AVIATION GASOLINE BY CATALYTIC CRACKING.

The following four catalytic cracking processes were experimentally investigated:

1. Fixed-bed catalytic cracking.

2. Moving-bed catalytic cracking.

3. Fluid-catalyst operation in the gas phase.

4. Fluid-catalyst operation in the liquid phase.

Fixed-bed Catalytic Cracking Process.

Insulated, unheated reactors of catalyst capacities of 0.35 cubic feet, 1.8 cubic feet and 3.5 cubic feet were used in the development of this process, especially the study of catalyst regeneration. A semi-commercial unit with a catalyst capacity of 35 cubic feet will be started up shortly.

Since the purpose of the development work on catalytic cracking was the manufacture of aviation gasoline, the use of natural, activated clays and of synthetic catalysts on the basis of magnesium silicate was excluded. It was found that only pure Al_2O_3-SiO_2 catalyst without the addition of other metals or their oxides were suitable.

The cracking catalyst used at present has a molar ratio of Al_2O_3 : SiO_2 of 1 : 9 and lies outside the patent claims of Houdry; it is especially characterized by its method of preparation. The activity of this catalyst could be considerably improved in the course of the last year. In contrast to the natural clays, the synthetic aluminum silicate catalysts are sensitive to water vapors.

The progress made from 1940 to the present time, especially the considerable improvement in the activity of the catalyst, is shown in Figure 1.

Conversion periods of 1 - 3 hours as compared to 20 - 30 minutes used previously still gave higher yields of gasoline than the former short conversion period. At the same time, the quality of the gasoline is improved as indicated in Figure 2.

It can be seen from this diagram that the olefin content as expressed by the bromine number could be reduced to a small fraction of the previous figure.

Figures 1 and 2 further indicate the effect of the length of the conversion period and of the space velocity on the production of gasoline as well as on its quality; lengthening of the conversion period and increase in the space velocity result in a decrease in the gasoline yield, an increase in the olefin content and a change in the type and quantity of by-products formed.

The cracking reaction is slightly endothermic and requires about 56 - 54 B. t. u. per pound of feed stock. The low heat requirement permits easy operation in unheated reactors. The product distribution is controlled by the length of the

conversion period, the space velocity, the temperature and the charge stock.

The reaction products formed, viz., stabilized gasoline (boiling up to 329°F.), liquefied gas, dry gas and coke are taken as 100 in the following Figures 3 - 5. Increasing the space velocity and lengthening the conversion period improves the product distribution, whereas the effect of raised cracking temperatures is unfavorable. It should be emphasized that the total conversion decreases with increasing space velocity and increasing length of the conversion period but increases when the temperature is raised.

The minimum in the carbon deposit curve in Figure 5 is explained by the fact that when the temperature is kept too low, unvaporized oil constituents are deposited on the catalyst which leads to increased carbon deposition. The minimum of the curve lies at the optimal cracking temperature (716 - 788°F.).

Which cracking condition should be selected for each individual case depends on the type of charging stock and must be determined experimentally. Naphthenic oils are best suited for this process and purely paraffinic oils give low gasoline yields and unfavorable product distribution.

The attached table shows the product distribution and data on the quality of gasolines produced at constant gasoline yields. It can be seen that prolongation of the cracking period and simultaneous lowering of the space velocity results in lowering of the carbon formation and has a favorable effect on the ratio of conversion to regeneration period.

The raised cetene number of the recycle oil should be noted because it indicates the possibility to process this material for the manufacture of diesel oil.

The average distribution of individual hydrocarbons in the liquefied and dry gas is shown in the following table:

H_2	1% by weight
CH_4	2% " "
$C_2H_4 + C_2H_6$	6% " "
C_3H_6	8% " "
C_3H_8	19% " "
n + isoC_4H_8	5% " "
n-C_4H_{10}	10% " "
isoC_4H_{10}	49% " "

The portion of C_1 and C_2 hydrocarbons, including hydrogen, accordingly amounts to only 10% of the total gas.

With respect to alkylate production it is important that isobutane represents about 50% of the total gas, or 77% of the total butanes.

The quality of the catalytically-cracked gasoline is affected by the operating conditions. Higher throughput, increased temperature and extended

cracking periods adversely affect the quality of the gasoline. When gasoline is made from natural petroleum, the olefin content amounts to between 5 - 10% and storage stability is good. The content of aromatics amounts to about 20 - 25% by volume, the Motor Method octane number of the clear gasoline is 76 - 78 and about 90 with 4.5 cc. TEL per gallon.

