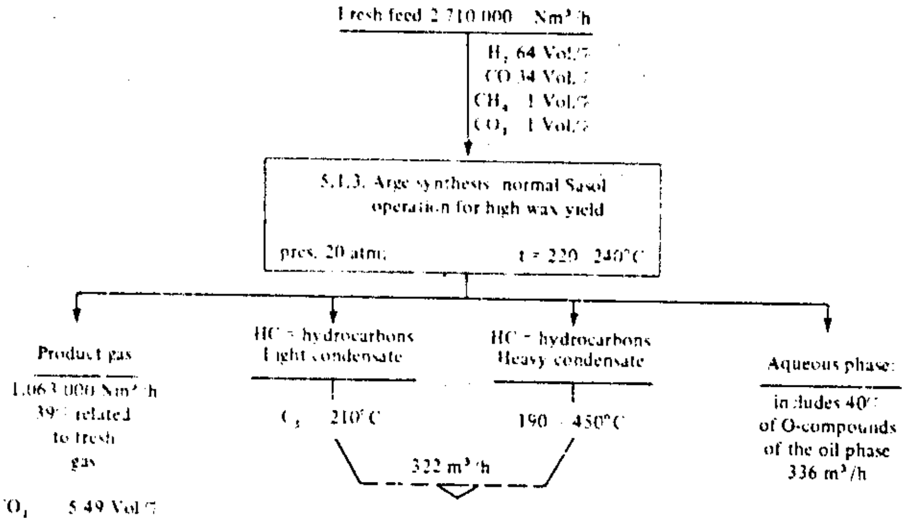
TABLE 2

Brief summary of 12 material balances

Standard: (1) 2.5 M [illegible]
(2) [illegible] oxygen compounds [illegible]
[illegible]
(3) Starting gas 1 [illegible] CO_2, 1 [illegible] CH_4, [illegible]

Method; mode of operation	Fresh gas tons 10³ Nm³/h	Net CO₂ free product gas [illegible]	Methane	C₂–C₄ Total	C₂–C₄ [illegible]	[illegible] Total	[illegible]	[illegible] compound
5.1.5 Arge normal	2710	[illegible]	267	[illegible]	[illegible]	2067	473	102
5.1.4 U.S. BOM Hot Gas Recycle	2904	[illegible]	[illegible]	962	[illegible]	1236	[illegible]	242
5.1.6 Fast synthesis	3465		[illegible]	1181	261	956	[illegible]	382
5.2 Synthol normal	1972	21	388	902	273	1360	85	229
5.2.1 Synthol selectivity for CH₄	2500	28	1137	1371	831	1001	[illegible]	100
5.2.2 Hydrol	1835		[illegible]	478	244	1327		206
5.2.3 U.S. BOM fluidized iron nitride catalyst	2534	[illegible]	647	1007	317	497		1005
5.3.2 Low pressure liquid phase, maximum gasoline	1317	15	240	811	[illegible]	1902	13	80
5.3.2 Medium pressure liquid phase maximum light products	1834		[illegible]	791		1640		65
5.3. U.S. BOM oil circulation expanded bed	2544	34	388	769	227	1356		[illegible]
5.3.6 U.S. BOM oil circulation iron chips	2187	32	394	926	279	1246	52	328
5.4 C₂H₄ direct synthesis	1364			2500	2500			

TABLE 3



CO_2	5.49 Vol.%
H_2	60.60 Vol.%
CO	27.18 Vol.%
CH_4	4.74 Vol.%
C_2H_4	0.05 Vol.%
C_2H_6	0.55 Vol.%
C_3H_6	0.32 Vol.%
C_3H_8	0.45 Vol.%
C_4H_8	0.37 Vol.%
C_4H_{10}	0.25 Vol.%

Overall yield

C_2H_4	6.372 MTy
C_2H_6	63.717 MTy
C_3H_6	52.100 MTy
C_3H_8	74.340 MTy
C_4H_8	78.580 MTy
C_4H_{10}	57.350 MTy
Σ	333.459

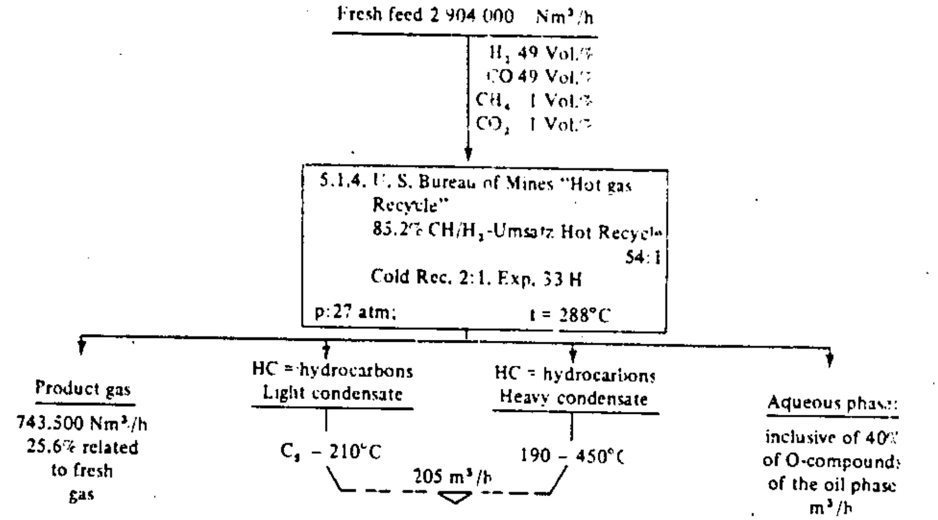
*Metric ton/year

C_5 – 190°C	469160 MTy*
190 – 316°C	527830 MTy*
316 – 450°C	597300 MTy*
>450°C	473300 MTy*
Σ	2067590 MTy*

