

CATALYTIC CRACKING OF HYDROCARBON OILS

In the spring of 1938 development work on catalytic cracking of hydrocarbon oils was started. The project was to be of a short-time nature since the experience of the contract partners in the U. S. was available. Catalysts and processing method were to be chosen in such a way that the patents of the Houdry Process Corporation were not violated.

The testing of catalysts was carried out in 8 small reactors with a catalyst capacity of 6.7 cu. inch and 10.4 cu. inch. 4 extended investigations were undertaken in 8 tubular reactors with a catalyst capacity of 103 cu. inch. Operation was discontinuous since each cracking period had to be followed by a regenerating period for the catalyst. Testing of the catalyst was carried out under identical conditions with the same oil without regard to product distribution. The cracking temperature for natural catalysts (activated clays) was kept between 842 - 860°F. and 752 - 797°F. for synthetic silica gel-aluminum oxide catalysts. The length of the cracking period for natural as well as synthetic catalysts was usually 30 - 60 minutes, but in special cases 2 hours, whereas the regeneration period was about twice as long. The space velocity for the synthetic catalysts was about 2 - 3 times that of the activated clays. Cracking with finely-divided catalyst in the vapor phase has been studied in equipment of varying design but these experiments are only continued at the side since cracking with finely-divided catalysts in the liquid phase under pressure has shown considerably more favorable results. The latter method was especially successful for the cracking of oils rich in hydrogen because, in this case, it permits extremely high throughput rates with low gas and coke formation and very high yield.

Natural Catalysts.

Some German clays, especially Terrana and Frankonit, could be activated by treatment with acids or salt solutions, especially chlorides and sulfides of magnesium, aluminum and manganese, so that they reach the cracking efficiency of Superfiltrol. In some cases the activated clays even exceeded the activity of Superfiltrol. The best catalyst of this type was found to be Frankonit activated with sulfuric acid or magnesium chloride solution. Its superiority consisted mainly in greater strength and lower sensitivity to temperature.

Synthetic Catalysts.

The combination silica gel-aluminum oxide was found best. The activity is strongly dependent on the pore size of the silica gel and suitable manufacturing methods for highly active catalysts were developed. Mechanical homogenizing of separately precipitated components seems to be especially desirable with respect to activity, resistance to deformation and economics of manufacture. The most active catalyst, whose strength, however, was not always satisfactory, surpassed the efficiency of a number of American products with respect to cracking efficiency. The silica gel-aluminum oxide catalyst, containing its constituents in the ratio patented by the Houdry Process Corporation, does not offer any advantages and the patent, therefore, need not be considered as a limitation.

Under suitable reaction conditions these highly active silica gel-alumina catalysts gave a similar product distribution as the activated clays. For instance,

from 100 parts by weight of West Texas gas oil, the following products were obtained with a loss of 2.1% using the $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst #1728 66/3B7.

Stabilized Gasoline: 33.7% by Weight (39.7% by Volume)

Recycle Stock: 50.6% by Weight

$\text{C}_3 + \text{C}_4$ Hydrocarbons: 8.2% by Weight

Gas: 1.7% by Weight

Coke: 3.7% by Weight

Besides foreign crudes, German petroleum fractions and fractions from the Fischer-Tropsch synthesis (Kogalin II) and products from the hydrogenation of brown coal were investigated. The results obtained with the latter 2 materials deviated partly from those obtained with petroleum fractions. Cracking of recycle stock gave, in all cases, less favorable results than cracking of the fresh feed.

Experimental Work.

Small-Scale Apparatus.

For catalyst testing 8 small reactors with a catalyst capacity of 6.7 cu. inch and 10.4 cu. inch, respectively are used. 4 reactors of equal size are arranged in a single electrically-heated aluminum block. The temperature is measured at 2 points in the aluminum block. The charge first enters an evaporation and heating zone which is packed with brass pellets and then passes in the vapor phase at the desired cracking temperature into the catalyst tube which immediately follows the preheater tube. The liquid reaction products are collected in glass receivers cooled with ice or CO_2 and methanol whereas the gas is collected in Mariotte bottles. The catalyst can be regenerated with air-nitrogen mixtures. Catalyst testing is carried out with the same charge stock under identical conditions. The assembled apparatus is shown in Figure 1.

Reactors with a Catalyst Capacity of 104 cu. inch (1.7 liters).

For more extensive investigations of catalyst and charge stock, 8 tubular reactors with a catalyst capacity of 104 cu. inch are available. The catalyst space has a diameter of 2.2 inches and a length of 2.6 feet. 3 thermocouples are arranged on the outer surface of the reactor and 4 are placed inside the reactor. The charge is injected into a preheater coil by means of a gear pump which can be controlled by changing its speed. The preheater coil is placed in an electrically-heated lead bath. The activated clays are used in the form of pellets with a height of 0.1 inch and a thickness of 0.16 inch; the synthetic catalysts are used as irregular pieces of the same size. In case that the latter are shaped in a press, a thickness of about 0.16 inches is maintained. The oil vapors enter the electrically heated reactor from the bottom. The product receiver is cooled with circulating brine and the receiver for low-boiling hydrocarbons is cooled with carbon dioxide and methanol. The gas is measured by means of gas meters. Regeneration usually is carried out with air-nitrogen mixtures of a pressure of 44 psi. The gases pass first through a silica gel dryer, but regeneration can also be carried out with steam-air or CO_2 -air mixtures. At the end of the cracking period the oil remaining on the catalyst and in the apparatus is recovered either by purging with steam or evacuation, depending on the type of catalyst.

Figures 2 and 3 show the experimental unit.

Regeneration of Fixed-Bed Catalysts.

In the first experiments with various Terrana clays and activated clays, regeneration was carried out with steam-air mixtures at atmospheric pressure. The regeneration times were sufficiently long so that complete removal of the carbon deposit was possible without difficulty.

When experiments were started with silica gel-aluminum oxide catalysts, it was soon found that the catalyst had to be regenerated in the absence of water vapors. At the same time, the application of slightly elevated pressures during the regeneration was started and this facilitated carbon combustion and temperature control. Regeneration is now carried out as follows: After the cracking period oil vapors are removed by purging and a nitrogen pressure of 44 psi. is obtained by means of a throttle valve at the reactor outlet under simultaneous maintenance of the desired gas velocity. Subsequently, air is added and the temperature is kept close to the max. permissible catalyst temperature by regulating the oxygen concentration. As soon as possible, regeneration is carried out by air alone. The progress of the combustion is followed by CO₂ determinations with simultaneous determination of CO after oxidation to CO₂.