Gasolines made by cracking of hydrogenation middle oils from brown coal and coal tar have a higher content of aromatics (about 30%) and a lower olefin content (between 2 and 5%). The storage stability is also good. The octane numbers are about 3 units higher. The supercharging characteristics of catalytically-cracked gasoline are shown in Fig. 6. The diagram compares the catalytically-cracked gasolines with a hydroformed gasoline and a regular aviation gasoline. The concentration of aromatics in these four gasolines is as follows:

Hydroformed gasoline	50% aromatics
Catalytically-cracked gasoline from middle oil from the high-pressure hydrogenation of coal tar	30% "
Catalytically-cracked gasoline from Roumanian crude oil	22% "
Aviation gasoline - approximately 10% "

The curves indicate that the aromatic content is of extreme importance with respect to the position of the performance curve; the catalytically-cracked gasoline from middle oil from coal tar hydrogenation approaches the performance of hydroformates. In spite of the fact that the catalytically-cracked gasoline from Roumanian naphtha has an aromatic content twice as high as that of regular aviation gasoline, the position of the performance curve is only slightly better. Numerous engine tests with catalytically-cracked gasolines of various origins seem to indicate that the most important factor for good performance in the supercharged engines is the amount of newly-formed aromatics rather than the branching of the paraffins. The quality of the non-aromatic portion of a cracked gasoline is dependent less on the cracking process itself than on the chemical composition of the charge stock.

The important ratio of conversion time to regeneration time is determined by the amount of carbon deposited on the catalyst and the conditions chosen for regeneration. In the subject experiment the heat of combustion of the carbon is removed only through the regeneration gas. To accomplish this the quantity of gas required is 3,000 - 5,000 volumes of gas per volume of catalyst. The maximum temperature to which the catalyst is exposed should not exceed 1,022°F. since otherwise the activity of the catalyst is lowered. The necessity to use such a large quantity of regenerating gas leads to the design of reactors with several catalyst beds. The catalyst beds are connected in series during the conversion period and parallel during the regeneration period in order to reduce resistance to gas flow.

The ratio of conversion to regeneration time lies between 1 : 1 and 1 : 3, according to experiments in a reactor with a catalyst volume of 3.5 cubic feet. The sensitivity of the catalyst to water vapors is an important consideration in the regeneration process. According to analysis, the approximate composition of the carbon deposit is C_1H_1 and, consequently, water is formed during regeneration. Since, on the other hand, large quantities of regenerating gas

make it necessary to carry out the regeneration in a cycle process, the water content in the recycle gas can reach about 50% if the water vapors are not removed by condensation and, consequently, the activity of the catalyst is affected. For this reason, separation of the water vapors is necessary and this affects the economics of the process adversely.

Moving-bed Catalytic Cracking Process.

It has been possible to raise the activity of the catalyst considerably. By special procedures used in its manufacture an unexpected high mechanical strength was obtained first about a year ago. The experience in the shaping of spheres gained in the manufacture of catalysts for butane dehydrogenation could also be utilized and small, regularly-shaped catalyst spheres of extreme resistance to attrition have been produced. These advances in catalyst preparation led to investigations on catalytic cracking with moving-bed catalysts. A semi-commercial reactor was developed which is shown in Figure 7. The catalyst spheres pass through a regeneration, purging and reaction zone. The regeneration zone is preceded by a tubular preheater in which the catalyst which comes from the reactor is heated to the temperature required for starting regeneration; part of the combustion of the carbon deposit by the regenerating gas takes place already in the preheater and the gas is not recycled. Since the hydrogen-containing portions of the deposit burn first, damage of the catalyst by water vapors would not even be experienced in case that hot recycle gas is used. After passing through the purging zone the catalyst spheres are introduced into the reactor through a double pocket-valve arrangement. After the catalyst has passed through the reactor it is freed from residual oil and gasoline in the purging zone and is removed from the reactor through a second double pocket-valve arrangement. By maintaining definite pressures in the various zones, the mixing of the different gas streams is avoided. The experimental reactor has been in operation for over four months. During this time no difficulties with the pocket-valve arrangement have been experienced.

It was found in numerous experiments that the loss by attrition of the catalyst amounts to 0.4 - 0.6 pounds per barrel of gasoline produced.

The yield and quality of the gasoline is approximately equal to that obtained in the fixed-bed process and the moving-bed process shows satisfactory flexibility with respect to various charge stocks. By changing the length of the cracking period, i.e., by changing the speed of moving the catalyst as well as by a difference in the space velocity, it is possible to keep the amount of carbon deposited on the catalyst approximately constant so that the same operating conditions can be maintained in a unit, especially with respect to regeneration. The pocket-valve type of process has the advantage over the fixed-bed type that it can be operated continuously and control valves operated at high temperatures as well as additional equipment for their automatic control becomes unnecessary.

Fluid-Type Catalytic Cracking Process.

Investigational work on the operation of the catalytic cracking process with fluid-catalyst in the vapor phase has been resumed since it became possible to produce satisfactory aviation gasoline by this process, provided that a sufficiently high catalyst concentration can be maintained in the reactor. However, equipment design has not yet sufficiently advanced to make definite claims for this kind of process.

Fluid-Type Catalytic Cracking in the Liquid Phase.

The work on this process can be summarized as follows:

For continuous operation a coiled pressure pipe was used both as heater and as reactor; the volume of the coil could be kept small since the throughput was very high. The oil was mixed with 3 - 10% catalyst and processed at about 842 - 932°F. and a pressure of 580 - 1,470 psi with a space velocity of 7 - 10 gallons per volume per hour. Natural clays were used as catalyst. As compared to thermal cracking, no increase in the yield is obtained in this process but the quality of the gasoline produced is considerably better. The process is especially suited for purely paraffinic oils, e. g., Kogasin from the Fischer-Tropsch synthesis. A greatly-improved product distribution is obtained as compared to cracking with a fixed-bed catalyst. The products made by this process, however, cannot be used for high-grade aviation fuels and, consequently, the interest in this method has lessened.