C_5 –	190°C
Olefins	50%
Iso-Verb.	8%
Naphthene	1%
Aromatics	1%
130° – 316°C	
Olefins	35%

Methanol	1.820 MTy
Ethanol	52.030 MTy
Propanol	16.420 MTy
Butanol	9.120 MTy
C_5^+ Alk.	11.800 MTy
Essigs.	10.750 MTy
Σ	101.940

TABLE 4



CO_2	10.6 Vol.%
H_2	37.4 Vol.%
CO	20.0 Vol.%
CH_4	21.9 Vol.%
C_2H_4	0.2 Vol.%
C_2H_6	5.4 Vol.%
C_3H_6	0.5 Vol.%
C_3H_8	2.0 Vol.%
C_4H_8	0.3 Vol.%
C_4H_{10}	0.9 Vol.%
N_2	0.8 Vol.%

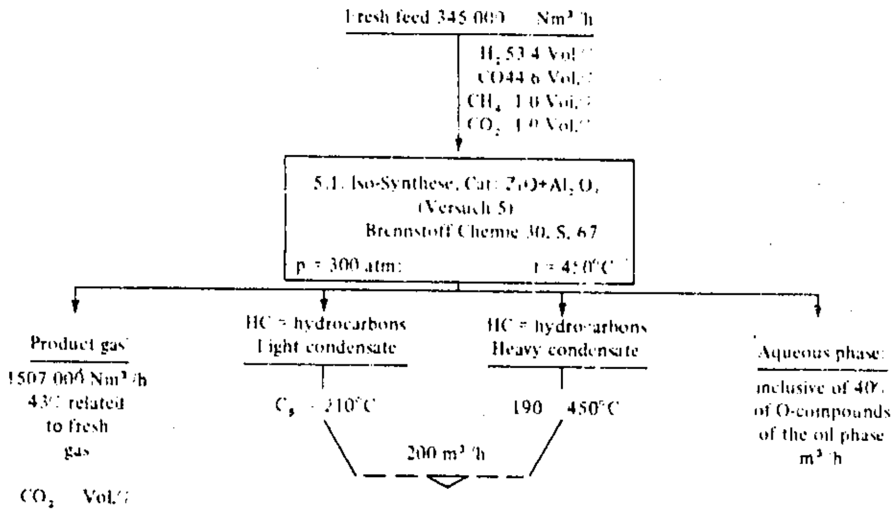
Overall yield

C_2H_4	13.900 MTy
C_2H_6	440.800 MTy
C_3H_6	58.300 MTy
C_3H_8	253.000 MTy
C_4H_8	42.600 MTy
C_4H_{10}	153.800 MTy
Σ	952.400

C_5 – 190°C	1020400 MTy
190 – 316°C	117000 MTy
316 – 450°C	126.000 MTy
> 450°C	33000 MTy
Σ	1296400 MTy

Methanol		MTy
Ethanol	198.600	MTy
Propanol		MTy
Butanol		MTy
Acetone		MTy
other O.-Verb.	44.000	
Essigs.		MTy
Σ	242.600	

TABLE 5



CO_2	Vol.%
H_2	Vol.%
CO	Vol.%
CH_4	Vol.%
C_2H_4	Vol.%
C_2H_6	Vol.%
C_3H_6	Vol.%
C_3H_8	Vol.%
C_4H_8	Vol.%
C_4H_{10}	Vol.%

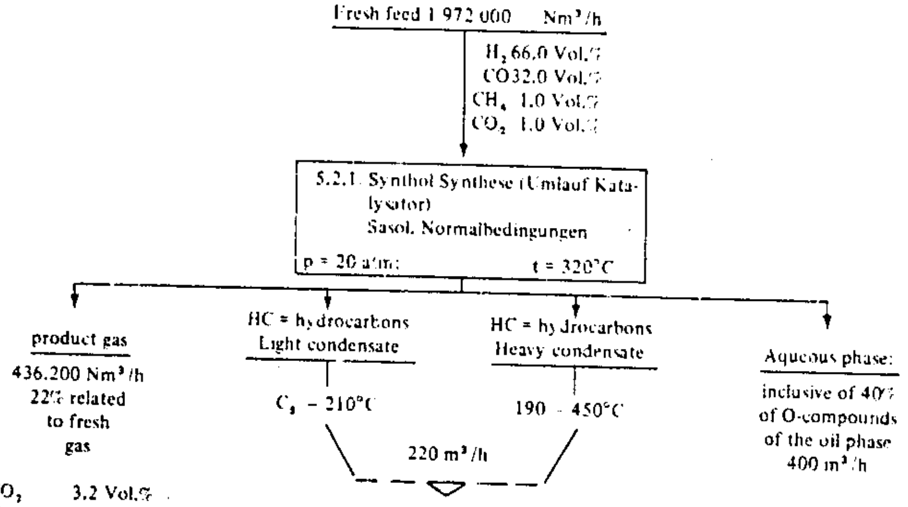
C_5 – 190°C	MTy
190 – 316°C	MTy
313 – 450°C	MTy
>450°C	MTy
Σ	956460

