CHAPTER IX.

INFORMATION SUPPLIED BY I.G. AND KELLOGG RELATIVE TO THEIR WORK ON THE PRODUCTION OF HYDROCARBONS FROM MIXTURES OF CO & H_2.

Discussions on Thursday 3rd and Friday 4th November.

A. INFORMATION SUPPLIED BY I.G.

Note: In this field I.G. express gas volumes at 0°C and 760 mm

In his introductory word Dr Pier stated that I.G. have for some years past been working on the problems involved in several places, namely:

Oppau Ammonia Lab.	Dr Scheuermann & Meisenheimer
Oppau	Dr Winkler
Ludwigshafen	Dr Michael
Leuna	Ober-Ing. Sabel, Dr Wentzel.

Results of the various laboratories have not yet been compared and correlated within I.G. themselves. A general report giving the overall picture of the work being done by I.G. only could be issued at some later date. A synopsis of the communications of the various I.G. gentlemen prepared by themselves is annexed (Annex D).

Information from Dr Scheuermann (Dr Meisenheimer).

Starting point: investigation of the possibility of producing paraffin according to a Fischer type reaction, the paraffin to be used as raw material for oxidation.

All experiments are carried out on a small scale in glass tubes and are mainly directed towards finding catalysts suitable for paraffin production.

In an investigation of the active component of Fischer catalysts they found Co to be responsible. According to the literature Co (without any carrier) gave 25 gr liquid products/m3; however, by careful slow cold precipitation (24 hrs) they prepared a catalyst producing 110 gr/m3 in one stage. Catalyst life, however, was short, as the catalyst contained no "stabilizer". (Catalyst sintered rather rapidly).

Paraffin % in product was lower than with Co-Kieselguhr catalysts.

Gas composition $CO:H_2 = 1:2$.

Apparent density (Schüttgewicht) of catalyst: 1.1 - 1.2.

Space velocity 1 l/grCo/h.

Further experiments were carried out to investigate the influence of a) activators
b) carriers.

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a) As MgO gives mixed crystals with CoO, this combination looked promising. Between 2-15% MgO there were no great differences in results.
Yield: 80 gr/m3.
Yield was lower than expected. In addition catalyst is very dense (app.dens. 1.2), which means large weight of catalyst required.

b) Co MgO on Kieselguhr gave catalysts somewhat inferior to $CoThO_2$ - Kieselguhr catalysts. Catalyst life unknown.
Co on Kieselguhr: Yield 105 gr. Catalyst life without regeneration 4 months.
The long life without regeneration might be attributed to the fact that only during the first 10 or 14 days some paraffin (of high melting point) was formed, so that the catalyst was not "blocked" by paraffin.
An explanation of this lack of paraffin formation might be the "sintering" of the most active spots on the catalyst surface during the first week or so, caused by the fact that no "stabilizer" was incorporated in this catalyst.

As Kieselguhr is a very good carrier, but may cause difficulties because it is a natural product and, therefore, liable to changes in structure and/or composition, other carriers with a more uniform and defined character were investigated, namely:

Al_2O_3
MgO
Kaolin
and pure silica gel.

It was found that Kaolin gave about the same results as Kieselguhr, whereas the other carriers were somewhat inferior.

They abandoned the above experiments after finding that Kieselguhr could be given a more uniform character by heating it to 500-700°C.

They then found that ThO_2 had a stabilizing effect on the precipitation of Co and furthermore a promoting influence on paraffin production. Paraffin production was found to increase with increase in ThO_2 content of the catalyst. Co Kieselguhr catalysts show a lower initial yield than Co ThO_2 Kieselguhr catalysts. However, probably on account of the low paraffin production, the former catalysts have a much slower decline in yield, so that after some time the yield of the Co Kieselguhr catalyst will approach and finally even surpass the yield of the $CoThO_2$ Kieselguhr catalyst.

The above experiments have all been carried out at normal pressure. It was found that Co-Kieselguhr under pressure gave more paraffin than a Co-Kieselguhr-ThO_2 catalyst. This is the reverse of what happens at normal pressure. An explanation may be that, whereas the tendency to form solid paraffin in general increases with increasing pressure, the Co-Kieselguhr catalyst makes more paraffin, the effect on the $CoThO_2$-Kieselguhr - already producing much paraffin at normal pressure - may be that under pressure it starts producing so much (and probably of so high molecular weight) paraffin that, according to the law of mass action its paraffin-producing tendency is partially lost already after a short time.

During another experiment a Co-Kieselguhr catalyst (which gave during 10 weeks at thoughput 1 constant results of 140-150 gr/m3 in 1 stage, the product containing 80-90 gr/m3 high molecular paraffin) was subjected to higher throughputs under pressure.

Throughput 2 1/grCo/h yield 120 gr
" 4 " " 90 "

At higher throughputs the percentage of paraffin in total product formed decreased.

INFORMATION FROM OBERING. SABEL. LEUNA.

