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Report by Dr. Kolling Ruhrchemie - Preparation of Iso-gasols and Aviation Gasoline from Synthesis Products

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Before discussing the actual process we must be clear about the technical requirements that are asked of an aviation fuel today. Previously the motor octane number was the decisive point. Namely, one differentiated between 87 and 100 octane aviation motor fuel. Today, one uses in place of the motor octane number the testing after the so-called super-charge method. Here one measures the highest permissible intake pressure or the resulting mean effective piston pressure at initial knocking depending on the excess air number. It is to be mentioned that motor octane numbers and super-charge curves lead to entirely different evaluations of the naphtha.

The obtaining of a high octane number or of a good super-charge capacity is made more difficult by a number of additional requirements in the preparation of aviation gasoline. Thus the aviation fuel must have a low Reid pressure, between 0.3 and 0.5, that means one can only add small amounts of low boiling, generally high octane, hydrocarbons. A further difficulty is caused by the iodine number requirement which makes it impossible to use olefin as knock number increasing agent. The iodine number must be smaller than 3. The other requirement like boiling limit, sulfur content, acid content, oxygen resistance in the bomb test, evaporation residue are generally of lesser importance than the requirement named above.

The aviation motor fuels that are used today can be divided into two groups. The first group includes naphtha which contains besides paraffinic resp. iso paraffinic hydrocarbon, also naphthenic and aromatic hydrocarbons. The naphtha of the second group contains only pure aliphatic hydrocarbon with very branched chain, thus a hydrocarbon of the type of isooctane. Naphthas of the second group have gained particular importance in recent times since they have an octane number of over 100 after addition of 0.9-1.2 Pb. Also, they are characterized by a particular flat course of the super-charge curve.

The hydrocarbons that are formed from the Fischer-Tropsch-Ruhrchemie synthesis are paraffinic or olefinic pure aliphatic hydrocarbons with practically unbranched chains. Only small portions of simply branched hydrocarbons of the methyl hexane class are present. Therefore, it seems first little promising to prepare high capacity motor fuels from these synthesis products.

The following two process groups for production of aviation fuel from gaseous hydrocarbons were developed by the petroleum industry:

1. The polymerization processes.
2. The condensation processes.

I can assume that these are known here. Of the first named processes, the so-called catalytic polymerization has attained importance. It is a catalytic polymerization using phosphoric acid catalysts. Among the processes named under (2), the so-called "alkylation" acquires importance.

Only polymerization need to be considered for the gasols of Ruhrchemie synthesis, because the iso content of the C_4-hydrocarbon is too small to allow economic processing with the other methods. But also the polymerization of C_3 and C_4 hydrocarbons with phosphoric acid catalyst is of little importance because of the relatively low olefin content of the hydrocarbons. The yields and properties of fuels that has been produced by polymerization of C_3 and C_4 hydrocarbon are presented in Table 1.

Table I

Hydrocarbons	Polym. yield in relation to charged olefins	Fraction 60° - 165°C: Of Polymer boiling between 60-165°C	Not. hydrog. Research Octane Number	Motor Octane Number	Hydrogenated Motor Octane Number +0.9Pb
C_3	90%	65%	95	64	86
C_4	90%	80%	96	73	87

One can recognize that, after addition of 0.9 lead, the hydrogenated polynaphtha gives motor octane numbers as they are required in aviation gasoline. But a test with the super-charge method showed that they do not attain the quality that is required directly as aviation fuel but only in mixtures with more valuable products.

The quantitative ratio of primary gasol to hydrocarbons that are liquid when prepared under normal conditions in the synthesis is about 10:90. Therefore, it is of far greater importance to investigate whether there are possibilities to produce high capacity (performance) fuel from these liquid products. In the main, there are three directions to be considered:

1. One can try to improve the products that lie in the naphtha range by isomerization.

2. One could produce highly valuable cyclic hydrocarbons by aromatization from the paraffinic hydrocarbons that lie in the naphtha boiling range.

3. One could produce suitable hydrocarbons from the primary hydrocarbons with the largest possible boiling range by thermal or catalytic cleavage.

I will not go into detail about the first group of methods. In my opinion this group is of little importance. It seems very difficult to isomerize long chain hydrocarbons without much cleavage. Also, so far as catalyst of the type of $AlCl_3$ is used there is a large consumption of catalyst. Also, the octane number increase is only small because the isomerization usually stops with a shift of a methyl group in the side chain.

I can also leave out a description of the process direction that is named under (2) since Dr. Rottig will report about this.

But there remains to be investigated how far the process of cleavage is suited for the production of aviation fuel from Fischer products. For the evaluation of the usability of the thermic cleavage process we can use the values that are recorded in column 1 of Table II. These values have been obtained by Ruhrchemie by splitting a Diesel oil fraction according to the Dubbs process.