Methanol	MTy
Ethanol	MTy
Propanol	MTy
Butanol	MTy
Acetone	MTy
Essigs.	MTy
Σ	382 070

Overall yield

C_2H_4		MTy
C_2H_6	260.900	MTy
C_3H_6		MTy
C_3H_8		MTy
C_4H_8		MTy
C_4H_{10}		MTy
Σ	1.161.470	

TABLE 6



CO_2	3.2 Vol.%
H_2	62.7 Vol.%
CO	4.1 Vol.%
CH_4	15.5 Vol.%
C_2H_4	2.5 Vol.%
C_2H_6	3.5 Vol.%
C_3H_6	5.0 Vol.%
C_3H_8	0.8 Vol.%
C_4H_8	2.4 Vol.%
C_4H_{10}	0.3 Vol.%

Overall yield

C_2H_4	109.000 MTy
C_2H_6	164.000 MTy
C_3H_6	328.000 MTy
C_3H_8	55.000 MTy
C_4H_8	219.000 MTy
C_4H_{10}	27.000 MTy
Σ	902.000 MTy

C_5 – 190°C	1013000 MTy
190 – 316°C	164000 MTy
316 – 450°	137000 MTy
> 450°C	55000 MTy
Σ	1369000 MTy

C_5 – 190°C
Olefins 70%
190°C – 255°C
Olefins 60%

Methanol	3.000 MTy
Ethanol	119.000 MTy
Propanol	34.000 MTy
Butanol	13.000 MTy

Acetone	23.000 MTy
MEK	6.000 MTy
C_5+ AlK	4.000 MTy
Essigs.	27.000 MTy
Σ	229.000 MTy

Calculations for Synthol method

Standard: 2.5 million t/a C_2+ and O-compounds: 8,000 h/a

Fresh gas composition:

H_2	66 Vol %
CO	32 Vol %
CH_4	1 Vol %
CO_2	1 Vol %

i.e. H_2 : CO ratio = 2.06 (from: Production of 2 Million t/a using Synthol Process. J. H. Cronje. Sep 74, p 4.)

Calculation of Conversion:

Fig. 9 and 15 of "The Sasol Story" lecture of J. C. Hoogendoorn, AIMF 23rd annual meeting.

From Fig. 9:

Fresh gas: in	Product gas: out
H_2: 152 × 0.6 = 91.2	54 × 0.5 = 27.0
CO: 152 × 0.25 = 38.0	54 × 0.02 = 1.08

Conversion of H_2 therefrom: $$\frac{91.2 - 27}{91.2} \times 100 = 70.3\%$$

CO - Conversion: $$\frac{38.0 - 1.08}{38.0} \times 100 = 97.2\%$$

Total conversion: $$\frac{129. - 28.08}{129.2} \times 100 = 78.27\%$$

According to Fig. 15 the conversion amounts to 85%. It is assumed that 85% is correct and the CO conversion remains at 97.2%, thus a figure of 79% results for the H_2 conversion.

Calculation of products/Nm^3 fresh gas

With a CO + H_2 conversion of 85% and a fresh gas of 98% CO + H_2 0.98 × 0.85 = 0.833 Nm^3 CO + H_2 are converted per Nm^3 fresh gas.

$$CO + 2\,H_2 \rightarrow -CH_2 + H_2O$$

$$3 \times 22.4 = 67.2\,l \rightarrow 14\ g$$

i.e. 0.67 Nm^3 CO + H_2 yield 140 g C_1+ compounds. 1 Nm^3 fresh gas (0.833 Nm^3 converted CO + H_2O) yields 173.5 g C_1+ compounds.

According to Fig. 15, 90% of these are C_2-compounds, i.e. per Nm^3 fresh gas 173.5 × 9 = 156 g C_2+ product are obtained. The oxygen-containing compounds are here calculated as hydrocarbons.

Calculation of the fresh gas amount/h for 2.5 million t/a C_2+ and oxygen-containing compounds

$$\frac{2.5 \times 10^6}{8 \times 10^3 \times 1.56 \times 10^{-4}} = 200\ 3000\ Nm^3/h$$

Calculation of the composition of the C_2^+ products (Fig. 15, Sasol Story):

Calculated from Selectivity

	Selectivity	g/Nm³ fresh gas	t/a x 10³
CH_4	10.0	17.3	227.2
C_2H_4	4.0	6.9	110.6
C_2H_6	6.0	10.4	166.7
C_3H_6	12.0	20.8	333.3
C_3H_8	2.0	3.5	56.1
C_4H_8	8.0	13.9	222.7
C_4H_{10}	1.0	1.7	27.2
C_5–190°C	37	64.2	1028.9
190°–316°	6	10.4	166.7
316°–450°	5	8.7	139.4
450°	2.0	3.5	56.1
Neutral O-comp.	6.0	10.5	168.3
Acids	1.0	1.7	27.2
	100.0	173.5	2503.2 C_2+
			2780.4 C_1+

Calculation of product gas composition:

(a)

	Fresh gas		converted	Unconverted fresh gas to product gas (of 100)
H_2	66	$\xrightarrow{\times 0.79}$	52.14	13.86
CO	32	$\xrightarrow{\times 0.972}$	31.1	0.90
CO_2	1.0			0.72*
CH_4	1.0			1.00
	100.0			16.46

(b) From the g/Nm³ fresh gas one calculates for C_1–C_4 hyurocarbons l/Nm³ fresh gas

	g/Nm³ Fresh gas	g mol/Nm³ Fresh gas	l/Nm³ Fresh gas	l/100 l Fresh gas
CH_4	17.3	1.08	24.2	2.42
C_2H_4	6.9	0.240	5.5	0.55
C_2H_6	10.4	0.347	7.8	0.78
C_3H_6	20.8	0.445	11.2	1.11
C_3H_8	3.5	0.079	1.6	0.16
C_4H_8	13.9	0.248	5.6	0.56
C_4H_{10}	1.7	0.029	0.6	0.06

---

*According to "Sasol Story" a small amount of CO_2 is consumed.