In an introductory word Herr Sabel stated that the main problem in the Fischer synthesis is the catalyst and that the question of working at normal or elevated pressure, of size and design of reactors and of methods of synthesis gas production are of secondary importance (for German conditions). As an example he mentioned that the Holten people have investigated up to now about 11.000 catalysts.

A) Re Catalysts.

a) Leuna find in general the same results as Fischer for the same catalysts, i.e.:

120 gr/m3 at normal pressure
140 " " higher "

b) Characteristics of product obtained at normal pressure:

S.G. 0.72
I.B.P. 35°C S.G. of fraction - 135° 0.674
-100° 30% " " " - 190° 0.692
-180° 50%
-300° 85%

c) I.G. have compared pilled catalysts (Schüttgewicht 1.0) and the normal catalyst (Schüttgewicht 0.3) and found that the apparent density plays no rôle even over long periods of time (up to 8 months), both catalysts giving the same results at the same throughput (= vol/vol. catalyst space/hr).

The above holds good both for working under normal and elevated pressure.

d) Mg catalysts seem to be somewhat more rugged and give about the same yield as Th catalysts.

Mg catalysts are better reproducible than Th catalysts.

e) The method of precipitation of catalysts is very important. It was found, for instance, that the composition of the primary products can be strongly influenced by the method of precipitation used.

At present I.G. are studying various catalysts with promising results.

This is a wide field. Conclusions cannot be arrived at easily, also because experiments have to be continued for a long time (say 6 months). As an example Mr Sabel mentioned that they are trying out a catalyst which will produce under 10 atm. pressure a product consisting practically only of solid paraffin.

Melting point higher than 120°C.

Working with such catalysts the solid wax contained in the catalyst must be periodically (e.g. every 10-14 days) removed, e.g. by extraction.

f) <u>Reduction of catalysts.</u>

I.G. find no difference (for CoTh and Mg catalysts) between reduction at 390°C and higher during a short time and in thin layers (10-30 cm) with large amounts of hydrogen on one hand and reduction at 200-250°C during 1 to 4 days in thick layers (1.5 - 2.0 m).

They even carried out reduction in the reaction oven itself.

The explanation why thick layers may be employed at low temperatures is perhaps that at 200-250° the reaction $CO_2 \longrightarrow CH_4$ does not yet take place.

g) Regeneration in situ. (CoTh and CoMg catalysts).

Is being carried out every two or three ~~weeks~~ with hydrogen at 200-300° or by extraction with gasoline or Xylol at 120°C. After Xylol extraction the regenerated catalyst comes up quicker to maximum activity.

Note: Extraction is done more often by I.G. than by Ruhrchemie, presumably as the preparation of catalysts (particularly the method of precipitation) is different.

B) Re experiments in pilot plants.

Leuna first used "Plattenöfen" (same construction as the low pressure Ruhrchemie oven), both for low and high pressure work, of the following sizes:

500 1 catalyst low pressure
150 - 1 " high " (up to 20 atm.)

Depth of catalyst bed 2 m in both types.

At normal pressure yields of 100-120 gr/m3 were obtained, at higher pressures (3-5 atm.), however, results were erratic due to varying temperatures (variations up to 40°C in different layers of the catalyst).

They then changed the reaction system and now only employ tube ovens (16 units) both for pressure and atmospheric work (catalyst inside tubes surrounded by water under pressure). Pressure ovens can withstand up to 25 atm.

Every unit is equipped with condensation and activated charcoal adsorption.

Size of catalyst-containing tubes: 6-15 mm i.d., length of tubes 1.5 to 4.5 m.
(An oven with a tube length of 10 m is under construction but may prove to be too long).

Volume of ovens: 3 l catalyst volume
12 l
40 l and 150 l

I.G. want to make the ovens as long as possible, because the covers and end pieces constitute a large part of the total expenditure.

They do not find, at constant space velocity, different yields when employing ovens of varying tube length.

~~They think that on a technical scale eventually~~ tube lengths of 8-10 m will be employed.

With still longer tubes the Δ P on the water side will become so high that the temperature at the bottom of the oven may become 3-5°C higher than at the top.

The flow is downflow. The upper part of the tubes is not filled with catalyst and serves as a preheating section for the gas entering cold.

INFLUENCE OF VARIATIONS OF THROUGHPUT.

It was found that this influence was very great, but was not materially different for ovens of 1.5 and 4.5 m length resp. (the latter ovens giving slightly better results).

Working at extremely high space velocities (entering with cold gas) the reaction will be "blown out".

However, within the limits explored (up to 3 vol/gr Co/hr up to now) it was found that the production per oven increases with increasing throughput (see graph fig. No 25). Annex A.

This checks with literature data from various sources, going up to higher space velocities.

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Mr Sabel finally stated that in Leuna the ovens are not run at "temperature" but according to the rate of Methane formation, which is recorded.

INFORMATION FROM Dr WINKLER (OPPAU).

The experiments of Dr Winkler and Dr Michael are being carried out with iron catalysts for two reasons:

a) in order to be independent of Fischer;
b) because Fe catalysts are very cheap.

About 2,000 small-scale experiments have been carried out with different Fe catalysts.