Table II

	Thermic Cleavage according to Dubbs process	Catalytic Cleavage	Catalytic Cleavage according to the Houdry process
Starting product	Ruhrchemie Diesel oil 200-350°	R.C. Diesel oil 180-350°	East-Texas gas oil 220-350°C 0.882/15°C
Cleavage Naphtha	15-20%	15-20%	about 45%
C_5	60 wt.%	60 wt.%	90 wt.%
C_4	10 " %	10 " %	1 " %
C_3	8 " %	14 " %	
C_2	12 " %	10 " %	
$C_1 + H_2$	8 " %	3 " %	6 " %
Carbon	2 " %	1 " %	
	-	2 " %	3 " %
Olefin content of naphtha			
C_5	85%	40%	The naphtha boils at 52-200°C acid heat 16°F
C_4	80%	50%	M. octane Nr. 77
C_3	75%	65%	" " + 0.5Pb = 85
C_2	65%	70%	
	50%	55%	
Iso content of			
C_5 Paraffins	-	65%	Of the total naphtha about 50% boil 54-140°C Acid heat 20°F
C_5 Olefins	-	40%	
C_4 Paraffins	25%	60%	
C_4 Olefins	6%	40%	
Naphtha 50-165° has			MO Nr. 78
R. Octane Nr. not hydrogenated	64	65	MO Nr. + 0.9 Pb 90
M. Octane Nr. hydrogenated	24	45	
M. Octane Nr. hydrogenated	-	70	

The high olefin content is characteristic for the cleavage products. The product that lies in the boiling range of aviation fuel has an octane number of about 64 but it declines after hydrogenation to a motor octane number of only 24. Therefore, it is entirely unsuited as aviation fuel. Also the gaseous cleavage products which contain a high portion of C_1 and C_2 hydrocarbons seem to be suited only to limited extent for the production of aviation fuel, because of their low iso content.

In recent times the catalytic cleavage process has been introduced more frequently particularly in America. This is particularly true of the catalytic cleavage process according to the Houdry process. This has been developed in the United States since about the year 1930, and 1935 about 15 large scale plants were in operation or under construction. Column 3 of Table II shows some yield numbers for the cleavage of East Texas gas oil according to the Houdry process. The values have been taken from a publication of Houdry in "The Oil and Gas Journal", 1938. It should be pointed out that the Houdry plants do not process the cracked stock completely. After the first or a few runs the unsplit material is further processed in a thermic cleavage plant. The values in column 3 of Table II have been obtained by a single run. About 55% gas oil remained unsplit. The extremely large naphtha portion of the cleavage product is striking. Of the total naphtha about 50% fell in the range of aviation fuel. The octane number is about 78-90 after admixture of 0.9 cc. lead per liter of naphtha. A considerable amount of true to type aviation gasoline of normal quality is formed.

Therefore it seems advisable to use these processes for processing the product of the Fischer-Tropsch Ruhrchemie synthesis in spite of the difficulties that are connected with the use of the catalytic cleavage process. Unfortunately we found that there were many considerable difficulties. Column 2 in Table II gives a general picture about the yield numbers and properties of the cleavage product of Fischer Diesel oil. Compared with the results of the thermic cleavage as represented in column 1 we find progress with regard to a smaller portion of C_1 and C_2 hydrocarbons and also with regard to a higher octane number of the hydrogenated naphtha. But the octane number after admixture of 0.9 cc lead per liter naphtha is only 70. Thus direct production of aviation gasoline in this manner cannot be carried out. According to our opinion the large difference between the results of column 2 and column 3 is caused by the different chemical compositions of the starting product which is also shown in the high density in the East Texas gas oil. This assumption is strengthened by our own experiments with German petroleum products which yield similar results as recorded in column 3. They show high yields of good octane gasoline and it was shown that petroleum products are more readily split catalytically than Fischer products.

The use of the catalytic cleavage process as developed in America for Fischer products seems little promising after all this. Therefore, we decided to pursue the solution of this problem in another direction. If possible, we shall not use the not very valuable cleavage naphtha. It is to be tried to split straight chain aliphatic hydrocarbon into small cleavage pieces and to build up from these a suitable hydrocarbon. The following six conditions have to be fulfilled in order to attain a successful utilization of such a process.

1. The point of gravity of the building products must lie near the C_4 hydrocarbons. The naphtha portion must be kept as small as possible. An increase in C_1 and C_2 portions must be avoided.

2. The construction to C_4 or C_5 hydrocarbons must be done by isomerization.

3. It has to be attempted to raise the percentage of unsaturation of the C_3-C_5 cleavage product as high as possible in order to make the new construction with simple polymerization possible, without recourse to complicated processes of dehydrogenation and alkylation.