For the product gas composition one obtains from (a) and (b) the following totals:

	Nm³/100 Nm³ FG	% of 22.12
H_2	13.86	62.7
CO_2	0.7	3.2
CO	0.9	4.1
CH_4	3.42	15.5
C_2H_4	0.55	2.5
C_2H_6	0.78	3.5
C_3H_6	1.11	5.0
C_3H_8	0.28	0.8
C_4H_8	0.56	2.4
C_4H_{10}	0.06	0.3
	22.12	100.0

Oxygen-containing compounds in the aqueous phase :

1. Calculation of the composition of the C_2^+ products according to Table 15 (Sasol Story) gives for the neutral O-compounds 168,000 t/a when the O-share is not considered. With consideration of the O-content one obtains, according to the following table, a value of 232,200 t/a

Source: J. H. Cronjé, Sept. 74, S.10 gC, gH, gO/mol/C + H/O

Neutral O-compounds	Wt.-%	C + H	O		
CH_3CHO	3.0	28	16	0.84	0.84
CH_3CH_2CHO	1.0	42	16	0.42	0.16
Aceton	10.6	42	16	4.45	1.70
CH_3OH	1.4	16	16	0.22	0.22
C_4-Aldehyde	0.6	56	16	0.34	0.01
C_2H_5OH	55.6	30	16	16.68	8.90
M E K	3.0	56	16	1.68	0.47
Propanol	3.0	44	16	1.32	0.48
n-Propanol	12.8	44	16	5.63	2.05
2-Butanol	0.8	58	16	0.46	0.01
EEK-MPK	0.8	70	16	0.56	0.01
i-Butanol	1.2	58	16	0.67	0.19
n Butanol	4.2	58	16	2.44	0.67
n-Butylketon	0.2	84	16	0.17	0.03
2-Pentanol	0.1	72	16	0.07	0.01
1-Pentanol	1.2	72	16	0.86	0.14
C_7^+ alcohol	0.6	90	16	0.54	0.01
				37.35	15.59

Instead of 168,300 t/a one obtains:

$$168{,}300 \times \frac{37.35 + 15.59}{37.35 + 1} = 232{,}300 \text{ t/a neutral O-compounds.}$$

When recalculating the numbers of the study of Cronje, Sep 74, p 4, to 2.5 Million t/a C_2^+ hydrocarbons + O-compounds[1] one obtains for C_1-C_3 alcohols, acetone and MEK alone 190,000 t/a. Recalculated for the total of neutral O-compounds this would give 219,000 t/a.

---

[1] Reference value for the recalculation is the sum of 1,694,600 t for the F-T products.

Here we assume a total production of 205,000 t/a on neutral O-compounds of the composition given in the Cronjé study, Sep 74, p 4.

	Weight % (neutral oxygenated compounds) (Studie J. H. Cronje P 10)	Metric ton/year
Methanol	1.4	2,037
Ethanol	55.6	120,614
Propanol	15.8	34,275
Acetone	10.6	22,995
MEK	3.0	6,508
Butanol	6.2	13,450
C_5^+ Alkohole	1.9	4,121
	94.5	205,000

Oxygen-containing compounds in the oil phase

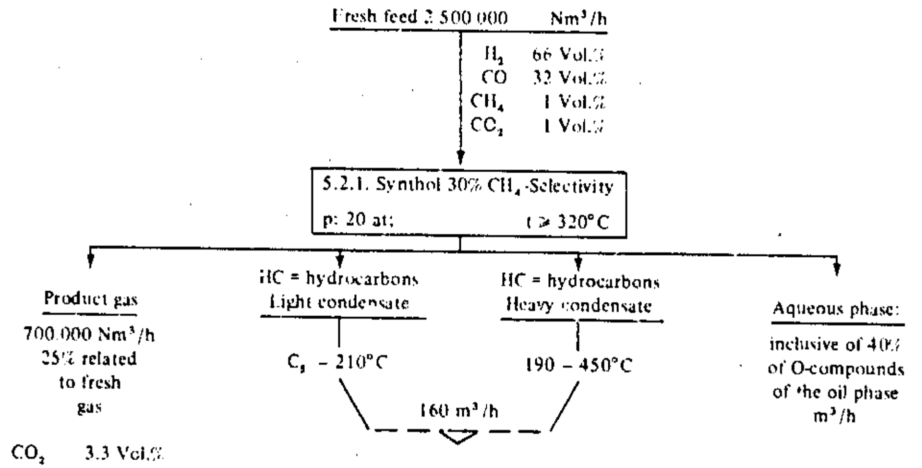
It must be assumed that the above yield of neutral O-compounds already contains those alcohols which can easily be washed from the oil by water.

Total balance of C_2^+ hydrocarbons amounts to:

C_2–C_4–HC	916,600 MTY (metric ton per year)
C_5^+ HC	1,391,100 MTY (metric ton per year)
neutral O-V	205,000 MTY (metric ton per year)
Essigsaure	27,000 MTY (metric ton per year)
	2,539,700

The sum was calculated for 2.5 Million metric tons per year. Factor = 0.98437.

