

Reel 138  
Document No. XV

Collection of Reports Made by the Research Laboratory  
Report No. 304

Research Laboratory  
Me 219  
Leuna Works,  
December 9, 1941.

The HF-Process and the Moosbierbaum Plant

Report given by Dr. Kaufmann at the  
Petroleum Conference held at Berlin on  
November 26, 1941.

Fundamental Observations Concerning the HF-Process

The HF process is a development of the hydroforming process started by the Standard Oil Company. As you know, it is an intermittent process.

We operate in a productive HF-period, followed by an unproductive period of catalyst regeneration.

I shall explain the fundamentals of the process on the basis of Figure 1. Initially, when we first set up our production schedule, we had to base it on the current experiences made with processing petroleum. We had to arrange for the two alternating periods on the basis of 1:1 ratio, that is, on the basis of a 10-hour regeneration period following a 10 hour production period. For this reason, we had to choose a two-unit system; one unit would be in operation, while the other would be regenerated.

1.) Moosbierbaum, First Stage of Plant Development (Mbb I)

Figure 1 demonstrates the technical equipment used at the first stage. Some of it is based on the personal experiences which I had gathered in the United States.

This unit is characterized by the following features: The large chamber reactor or converter is unheated; the necessary heat is introduced into the reaction mixture outside of the catalyst chamber (indicated by arrows); both groups share one preheater. The hot switch valves are placed between the preheater and the reactor. This figure shows only two reactors.

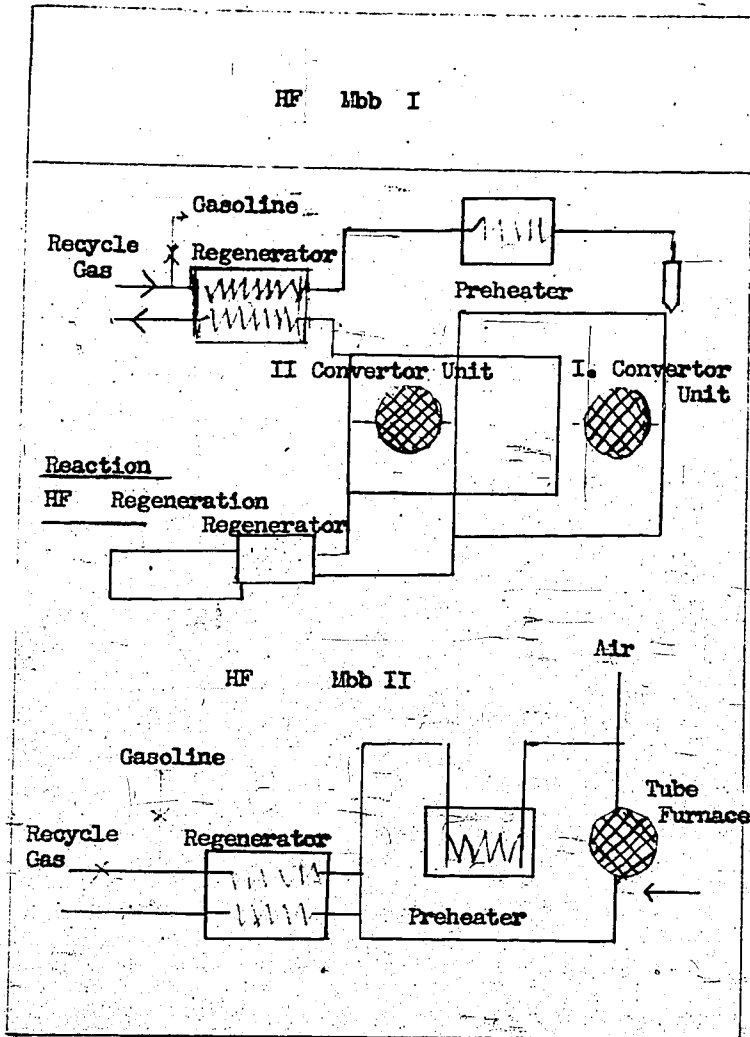


Figure 1

In fact we operate with two reactor units comprising three reactors each; and between each of the reactors an intermediate preheater has been placed for reheating the reaction mixture, the HF-reaction being of a strongly endothermic nature.