4. It must be attempted to split the total cracked charge without residue.

5. The boiling range of the hydrocarbons that are to be processed by the catalytic cleavage has to be as large as possible. Particularly it is desirable to charge also hydrocarbons that boil between 100 and 200°C.

6. Finally, it was to be tried to arrange the technical construction of such a catalytic cracking process so that the complicated arrangement of the American process can be avoided.

In order to make the following part clear will you allow me to discuss briefly the apparatus aspects of the American catalyst cleavage process. The Houdry process has been described most extensively and is also the best developed process. There exists an interesting description of a Houdry plant at the Magnolia Petroleum Co. It reports a daily throughput of about 2,000 tons. It was published by Voorhis in the National Petroleum News of August, 1939. According to this publication the cracking charge goes from the charge pump through a number of heat exchangers to a pipe oven where it is heated to about 440°C. Then it reaches a tar separator, steam is added and it is heated again in a pipe oven up to 470°C and finally it goes to the automatically steered check valve of the cracking chamber. There exist three groups of reactors, one of which is always in reaction. The pressure of the reactors is 2.1 atm. absolute pressure. The cleavage vapors pass through the reactors, through the heat exchangers as mentioned above to the processing in fractionating and stabilizing columns.

Precipitates which contain carbon are formed in the reaction at the catalyst surface and have to be burned off in a regeneration period. The quantities of air that are required for this are sucked in by Brown-Bovery-turbine compressors. After appropriate heating it is conducted to the reactors. The smoke gases that leave the reactors are burned first using a catalyst and then they go into a Brown-Bovery hot gas turbine which is connected with the compressor.

A circulating fused salt is used to maintain suitable temperatures in the reaction chambers. In this plant the salt system requires the filling of 500 tonnes. After leaving the reactors the fused salt goes into an

expansion tank and then into a pump tank. From there it goes part into the reactors and part it is pumped into a steam producing plant to give off heat.

About the construction of the catalyst chambers the article only states that it has a diameter of 3.2 meters and a height of about 11 meters and that the construction has been done very precisely. One may assume that we are dealing with the reactors of similar construction as described in A.P. 2,161,677. The main principle of the Houdry process is the temperature regulation of the catalyst with aid of the catalyst chambers and the pipe systems that surround the contact chambers through which one pumps the heat carrying medium, in this case fused salt.

It should be specifically emphasized that the distance between two heat exchange surfaces in all places of contact must not be more than 1 inch. The salt fusion brings on the one hand the heat that is necessary for the endothermic reaction and carries out the hydrcarbon combustion heat that is liberated by regeneration. As mentioned before the excess heat quantities are used to produce steam. The rest of the construction of the catalyst chambers can be seen from the representation. The entire catalyst tower is divided into six single layers obviously for better gas distribution. In this way it is possible to carry out various arrangements. For instance, the charge product can be introduced from the top and bottom and taken off from the middle, etc. One can see from the picture that such a catalyst apparatus is a very complicated construction. One also has to consider that only especially selected steels can be used because of the high reaction temperature and because of the change in stress of the oxidizing and reducing atmospheres in the cooling system. One must not neglect entirely the influence of the large steel surface on the course of the reaction according to our experience. The Houdry had to arrange for a special manufacturing by the Sun Ship Building Co. with large machine arrangements. Also, the requirements for the apparatus of the salt circulation will have to be considered. Therefore, one must assume that Houdry plant may be economical for large units such as is possible in the American petroleum industry but not for plants on the scale as it would be necessary for the Fischer plant.

I also have to mention the time scheme of the Magnolia Houdry plant.

Ten minute reaction
Five minute steam blowing
Ten minute air treatment
Five minute steam blowing
Ten minute reaction, etc.

The reaction time is in the ratio of 1:2 to the regeneration time.

The catalyst that is used was not described in detail. But it is to be assumed that it is the pure aluminum hydrosilicate catalyst prepared according to the Houdry patent A.P. 2,073,945 by pressure formation.

In contrast to the Houdry process the processes worked out by Standard and by Kellog operate with moving catalyst. Here the difficulty that is caused by the change of endothermic cleavage reaction and exothermic regeneration is solved by carrying out the reaction and regeneration in different places. A schematic presentation of this process is contained in the Standard patent F.P. 865,901 in the year 1941. This ought to correspond with the state of development up to date. The cracking charge is first heated on a pre-heater to 205°C. Then it is mixed with a pulverized regenerated catalyst in a mixer and with a preheated inert gas, for instance, nitrogen. Then it is cracked in the cracking coil at 0.35 atm. absolute pressure about 400°C and a residence time of about 15 seconds. The ratio catalyst:oil amounts to 3 to 1 in weight %.(Trans.:sic). The catalyst is separated from the oil vapors by blowing out with nitrogen in a catalyst separation apparatus. Then the catalyst reaches a collecting vessel after passing through several sluices. Heated air or air inert gas mixtures are added. Then it is put into the coil that is heated from the outside, where the separated hydrocarbon is burned off at 3.5 atm. absolute pressure and temperatures between 315 and 760°C. After blowing out again with inert gas in a second catalyst separation apparatus the catalyst can be used again for the reaction.