The attached flow-sheets show four possibilities to use natural petroleum for the manufacture of high-grade aviation fuels. The figures used in the diagrams are only estimates but they are based on the extensive material obtained in numerous individual experiments.

1. Processing of crude oil by pressure distillation, catalytic cracking and hydroforming. Besides aviation gasoline, much diesel oil, lubricating oil and fuel oil is obtained.

2. Crude oil processing by hydrogenation, catalytic cracking of straight run middle oil and hydroforming. The main product is hydroformed gasoline.

3. Crude oil processing by hydrogenation, catalytic cracking of straight run and sump-phase middle oil and hydroforming. In this process considerably more catalytically-cracked gasoline is obtained in spite of the fact that large amounts of hydroformate are also made.

4. Crude oil processing by hydrogenation, catalytic cracking of straight run sump-phase middle oil and cracked recycle stock (with simultaneous use of hydrogenation) followed by hydroforming. This method of operation produces the largest amount of catalytic gasoline.

The following statements can be made with respect to the design of a commercial unit: Sufficient experimental data are available for the design of a fixed-bed unit. The development of the moving-bed catalytic process has not yet reached completion. However, it is believed that this will be possible in a short time. The very promising process using a fluid-type catalyst will certainly require a long time until it is completely developed and ready for use on a commercial scale.
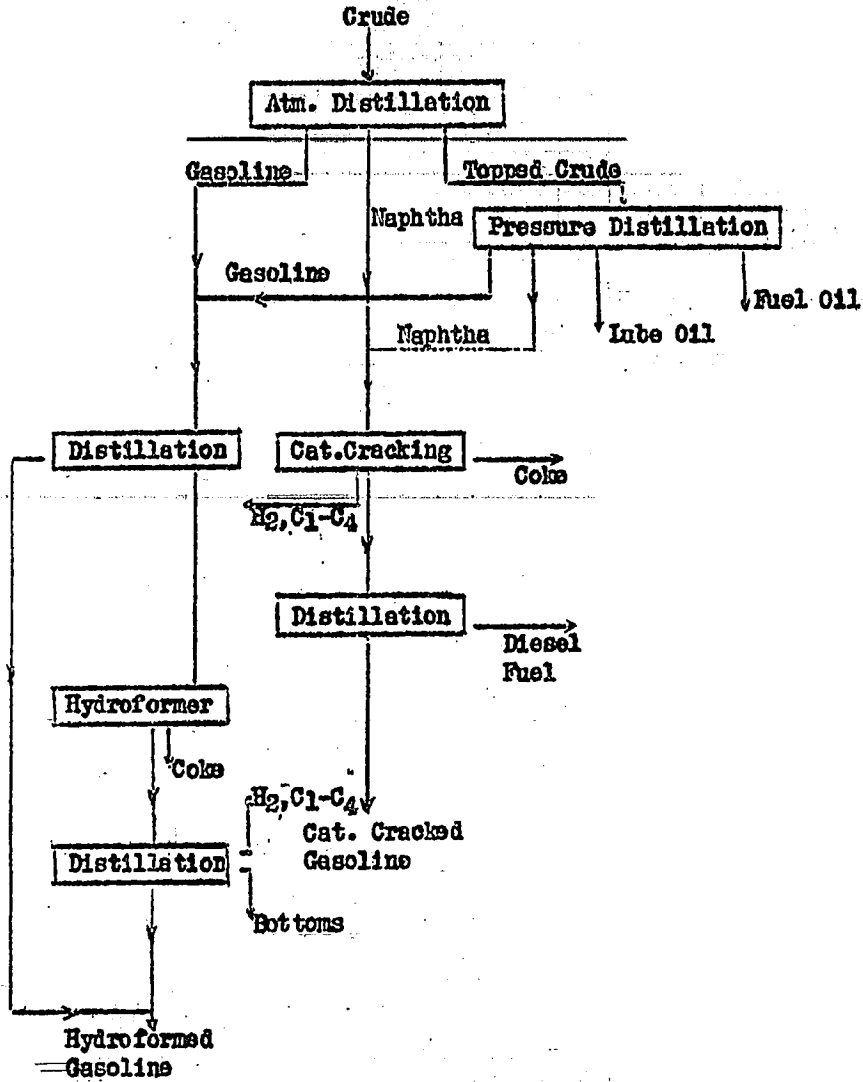
Operating Conditions for Maximum Gasoline Yield

Charge Stock: Roumanian mixed-base gas oil, API gravity 32.3, IBP 329°F.