TABLE 7



CO_2	3.3 Vol.%
H_2	51.4 Vol.%
CO	3.3 Vol.%
CH_4	28.4 Vol.%
C_2H_4	2.3 Vol.%
C_2H_6	4.3 Vol.%
C_3H_6	3.7 Vol.%
C_3H_8	1.3 Vol.%
C_4H_8	1.3 Vol.%
C_4H_{10}	0.7 Vol.%

Overall yield

C_2H_4	176.000 MTy
C_2H_6	355.000 MTy
C_3H_6	385.000 MTy
C_3H_8	140 000 MTy
C_4H_8	210.000 MTy
C_4H_{10}	105.000 MTy
Σ	1.371.000 MTy

C_5 – 190°C MTy
190 – 316°C MTy
316 – 450°C MTy
> 450°C MTy
Σ 1030000

Rough estimates according to poorly detailed pilot data

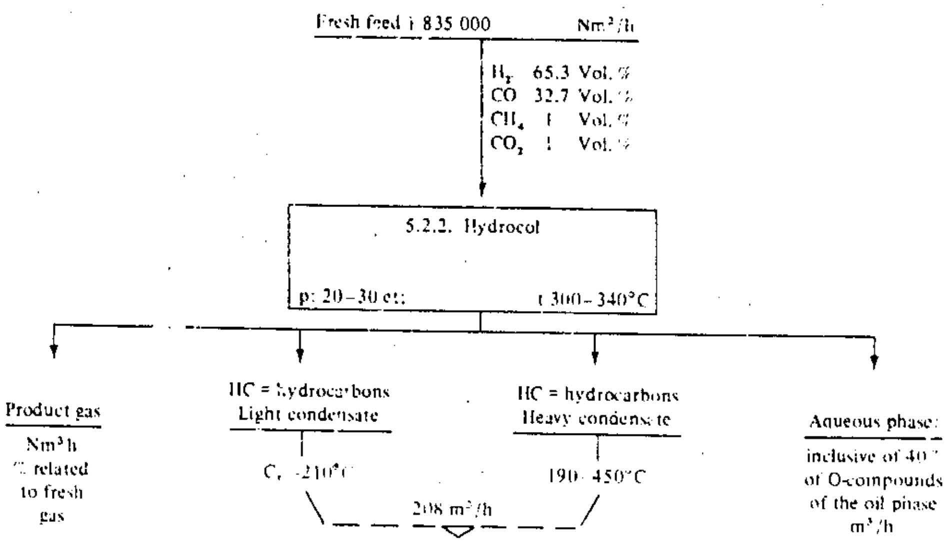
Fig. 3, The Sasol Story

Methanol MTy
Ethanol MTy
Propanol MTy
Butanol MTy

Acetone MTy

Essigs. MTy
Σ 100.000

TABLE 8



CO_2	Vol. %
H_2	Vol. %
CO	Vol. %
CH_4	Vol. %
C_2H_4	Vol. %
C_2H_6	Vol. %
C_3H_6	Vol. %
C_3H_8	Vol. %
C_4H_8	Vol. %
C_4H_{10}	Vol. %

C_4 - 190°C	1017920 MTy
190 - 316°C	217900 MTy
316 - 450°C	81500 MTy
>450°C	MTy
Σ	1317320

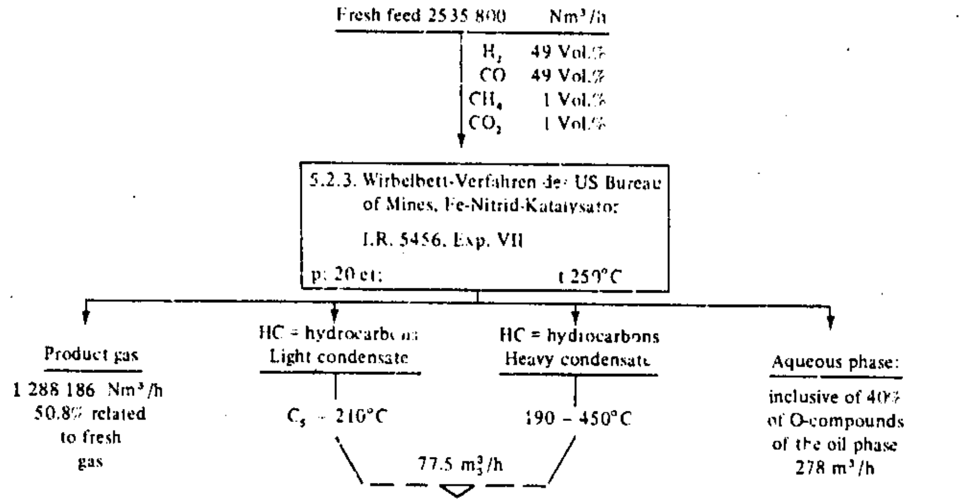
Methanol	503 MTy
Ethanol	51.800 MTy
Propanol	28.370 MTy
Butanol	6.750 MTy

overall yield

C_2H_4	61.570 MTy
C_2H_6	188.000 MTy
C_3H_6	319.200 MTy
C_3H_8	72.600 MTy
C_4H_8	296.400 MTy
C_4H_{10}	45.500 MTy
Σ	978.270 MTy