The usability of the processes with moving catalyst cannot be judged from the patent publication. But at any rate it seems to be a technically very difficult process to circulate a pulverized catalyst mass at such high temperatures and particularly to transport them through narrow reaction pipes. Basically, this process comprises a step back to the thermic cleavage process. As in that process the total heat that is necessary for the reaction is passed through the walls of thin pipes. It probably is also very difficult with regard to the material choice to eliminate the influence of wall surfaces.

All these difficulties have been avoided in the process that has been developed by the main laboratory of Ruhrchemie by Dr. Trauna, cooperatively with Dr. Dahm, engineer Stuhlpfarrer, Dr. Kalippke and the lecturer. The important technical problem is the control of the heat moving between endothermic cleavage reaction and exothermic catalyst regeneration. This was solved in a simple manner. A small number example may throw light on the situation. One can assume for instance that 100 kilograms charged material can be cracked to 50% by a single throughput of the catalyst. To split 50 kgs. one needs 50 x 300 = 15,000 heat units. We attempted to arrange the whole process in such a manner that exactly the 15,000 heat units would be produced during the regeneration of the catalyst. Thus, we did not need the complicated heat carrying system in which salt solution circulates as in the Houdry plant and also not the complicated arrangement of catalyst moving. But it was possible to operate with simply arranged stationary catalyst. Thereby a catalyst mass is at the same time heat regenerator for the cleavage. In order to fulfill this task we would have to succeed to separate just enough carbon on the catalyst surface that the heat that is produced by its burning off is enough as cleavage heat. Burning 1 kg. carbon liberates about 9,000 heat units, thus there had to be burned about 1.7 kgs. carbon. First it seemed very hopeless to regulate such a complicated process as the catalytic cleavage in such a manner, particularly if various catalysts and various

cleavage charges were to be used. Through tedious careful study in laboratory tests and half technical tests we succeeded finally to get to know all the operation conditions that affect the hydrocarbon precipitation. Thus, today we are able to regulate the cleavage in desired direction. Among the operation conditions there are catalyst load, duration of reaction period, reaction temperature, catalyst activity, and even the size of the reactors.

With the exact adjustment of heat yields according to heat requirements it is also possible to effect extremely short regeneration times. The ratio between reaction time and regeneration time is 2:1 (this includes als. the intermediate steam blowing in the regeneration plant). In the Houdry process the ratio is 1:2. This is an important fact. Of 100 cu.meters of stationary catalyst in the Houdry process only about 33 cu.meters are in constant operation, while in our process there are 66 cu.meters in constant operation, therefore the double amount.

In the large scale plant that is under construction three groups of reactors are provided of which two groups are always in reaction and one group in regeneration. The course of operation in this plant is as follows (compare appendix).

From intake tanks that are in alternating arrangement the products that are to be split go to a pipe oven. There they are evaporated and preheated to the reaction temperature. The pipe oven has also a special oven part in which the so-called cracking reflux is preheated. This cracking reflux is not split in one throughput. The evaporated products go into a mixing chamber where water steam can be added and then into the reactors. The reactors are formed especially from a special material. They consist of a container in which the catalyst rests. The reaction is carried out at normal pressure and temperatures of 500°C. The products that leave the reactor go first to a de-heating kettle where they are cooled off to about 260°C with a production of corresponding amount of steam.

Also, the air that is necessary for the carbon burning which has been preheated in the pipe heater to reaction temperature pass through the reactors and are finally passed through the deheating kettle. The steam that is necessary for blowing out and mixing to the charge product is also heated in the same pipe heaters as the air.

Conversion of the reaction to air or steam blowing occurs by a fully automatic gear arrangement that operates by an electric-pneumatic method. Electric connections are operated by a steering cylinder. These three valves by magnetically steered through which a pneumatic medium such as compressed air operates the actual regulating valves. Appropriate back-indicating devices assure absolute technical safety of the arrangement.

Now I shall speak about the further processing of these products. A mixture of cracked products goes from the heat reduction kettles into a cooling installation which consists of a rinsing cooler and adjoining indirect cooler.

The liquid hydrocarbons go to the fractionation, the gaseous hydrocarbons pass through a gas meter into a compression station. In the first column one takes off the cracking reflux at the bottom, a heavy naphtha that boils above 100°C as a side stream, and on top the hydrocarbons boiling below C_7. These hydrocarbons are mixed with the products that are formed in the first compressor stage which operates at 10 atm. Then they are separated in a second pressure distillation in a C_5 (and C_6-) bottom product and a C_3, C_4, C_5 top product. The top product is mixed with a product that is formed in the second compressor stage which operates at 35 atm. absolute pressure. Then it is separated in a third column into a bottom product of C_5 and a top product of C_3 and C_4. The C_3, C_4 is then divided in a fourth column into C_3 and C_4.