With this type of regeneration procedure a prolonged regeneration period is used. Pelleted natural catalysts with a coke deposit of 0.63 - 0.76 pounds per cu. ft. of catalyst could be regenerated in 36 - 40 minutes with a gas velocity of 3,600 volumes per volume of catalyst per hour, a gas inlet temperature of 860°F., and a regeneration maximum temperature of 1,022°F.; when the coke deposit was 1.13 - 1.39 pounds per cu. ft. of catalyst, 45 - 52 minutes of regenerating time were necessary under the same conditions.

The regeneration of synthetic silica gel-alumina catalysts was more difficult because the carbon deposit was greater due to the higher activity of the catalyst and because passage of oxygen into the fine pores of the gel was difficult to obtain; on the other hand, the best cracking temperatures lie usually below the most favorable combustion temperatures. The catalyst temperature of 752 - 788°F. at the end of the cracking period is sufficient for ignition of the carbon deposit, but complete removal of the deposit can hardly be accomplished after the high regeneration temperatures have decreased to the approximate inlet temperature of the oxygen-containing gases (797°F.). With a silica gel-alumina catalyst containing 1.77 pounds of carbon per cu. ft. of catalyst, a CO₂ content below 0.2% in the combustion gas was only reached after 50 - 55 minutes when 3,700 volumes of regeneration gas per volume of catalyst per hour were used with an inlet temperature of 842°F. and a maximum temperature of 1,112°F. At an inlet temperature of 842°F., and under otherwise equal conditions, the CO₂ content of 0.2% was reached already after 30 - 38 minutes, whereas noticeable CO₂ formation could no longer be detected after 55 - 65 minutes.

Experiments with Fluid-Type Catalysts.

Experiments with fluid-type catalysts in the vapor phase were carried out in 2 basically different units. In one case a controlled amount of catalyst is passed in parallel flow with oil vapors from the top to the bottom of a vertical reactor by means of baffles which are partly mechanically moved. The second design consists of a coil in a lead bath. The oil vapors mixed with steam are passed through the coil at great velocity and carry the catalyst in turbulent flow with them. The vapors are condensed together with the dust, and liquid and gas are analyzed in the usual way. The best and most unambiguous results were obtained by the latter method. However, this work was discontinued in favor of the liquid-phase process described below.

In a high-pressure apparatus, which consists of a preheater coil and an electrically-heated reactor with stirrer, suspensions of the charge stock with powdered catalyst (5 - 20%) are processed. The process is operated at pressures ranging from 1,470 - 8,820 psi. and at temperatures from 788 - 898°F. It was found that under these conditions liquid phase was definitely present, which made a convenient, continuous operation possible. In contrast to the results of vapor phase operation with fixed-bed catalysts, the latter process yields more gasoline with noticeably lower gas and coke formation.

Product Evaluation.

The analytical evaluation of the small-scale experiments pertains only to testing catalyst activity. Consequently, the liquid products, including the hydrocarbons condensed at 112°F., are fractionated to yield a distillate (E.-P. 392°F.) and a residue. The entire yield of C₃ and C₄ hydrocarbons is also determined. In this way up to 8 different catalysts can be tested daily for their activity (production of distillate up to 392°F.)

The products from the experiments in the larger reactors are investigated in greater detail since it is desired to determine the exact product distribution and thereby not only to estimate the activity but also the selectivity of the catalyst. The products from several, e.g., 3 - 5 cracking periods, are combined and distilled to yield gasoline with an end point of 392°F., recycle stock and low-boiling hydrocarbons. Gasoline of 9 - 10 pounds RVP is prepared by stabilization. The excess of C₄ hydrocarbons is collected together with the C₃ hydrocarbons. The dry gas is determined quantitatively and qualitatively and coke formation is determined by analysis of the carbon-oxygen compounds formed during regeneration or by direct determination of the carbon on the catalyst removed from the reactor.

Charge Stock.

For testing of the activity of several catalysts, usually American and very similar Iranian petroleum fractions were used. German petroleum fractions, as well as brown coal hydrogenation and Fischer-Tropsch products, were also used. Recycle stock was cracked in several cases.

In order to obtain uniform behavior of the vaporized oils, the charge was usually distilled to give 1 - 5% residue, maintaining a maximum overhead temperature of 752°F. This procedure was used in spite of the fact that in most cases the experimental results were not affected by omission of the preliminary distillation.

The principal inspection data of the charge stocks used in the investigation are given in Table 1.

Experiments with Natural Catalysts.

A large number of commercial filter clays prepared by activation with acids were used as such or after additional treatment. Increased cracking activity could be obtained by activation with acid, especially sulfuric acid, and also by treatment with salt solutions.

For additional activation, the clays were treated for several hours with acid or aqueous solutions of magnesium chloride or sulfate or aluminum or manganese chloride or sulfate. After removal of the electrolytes by washing with water and drying, the catalyst was formed into pellets, if necessary, after addition of 1 - 2% graphite. The following clays were investigated:

Several Terrana clays (lower Bavaria)	
Several Frankonites (lower Franconia)	
Fullers Earth	(U. S. A.)
Florida Clays	(U. S. A.)
Superfiltrol	(U. S. A.)
Niho Clay	(Japan)

In addition, several natural clays, as well as bentonites, bauxites, and silica gel, were investigated. Although the latter materials showed quite considerable cracking activity after the above-described treatment, they did not reach the activity obtained with the clays listed above.

For these comparative tests, oil #1 was used which was cracked at a temperature of 842°F., a space velocity of 0.6 volumes per volume per hour and a cracking time of 2 hours. The results are given in Table 2.

Synthetic Catalysts.

Using experiences with other catalytic processes which were considered to be related to catalytic cracking, different catalyst combinations were prepared and tested. It was, however, soon found that the most favorable results were obtained with catalysts on the basis of silica gel in admixture with alumina or magnesia. Further development work was concentrated on these combinations and previous experience in the manufacture of silica gel was found helpful.

The structure, especially the pore size of the silica gel, is mainly responsible for the activity of the catalyst. The amount of alumina added has only a slight effect within large limits, both with respect to cracking efficiency and product distribution. In order to obtain a high and uniform activity it is important to maintain a favorable pH value when the silica gel is precipitated and also during manufacture of the catalyst since a change in the pore size can occur during washing or when the pH is changed by the addition of a second component. A considerable decrease of activity can occur even in the dry state with insufficiently-washed catalysts because of volatilization of an acid or a base on heating.