Acetone	34.630 MTy
Aldeh	13.590 MTy
Ester	725 MTy
Ketone	11.050 MTy
höh.aldehyde	1.950 MTy
Esters	40.987 MTy
Acetic acid	15.913
Σ	206.268

TABLE 9



CO_2	23.4 Vol.%
H_2	26.9 Vol.%
CO	35.8 Vol.%
CH_4	9.5 Vol.%
C_2H_4	0.1 Vol.%
C_2H_6	2.26 Vol.%
C_3H_6	1.0 Vol.%
C_3H_8	1.0 Vol.%
C_4H_8	0.8 Vol.%
C_4H_{10}	0.5 Vol.%

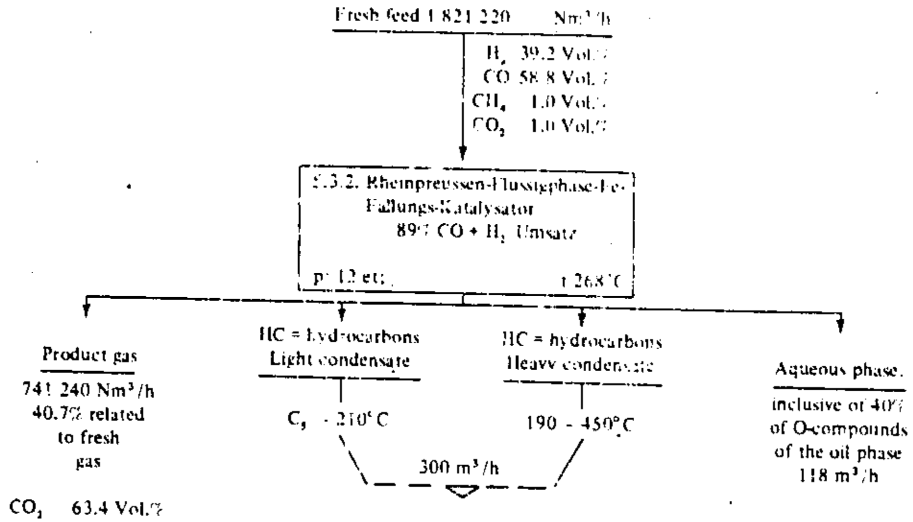
Overall yield

C_3H_6	195.351 MTy
C_3H_8	205.687 MTy
C_4H_8	152.753 MTy
C_4H_{10}	136.620 MTy
Σ	1.007.107 MTy

C_5 – 190°C MTY
190 – 316°C MTY
316 – 450°C MTy
> 450°C MTy
Σ 497.448

Methanol	144.178 MTY
Ethanol	405.579 MTy
Propanol	177.196 MTy
Butanol	51.618 MTy
Acetone	27.021 MTy
Essigs.	10.000 MTy
Uebrige O-Verb.	189.554 MTy
Σ	1.005.146 MTy

TABLE 10



CO_2	63.4 Vol.%
H_2	13.5 Vol.%
CO	13.1 Vol.%
CH_4	5.7 Vol.%
C_2H_4	Vol.%
C_2H_6	1.1 Vol.%
C_3H_6	Vol.%
C_3H_8	3.2 Vol.%
C_4H_8	Vol.%
C_4H_{10}	Vol.%

Overall Yield

C_2H_4	58 940 MTy
C_2H_6	26 520 MTy
C_3H_6	MTy
C_3H_8	427 310 MTy
C_4H_8	MTy
C_4H_{10}	MTy
Σ	512 770 MTy

C_5 - 190°C	1577 480 MTy
190 - 316°C	258 350 MTy
316 - 450°C	25 990 MTy
> 450°C	14 740 MTy
Σ	1906 560

Methanol	3 190 MTy
Ethanol	46 620 MTy
Propanol	8 850 MTy
Butanol	2 980 MTy
Pentanol	1 020 MTy
Acetone	2 240 MTy
Aldehyde	750 MTy
MEK	610 MTy
Ethylacetate	560 MTy
Essigs.	12 810
Σ	80 670 MTy