The C_3, C_4 and C_5 hydrocarbons can now be polymerized in a polymerization plant over stationary catalysts. After polymerization there follow stabilizing columns and distillation columns. In these the aviation fuels are adjusted to boiling ranges true to type and accurate Reid pressure. And finally, there follows a hydrogenation column.

I do not wish to go into further details about this scheme, but I hope that I have showed you that we succeeded to develop a technically simple catalytic cleavage process, which can be used also for small cleavage plants as it is required for the Fischer work. It can be done economically. The six requirements that were named at the beginning for a usable catalytic cleavage process seem to be fulfilled.

In the following I should like to show how far the points 1-5 could be realized. Table III shows a summary of yield numbers as they were obtained by splitting of a product that boils between 160-350°C. This Fischer-Tropsch-Ruhrchemie synthesis product has been used in our technical pilot plant for many months.

Table III

	Ruhrchemie Products
Charge material	
Boiling limits	170-350°C
Density$_{20}$	0.763
Wt.% conversion	about 40%
The converted products are divided into	
wt.% naphtha	15-20
" C_5	19-24
" C_4	25-30
" C_3	20-25
" C_2	5-7
" C_1 + H_2 + carbon	1-2
	3-4
Olefin content of	
C_5	35-90%
C_4	90-95%
C_3	90-95%
C_2	60-65%

Table III (Cont.)

Iso content of	
C_5 Paraffins	60-65%
C_5 Olefins	45-50%
C_4 Paraffins	60-65%
C_4 Olefins	38-43%

Thereby no cleavage residue was taken off. With one throughput the cleavage is about 30% as can be seen in Table III. The converted products are distributed as follows: 15-20 wt.% naphtha, 19-24 wt.% C_5, 25-30 wt.% C_4, 20-25 wt.% C_3, 5-7 wt.% C_2, 1-2 wt.% C_1 and H_2 3-4 wt.% carbon.

Thus, we succeeded not only in shifting the center of gravity of the cleavage product away from the naphtha to the C_4 with only a small increase of the C_1, C_2 portion but also in producing C_4 and C_5 cleavage fragments with sufficient iso content. It is particularly important that we succeeded to produce C_3, C_4 and C_5 hydrocarbon with 90-95% olefin content. Thus, it is possible to convert C_3 to C_5 hydrocarbons with good yields into highly valuable polynaphthas by simple polymerisation with sulfuric acid catalyst. Later we shall go into detail about these processes.

It is necessary to make some statements about the catalyst that was used in order to evaluate our catalytic cleavage process. Table IV shows what differences were caused by the choice of various catalysts.

Table IV

Catalyst	Wt.% Conversion	The converted are divided wt.% Naphtha	C_5	C_4	C_3	$C_2C_1H_2$	Carbon	$\%C_4$	% Iso-C_4-C_4
A	about 30	53	12	11	7	7	11	85	40
B	" 30	36	16	17	14	6	11	80	40
C	" 45	11	15	33	27	9	5	35	34
D	" 40	10	13	38	31	4	4	40	38
E	" 40	11	16	35	29	6	3	85	40

The catalysts A to E were run under similar conditions. Nevertheless, large deviations in distribution of the analysis of cleavage products occurred. For example, catalyst A shifts again to the naphtha side although the same experimental conditions were chosen as in the experiments that were summarized in Table III. Also the great carbon precipitation is remarkable. Catalyst B shows similar results. On the other hand, Catalysts C and D give even better yields than those obtained in the experiment of Table III with regard to naphtha and C_4 values. Unfortunately, the olefin numbers are very poor and with Catalyst C also the iso values are low. The yield values of Catalyst E approach the values of Table III. If we succeed to increase the olefin content of the cleavage pieces somewhat then this catalyst will be better than the one used up till now.

The life span of the catalyst is generally very good. For example, the catalyst that has been used in our pilot plant was run in a experiment up to the age of 3,500 reaction hours, this is five months of pure operation time. The decline of activity of the catalyst can be equalized by changing experimental conditions. It is true thereby occurs a small increase of the C_1, C_2 values. Therefore, it seems to be practical to change the catalyst two to three times a year.