The manufacture of synthetic silica gel catalyst is only economically feasible when the gel is precipitated from a waterglass solution which contains at least 1 pound SiO_2 per gallon. When more dilute waterglass solutions are used, the complete precipitation at low pH , especially between 3 and 4, requires too much time; washing of a gel prepared in this way is difficult and requires large amounts of liquid and large reaction vessels. The control of the pore size, also, is only possible by precipitation from concentrated solutions. This is carried out by adding a waterglass solution of the exact concentration to the calculated amount of acid at not too high a temperature so that a clear sol still exists when the desired pH has been reached. On heating, complete precipitation to an entirely homogeneous solid gel takes place which can be washed very easily.

The combination of silica gel and alumina can be carried out by various methods. In case that these methods permit to maintain a favorable pH value over the entire manufacturing period, they yield catalysts of approximately the same activity. The mechanical strength of the catalysts, however, is not the same with all manufacturing methods. Details of the manufacturing methods are given below:

The effect of the pore size of the silica gel is shown clearly by experiments with silica gel with narrow pores (A) and silica gel with wide pores (B). Both are commercial I. G. products which are mainly used as dryers and absorbents and represent transparent particles of varying size. Whereas silica gel A which contains traces of alumina, shows an average activity, silica gel B is almost completely inactive. Comparative results of various silica gels are shown in Table 3.

After the incorporation of alumina by soaking the gel with aluminum nitrate solution and heating to 842°F., silica gel A shows an extreme increase in the cracking efficiency already at an aluminum concentration of 0.4%. After 3 - 4% aluminum oxide have been added, further activation has taken place. Silica gel B is only slightly activated by this method; a slightly higher cracking activity is obtained after treatment with acid. The increase in activity becomes considerably smaller when the nitrate is converted into the oxide by precipitation with ammonia. The activity of silica gel A can be further increased by more thorough washing. The disadvantage of this manufacturing method consists in the fact that only small, although very hard, particles are obtained on treating the water-sensitive, narrow-pore silica gel with aluminum nitrate solution, and the aluminum oxide film in the gel pores is probably not very uniform. Bursting of the particles can be considerably inhibited by heating the gel at first to 1,112°F. or by subjecting to a suitable treatment with steam; in this way the development of high pressure in the interior of the gel particle by water is avoided, either by enlarging the pores or displacement of the occluded air.

By intensive mixing of silica hydrogel precipitated at PH 3.6 - 4 (partly 5) with aluminum nitrate solution, drying and subsequent heating to 842°F., the most active cracking catalyst was prepared. The strength of these catalysts are not yet as satisfactory as desired since the larger pieces disintegrate into preformed smaller pieces at higher loads.

Almost equally active and at the same time extremely strong are the silica gel-aluminum oxide mixtures which are obtained by mechanical homogenization of narrow pore silica hydrogel (PH 3.5 - 5.0) and aluminum hydroxide. In place of aluminum hydroxide, its sol can be used which is obtained by peptization with a small amount of nitric acid. Depending on the conditions maintained during homogenizing and depending on the aluminum hydroxide content, non-transparent pieces with rough or porcelain-like surfaces or transparent particles of any desired size with the appearance of pure silica gel are obtained. This method of manufacture appears very advantageous and permits shaping by means of a string press which avoids all loss of material.

By simultaneous precipitation of silica gel and aluminum hydroxide from waterglass and aluminum nitrate solution, strong catalysts were also obtained but their activity is below the maximum value obtainable with other catalysts. The PH of 3.5 - 4.0 which is the best for the manufacture of narrow pore silica gel cannot be maintained during the simultaneous precipitation since, at that hydrogen-ion concentration, aluminum hydroxide is not precipitated completely and simultaneously. It appears much better to carry out the simultaneous precipitation using aluminum hydroxide sol which results in the formation of strong and highly active catalysts.

Another type of simultaneous precipitation consists in dissolving silicon tetrachloride and aluminum chloride in methanol and precipitating it by passing the solution into water.

These catalysts show great mechanical strength, but their cracking efficiency is not quite satisfactory.

Besides aluminum oxide, a series of other oxides was tested for the use as second component of the silica gel catalyst; among the oxides tested were those of Be, Ca, Zn, B, Ti, Zr, Cr, Mo, V, Mn, Fe, Co, and Ni. The activity was, in all cases, lower than that obtained with aluminum.

The magnesium oxide-silica gel catalyst should be especially mentioned because of the mechanism of its cracking effect. The formation of C₃ and C₄ hydrocarbons is considerably decreased as compared to natural and other synthetic catalysts. The propane and butane formation, e. g., is about 100% higher with an aluminum oxide catalyst of the same activity. This behavior is especially noticeable when Kogasin II is cracked. In spite of much effort, the activity of these catalysts could not be raised appreciably so that it is still below that of the natural catalysts. The most active catalysts of this type were obtained by homogenizing and simultaneous drying of peptized magnesium oxide with silica sol free from electrolytes.

Three-component catalysts also did not exceed the cracking efficiency of the most active silica gel-alumina catalyst; these three-component catalysts were prepared by adding magnesium, zinc, manganese or iron oxide to silica gel and aluminum oxide. The addition of manganese or iron oxide was thought to decrease the regeneration time required. The improvement, however, does not seem to be very great, but the detrimental effect on the activity as compared to the pure silica gel-alumina catalyst is noticeable. Since, however, with some other oxides, a favorable effect, especially on the product distribution, seems possible, these experiments will be continued.

The comparative tests with these catalysts, which are shown in Table 3, are carried out on East Texas gas oil at a cracking temperature of 842°F. with a space velocity of 0.6 volumes per volume per hour and a cracking period of 2 hours.

Pilot Plant Studies on Catalysts.

A number of treated clays, synthetic silica gel-alumina and silica gel-magnesia catalysts, were tested in long-time runs. The best product distribution was empirically determined by changing the reaction conditions until a maximum yield of gasoline was obtained. Whereas the activated clays and the synthetic silica gel-magnesia catalysts gave the best results for cracking of gas oils at temperatures of 833°F. - 860°F., a space velocity of 0.5 - 0.8 volume per volume per hour, and cracking periods of 30 - 60 minutes (in some cases, 2 hours), the considerably more active silica gel-alumina catalysts required only temperatures of 752 - 797°F. and preferably higher space velocities. The extremely high formation of low boiling hydrocarbons which was obtained with these catalysts at higher temperatures and lower space velocities could be decreased to such an extent that the product distribution becomes similar to that obtained in cracking with activated clays. In spite of the decrease in temperature, the higher activity can be seen in higher space velocities and longer operating periods. Gasoline formation amounting to about 40% by volume, based on the liquid products obtained, seems to be the most advantageous operating condition.