The types used at present are produced by burning Fe (possibly mixed with certain additions) with oxygen. This gives Fe_3O_4, which is reduced in a hydrogen stream.

The method of preparation for the best catalyst found up to now is as follows:

Raw materials: 1000 gr Fe powder
25 gr Si "
25 gr Ti-oxide
50 gr $KMnO_4$.

These ingredients are pasted with a small amount of water and burned with oxygen. The reaction product is broken into pieces of 6-8 mm and reduced with hydrogen at 500-600°C.

Schüttgewicht (apparent density) 2.0 kg/l.

These catalysts do not work at atmospheric pressure, because their activity is too low.

The experiments are, therefore, carried out at high pressures and were begun at 100 atm.

They first tried out working in vapour phase with recycling of tail gas.

Oven 6 m long 120 mm Ø
20 layers of catalyst
cat. volume 20 l total

Throughput 10 m3 fresh gas/hr
250 m3 recycle gas/hr to remove heat of reaction

Downflow

The results were not encouraging. Best yields were:

95 gr propane plus per m3 $CO + H_2$ converted,
of which 30-35% consisted of C_3 and C_4.
Expressed on fresh $CO + H_2$ the yield amounted to 40 gr/m3. Methane formation was high. No actual figures were given. After 10 days much solid paraffin was being formed and the activity of the catalyst decreased.

Thereupon vapour-phase experiments were stopped.

LIQUID-PHASE EXPERIMENTS.

Same catalyst is used.

With this arrangement the heavier part of the oil produced is recycled and goes concurrently with the gas from bottom to top of the oven. The heat of reaction is removed by heating up and partly vaporization of these recycled liquid products.

Pressure 100 atm.
Oven 6 m long 120 mm dia. 50 l catalyst
60 l free volume
catalyst 6-8 mm pieces.
Temperature 350°C or lower.

It is possible to vary the composition of the fresh gas, but normally a ratio 1:1 is employed. Also runs with gas containing even 55% CO have been made.

Practically all of the oxygen is expelled in the form of CO_2.

Results of an experiment:

Duration 1500 hrs
Throughput 130 m3/hr fresh gas (55 CO 45 H_2)
% conversion of fresh gas: 50%

Produced per m3 fresh gas converted about 145 gr $C_3C_4C_5$
" 28 " C_1
" 400 " CO_2
" 70 " H_2O
" 643

Leistung $C_3C_4C_5$+: $\frac{130 \times 0.50 \times 0.145}{60} = \underline{0.155}$ kg/l/hr

The 145 gr $C_3C_4C_5$ + products were found to consist of:

Gasol (C_3C_4)	16-18%	
Gasoline -200°C	42%	(about 42% unsaturates O.N. Research 68)
Diesel oil about 400°C	20-27%	Gasoil 300-400°C showed C.N.78
Lubricating oil	7-8%	
Low-melting point wax	2.7%	
Distillation loss and residue	5-6%	
Oxygen-containing products	6%	

Recently experiments are being carried out at 20 atm. at temperatures of 250-260°C.

Although it looks as if under those conditions the wax production increases, further results are not yet conclusive, so that Dr Winkler refrained from giving any figures for the time being, another reason being that with these types of reactions results obtained vary with varying size of apparatus.

Next day the experimental plant was visited. The 60 l 100 atm. plant proved to be practically totally enclosed within a stall, so that not much could be seen. The flow of the products is as follows:

The products plus tail gas leaving the oven pass a heat exchanger (against the recycled oil), are partly further cooled and then a separation between gaseous and heavier liquid products takes place in a kind of hot separator. The final products are further cooled down and then expanded.

The recirculation pump takes suction from the hot catchpot and delivers the recycle liquid through heat exchanger and a heated coil back to the bottom of the oven.

No steam is being produced from the excess heat of reaction owing to the heavy heat losses of this small system.

There are further three 20 atm. plants of 150, 800 litres and 1.2 m3 respectively, whereas a unit with an oven of 2.0 m3 is in course of erection.

INFORMATION FROM Dr MICHAEL (Ludwigshafen).

Before describing his own experiments Dr Michael gave a lecture on the problems involved in general in the conversion of CO and H_2 into hydrocarbons due to the excessive heat of reaction and in connection therewith the possible and most advantageous types of reaction ovens to be used.

In oven types carrying off the reaction heat through the walls, the following "lag" is observed (see fig. 26). Annex A.

In addition the temperature diagram taken over the cross section of a tube is not a straight line, but shows higher temperatures in the middle of the tube. The difference between t_1 and t_2 (see figure 27) depends on the diameter of the tube, the heat conductivity of the catalyst, etc., but is primarily dependent on the diameter of the tube.

The above clearly shows that, with a surrounding hot water bath of constant temperature, it will be, practically speaking, impossible to obtain constant temperatures within the catalyst space measured, neither over the length nor over the cross section of the tubes.

With tubes of too large a diameter the temperature "runs away", this being caused by an excessive CH_4 formation once a certain temperature somewhere in the tube has been reached, the CH_4 formation velocity increasing much faster with temperature than the oil formation.