It is interesting to regard once the distribution according to C-numbers of the products that are charged into the cleavage and the products that were obtained. In Table V (Appendix 1) the results of such an investigation have been represented graphically. The dotted curve is the distribution of the charged material, the solid line shows the total end product by percent weight for the various hydrocarbons. Also, the corresponding olefin curves have been corded. One can see again the shift of the cleavage of C_3 to C_5 hydrocarbons particularly to the C_4 hydrocarbon and extensive depression of naphtha formation with a minimum at C_8 is also shown. The continuation of the curve to the R cycle material shows a greater cleavage of the highest boiling fraction and obviously also a favored cleavage of the C_{12} and C_{15} hydrocarbons. One would assume that there occurred a certain median cleavage that goes, for example, over C_8 to C_4. If one compares the olefin curves one can see that the hydrocarbons of the split product has a high olefin content as has been mentioned before.

The hydrocarbons of the cleavage reflux on the other hand have lower olefin numbers than the charged material. We could confirm the assumption that a median cleavage occurred in the catalytic cleavage of the charged hydrocarbon by the results of cleavage experiments in which C_6-C_9 hydrocarbons from the Fischer synthesis were used. Table VI (Appendix 2) shows first the results of a charge of C_8-C_9 mixture. One can see clearly the favored cleavage of C_8 hydrocarbons and particularly C_8 olefins into two C_4 hydrocarbons. The distribution of cleavage products corresponds otherwise to the values recorded in Table III. Also the olefin and iso values of the cleavage pieces are the same as there. Table VII (Appendix 3) gives the cleavage results of C_7 hydrocarbons. As can be seen clearly from the picture the cleavage is favored in the following directions: C_7 into C_3 and C_4. Distribution of the cleavage product amounts to 5 wt.% C_6, 15 wt.% C_5, 35 wt.% C_4, 38 wt.% C_3, 5 wt.% C_1,C_2, and 3 wt.% carbon. The other values correspond with those of Table III. Figure 8 (Appendix 4) shows finally the results of the cleavage of a C_6 fraction that was slightly contaminated with C_4 and C_5. The cleavage reaction runs almost entirely according to the equation $C_6 = 2C_3$.

Thus, it is possible to separate hydrocarbons down to C_6 in our catalytic cleavage process predominantly into C_3 to C_5 cleavage pieces with high olefin content and sufficient iso content. From these one can build up aviation motor fuels by polymerization with phosphoric acid catalyst with good yields. The only limit consists in the decrease of cleavability with falling C number as can be seen in Table IX.

Table IX

Charge 160-350°	C_8-C_9 Fraction	C_7 Fraction	C_6 Fraction	C_5 Fraction
Wt.% conversion 46	33	32	19	10

For example at equal experimental conditions the cleavage falls from 46% to 33%, 32%, 19% and with C_5 even to 10%.

Therefore, a catalytic cleavage of C_5 hydrocarbons should not be done. Also, a cleavage of C_6 hydrocarbons is only advisable in exceptional cases. But it seems easily possible to charge all hydrocarbons of the Fischer synthesis down to C_7 into the catalytic cleavage.

An additional effect of our catalytic cleavage process must be emphasized that it is possible to isomerize C_4 and C_5 olefins that can be put through the reactors up to 40-50% without decreasing the cleavage performance of the plant. For the Fischer plant where C_4 and C_5 olefins are available from other sources this means a considerable increase of aviation motor fuel yields. The C_4 isomerization operates completely without loss, in a C_5 isomerization there is a small loss in conversion of part of the C_5 olefins primarily into C_3 and C_2 cleavage pieces.

There still remains to be discussed the processing of the catalytic cleavage product of C_3 to C_5 hydrocarbons into aviation motor fuel. It would not be in the scope of this lecture to go into details about the polymerization and hydrogenation. Only the obtained yields and qualities of polynaphthas are interesting here. I give a summary of these values in Table X.

Table X

Hydrocarbons	Polym.yield referred to charged olefins	Of Polymers boiling from 60-165°	Fraction 60-165° Hydr. MONr	MONr + 0.9Pb	MONr + 1.2Pb
C_3	90%	65%	64	86	88
C_4	90%	88%	91	104	106
C_5	70%	80%	89	103	104

One can see clearly the improvement of the quality of the C_4 polynaphtha because of their increased iso content as compared with the polymerization of primary gasols whose result have been reported in the beginning of this lecture in Table I. It is surprising that it is also possible

to produce polynaphthas of similarly good quality from C_5 olefins without increasing the portion of higher boiling products considerably.

The yields of polynaphtha in the boiling range of the aviation gasoline and of the by-products that are formed in the polymerization in relation to cracked charge is presented in Table XI.

Table XI

Hydrocarbons	C_3	C_4	C_5		
Wt.%	22.5	27.5	21.5		
Olefin content	92.5%	92.5%	87.5%		
Fraction 60°-165°	12.2	24.1	10.5	Total	42.8
" -60°	—	—	8.3	"	8.3
" 165°-200	4.6	2.0	1.8	"	8.4
200°C boiling polyends	1.9	0.8	0.8	"	3.5
Motor fuel gas	3.8	4.7	—	"	8.5

According to this, there forms in total 42.8% polynaphthas that boil between 60-165°C, 8.4% between 165-200° boiling polynaphthas, 8.3% between 60° boiling products from the C_5 polymerization, 3.5% over 200° boiling so-called polyends and 8.5% motor gas.