## 2.) Moosbierbaum, Second Stage of Plant Development (MbbII)

Taking into consideration the endothermic nature of the HF-reaction and the exothermic nature of the regeneration reaction, when we erected the second stage units, we chose a tube furnace having a heated jacket. Furthermore, we gave up the principle of using one preheater for two reactors. An entirely self-contained reactor unit having a preheater of its own is more independent; another advantage of this arrangement is that the sensitive hot-valve mechanism between the preheater and the reactor is not needed any-more.

### Initial Tasks

May I mention that at the end of 1939, when we decided to build a technical plant, the following tasks had been assigned to us: We were supposed to prepare a suitable aviation gasoline having about a B<sub>4</sub> quality, from Roumanian straight-run gasolines, which contain too much paraffin.

Later on, we received the data obtained by DVL, where one of our first pilot plant products had been subject to the motor test. It turned out to have such an outstanding supercharging capacity in the aviation motor, that it was not designated as an "aviation gasoline", but as a "high-efficiency gasoline". From that time, Moosbierbaum had to supply high efficiency gasoline. And at that: by a process working up petroleum. Hitherto, in general, only mineral coal and its derivatives had been used as a parent material for such purposes ("Aromatization").

Furthermore, the continuous development of aviation motors resulted in continuously stricter requirements concerning the quality of HF-gasoline.

However, we succeeded in meeting these ever stricter requirements, too, even while using the unheated converter, by systematically developing the process, particularly the catalysts.

In these converters we have partitioned the catalyst beds in such a manner that in the course of the reaction the vapors will pass over constantly more and more active catalysts, within each of the individual reactors as well as on passing from one reactor to the next one.

Only by choosing this mode of action we succeeded more or less in distributing the HF reaction over the whole length of the catalyst bed; thereby we obtained good results. However, the results in the tube-furnace were still 4-5% more favorable.

# Supercharging Capacity

(DVL - Simplified 138°)

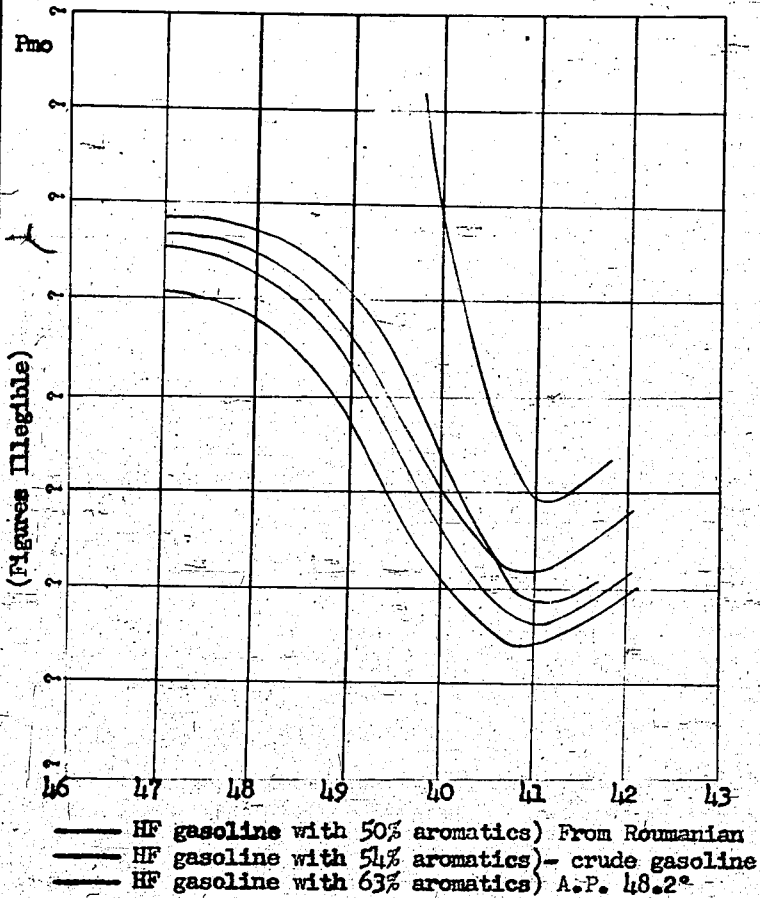


Figure 2

## Chemical Reactions and Mode of Operation

I want now to discuss briefly the chemical changes taking place and the mode of operation to be used.