Another reason for temperature runaways is the fact that a fresh catalyst always contains particles or parts of particles with an extremely high activity. It is fortunate that such high activity particles are rather rare, otherwise it would not be possible at all to start a newly filled oven.

The runaway danger is larger with Fe catalysts than with Ni and Co, particularly as Fe works at a higher temperature than Ni and Co and is not only nearer to its CH_4-forming field but in addition is close to its temperature range of carbon formation (see figs 28 and 29).

With Fe catalysts one must, therefore, be extremely careful to operate in such a way that no temperature peaks can possibly be formed.

At this point Dr Pier interrupted by stating that the above holds good for the Fe catalysts in use with I.G. at present, which catalysts are rugged and less sensitive to poisons than other catalysts. There are, however, other Fe catalysts, operating at a lower temperature and which, therefore, are not as vulnerable with respect to CH_4 and carbon formation as the present type.

The neighbourhood of the CH_4-forming zone is very dangerous, because contrary to what happens during the oil-forming reaction the reaction product (CH_4) is desorbed very fast from the catalyst surface, so that once favourable conditions for CH_4-formation are reached, immediately large amounts of CH_4 are formed.

Thus it is, for instance, impossible to use .
Fe catalysts in long tubes (even of very small diameter).
They also found that once carbon is being formed this acts

as an insulator promoting, with temperature increase, the formation of further amounts of carbon.

The conclusion, therefore, is that (the present) Fe catalysts are much more difficult to work with than Ni and Co catalysts.

However, Fe catalysts were adopted for the following reasons:

1) being cheap
2) being much more active (larger production (= Leistung) under optimum conditions)
3) products are different from the normal Fischer primary products
4) the catalysts were independent of Fischer patents and furthermore were a continuation of former I.G. work. (NH$_3$ catalysts are being prepared in a similar manner).

REASONS FOR THE ADOPTION OF A DIFFERENT TYPE OF REACTION SYSTEM.

Means were sought which would reduce the extent of carbon and CH$_4$-formation.

Very active finely divided catalysts proved to give great difficulties. A small particle of carbon formed within one piece of catalyst sufficed to cause the oven to be filled with carbon within a short time. Twice an oven had to be drilled out for this reason.

They, therefore, tried to increase the heat conductivity of the catalyst:

1) by incorporating metal strips of good heat conductivity within the catalyst layer, but
2) best results were obtained by preparing a catalyst which itself had a good heat conductivity, thereby avoiding formation of hot spots within the catalyst pieces. This could be achieved by starting from finely divided Fe, which is sintered in order to increase its density.

The catalyst is produced by sintering finely divided Fe (every kind of pure iron is suitable - best results are achieved with Fe obtained from decomposition of Fe carbonyl) at 900°. A small amount of alkali (less than 1% Na_2CO_3) is added and proved to be useful, but is not essential.

The sintered material is reduced with hydrogen during several hours at 850°C and is used in the form of lumps.

Density nearly 7.5

"Schüttgewicht" (apparent density) about 2.5 kg/l.

These catalysts are inactive during the first one or two days, and only after this period show their full activity.

Small-scale experiments gave a Leistung of:

1 kg $C_3C_4C_5$ + /l/day, at 310-330°C.

They then tried out the catalyst in a semi-technical tube oven with tubes up to 60 mm dia. with vanes inside. It worked, but they were not content with the results.

After this experience the principle of removing the heat of reaction through the walls was abandoned and a system of about a hundredfold recirculation of tail gas was adopted, the underlying idea being as follows.

Assuming the specific heat of synthesis gas and of tail gas to be the same and independent of temperature, it can be calculated that the temperature increase by the heat of reaction when converting 75% of the CO present in synthesis gas amounts to more than 1000°C.

As the allowable temperature increase is only of the order of 10°C, one could picture sub-dividing the reaction space into 100 sections, inserting a cooler between every two sections. A less complicated way is to pass the gas through the catalyst at such a rate that only such a fraction of the CO and hydrogen is converted that the temperature rise is restricted to about 10°C. This can be accomplished by recirculation of tail gas back to the reaction space.

In order to obtain a temperature increase of, say, 5, 10 and 20°C respectively, it is, therefore, necessary to recirculate 200, 100 and 50 m3 of tail gas per m3 of fresh gas respectively.

It was found that a temperature increase of 10° could be tolerated and that, therefore, the recirculation could be limited to 1:100. In principle, the operation ~~is carried out as shown in fig. 30. Annex A.~~

The mixture of fresh and recycle gas only contains a relatively small % of CO + H_2, but this proved to be of no influence on the results obtained as regards the "Leistung" of the catalyst.

Incidentally the fact that the recycle gas in practice has a higher specific heat than fresh gas and the fact that it is no longer "wild" ensures very smooth operation.

In a plant with 400 l catalyst the Leistung at present is 0.7 kg/l/day, but they hope to obtain 1.0 (as obtained on a small scale).

A temperature increase of 10, 20 or even 30° would be possible, but the latter would not yield any advantage as part of the catalyst zone would be too cold for optimum production.

PRESSURE.