TABLE 11

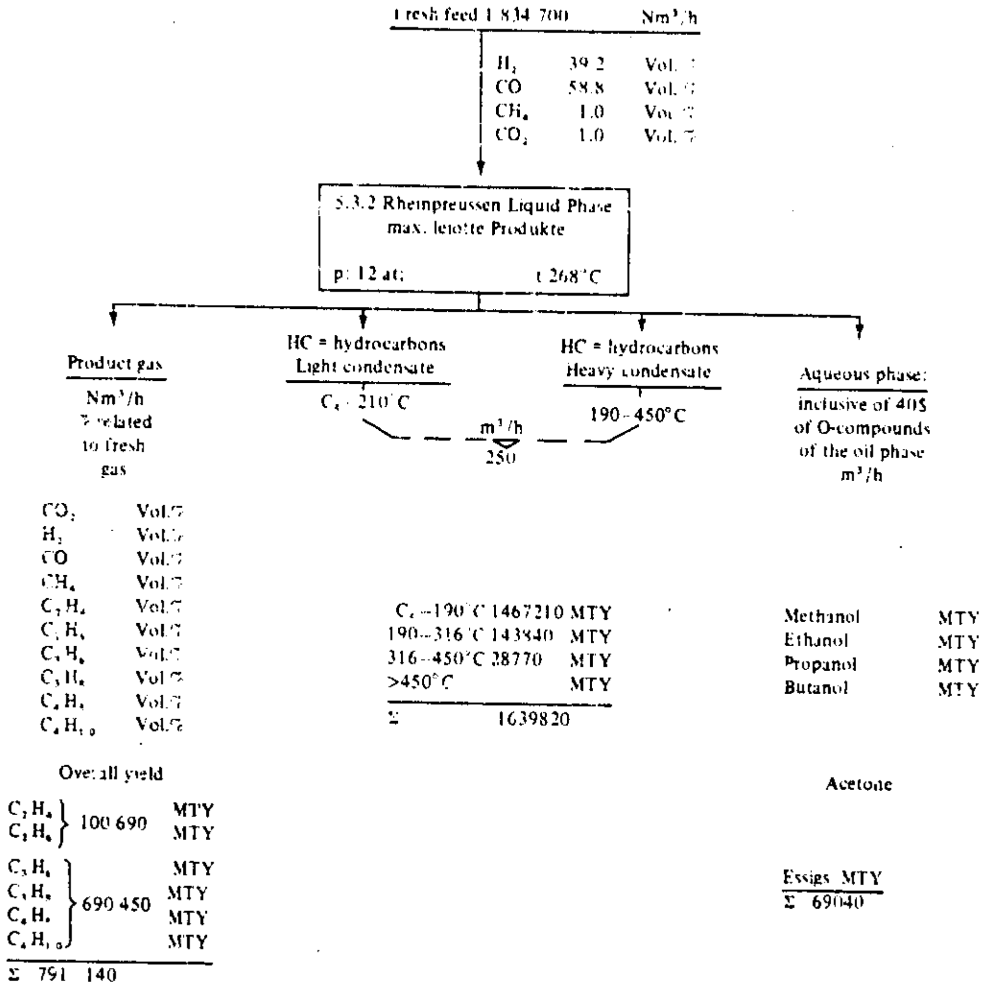
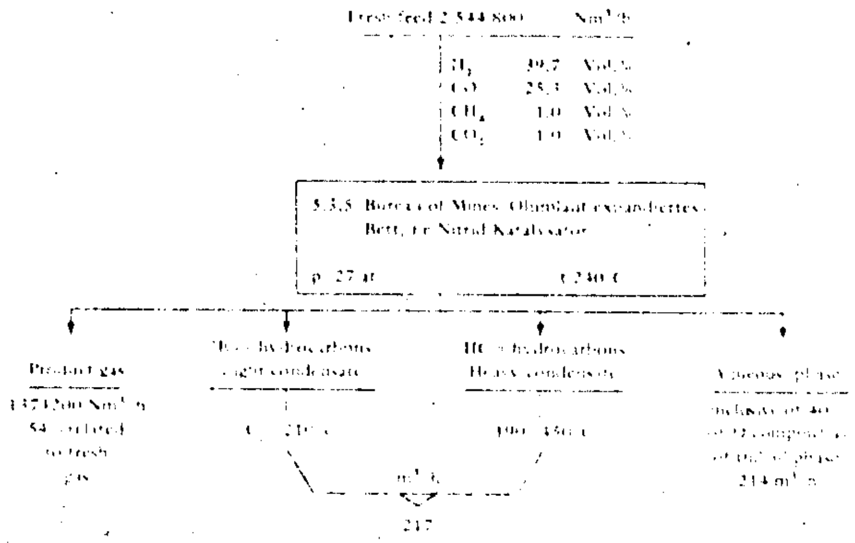

Fresh feed 1 834 700 Nm³/h
H_2 39.2 Vol.%
CO 58.8 Vol.%
CH_4 1.0 Vol.%
CO_2 1.0 Vol.%
5.3.2 Rheinpreussen Liquid Phase
max. leiotte Produkte
p: 12 at; t 268°C
Product gas
Nm³/h
% related to fresh gas
CO_2 Vol.%
H_2 Vol.%
CO Vol.%
CH_4 Vol.%
C_2H_4 Vol.%
C_2H_6 Vol.%
C_3H_6 Vol.%
C_3H_8 Vol.%
C_4H_8 Vol.%
C_4H_{10} Vol.%
Overall yield
C_2H_4 } 100 690 MTY
C_2H_6 MTY
C_3H_6 MTY
C_3H_8 } 690 450 MTY
C_4H_8 MTY
C_4H_{10} MTY
Σ 791 140
HC = hydrocarbons
Light condensate
C_4 - 210°C
m³/h
250
HC = hydrocarbons
Heavy condensate
190 - 450°C
C_4 -190°C 1467210 MTY
190-316°C 143840 MTY
316-450°C 28770 MTY
>450°C MTY
Σ 1639820
Aqueous phase:
inclusive of 40$ of O-compounds of the oil phase
m³/h
Methanol MTY
Ethanol MTY
Propanol MTY
Butanol MTY
Acetone
Essigs MTY
Σ 69040

TABLE 12



CO_2	37,22	Vol.%
H_2	20,4	Vol.%
CO	23,1	Vol.%
CH_4	4,98	Vol.%
C_2H_4	0,50	Vol.%
C_2H_6	1,12	Vol.%
C_3H_6	1,25	Vol.%
C_3H_8	0,50	Vol.%
C_4H_8	0,41	Vol.%
C_4H_{10}	0,23	Vol.%

C – 190 °C	742 619	Mt/a
190 – 316 °C	81.250	Mt/a
316 – 450 °C > 450 °C	552 225	Mt/a
Σ	1 356 097	