The quality of a high efficiency gasoline is nowadays principally expressed by its supercharging capacity in the motor up to the knock limit. A desirable supercharging capacity results either from the presence of aromatics or of widely branched hydrocarbons.

The formation of aromatics occurs along with the formation of hydrogen.

- 1.) By the dehydrogenation of naphthenic hydrocarbons.
- 2.) By converting paraffin hydrocarbons into cyclic hydrocarbons and by dehydrogenating them thereafter.

These conversions occasion an endothermic reaction of about 150-200 cal/kg of reactor charge (Roumanian-petroleum gasoline). An important, although undesirable side reaction consists in the splitting of the thermally relatively unstable paraffin hydrocarbons. Principally, coke and hydrocarbon gas are thereby formed and the output is thus reduced. The more paraffins are contained in the parent material, and the higher the requirements the HF-gasoline has to meet in regard to its aromatic contents, the more losses will be incurred in the processing.

### Operating Conditions

The optimum pressure for such petroleum gasolines is 15 atm. Both units in Moosbierbaum, however, have been built for 15-30 atm., in order to be able to process also gasolines having a high naphthene content, if necessary. The  $H_2$  partial pressure in the recycle gas is kept at about 65-70% of the total pressure by means of washing and cooling.

The reaction temperatures average about 500°.

We are using activated aluminum catalysts combined with 5-10% of molybdic acid. The Moosbierbaum catalysts are prepared at Leuna.

The rotation between the HF reaction and the catalyst regeneration depends extensively upon the quantity and quality of the feed stock on the one hand, and upon the quality of the final product, on the other hand. In the course of time, we could render it more profitable. In the actual case, with Roumanian gasolines having a high paraffin content, the conversion period lasts about 17 hours; the catalyst regeneration, the unproductive

part of the process requires about 9 hours. On processing petroleum gasoline containing more naphtha, the ratio would become about 30:9 or better, according to the actual qualities.

The normal catalyst charge was 0.5-0.6 kg/l/h.

	<u>Crude Gasoline</u>	<u>HF-Gasoline</u>
Density at 20°C.	0.750	0.776
(Lowest Boiling Point °C.	62	44
(Vol. % up to 100°C.	18	36
Boiling Range (Vol. % up to 160°C.	95	94
(Highest Boiling Point °C.	165	164
API °C.	48.2	-0.6
APII °C.	59.5	64.5
Bromine Number	0.51	2.3
Olefins Vol. %	0.5	1.5
Aromatics Vol. %	14	54
Naphthenes Vol. %	44	8
C %	85.46	87.94
H %	14.53	12.16
Steam Pressure (Reid)	0.36	0.35
Lead Bomb Test mg	-	8
Octane Number	58.5	80
Octane Number + 0.12 Pb	79.0	91

Results

I am now going to discuss the principal results of the process.

The picture (Fig. 3) demonstrates how some properties of the gasolines were changed by the HF-processing. The aniline point I of 48.2°

would be sufficient for indicating that in this case we are dealing with a semi-paraffinic gasoline. Now I am referring to the aniline point of the HF-gasoline; it is  $-0.6^{\circ}$ . I want to add that the aniline point gives a very satisfactory criterium for a rapid first evaluation of the whole reaction. Practically, the operation of the convertors is checked by means of the aniline point, to a large extent.

I want further to remind you that not all of the crude gasoline undergoes the HF-process proper, but only 80-90% of it. The lightest fractions, up to about 70 or 80° are admixed to the HF-product ("HF-fraction") without further processing ("HF-gasoline").

The olefin contents rise from 0.5 to 1.5%. The lead bomb test is unobjectionable. The analyses refer to an HF-gasoline refined with sulfuric acid. After careful studies we have found it most suitable to refine petroleum HF gasolines, using very exiguous quantities of sulfuric acid. The table shows the aromatic contents to have risen from 14 to 54.