Tables 4 - 6 show the product distribution and experimental conditions for the cracking of various charge stocks with the following activated clays:

1. Superfiltrol GOC 12X and Superfiltrol GOC 12E
2. Frankonit (#1444, treated with sulfuric acid)
3. Terrana (#1384, treated with sulfuric acid)

4. Superfiltrol GOC 12E (#1534, treated with $MgCl_2$ solution)

5. Frankonit (#1505, treated with $MgCl_2$ solution)

The data in each vertical column of the tables refer to several, usually 5, consecutive cracking periods. Only a few of the experiments from longer experimental series (containing up to 300 cracking periods) are given. In the course of testing the catalysts in extended tests, various conditions were tried out. In the beginning, the oil vapors, together with steam, usually 2% water calculated on oil, were passed over the catalyst. No effect on yields and reaction products was found, but the temperature differential in the catalyst bed was smaller in these cases. The latter observation might explain the fact that shortening of the residence time caused by the addition of steam did not affect the cracking process. The experiments shown in the Tables 5 and 6 were carried out without the addition of steam.

The various natural clays do not show great differences with respect to their cracking activity and the product distribution under equal experimental conditions. Superfiltrol treated with magnesium chloride (#1534), however, appears to be more active so that the temperature and space velocity chosen in these experiments are not the most favorable ones. Frankonit also treated with magnesium chloride (#1505) gave a space velocity of 0.6 volume per volume per hour a satisfactory product distribution only at $824^{\circ}F$. The decrease in activity with increasing total cracking time (age), is shown most clearly on Superfiltrol GOC 12X. A similar decrease was observed with all clays investigated; Frankonit, which is also less sensitive towards higher temperatures (up to $1112^{\circ}F$.) shows this effect less pronounced. The greater decrease in activity which is shown in Table 6 is mainly due to frequent and longer regeneration periods reaching $1112^{\circ}F$. This decrease, however, is considerably smaller than found for all other natural catalysts investigated. Usually, a maximum regeneration temperature of $1,022^{\circ}F$. was not exceeded.

The gasoline which was stabilized to 9 - 10 pounds RVP was colorless, stable to light, and did not have the characteristic odor of cracked gasolines. The untreated gasolines, however, did frequently have a high glass dish gum and, in some cases, gums as high as 20 - 30 mg. per 100 cc. were found. The hydrocarbon composition of the gasoline obtained by cracking of East and West Texas, and Iranian gas oil, using catalyst #1444 (35% by volume) was as follows: East Texas gas oil 19% aromatics, 29.0% olefins; West Texas gas oil 28% aromatics, 27% olefins; Iranian gas oil 27% aromatics and 23% olefins.

The octane number of the higher-boiling gasoline fractions is not appreciably lower than that of the lower-boiling fractions, which is due, partly, to the higher aromatic content of the higher fractions. Definite signs of isomerisation were also found. In spite of the fact that the inspection data of the gasolines vary in accordance with the charge stocks, their knock behavior is astonishingly similar.

Aniline point, pour point, and end point of the recycle stock was decreased, whereas the specific gravity had increased.

Inspection data of various gasolines and recycle stocks are given in Table 7.

Experiments with Synthetic $SiO_2 \cdot Al_2O_3$ and $SiO_2 \cdot MgO$ Catalysts.

The product distribution and experimental conditions for the cracking of various gas oils in the presence of some synthetic silica gel-alumina catalysts and a silica gel-magnesia catalyst are shown in Tables 8, 9, 10 and 11. The following catalysts were used in the experiments:

#1642 $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$; 12.5% Al_2O_3 (55.3% distillate in evaluation tests)

#1726 55/3 B7 $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$; 14.6% Al_2O_3 (58.1% distillate in evaluation tests)

#1447/1 $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$; 4.2% Al_2O_3 (52.8% distillate in evaluation tests)

#1427 $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$; 34% Al_2O_3 (50.0% distillate in evaluation tests)

#1308 $\text{SiO}_2 \cdot \text{MgO}$; 40% MgO (30.2% distillate in evaluation tests)

Whereas the cracking efficiency of natural clays decreases considerably with increasing age, no appreciable loss in activity is found with synthetic catalysts (even after 400 regenerations). The unchanged activity in extended tests is, however, conserved only in the absence of water vapors, especially during regeneration. A further advantage of synthetic catalysts consists in the fact that they are almost entirely insensitive to higher temperatures (up to 1,472°F.), in contrast to the natural clays; in this way the necessity to maintain a regeneration temperature below a certain maximum becomes unnecessary. It is, consequently, possible to balance the difficulties encountered in completely removing carbon from narrow-pore catalysts by using higher regeneration temperatures. In the previous investigations it was found advantageous to reach a temperature of 60° to about 100°F. above the cracking temperatures (752 - 788°F.) at the end of the regenerating period.

In the previously-described catalyst studies, petroleum fractions of different origin were used. These did not show basic differences in the ease of cracking, product distribution and the quality of the products. A fraction from Austrian crude (Zisterstorf) which contained more than 50% of the crude (oil #4) was very easily cracked; in spite of extremely high gasoline yields, the distribution of the reacted products is very favorable so that this material can be considered a suitable charge stock for catalytic cracking. Extensive studies were also made on the cracking of recycle stock from catalytic cracking. These oils can be used as diesel oils after very slight treating.

When subjected to the same reaction conditions as the fresh feed, the recycle stocks were found to be less easily cracked. By raising the cracking temperature or lowering the space velocity and shortening the cracking period, this disadvantage can be balanced only to a certain degree since gas and coke formation increases considerably. The results of cracking experiments are shown in Table 12.

Some middle oils obtained by high-pressure hydrogenation of brown coal were also investigated with respect to their cracking behavior. The charge stock represented a paraffinic oil which had been obtained by high-pressure hydrogenation of brown coal tar in the sump phase, using a fixed-bed catalyst at a temperature of 716°F. The distillate from this material with a boiling range of 500 - 788°F. was an oil with a pour point of 36° which was further fractionated after dewaxing.

As indicated by the data in Table 13, the oil could be easily cracked catalytically and yielded a very knock-resistant gasoline in spite of the low specific gravity. The recycle stock, whose pour point was lowered by about 40°F. and whose end point was about 80°F. higher as compared with the charge stock, gave a good diesel oil when blended with a lighter distillate from the hydrogenation product. By blending the cracked gasoline and the hydrogenation gasoline, a good automotive fuel could be obtained. Since the paraffinic oil from brown coal tar hydrogenation was cracked so very easily it was assumed that the middle oil fraction from Fischer-Tropsch synthesis (Kogasin II) would behave similarly. These oils con-

tain, as is well known, mainly straight-chain or very slightly branched paraffins besides more or less olefins.