The optimum pressure found is 20 atm. Lower pressure gives a lower Leistung and a smaller conversion. At higher pressures more oxygen compounds are formed.

(Dr Pier again stressed the fact that the above only holds good for the sintered Fe cat. and that the optimum for these catalysts may even be different for gases with different CO:H_2 ratios.)

Dr Michael mentioned that the principle adopted may also be applied for the normal Fischer catalysts.

The % conversion obtained has been max. 80% in one stage, but it will be advantageous not to go over 75% in the first stage, and then to cool the products, remove CO_2 present and effect conversion of residual CO in a second stage.

The gas employed is watergas CO,H_2 ratio 4:5.

For a flow sheet of a semi-technical plant, see fig.31 in which the incorporation of a so-called "Kaltkreislauf" is especially noteworthy.

The "Kaltkreislauf" serves to remove the higher boiling products or more exactly to lower the partial pressure of such products in the recirculated gas.

With watergas the reactions taking place may be summarized as follows:

$$CO + 2H_2 \longrightarrow (CH_2) + H_2O$$
$$2CO + H_2 \longrightarrow (CH_2) + CO_2$$

Both reactions take place to about the same extent.

If the gas going to the second stage is purified by refrigeration followed by CO_2 removal, it then only contains about 20% inerts.

The size of apparatuses for the second stage has only to be proportional to the extent of CO conversion in that stage (say 75:25 = size 1st to 2nd stage 3:1). Only small correction has to be made for the increased percentage of inerts, which necessitates a little more catalyst or a slight increase in pressure in the second stage. Incidentally another advantage of the Michael principle of heat removal is that the amount of recirculation required is strictly proportional to the amount of liquid produced (= reaction heat evolved), so that from the point of view of power consumption it does not matter in how many stages the process is carried out.

POWER FOR GAS RECIRCULATION.

At first it was thought to be very high. One, however, is quite free to choose the dimensions of the reaction space. Dr Michael now employs a layer of 85 cm and may eventually use 1.0 or 1.5 m.

Power for recirculation amounts to 0.5 kWh/kg primary product. This figure may be reduced to 0.25 kWh or even less.

Note: Heat of reaction is recovered as super pressure steam (temp. high) and was stated to amount to 4000 cal/kg primary product.

In large-scale operation they propose to use parallel flow as indicated in the sketch fig. 32, because increasing catalyst depth is very expensive, as doubling the depth means 8 times increase in power consumption. Also the dimensions of the catalyst lumps play a role in power consumption. At present 12 mm lumps are used.

Catalyst life is not yet known. In a small-scale experiment (with varying temperature) a life of 2.5 months was obtained. The temp. changes ruined the catalyst and it also fell to pieces.

Dr Michael believed that in large-scale operation a very long catalyst life can be obtained.

REGENERATION is very simple and consists of roasting and reducing. Often a regenerated catalyst proved to be better than a new one.

Power saving for recirculation could be effected by the injection of cold gas. This is not attractive for German conditions, because the W.H. steam production is smaller. It might be attractive for places where cheap fuel is available. One could, for instance, picture dividing the total catalyst into 3 beds and removing heat of the first two beds with cold gas and that of the third bed with steam.

Another possibility for countries with cheap fuel is omitting the second stage and returning the tail gas of the first stage to the methane steam plant.

Dr Pier then said that the principle employed had proved to be a great success. They had started to use a Fe cat. for the reasons given by Dr Michael, but comparative experiments in the Michael system would have to be made also with other catalysts.

It is clear that the principle (recirculation of gas) can be combined with various other means of removing heat of reaction, e.g. injection of cold gas - of oil - etc., or one could combine direct and indirect heat removal.

An interesting feature is that the purification of the gas may be the same as for NH_3 synthesis gas. (Afterwards we heard that in Oppau org.S content is 2-3 mg/m3).

Also the Fe cat. seems to have a purifying action, so that, for instance, one could use a Fischer cat. in the second stage.

Another interesting thing about the Fe cat. is that it recovers after having been subjected to a gas containing too much S.

PRODUCTS:

The fraction -200° contains 3 - 3.5 % oxygen
The Diesel-oil fraction " 1.5 - 2 % "
Olefine content of total product: about 80 %, is fairly constant for all fractions,

	% by weight
Paraffin	2
Diesel oil	13 (cetene number 53 pourpoint -24°C)
Gasoline	45 raw gasoline O.N. 80 (Research see also below)
Alcohols, etc.	8-10
C_4	9 (90% olefines)
C_3	9 (75-80% ")
C_2H_4	12
	100
$CH_4 + C_2H_6$	about 20 (up to 30)

PROPERTIES OF GASOLINE.

As the gasoline contains oxygen compounds and is unstable it must be refined. I.G. are busy working out two methods, both of which were stated to be very cheap, as it would be possible to incorporate the refining within the synthesis apparatus. Details could not yet be divulged, but will be communicated at a later date.

The 1st method removes O_2-content in product boiling to 200°C down to 0.5% with a yield of 94% (rest H_2O and gas).

Properties of refined gasoline.