The change in the octane number is interesting. I should like to say that we have determined these values at Leuna; DVL found an octane number of 95 for the same gasoline.

The curves (Fig. 3) demonstrate the practical results of the variegated correlations between the qualities of the parent and of the final product.

I want to say here what I failed to mention when I discussed the equipment used for the I. and for the II. stage at the Moosbierbaum plant: The first-stage catalyst chamber measures 42 m<sup>3</sup> and the second-stage catalyst chamber measures 22 m<sup>3</sup>.

These curves (Fig. 3) are influenced by the following facts: The changes in output depending upon the qualities of the feed stock and of the final products, along with some important changes in the operating conditions. You are seeing here, the figures for the charges and for the ratio of the HF reaction period to the catalyst regeneration period, incl. the time needed for rinsing. The more paraffins are contained in the feed stock gasoline, the lower must be the charge chosen. This tendency effects still more decisively the time ratio. The same applies, of course, when different qualities of HF gasoline are to be obtained on using the same feed stock.

At this time we cannot discuss other important effects, such as the influence exercised by the boiling range of the crude gasoline, by the nature of the so-called residual gasoline which contains no aromatics and particularly by the catalyst.

22 m<sup>3</sup> Plant (Hbb II)  
 Crude Gasoline Feedstock  
 HF-gasoline output

— Crude Gasoline Having A.P. 45°  
 — " " " " 48°

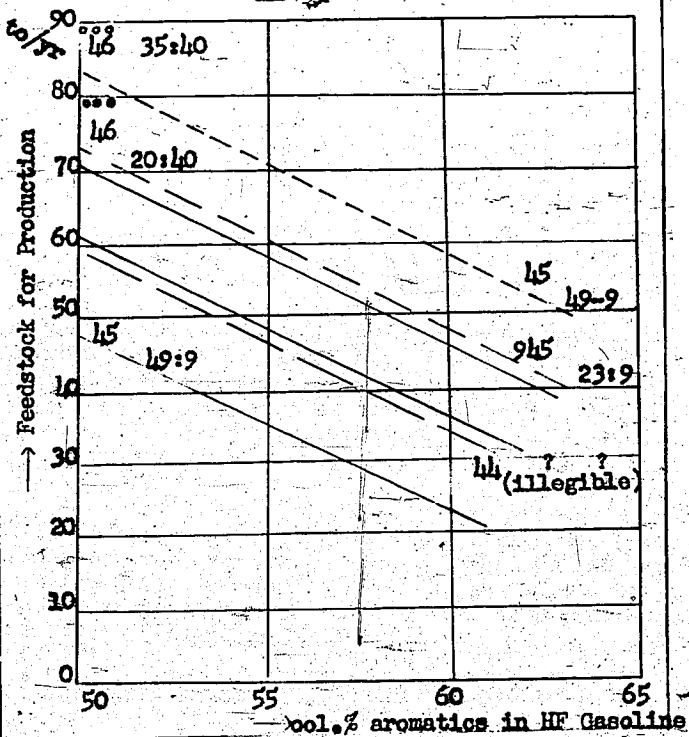


Figure 3



The following table shows in detail the principal and side products to be expected at Moosbierbaum. The Ammonia Plant at Merseberg is buying the crude gasolines directly from the individual Roumanian firms, since we failed to get the support of the "Wifo".

Moosbierbaum Stage I and II

Crude Gasoline AP 50°; HF-Gasoline 50 vol. % Aromatics

	STAGE I		STAGE II	
	42 m <sup>3</sup> to/yr	catalyst weight %	22 m <sup>3</sup> to/yr	catalyst weight %
Input, crude gasoline	80,000	100	60,000	100
Output, HF-gasoline	59,000	73.7	47,400	79
Redistilled residue	2,900	3.6	2,100	3.5
Coke	1,100	1.4	650	1.1
N <sub>2</sub>	950	1.2	850	1.4
C <sub>1</sub>	4,700	5.9	1,950	2.9
C <sub>2</sub>	4,350	5.4	2,250	3.8
C <sub>3</sub>	3,600	4.5	2,600	4.3
iC <sub>4</sub>	1,200	1.5	800	1.3
nC <sub>4</sub>	2,200	2.8	1,600	2.7

This table contains also the side products, which had not been mentioned hitherto. I want to stress that these figures may vary within a fairly wide range when the given conditions vary (aniline point of the feed-stock gasoline 50°; aromatics contents of the HF-gasoline 50 vol. %). I should like to add that the hydrocarbon side-products consist nearly exclusively of paraffin hydrocarbons. They are used as heating and motor gas.