It was found, however, that this product behaved entirely differently from the other oils investigated. The synthetic silica gel-alumina catalysts cannot be used at all because of their high activity and the "overcracking" caused by them. The activated clays, on the other hand, gave only very unsatisfactory results since octane numbers exceeding 65 were only obtained when an exceedingly high amount of C_3 and C_4 hydrocarbons (mainly C_3H_6 and C_4H_8) was made. Under experimental conditions which gave a more favorable product distribution, the gasoline formation amounted to 30% by volume and the octane number was below 60. The recycle oil, which was very little different from the fresh oil, showed a considerably greater resistance to cracking. More favorable results were obtained by cracking Kogasin with synthetic silica gel-magnesia catalysts.

In spite of the fact that the activity of these catalysts was not very satisfactory and that the product distribution was not too good, the magnesia-containing catalysts were in this case superior to the other catalysts used.

Table 1

Oil No.	East Texas Gas Oil		West Texas Gas Oil		Iranian Gas Oil		German Petroleum Fraction		Brown Coal Tar Hydrogenation Product		Recycle Stock From No. 6		Kogasin II		Recycle Stock From No. 8	
	1	2	3	4	5	6	7	8	9	10						
API Gravity	33.7	31.0	35.6	30.4	33.1	38.1	35.3	52.1	51.4	51.6						
Aniline Point, °F.	173	153	144	159	147	201	165	191	201	187						
Pour Point, °F.	43	27	3	34	50	81	45	-	-	-						
IB ₁₀	522	482	410	414	408	473	462	408	410	428						
5%	549	505	442	464	437	509	482	430	424	441						
50%	624	597	511	603	545	630	536	496	527	491						
95%	702	716	675	756	707	766	707	594	716	590						
BP	734	729	698	770	725	784	725	626	743	606						
Cetane No.	69.0	62.0	66.0	-	-	-	-	-	-	-						

Table 2

Catalyst	Apparent Density g/100 cc.	Gas (without hydrocarbons) l/l of oil	Distillate up to 392°F. (incl. C ₃ hydrocarbons) (1. cracking period) % by vol.
<u>Superfiltrol-GGG12E</u>			
Original	78.5	35.0	41.0
treated with MgSO ₄ solution (#1534/2)	81.0	37.0	46.6
treated with MgCl ₂ solution (#1534)	81.5	37.0	45.9
<u>Terrana</u>			
comm. product	72.0	20.0	29.8
treated with HCl #1796	68.0	19.0	21.7
treated with H ₂ SO ₄ #1384	70.0	41.0	43.4
treated with MgCl ₂ solution, #1744	73.2	44.5	41.1
treated with AlCl ₃ solution, #1779	69.0	45.5	43.5
treated with MnCl ₂ solution, #1816	70.0	40.0	40.0
<u>Frankonit</u>			
comm. product	75.8	26.5	32.2
treated with H ₂ SO ₄ #1444	70.8	37.0	42.2
treated with MgCl ₂ solution, #1505	69.5	44.5	45.7
treated with MnSO ₄ solution, #1510	64.1	31.0	38.5
<u>Japanese clay, activated electrolytically (Niho process)</u>			
	88.8	14.5	21.4

Catalyst	Apparent Density g/100 cc.	Gas (without C ₃ hydrocarbons) 1/liter of oil	Distillate up to 392°F. (+ C ₃ hydrocarbons) (1. cracking period) % by vol.
SiO ₂ -Gel A	72.0	17.0	22.5
SiO ₂ -Gel B	44.0	9.6	3.3
SiO ₂ -Gel B #1280 (treated with acid and contg. 5% Al ₂ O ₃)	-	22.0	18.2
SiO ₂ -Gel A #1750/1 (contg. 0.4% Al ₂ O ₃)	74.3	27.5	41.1
SiO ₂ -Gel A #1776 (contg. 3% Al ₂ O ₃)	75.0	38.5	51.5
SiO ₂ -Gel A #1747/1 (contg. 4.2% Al ₂ O ₃)	79.5	32.5	52.8
SiO ₂ -Gel A #1747/2 (contg. 4.2% Al ₂ O ₃ (NH ₃))	70.0	19.0	34.6
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SiO ₂ .Al ₂ O ₃ (17.5% Al ₂ O ₃) #1670 58/1 B ₇	64.7	52.0	61.9
SiO ₂ .Al ₂ O ₃ (14.6% Al ₂ O ₃) #1726 55/3 B ₇	73.5	51.0	58.1
SiO ₂ .Al ₂ O ₃ (12.5% Al ₂ O ₃) #1823	75.0	42.0	62.2
SiO ₂ .Al ₂ O ₃ (10.6% Al ₂ O ₃) #1792	62.7	55.0	58.9
SiO ₂ .Al ₂ O ₃ (8.6% Al ₂ O ₃) #1675	80.4	50.0	59.7
<hr/>			
SiO ₂ .Al ₂ O ₃ (17.5% Al ₂ O ₃) #1765	62.9	52.0	52.8
SiO ₂ .Al ₂ O ₃ (14.6% Al ₂ O ₃) #1766 55/5 B ₇	62.5	52.0	57.8
SiO ₂ .Al ₂ O ₃ (12.4% Al ₂ O ₃) #1759	63.5	44.5	54.5
SiO ₂ .Al ₂ O ₃ (10.8% Al ₂ O ₃) #1786	53.8	43.0	53.9
SiO ₂ .Al ₂ O ₃ (9.6% Al ₂ O ₃) #1787	58.9	50.0	55.2
<hr/>			
SiO ₂ .Al ₂ O ₃ (34.0% Al ₂ O ₃) #1427	80.0	64.0	50.0
SiO ₂ .Al ₂ O ₃ (9.6% Al ₂ O ₃) #1778	60.5	41.0	53.9
SiO ₂ .Al ₂ O ₃ (46.0% Al ₂ O ₃) #1492	-	-	46.2
SiO ₂ .Al ₂ O ₃ (30.0% Al ₂ O ₃) #1509	-	20.0	48.0
<hr/>			
SiO ₂ .MgO (40% MgO) #1308	65.0	34.0	30.2
SiO ₂ .MgO (31% MgO) #1495	-	41.0	33.4

TABLE 4

Product Distribution for Cracking of Various Oils with Superfiltral GOC 12X and GOC 12E