As shown in Table X the polynaphthas that boil between 60-165° (after hydrogenation and after addition at 0.9 or 1.2 lead) have octane numbers that correspond partly to the normal 87 and partly to the 100 octane aviation motor fuel. As I have said in the beginning it is customary now to test aviation fuel according to the super-charge method. Based on these measurements there resulted two possibilities for the preparation of aviation motor fuel. Either one can produce a product with highest values corresponding to iso-octane which we shall call aviation fuel #I in the following, or one can produce an aviation motor fuel of normal quality which we shall call aviation fuel #II.

Based on the super-charge test only C_4 and C_5 polynaphthas are suitable for aviation naphtha #I. The C_3 polynaphtha, the polymerizates of C_4 and C_5 hydrocarbons which boil between 165-200°C, the portions from the C_5 polymerization which boil under 60° and the catalytic cleavage naphtha that boils between 60 and 160° make up the automobile fuel. The octane number of this mixture without admixture of lead is 87. Table XII gives a survey about the quantitative ratio.

Table XII

	Wt.%	Wt.%	Wt.%
Aviation fuel #1	31.7	32	
Automobile fuel(Research octane number without Pb = 78)	48.1	48	80
Motor gas	8.8	9	
C_2 - Hydrocarbon with 80% olefins	4.2		
$CH_4 + H_2$	1.6	11	
Carbon	3.6		

Our values refer to cracked charge. The 3.5 polyends that are mentioned above are not recorded again, since these polyends can always be split catalytically in the same manner. For the rest of the cleavage charge the yield values can be stated without consideration of the polyends by corresponding recalculation. As shown in Table XII the yields of aviation fuel #I amount to about 32%. The yields of C_4 the automobile fuel to about 48% and the yield of fuel gas about 9%. Thus the total naphtha yields is about 80%, the total yields of motor fuel material about 89%. The other 11% consists of about 67% C_2 hydrocarbons or about 4% CH_4. Even the 4% carbon that is formed in the cleavage process is not to be considered as a total loss since the heat that is liberated in the carbon burning is again used. As I have pointed out before, it furnishes the total cleavage heat. Thus we succeeded to produce a relatively high amount of highly valuable aviation motor fuel from the straight chain products of the Fischer-Tropsch-Ruhrchemie synthesis by catalytic cleavage combined with polymerisation of the olefin obtained in the cleavage and following hydrogenation. Thereby an automobile fuel is formed with an octane number of 87 without lead admixture which makes up a valuable admixture for improvement of primary naphthas.

This can be of particular importance if for some reason one has to decrease the quality of the primary naphtha by taking out a certain hydrocarbon as, for instance, olefin hydrocarbon. The aviation gasoline #I can be used technically just like isooctane. It can be used as highly valuable isoparaffinic component which is necessary for the improvement of the very steep course of supercharged curves of the aromatic hydrogenated naphthas, in order to make them suitable aviation operation. Therefore, its production is very urgent. To make that clear I show you the corresponding supercharged curves in picture 13 (Appendix 5). Curve 1 corresponds to our aviation gasoline #I. Curve 2 corresponds to aromatic hydrogenated naphtha. Curve 3 corresponds to a mixture of 80% hydrogenated naphtha with 20% aviation gasoline #I.

If one foregoes the production of aviation fuel with top-quality as it is presented by our aviation gasoline #I, one can produce a larger amount of aviation fuel of normal quality which we have called aviation fuel #II. In this case it is possible to mix in also the C_3 polymerisate and even the portion of hydrogenated catalytic cleavage naphtha boiling up to 120°. The aviation naphtha II that is obtained that way yields curve 4 recorded in picture 13 which corresponds in its position to the aviation fuel "B_4" (curve 5). Yield numbers in relation to cracked charge are summarised in Table XIV.

Table XIV

	Wt.%	Wt.%	Wt.%
Aviation fuel II	56.1	56	80
Automobile fuel RONr. without Pb ≈80	23.7	24	
Fuel gas	8.8	9	
C_2 Hydrocarbons with 60% olefins	6.2		
CH_4 + H_2	1.6	11	
Carbon	3.6		

According to this one obtains about 56% aviation fuel II, about 24% automobile fuel with a research octane number of 80, and about 9% fuel gas and about 11% C_1C_2 hydrocarbon and carbon. Thus one succeeds in the production of aviation fuel of normal quality with surprisingly good yields.

It may be interesting for the evaluation of the economy of the Ruhrchemie process to compare the energy requirement values with the statement about energy use of the Houdry process in the publication that has been mentioned before by van Voorhis about the Houdry Magnolia plant. Table XV gives this comparison.