E.P. 200°C
45 - 65% - 100°
O.N. Res. 84-88
O.N. M.M. 77 (45% - 100° ?)

2nd method: losses less than 1%. No oxygen removed, but only gum. O.N. research 86.

Blending value: with gasoline O.N. 60
10% synthetic gasoline in blend 107 (research M.)
50% " " " " 95 "

By catalytic cracking of the gasoil produced gasoline is obtained with an O.N. M.M. 76.5 clear (research method 85).

After storing the refined primary gasoline for months the gum content (about 2.5 mgr per 100 cc according to I.G. method) had not increased. These tests, however, have not yet been completed and are not conclusive.

Properties of alcohols, etc.

Acetaldehyde	0.5	total 8-10 parts
Acetone	1.1	
Ethyl alcohol	5.7	
Propanol	2.5	
C_4C_5 alc.	rest	

The above compounds are practically wholly contained in the water layer.

C_3 and C_4 unsaturated may, of course, be polymerized.

C_2H_4 is obtained in large amounts. A polymerization process for ethylene has been worked out by I.G.

Paraffin content of products is small. By decreasing the reaction temperature during synthesis by about 20-25°, about 7-8% wax is obtained containing some wax of very high melting point, which has not yet been investigated.

Catalyst costs. New: 60-70 Pfennig/1 catalyst
Regenerated: 5-10 " 1 "

Next day the semi-technical plant was visited, which proved to have a very simple layout. Heavy products are cooled down in two stages, the heaviest part being cooled only to 50-60°C on account of the presence of solid wax. In the second stage of the "Kaltkreislauf" the temperature is reduced to 20°C.

The Kaltkreislauf in this plant only contained coolers. It is clear that in large-scale operations use will be made of heat exchangers in order not to waste heat of reaction in cooling water.

The tail gas is dried by $CaCl_2$ and then cooled by NH_3 to about -40°C. Products obtained from the three cooling stages are then combined after having removed C_3 and lighter.

The operation of the plant was stated to be extremely simple, the pressure in the plant being maintained by a back pressure regulator for the tail gas.

Continuous supervision is needed only for control of cooling water temperatures.

It may be stated that the plant receives CO and H_2 through separate lines, the components being blended at the panel, so that experiments with varying CO-H_2 ratios can be carried out.

Dr Michael mentioned that very soon a decision might be taken to erect a plant for a production of 5000 t/year of liquid products in Ludwigshafen.

B. INFORMATION SUPPLIED BY KELLOGG (MR KEITH).

A rough survey has been made by Kellogg of the CH_4 now wasted in the U.S.A. Leaving out those quantities produced in too far remote places, Mr Keith thinks that 5×10^9 cub.ft = 142×10^6 m3/day is a conservative figure for methane available, if wanted, for conversion into gasoline, etc. in the U.S.A.

The price to be calculated for this gas is purely ficticious. If now a consumer wants to buy a few thousand cub.ft in places where millions of cub.ft are lost daily, he has to pay the price for fuel (5 cts/1000 cub.ft), but if a new market for this gas is established, Mr K. thinks large quantities would be obtainable at, say, 2 cts per 1000 cub.ft, incl. transportation costs. This works out at $ 1.15/ton.

<u>Catalyst investigations</u> (chronologically recited).
(Further details may be found in nine Kellogg Laboratory Reports handed over during the discussions.)

1) Kellogg started 2 years ago with Ni, because this metal is specially excluded from Fischer patents in the U.S.A. and Canada.

A catalyst, consisting of: 40 Ni
10 MnO
4 Al_2O_3
and Kieselguhr

gave the same yield as obtained by Fischer: 130-160 cc/m3 = 95-118 gr.

Precipitation of nitrates is carried out with K_2CO_3

" from chlorides gives less active catalysts

" " sulphates gives no good catalysts at all.

Temperature measurements during these experiments were not reliable, which explains several erratic results obtained.

2) The apparatus used at first consisted of a tube 7.5 cm dia. Good heat transport was obtained by inserting in the tube 2 corrugated tubes of slightly larger dimensions; in addition, in the centre, a rod was inserted, pressing the corrugated tubes against the wall. The whole aggregate was filled with catalyst. The catalyst particles were at the maximum 6 mm distance away from a steel surface (see fig. 33).

Length of tubes varied from 16' to 24'.

Metal temperatures proved to be even all over.

Two kinds of pressed pellets were tried out in these tubes, apparent density 0.7 and 1.1 resp.; dimensions 3 x 3 mm.

	YIELD
Throughput 0.5 l/gr Ni/h	110 cm3 1 stage
" 1.0 "	70 "

Results, therefore, were not encouraging.

The above tube may be good, however, for catalysts of low density.

3) Next, the Robinson Bindley principle of catalyst preparation (ethyl ortho silicate as a carrier) was tried out for making catalysts of lower apparent density. Gave great difficulties at first. Then it was found that the mixture had to be hydrolysed for several days in a wet atmosphere. Catalysts were then good, but very expensive.

A variation consisted in cementing Kieselguhr using ethyl ortho silicate. Results were good, but the cat. is still expensive.