Operating Conditions			Yield % by Wt.					Inspection Data of Gasoline					Inspection Data of Recycle Stock			Ratio of Carbon to Catalyst	
Temp. °F.	Space Velocity vol/vol/hour	Cracking Time, Min.	Gasoline 329°F. E.P. 6# Reid	Liquefied Gas	Dry Gas	Carbon Deposit	Recycle Stock IBP 329°F.	Octane No.	Bromine No.	Aniline Point °F.	Olefins & Aromatics % by Vol.	API Gravity	Cetane No.	Aniline Point, °F.	API Gravity	lb. carbon per cu.ft. Catalyst	Carbon % by Wt. of Catalyst
788	1.0	20	30	12-14	1.5-2	5-6	40-50	78	6.5	109	24.4	63.7	32.0	92	29.6	0.89-1.07	2-2.4
788	0.6	60	30	13-14	2-2.5	4-4.5	48-50	78	6.8	109	26.3	62.9	32.5	93	29.2	1.29-1.45	2.86-3.2
788	0.5	120	30	13.5-14.5	2.5	3-3.5	49-50	78	8.2	104	26.9	61.6	36.0	95	28.2	1.61-1.88	3.6-4.2
788	0.4	180	30	14-15	2.7	2.7-3	50	78	8.6	102	28.8	61.1	38.5	96	28.0	1.74-1.93	3.9-4.3

PRESSURE DISTILLATION, CATALYTIC CRACKING AND HYDROFORMING

Crude
↓

Atm. Distillation

Gasoline — Topped Crude

Naphtha → Pressure Distillation

Gasoline

Naphtha → Fuel Oil

Lube Oil

Distillation — Cat. Cracking → Coke

H_2, C_1-C_4

Distillation → Diesel Fuel

Hydroformer

Coke

H_2, C_1-C_4 → Cat. Cracked Gasoline

Distillation

Bottoms

Hydroformed Gasoline

	% by wt.
Cat. cracked gasoline	13.7
Hydroformed gasoline	13.1
Diesel fuel	24.6
Lube oil	13.6
iC_4	4.3
nC_4	1.7
H_2	0.3
C_1-C_3	4.8
Residual oil	0.6
Heavy fuel oil	20.7
Coke	2.6
Sludge	

HYDROGENATION, CATALYTIC CRACKING OF STRAIGHT-RUN NAPHTHA, HYDROFORMING

Crude

Atm. Distillation

Topped Crude

Gasoline   Naphtha

Sumpphase Hydrog.

H_2, C_1-C_4 Cat. Cracking

C_1-C_4

Separator Residue

Cat.cracked gasoline   Distillation

Distillation

Recycle stock

Middle oil

Sludge

C_1-C_4 Vap. Phase Hydrog.

Middle Oil

Distillation

Distillation

Hydroformer   Coke

Stabilizer H_2, C_1-C_4

Bottoms

Hydroformed Gasoline
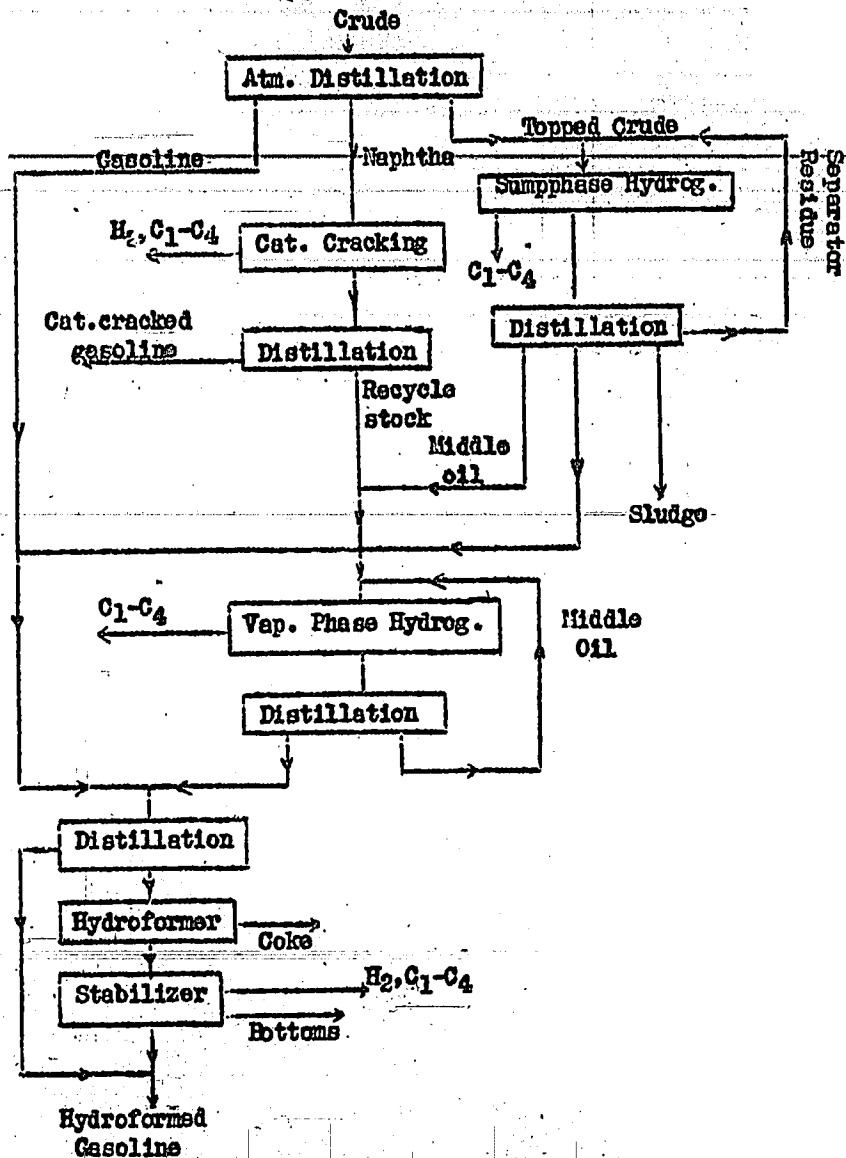
	% by wt.
Cat. cracked gasoline	12.0
Hydroformed gasoline	52.0
Diesel fuel	-
Lube oil	-
iC_4	9.0
nC_4	5.3
H_2	1.0
C_1-C_3	15.9
Residual oil	2.3
Heavy fuel oil	-
Coke	2.3
Sludge	0.2