Table XV

	Ruhrchemie Process		Houdry Process	
		RM		RM
Fuel gas	300,000 heat units	3.52	320,000 heat units	1.41
Electricity	55 KWh	0.99	10 Kwh	0.18
Steam	0.6 tonnes, 15 atm.	1.80	0.05 tonnes	0.15
Fresh water	3 cu. meters	0.21	1.2 cu.m.	0.08
	Total	6.52		1.82
That is 0.65 Pfg per kg cleavage charge			0.18 pfg per kg charge	
or 1.62 " " " " products			or 0.45 " " " product	

The values refer to one tonne of cracked charge and include in both cases the distillative processing of the cracked product. It is clear that the energy requirement of our process must be higher. In contrast to the Houdry process in which one works directly towards the naphtha we must process large amounts of gaseous cleavage products. As one can see in Table XV the excess consumption of energy amounts to about 0.5 pfg. per kg. cleavage charge. If one determines the cleavage degree in single throughput for the Houdry process similarly as the values in Table III at 40% this amounts to about 1.2 pfg per kg. of converted cleavage charge material. If one adds to this the cost of polymerization, stabilization and hydrogenation which are not included in Table XV one can obtain a total price excess of about 1.8 pfg. per kg. converted cleavage charge. If one considers that in the Houdry process about 45% aviation fuel of normal quality is produced,

by our process we produce 56%, and further that in our process one has the possibility to produce aviation fuel #1 a product is technically an isooctane then this result must be considered entirely satisfactory. Particularly, since, in comparison to the Houdry process, the Fischer product aviation fuels are much more difficult to produce.

We should like to say a few words about the entire economy of an aviation fuel plant. We have chosen 26 to 27,000 tonnes of material which results in 15,000 tonnes per year of aviation fuel. We are concerned here with a plant of the size which could be constructed in the various synthesis plants without the plant having to buy cracked stock from another source. The size of the plant is the same as we have shown in Table V. The construction cost amounts to 430 marks per tonne of produced aviation fuel. Besides the 15,000 tonnes aviation naphtha there is formed 6,400 tonnes of automobile naphtha with an octane number of 80, and 2,400 tonnes fuel gas, 960 tonnes ethylene, and 1,070 tonnes of gas. 26,300 tonnes charge is necessary which has to be counted as 30 pfg. The automobile fuel is credited with 32 pfg per kg., a fuel gas 29 pfg, the ethylene with 13 pfg and the fuel gas with 1.7 pfg per kg. After subtracting the credit one obtains a charge price for the aviation fuel of 34 pfg. The construction costs amount to about 6½ million marks. From this one calculates amortization and interest of 6.5 pfg. The operation costs are calculated including the catalyst cost at 5.7 pfg., wages and salaries amount to 2.6 pfg. repairs to 2.2 pfg. The total price for aviation fuel on this basis comes to 51 pfg per kg. One has to consider in calculating the economy that the resulting 6,400 tonnes of automobile naphtha is very highly valuable and could be sold at a higher price than 32 pfg.

In conclusion I would like to say that the Ruhrchemie cleavage process has only been worked out for the production of aviation fuel from products of the Ruhrchemie-Fischer-Tropsch synthesis. But we know today that it can be used also for petroleum products. Of course, there are different yield numbers because of the different chemical compositions of the starting product. Also here interesting prospects are opened because of the simplicity of our process.

Signed Kolling

Martin: The investigations had already been started before the war and were carried out with the int ntion to improve the quality of Fischer naphtha. The results that were just reported have been obtained in a pilot plant. In a short time large scale values will be available because a large scale plant is under construction. While the Houdry process in the U.S.A. is only built as plants with large capacity of about one million tonnes per year or more, the present process is also suited for smaller charges and particularly for the German conditions. It is remarkable that in this method of cleavage hydrocarbons with a C number that is divisible by 4 decomposed into C_4 hydrocarbons, and that mostly isoparaffins are formed.

Lopmann points out that favorable operation of such a plant is very dependent on the equalization of the heat. He asks whether the heat exchange can also be well controlled when a non-uniform charge is used. Kolling explained that no difficulties occur when C_5-C_8 hydrocarbons are charged. Martin throught that higher molecular mist may cause trouble. Ullrich asks whether the presence of C_3 and C_4 hydrocarbons disturbs the balance of the cleavage. Kolling remarks to this that neither C_4 nor C_5 hydrocarbons disturb the balance. That also C_5 hydrocarbons split partly into C_3 and C_2 and there occurs some carbon precipitation. But the losses through carbon precipitation are small.

Kolling points out that while the temperatures of the Ruhrchemie cleavage process are higher than in the Houdry process and they fluctuate during the process between 30° and 40°C, the catalyst is very stable and sensitive against temperature changes.

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