This demonstrates again the greater efficiency of the tube furnace in comparison with the convertor, in regard to the ratios as well as in regard to the absolute quantities of the products obtained. (The difference in the time ratio which we have previously mentioned, is important; there: 10:10, and here: 17:10 hours.)

Investment and Operating Costs

A few data will be given concerning the investment and operating costs, including the energy requirements.

Moosbierbaum I and II (100,000 to/yr HF Gasoline)

Investment Costs

Total: RM 17,050,000.-  
contained therein

Preheaters for con-  
vertors 3,080,000

Electricity and op-  
erating equipment  
2,000,000

Piping 2,750,000

Scaffolding, girders  
installation 1,610,000

Storage tanks 1,080,000

Office Buildings  
1,125,000

Roads, trucks, etc.  
650,000

Air Shelter 980,000

Total: RM 105.60/to  
HF-gasoline

Auxiliary material  
11.10/t HF-gasoline

Operating costs  
66.00/t HF-gasoline  
(Energy 29 RM)  
(Repairs 20.50)

Amortization 28.50/t  
HF-gasoline  
(20% of 15,080,000)  
(7% of 1,970,000)

Conditions presumed  
Crude gasoline AP 51°  
Yields 73%

Total: RM 29/to  
HF-gasoline

Steam 2.7 t/t

High tension  
steam 258 kwh/t

Water 70 m<sup>3</sup>/t

The investment costs will appear to be very high. However, it must be taken into consideration that we were building on a tract of land which had not been opened up; when the first stage was planned, the general conditions were not such that the need for expansion could be foreseen; thus, the second stage had to be build quite separately, too.

The operating costs are cautiously calculated. A very poor feed stock was chosen as the basis of our calculation; that is why we assumed that it would yield only 73% of HF-gasoline. This calculation gives a cost of 105.60 RM per ton of gasoline.

When the yields increase the specific operating costs may be expected to decrease. Our low yearly output and our expanding in separate steps affected the prices adversely, too. At Moosbierbaum, we are also

paying high prices for energy. Furthermore, the Moosbierbaum plant operates isolated from any similar large work, such as hydrogenation units.

### Catalytic Cracking

Our laboratory is not only studying the use and refinement of petroleum products; already before the war started, and now again, we have extensively investigated the problem of catalytic cracking. This process, too, is an intermittent process used for converting a part of the middle oils boiling up to 400°C. into gasoline. When the process is adequately controlled, it yields good aviation fuels, too.

Middle oil vapors are passed without pressure at about 400° over a synthetic aluminum silicate catalyst, without any hydrogen admixture. More coke is formed. At the HF-process, 1-1 1/2% of coke were formed; with catalytic cracking, 3-5% of the feed-stock are converted into coke. Therefore, the operating periods are much shorter, only 15-30 minutes. In comparison thereto, the regeneration and rinsing periods are much longer than with the HF-process, namely about 2-4 times as long as the operating period.

### Yields

Again, there is an extensive correlation between the output and quality of the catalytic cracking products and the properties of the middle oils. Oil having a naphthene base is easiest to work up; oils containing pre-eminently paraffins are hardest to work up. They yield a lower gasoline output, while the portion of gaseous hydrocarbons is increased at the same time.

Furthermore, the quality of the gasolines produced is somewhat inferior to that of the naphthene oils.