HYDROGENATION, CATALYTIC CRACKING OF STRAIGHT-RUN AND SUMP PHASE NAPHTHAS, HYDROFORMING

Crude
↓

| Atm. Distillation |

Gasoline　　　　　　　　　　Topped Crude

Naphtha

H_2, C_1-C_4 ← | Cat. Cracking | Coke　　　| Sumpphase Hydrog. |

C_1-C_4　　　　Sep.

Cat.cracked Gasoline　| Distillation |　　　| Distillation |

Gasoline　　　　　Sludge

C_1-C_4 ← | Gas phase Hydrog. |

| Distillation |

Gasoline

| Distillation |

| Hydroformer | Coke →

H_2, C_1-C_4

| Stabilizer |　　Bottoms →

Hydroformed Gasoline

Sep. Residue
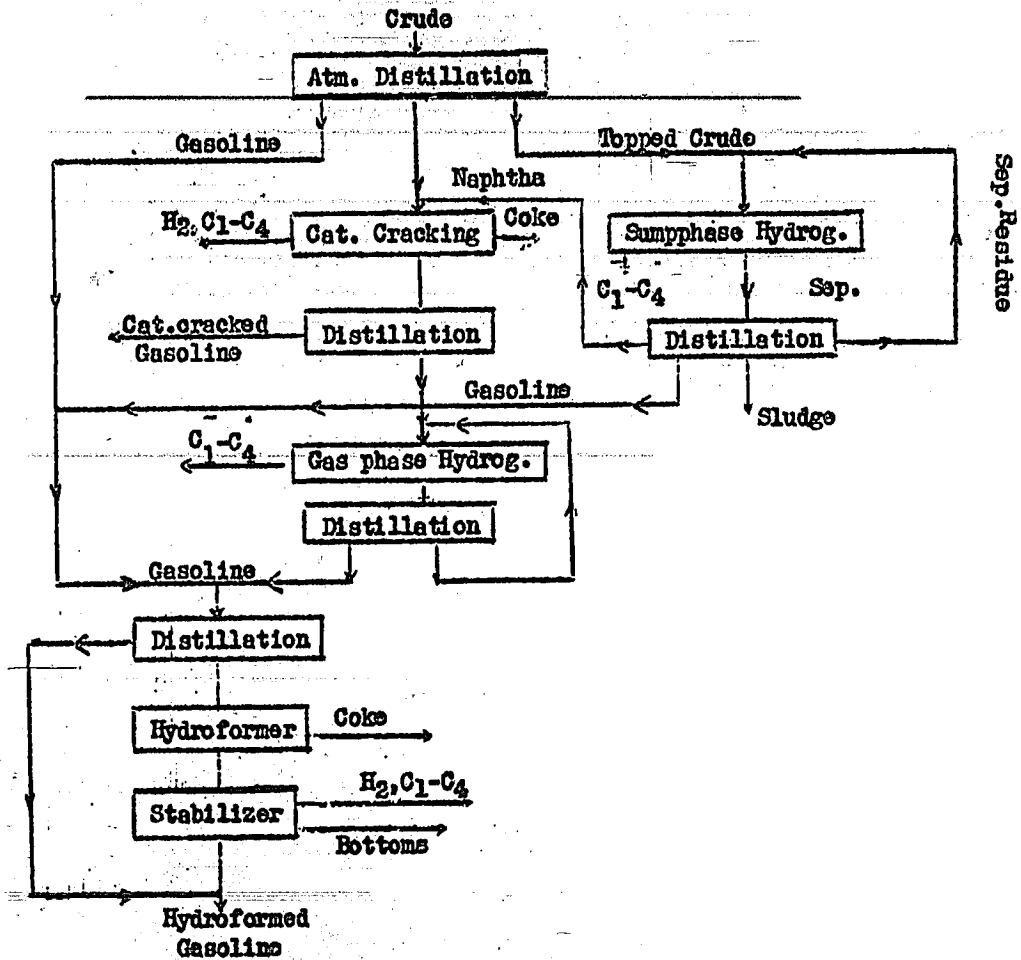
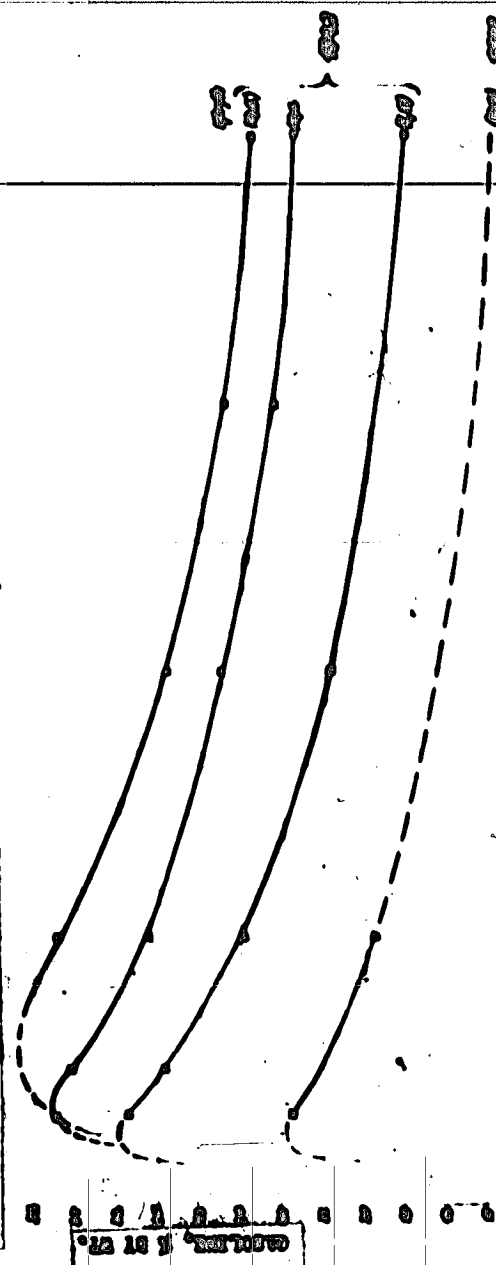|	% by wt.
Cat. cracked gasoline	20.9
Hydroformed　"	42.2
iso-C_4	9.8
n-C_4	5.1
H_2	0.9
C_1-C_3	15.7
Residual Oil	1.8
Coke	3.4
Sludge	0.2