4) Ni-Mn catalysts showed decreasing CH_4 and CO_2 formation ~~if precipitates were washed with increasing amounts of water~~ (= repeated washings with 450 cc water/gr Ni).

No effect when re-adding some K_2CO_3 to a well-washed catalyst.

Oil production increased with catalysts of lower apparent density; also CO conversion increased.

9% graphite (added to get better pills) had no effect on activity.

Increase in Mn content over 10% had no influence.

Yields: 130-140 cc in 1 stage in glass tubes 16 mm. dia. at space velocity of 1 l/gr Ni/hr.

At this stage, before continuing their experiment, an extensive review of the literature on the whole subject was made (see special report).

They then started investigating:

5) CoTh catalysts. Example
1 Co
0.17 Th oxide
1.9 Kieselguhr.

At throughput 1 l/gr Co/hr 150-160 cc yield/m3 was obtained. Again it was found that better conversion occurred with catalysts of lower density. Lower density catalysts allowed better temperature control.

All these experiments were carried out in 16 mm glass tubes. During experiments with catalysts containing varying amounts of Kieselguhr (10-88%) it was found that one must not compare catalysts at the same, but at their optimum temperature, which will be different for different catalysts. In this connection optimum temperature means the temperature at which the maximum yield is obtained. This procedure has been followed since (also by Ruhrchemie).

A catalyst consisting of 1 Co and 0.17 Th without Kieselguhr gave a yield of about 75 cc, of which over 90% consisted of wax.

Additions of Kieselguhr varying from 1 to 7 parts per part Co were then investigated. It was found that the optimum temperature varied from 410-440°F (measured in catalyst at spot of maximum temperature).

A cat. containing 50% Kieselguhr showed the smallest variations of yield with temperature. Highest yield was obtained with a catalyst containing 30-33% Co (143 cc one stage).

No differences in results were found between precipitating in presence of Kieselguhr or adding it after precipitation.

Pelleting and mixing of pellets with porcelain beds had no effect.

Difference between temperature in centre of catalyst and temperature at tube surface was found to be 40°F larger in case of glass tubes than when using metal tubes.

50 mm tubes gave much inferior results than 20 mm tubes.

It was found that better results were obtained in short than in long tubes, probably because in the former the end layers of the catalysts were better cooled. In order to eliminate this effect, in all experiments the gas was preheated.

Decrease in throughput from 1 l/gr Co to 0.1 l/gr Co has no effect on yield.

At 7 atm. yield was higher - more wax was produced - but not yet oxygen compounds.

By electrolytically washing (osmosis) the precipitate in several cases, the yield increased to 180-185 cc in 1 stage.

(Perhaps adsorbed ions are removed in this way and not by an ordinary water wash).

Note: All experiments only lasted about one week. No life-time tests have been made. Further experiments recorded were mostly made in 16 mm i.d. tube, containing 4 gr Co.

6) Kieselguhr plus Co (30%) plus Mn, varying % Mn between 0 and 50 %.

No difference was found between hot and cold precipitation.

Best cat.: 45 % Mn on Co, which gave yields of 150-160 cc/m3.

Mn additions give catalysts producing more wax than those containing Th.

For precipitation both Na_2CO_3 and K_2CO_3 could be used. Influence of variations in wash procedure is small and no effect was noticed when using more than 150 cc wash water/gr Co.

7) American Kieselguhr is very pure. It contains no Al_2O_3 and no Ca and only small amounts of Fe. Pretreatment with HCl or HNO_3 gave no improvement.

8) Thus far wet H_2 (passing a wet gasmeter) was used for reduction. It was found that dry H_2 is much better for this purpose.

9) In order to lower the alkali content of catalysts, precipitation with oxalic acid was tried. No good catalyst was obtained, presumably because of non-careful reduction (formation of water and watergas by decomposition of oxalic acid). Better results might be possible when carefully reducing according to Ruhrchemie's practice, with a very large excess of hydrogen.

10) Co-Al_2O_3 catalyst co-precipitated with 2% Al_2O_3 on Co gave a yield of 115 cc/m3. The product contained no wax. ~~The end boiling point of total product was 200°C. The~~ permissible Al_2O_3 range is very small: 2 - 4 %; e.g. a catalyst with 6% Al_2O_3 on Co only gave 60 cc yield.

11) Co (100) MnO (20) Al_2O_3 (2). Results were very good and equal to CoTh and CoMg catalysts, i.e. 150 cc yield.

12) Co (100) Ce_2O_3 (5-20%). These catalysts were not so active as the CoTh ones. Max. yield 140 cc. When preparing these catalysts by precipitation with KOH the yield dropped to 90 cc.

13) Co (100) MgO (280-20%) without Kieselguhr. Kellogg seem to have used too much MgO in all cases, seen in the light of Ruhrchemie's experience. Kellogg, however, wanted to use MgO as a carrier. These catalysts were unsatisfactory. A catalyst containing 20% MgO gave only 75-80 cc yield; the ot still less. All these catalysts were prepared by careful slow precipitation (about one day) from diluted solutions.