The yields to be expected on working up a pre-eminently naphthene middle oil average:

Gasoline up to 165°	25 - 30%
C <sub>3</sub> and C <sub>4</sub> Hydrocarbons	10 - 15%
H <sub>2</sub> , methane and ethane (ethylene)	2 - 3%
Coke	3 - 5%
R-oil/Diesel oil	50 - 58%

Production Scheme

(Moosbierbaum)

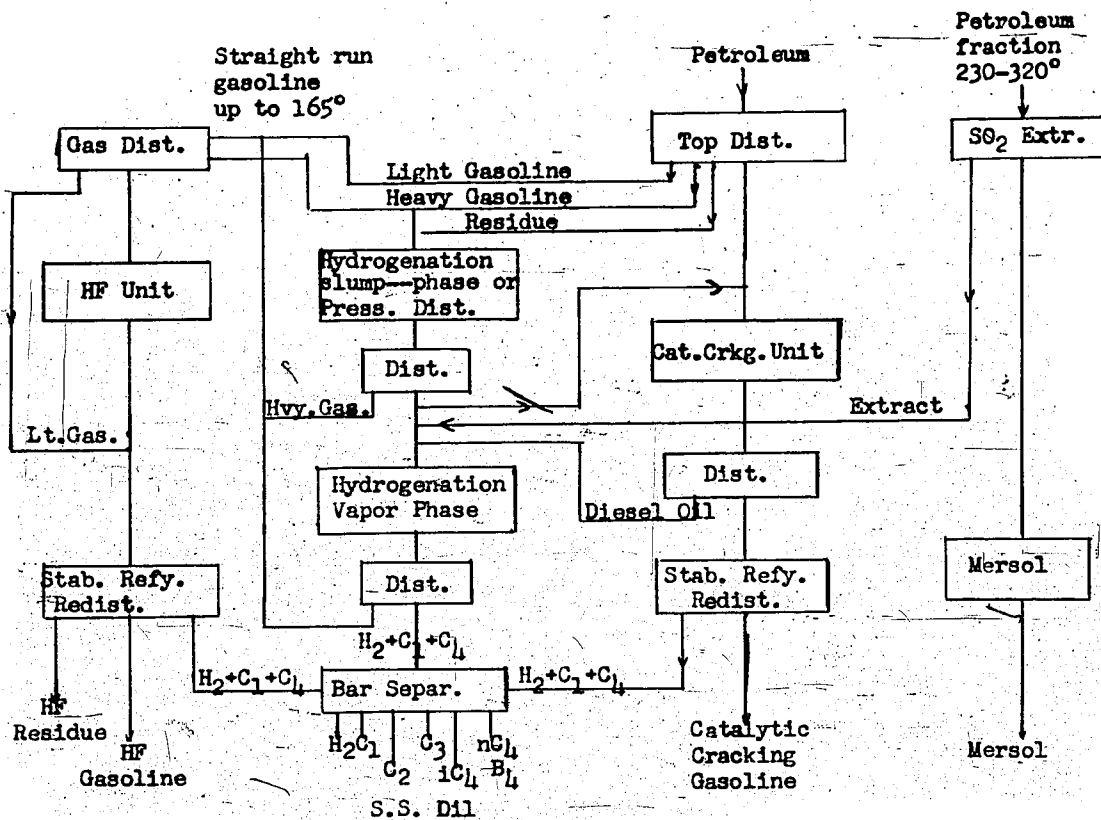


Figure 4

### The KK-Gasoline

The catalytic cracking gasoline has a good octane number (MM) of 78-80, with an addition of 0.12 lead it reaches about 90, although it contains much less aromatics (25-30%, while the HF gasoline contains 50-55%).

The olefin contents are higher in cracking gasoline than they are in HF-gasoline. But they are absolutely harmless uni-olefins. The storage stability of cracking gasoline is excellent.

### Overcharging Capacity

Authentic DVL data concerning the super-charging capacity of the KK gasolines are not yet available. The results of tests made at our own testing unit at Leuna demonstrated their excellent behavior in the aviation motor. The super-charging curve lies considerably higher than that of B4 gasolines.

This desirable property of this gasoline is to a large extent due to the fact that the paraffin hydrocarbons in the cracking gasoline are widely branched.

### Hydrocarbon Gases

Because of the peculiar composition of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons formed, it seems very desirable to follow up the cracking process with an alkylation process, thus causing a further amelioration of the quantity and quality of the gasoline.

Figure 4 shows the plans made in regard to our future expansion at Moosbierbaum.

Kaufmann

M. Beth

MB:hlm  
7-9-47