Catalyst	GOC 12 X				GOC 12 E	
	842	60	0.6	835	60	0.6
Av. Catalyst Temp. °F.						
Cracking Time, Min.					30	30
Space Velocity vol/vol/hour					11-15	106-112
Cracking Periods	13-17	58-62	94-98	160-164	1	1
Oil No.	1	2	1	1	1	1
Yield, based on charge						
Liquid product, % by vol. (% by wt.) (incl. C ₃ hydrocarbons)	98.3(91.4)	97.3(90.2)	98.9(92.0)	99.4(93.2)	98.1(92.3)	96.6(90.6)
Gas + Coke + Loss, % by wt.	8.6	9.8	8.0	6.8	7.7	9.4
Gasoline 10# RVP, % by vol. (% by wt.)	38.8(33.4)	36.1(30.8)	36.0(30.6)	34.2(29.5)	34.8(30.1)	39.1(33.7)
Recycle Stock, % by vol. (% by wt.)	48.9(49.8)	51.5(52.1)	53.1(53.8)	56.4(57.0)	55.3(56.1)	49.5(50.4)
C ₂ H ₄ fraction, % by vol.	10.6	9.7	9.8	8.8	8.0	8.0
Gas, % by Wt.	1.9	1.8	1.9	1.8	1.8	2.0
Coke % by Wt.	-	-	-	3.1	-	3.7

TABLE 6

Product Distribution for Cat. Cracking of various oils

Catalyst	1384	1534	1505
Av. Cracking Temp. °F.	842	842	824
Cracking Time, Min.		60	
Space Velocity, vol/vol/hour		0.60	
Oil No.	1	3	1
Yield, based on charge			
Liquid product, % by vol. (% by wt.) (incl. C ₃ hydrocarbons)	100.1(93.7)	97.6(90.6)	99.1(93.1)
Coke + gas + loss % by wt.	6.8	9.4	6.9
Gasoline 10# RVP % by vol. (% by wt.)	34.5(29.6)	37.5(33.0)	33.9(29.1)
Recycle stock % by vol. (% by wt.)	56.4(57.3)	45.4(46.3)	56.1(57.1)
C ₃ ,C ₄ fraction % by vol.	9.2	14.9	9.1
Gas % by wt.	2.6	3.2	2.0
Coke % by wt.	3.0	-	-

TABLE 7

Inspection Data for gasoline and recycle stock -
obtained by Cat. Cracking with activated clays

Oil No.	1	1	1	2	3	4
Catalyst	GOC 12 X		1444	GOC 12 X	1444	1444
Cracking Temp., °F.	842		851	842	851	851
Gasoline Yield, % by vol. (Gasoline 10 $\frac{1}{2}$ RVP)	38.9	34.2	36.7	36.0	36.1	43.0
API Gravity	61.3	59.8	61.6	59.5	57.2	57.0
Aniline Point, °F.	104	106	100	89	88	94
IBP °F.	97	102	97	100	100	97
5% °F.	122	122	117	120	122	117
50% °F.	230	244	221	230	252	259
95% °F.	370	374	381	379	385	388
EP °F.	392	390	392	392	394	392
Bromine No.	-	-	40.8	40.0	37.0	32.7
Octane No.						
IG-Research	84.0	84.5	85.5	86.5	86.5	85.0
Motor Method	-	-	79.5	-	79.5	79.0
Recycle Stock						
API Gravity	30.8	31.7	31.0	28.1	32.7	26.8
Aniline Point °F.	139	144	144	123	127	117
Pour Point °F.	31	34	-	5	-	12
IBP °F.	457	462	464	455	446	446
5% °F.	476	482	491	477	455	468
50% °F.	554	563	566	534	491	531
95% °F.	689	689	678	698	621	673
EP °F.	698	698	692	712	553	725
Cetane No.	62	-	-	51.5	57.5	50.5

TABLE 9

Product Distribution for Cat. Cracking of Various Oils

Catalyst	1726 55/3 B7			1747/1			1427		
	779	779	779	779	788	770	770	770	770
Av. cracking temp. °F.	779	45	30	779	788	770	770	770	770
Cracking Time, min.	30	45	30	30	30	120	120	30	30
Space Velocity, vol/vol/hour	1.3	1.2	1.3	1.3	1.3	0.58	0.58	1.2	1.2
Oil No.	3	3	3	2	3	3	3	3	3
Yield, based on charge									
Liquid product % by vol. (% by wt.)	99.8(93.5)	100.7(94.2)	99.9(92.5)	99.0(92.7)	99.0(92.7)	99.6(93.7)	99.6(93.7)	98.9(93.2)	98.9(93.2)
(Incl. C ₃ hydrocarbon)									
Coke + Gas + Loss % by wt.	6.5	5.8	7.5	7.3	7.3	6.3	6.3	6.8	6.8
Gasoline 10# RVP % by vol. (% by wt.)	59.7(35.0)	58.0(33.4)	59.7(33.7)	35.7(31.2)	35.7(31.2)	54.2(30.2)	54.2(30.2)	35.4(31.1)	35.4(31.1)
Recycle Stock % by vol. (% by wt.)	49.1(50.0)	52.3(53.2)	49.6(50.6)	54.5(55.0)	54.5(55.0)	54.8(55.4)	54.8(55.4)	54.9(55.7)	54.9(55.7)
C ₃ -C ₄ fraction % by vol.	11.0	10.4	10.6	8.8	8.8	10.5	10.5	8.6	8.6
Gas % by wt.	1.2	1.2	1.7	1.1	1.1	1.6	1.6	1.4	1.4
Coke % by wt.	4.1	3.6	3.7	3.0	3.0	2.6	2.6	-	-

TABLE 10

Product Distribution for Cat. Cracking of East and West Texas Gas Oil

Catalyst	1308			
Av. cracking temp., °F.	842			
Cracking time, min.	60	60		60
Space Velocity, vol./vol./hour	0.6			
Oil No.	1	1	1	2
Yield, based on charge				
Liquid product % by vol. (% by wt.)		97.0(92.4)	94.7(89.4)	98.0(93.6)
(incl. C ₃ hydrocarbon)				
Coke + gas + loss % by wt.		7.6	10.6	6.4
Gasoline 10 # HVP % by vol. (% by wt.)		29.7(25.6)	34.1(29.5)	28.9(24.9)
Recycle Stock % by vol. (% by wt.)		63.4(63.8)	55.3(56.1)	65.6(66.1)
C ₃ , C ₄ fraction % by vol.		3.9	5.3	3.5
Gas % by wt.		1.7	2.4	1.4
Coke % by wt.		-	3.6	1.7

TABLE 11

Inspection Data for gasoline and recycle stock obtained by cat. cracking with silica gel-alumina catalysts.