HYDROGENATION, CATALYTIC CRACKING OF STRAIGHT-RUN AND SUMP PHASE NAPHTHAS AND RECYCLE STOCK, HYDROFORMING

Crude

Atm. Distillation

Gasoline

Topped Crude

Sep. Residue

Naphtha

H_2, C_1-C_4

Cat. Cracking

Sumpphase Hydrog.

Coke

C_1-C_4

Cat. cracked Gasoline

Distillation

Distillation

Sludge

Hydrog. without cracking

Hydrogenated Recycle Stock

Distillation

Hydroformer

Coke

Stabilizer

H_2, C_1-C_4

Bottoms

Hydroformed Gasoline
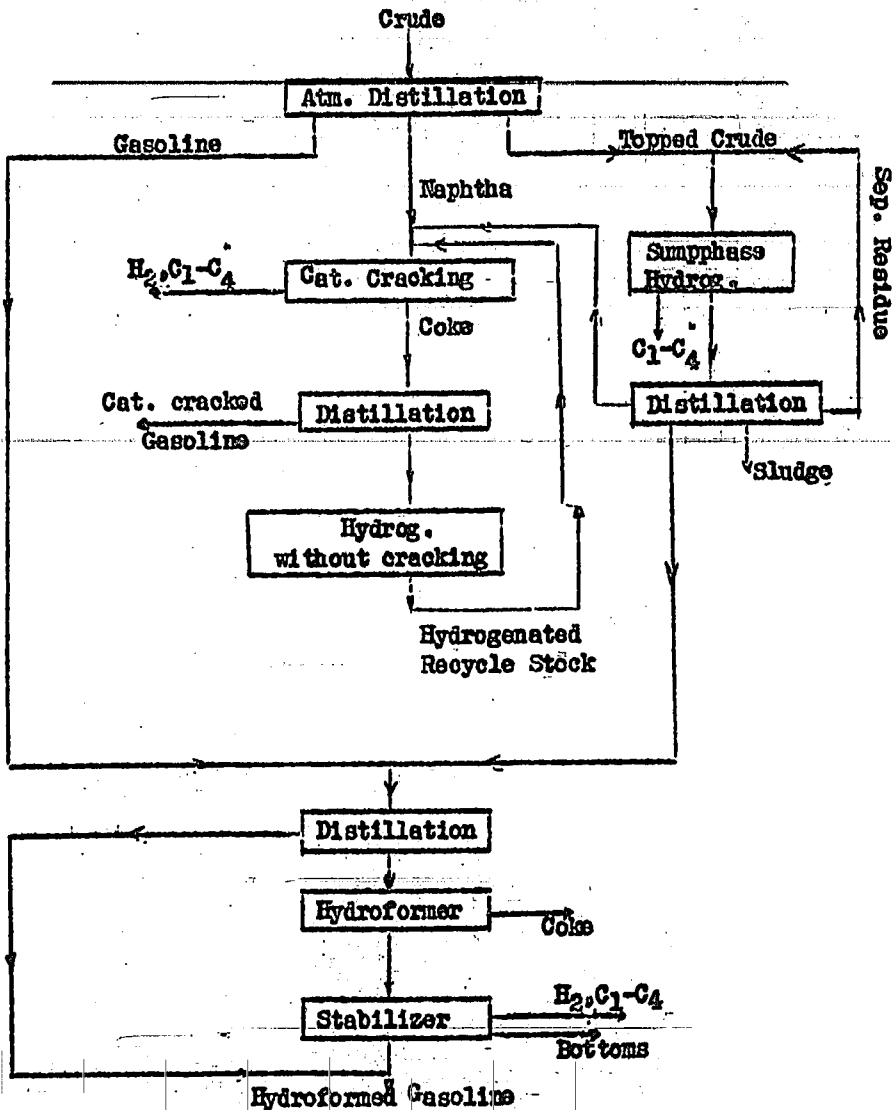
	% by wt.
Cat. cracked gasoline	43.2
Hydroformed "	19.6
iso C_4	10.8
n-C_4	4.6
H_2	0.5
C_1-C_3	14.5
Residual Oil	0.8
Coke	5.8
Sludge	0.2