Methanol	18 800	Mt/a
Ethanol	138 750	Mt/a
Propanol	81 620	Mt/a
Butanol	25 770	Mt/a
C_5OH	35 600	Mt/a

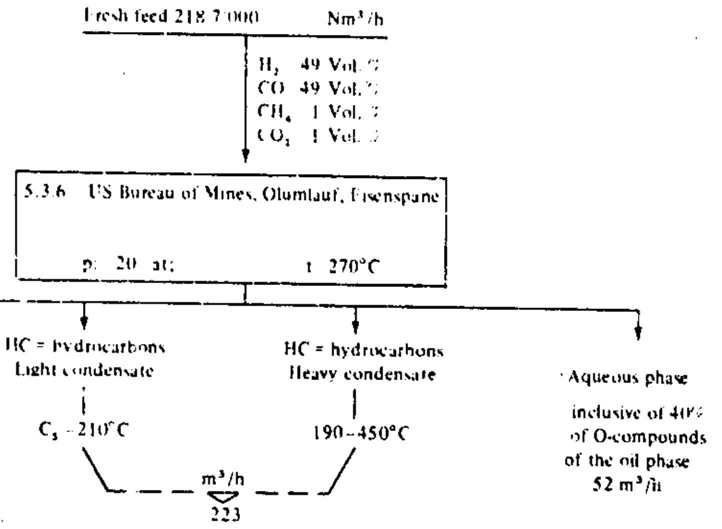
Overall yield

C_2H_4	65 850	Mt/a
C_2H_6	161.100	Mt/a
C_3H_6	252.100	Mt/a
C_3H_8	105 000	Mt/a
C_4H_8	116 250	Mt/a
C_4H_{10}	68 600	Mt/a
Σ	768,886	

Aceton

Ald. + Ket.	20 750	
Ester	18 880	
as free C6		
Carbons.	7 500	Mt
Säuren	5 675	Mt
Σ	372 500	Mt

TABLE 13



Product gas

999.000 Nm³/h
45.7 % related
to fresh
gas

CO_2	30.9 Vol. %
H_2	30.9 Vol. %
CO	26.27 Vol. %
CH_4	6.87 Vol. %
C_2H_4	0.65 Vol. %
C_2H_6	2.01 Vol. %
C_3H_6	1.86 Vol. %
C_3H_8	0.55 Vol. %
C_4H_8	0.98 Vol. %
C_4H_{10}	0.49 Vol. %

overall yield

C_2H_4	64.940 MTy
C_2H_6	214 600 MTy
C_3H_6	279 600 MTy
C_3H_8	87.500 MTy
C_4H_8	192.100 MTy
C_4H_{10}	87.500 MTy
Σ	926.240

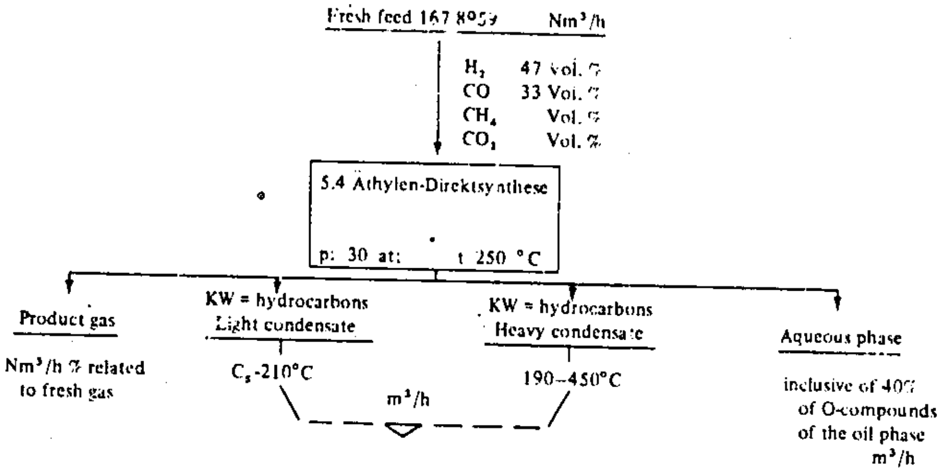
C_5 -190°C	668.900 MTy
190 -316°C	350.500 MTy
316 -450°C	175 000 MTy
>450°C	52 500 MTy
Σ	1.246.400

C_5 -190°C	Olefine 61%
190 -316°C	Olefine 40%
316 -450°C	Olefine 25%

Methanol	42.000 MTy
Ethanol	149.700 MTy
Propanol	47.000 MTy
Butanol	30 200 MTy

Acetone	4.800 MTy
Essigs.	54.200 MTy
Σ	327.900

TABLE 14



CO_2	Vol. %
H_2	Vol. %
CO	Vol. %
CH_4	Vol. %
C_2H_4	Vol. %
C_2H_6	Vol. %
C_3H_6	Vol. %
C_3H_8	Vol. %
C_4H_8	Vol. %
C_4H_{10}	Vol. %

C_5 — 190°C	MTY
190 — 316°C	MTy
316 — 450°C	MTy
> 450°C	MTy
Σ	

Methanol	MTY
Ethanol	MTy
Propanol	MTy
Butanol	MTy

overall yield

CH_4	182.291	
C_2H_4	2.500.000	MTy
C_2H_6		MTy
C_3H_6		MTy
C_3H_8		MTy
C_4H_8		MTy
C_4H_{10}		MTy
Σ	2.682.291	

Actone	MTy
Essigs.	MTy
Σ	