They experienced large MgO losses during washing of the precipitates; for instance, when using 500% MgO the catalyst contained 280%; when using 200% MgO the catalyst contained only 20% MgO.

14) Co. Ni (1:1) + promotors gave same results as Co plus promotors.

14a) Dr Pier enquired whether the Co used in the various experiments all originated from the same source, recalling in this respect that according to Ruhrchemie there is a difference between Co and Co.

Mr Keith answered that Co from different sources had been used, but that no differences in activity had been observe

15) <u>Influence of apparatus and space velocity on results.</u>

During these experiments (which have not yet been laid down in Laboratory reports), they changed to steel tubes surrounded by a steam bath. Inlet gas was preheated.

Investigations were carried out relative to the ~~influence of tube diameter - Catalyst depth and space~~ velocity.

Basis of the experiments: As natural gas (and therefore synthesis gas) is cheap in the U.S.A., the yield per m3 is not of much importance, the more so as the tail gas may be recycled to the synthesis gas plant and worked up again. They are, therefore, aiming at the <u>largest yield per gram of COBALT</u> (= the smallest synthesis plant).

In order to give an idea of the yields obtained it was stated that these amounted to about 90-150 cc/m3.

Space velocities from 1 to 50 l/gr Co/hr were investigated.

The results are always reported from now on as liquid/gr Co/hr.

Tubes: 2" to 9/16".

Catalyst depth constant: 1 ft.

The following table (see fig. 34) shows that production (per gram of Co) depends on diameter of tube and on space velocity:

Space velocity litre/gr Co	tube Ø 2"	1.5"	1.0"	3/4"
	production cc/gr Co/hr			
1	0.14	0.14	0.16	0.16
2	0.18	0.24	0.26	0.27
3	0.12	0.16	0.31	-
4	0.04	0.16	0.32	0.43

16) These experiments led to the conclusion that there must be an optimum catalyst depth for every diameter, at which the production per gr Co/hr is a maximum. The longer the tube, the higher the S.V. taken over the top section only of the tube in question.

By increasing tube length (at constant space velocity for the whole tube) at last such a space velocity, calculated on the top section, is reached that the production of this section is on the right hand side of the optimum (see fig.   ).

On the other hand with very short tubes one works mostly on the left hand side. Theoretically one ought, therefore, to work with conically shaped tubes, in order to stay at the optimum. However, this is no practical proposition.

The experiments with variations of tube length at constant space velocity have not yet been completed. Some results for a space velocity of 2 l/gr Co/hr are given below for two tube diameters.

Cat. depth	9/16" tube	1" ø
1 ft	0.24 cc/grCo/hr	0.16 cc/grCo/hr
2 "	- "	0.32
3 "	0.30 "	0.30

(Dr Pier: In addition the density and form of the catalyst, the pressure and perhaps also other factors play a rôle).

17) Kellogg feel that optimum results may be obtained in an oven of the following construction (see fig.).

The flow passes the catalyst in a direction radial to the centre, the reaction products leaving through the central tube.

~~It was felt that a high velocity would result in~~ a pressure drop sufficient to ensure good gas distribution. This oven is under construction.

Dr Michael interrupted at this moment and stated that he had used this type of oven with his Fe catalyst. It does not work properly for the following reason: Assuming a contraction of, say, 50%, the density of the vaporous reaction product in the central tube is twice as large as that of the fresh gas.

Now the pressure drop through the catalyst bed is very small (das Gas schleicht durch). The result is that in the lower half of the oven, the reaction products partly pass back into the catalyst and even to the outer gas space. At last an equilibrium is attained and it was found that only the upper part of the oven was working properly.

One could, of course, think of some tricks in order to improve matters, but Dr. Michael was convinced that the design is wrong in principle.

18) Another idea of Kellogg's is the upflow oven.

In downflow tubes the liquid drops downwards. Each section of a tube has to get rid of the reaction heat through the tube surface surrounding this section only.

As in different sections different amounts of heat are evolved, temperatures must be uneven in the different sections.

In upflow tubes things are different. Liquid is stirred up and in a bottom section (large heat evolution - fresh gas) part of the heat will be taken up by vaporization of liquid reaction products. The vapours are carried upwards and condense again in a section having a smaller heat production.

In this way heat absorption by the walls is more evenly distributed over the whole tube length.

Upflow gives much lighter products, e.g. a CoTh catalyst gave on downflow 5% parrafin. On upflow a product with 550°F end point only was obtained. After 10 days the catalyst was found to contain only 0.5% paraffin calculated on total product.

19) Kellogg have issued an Engineering Report (dated 9th August 1938) outlining the economies of the Fischer process, based on the following assumptions:

Yield:	100 cc/m3 ideal gas
Throughput:	4. l/grCo/hr
Liquid production rate:	0.4 cc/grCo/hr
Cat. life:	600 t product/tCo before complete regeneration.

Catalyst volume required for 5000 B/D liquid products: 55000 cub.f

Mr Keith expressed as his opinion that a Fischer plant on this basis would be a paying proposition.