GASOLINE YIELD AT VARIOUS SPACE VELOCITIES

(STABILIZED AVIATION GASOLINE E.P. 329°F)

OLEFIN CONTENT (BROMINE NO.) AT VARIOUS SPACE VELOCITIES

CRACKING TIME, MIN.

PRODUCT DISTRIBUTION FOR VARIOUS CRACKING TIMES
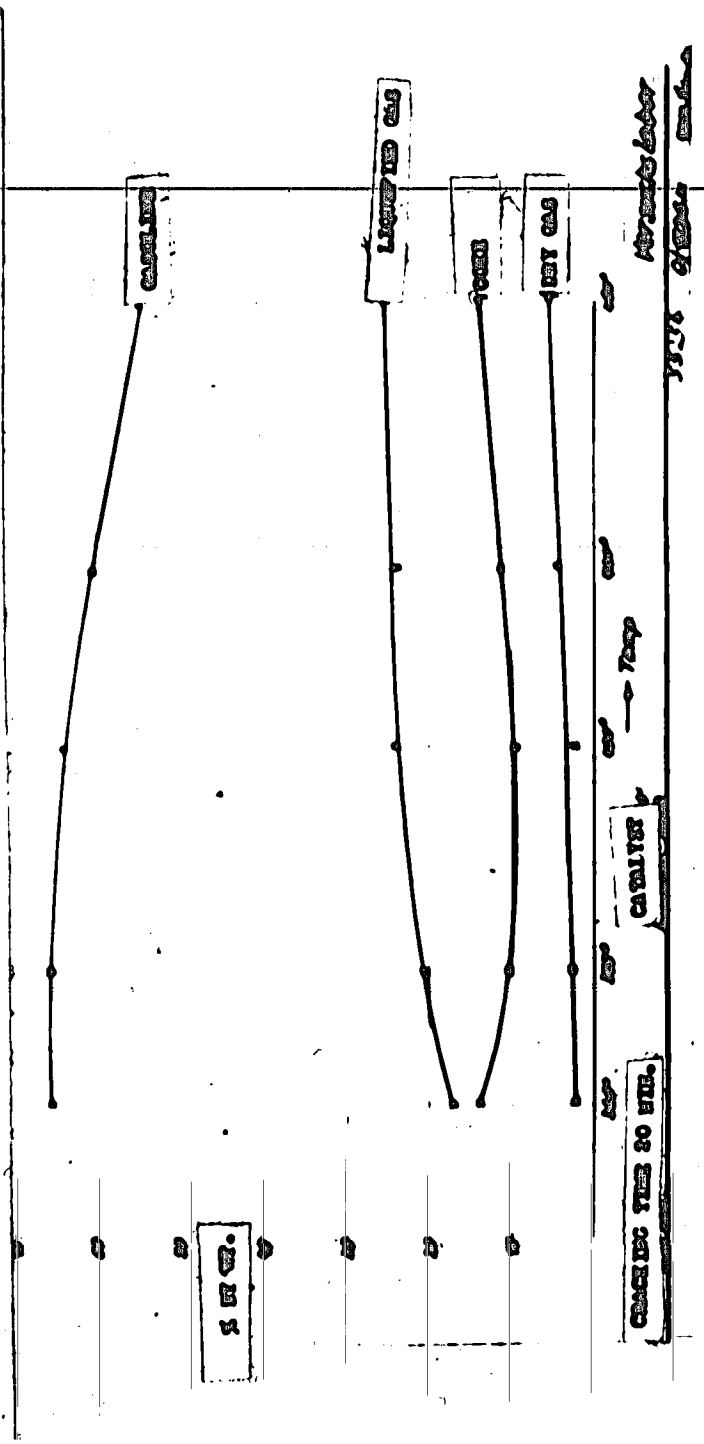
PRODUCT DISTRIBUTION AT VARIOUS SPACE VELOCITIES