Oil No.	2				1		3	2
Catalyst	1642	1642	1308	1447/1	1642	1308	1726	53/3 B7
Cracking Temp., °F.	761	779	842	779	761	842	779	779
Gasoline Yield, % by vol.	39.5	35.2	28.9	35.5	37.8	34.1	39.7	39.7
Gasoline 10 # RVP								
API Gravity	61.3	60.5	58.0	60.0	62.4	61.3	59.0	59.5
Aniline Point, °F.	98	97	89	96	108	105	94	100
IBP °F.	93	97	91	102	97	97	102	99
5% °F.	117	117	124	115	115	118	124	117
50% °F.	219	212	248	217	216	237	244	219
95% °F.	381	356	370	365	367	365	387	381
EP °F.	388	387	392	383	385	388	392	388
Bromine No.	18.4	23.8	-	20.8	22.1	-	19.4	18.1
Octane No.								
I G - Research	87.0	85.5	88.0	85.8	84.5	88.0	83.0	84.5
Motor Method	78.5	77.5	-	79.0	78.5	-	77.0	78.0
Recycle Stock								
API Gravity	27.9	28.2	29.2	28.5	30.6	31.6	32.3	27.4
Aniline Point °F.	121	128	130	124	144	145	126	118
Pour Point °F.	-	-	-	-	-	-	-	-
IBP °F.	463	460	457	459	464	457	442	455
5% °F.	471	473	473	475	489	482	457	473
50% °F.	529	540	536	534	565	563	495	529
95% °F.	693	698	680	687	687	671	624	698
EP °F.	748	734	698	730	707	689	680	734
Cetene No.								

TABLE 12

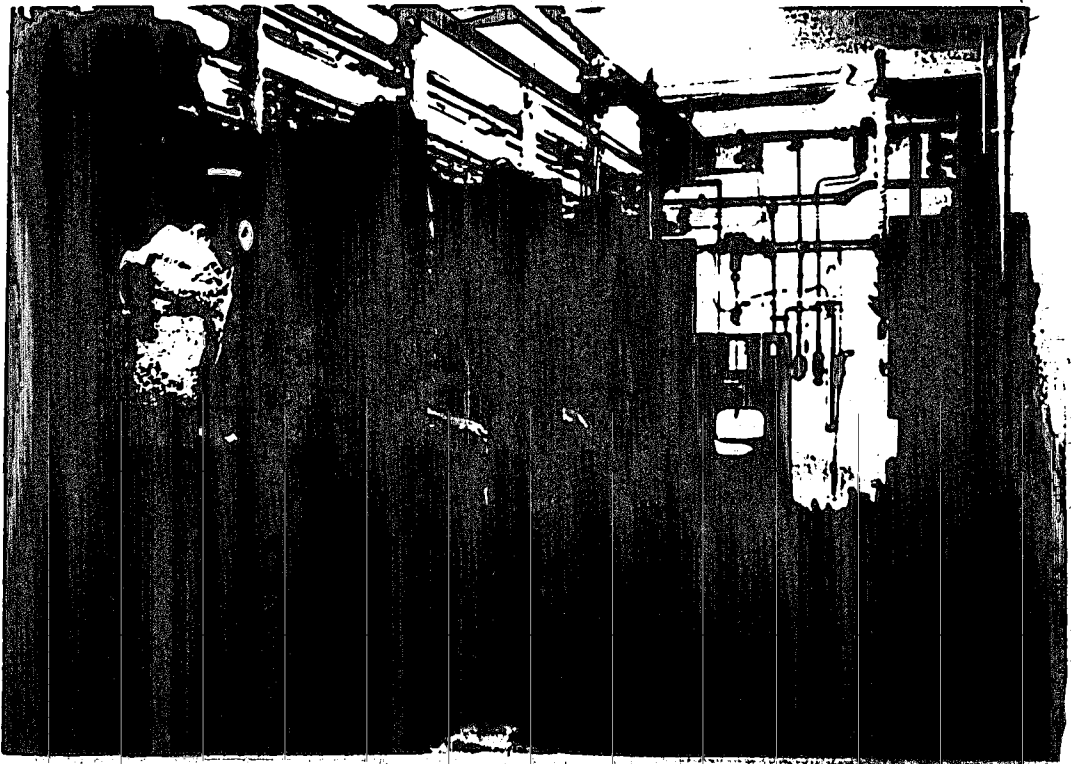
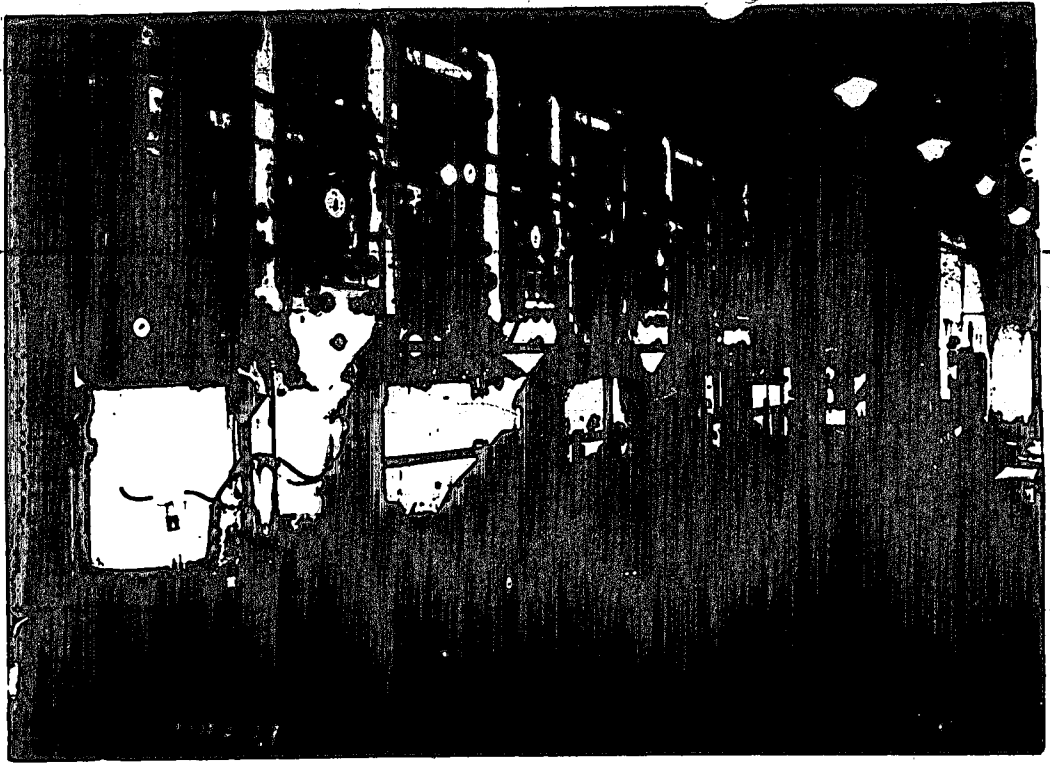
Catalyst	1726 55/3 B7	1642
Av. Cracking Temp. °F.	779	770
Cracking Time, min.	30	30
Space Velocity /vol/vol/hour	1.65	1.45
Oil No.	1	2
Yield, based on charge	Recycle stock from 1	Recycle stock from 2
Gasoline-10 # RVP % by vol. (% by wt.)	21.5(18.2)	21.1(17.7)
Recycle stock % by vol. (% by wt.)	56.5(57.1)	55.6(56.6)
C ₃ , C ₄ fraction % by wt.	6.9	7.2
Gas, coke + loss % by wt.	6.3	6.6
Data of Gasoline		
API Gravity	61.6	58.7
Aniline Point °F.	102	90
Examine No.	21.0	19.7
5% distilled °F.	115	117
50% distilled °F.	221	212
95% distilled °F.	379	378
Data of recycle stock		
API Gravity	32.1	27.2
Aniline Point °F.	145	115
5% distilled °F.	487	454
50% distilled °F.	531	520
95% distilled °F.	678	675
	30.4	28.6
	133	126
	480	475
	532	536
	684	685
	29.9	26.1
	151	106
	475	468
	529	518
	658	673
	59.4(60.6)	60.5(61.6)
	5.9	5.1
	6.4	8.9
	62.6	60.0
	100	97
	20.5	18.3
	109	118
	214	230
	379	383
	62.1	60.0
	102	97
	22.3	18.3
	117	118
	212	230
	374	383
	30.4	28.6
	133	126
	480	475
	532	536
	684	685
	29.9	26.1
	151	106
	475	468
	529	518
	658	673