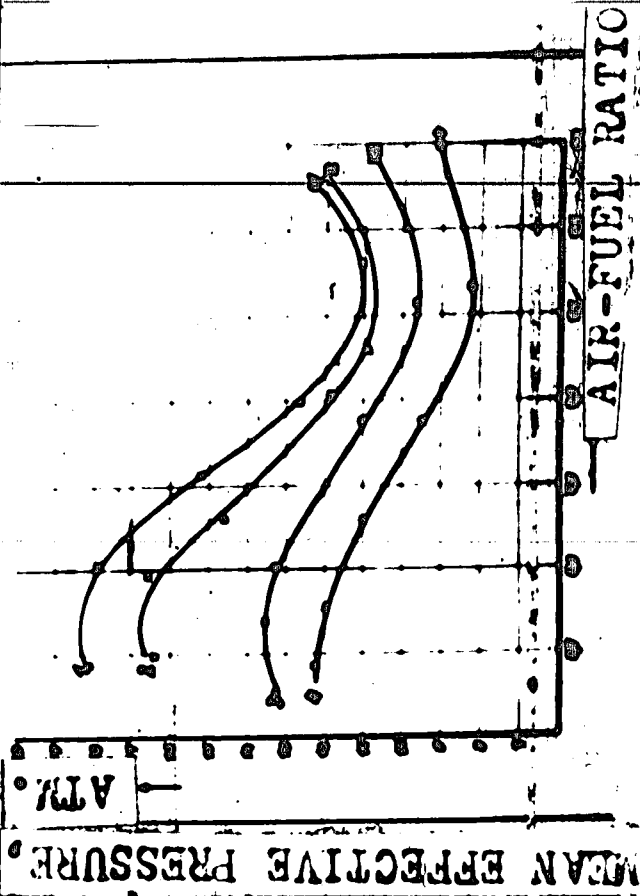# PRODUCT DISTRIBUTION AT VARIOUS CRACKING TEMPERATURES
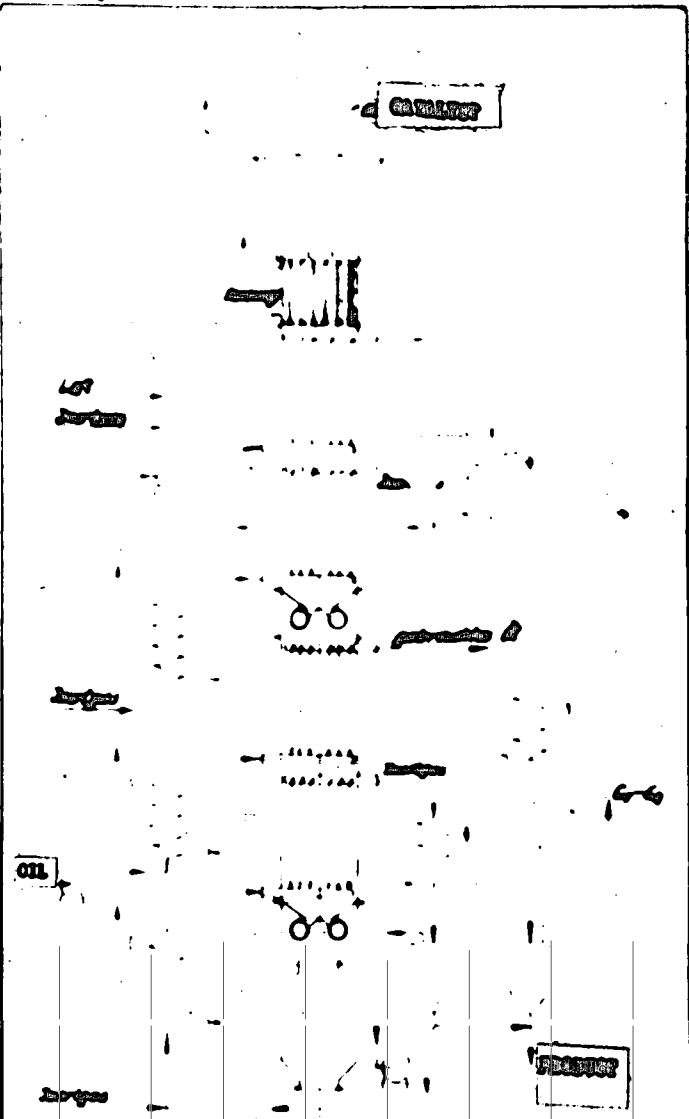
PERFORMANCE

Tafel 7

266°F.

1. HYDROFORMED GASOLINE
2. CAT. CRACKED GASOLINE FROM HYDROGENATED COAL MIDDLE OIL
3. CAT. CRACKED GASOLINE FROM NATURAL CRUDE
4. HYDROFORMED GASOLINE + 4.5 cc TEL

MEAN EFFECTIVE PRESSURE

ATM.

AIR-FUEL RATIO