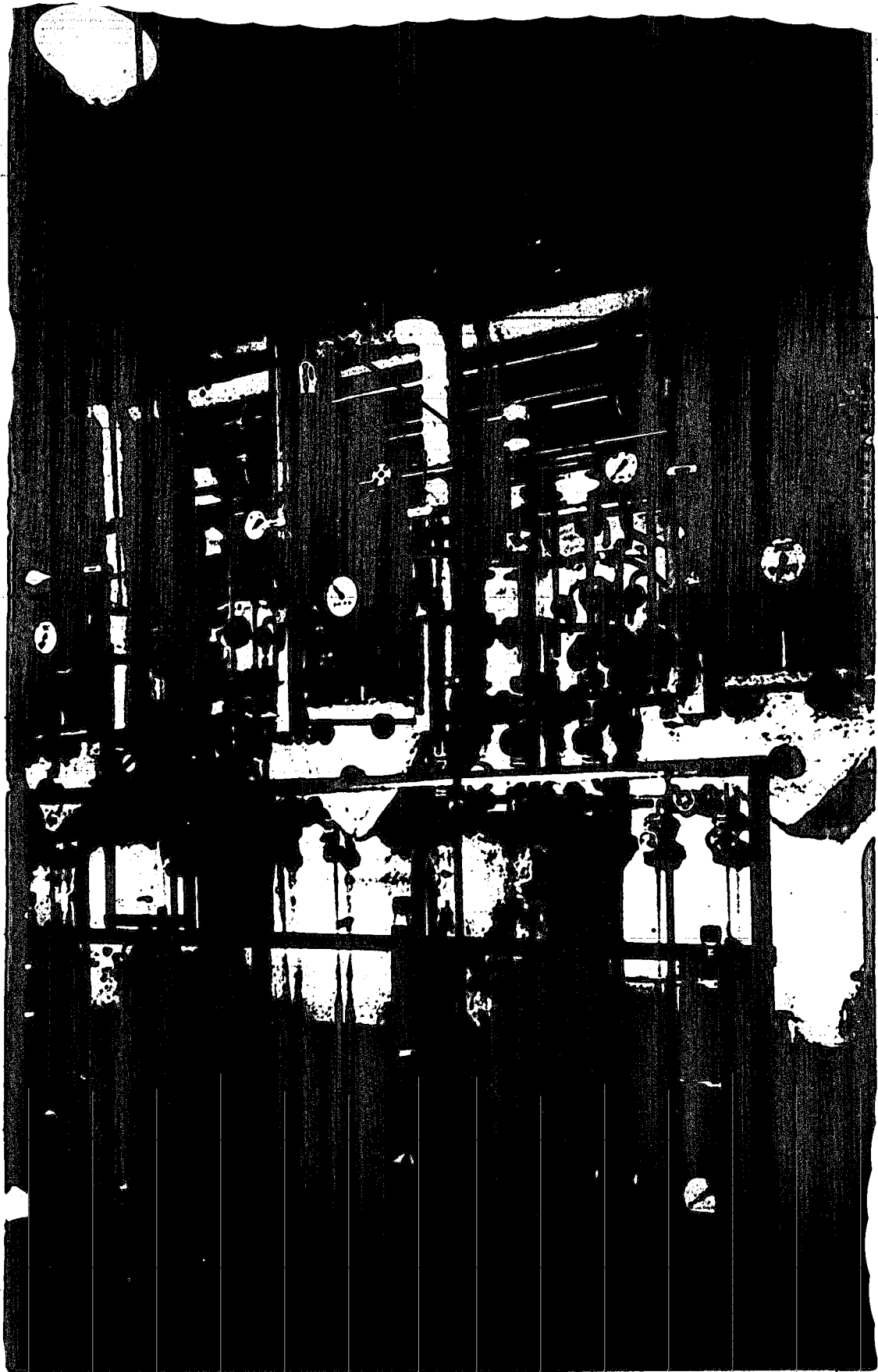
TABLE 13

Cracking of various fractions of a brown coal tar hydrogenation product with Superfiltral GOC 12X

Av. Cracking Temp. °F.	770		808
Cracking Time, min.	120		60
Space Velocity vol/vol/hour	0.52		0.62
Oil No.	5	6	7 (recycle stock)
Yield, based on charge			
Gasoline 10# RVP % by vol.	39.0	41.9	29.0
Recycle Oil % by vol.	54.6	48.9	64.3
C ₃ , C ₄ fraction % by vol.	6.0	9.7	5.0
Gas % by vol.	1.4	2.0	1.8
Coke % by vol.	-	3.9	-
Data of gasoline			
API gravity	56.7	66.4	61.3
Bromine No.	14.6	27.0	23.2
5% distilled °F.	122	120	116
50% distilled °F.	259	216	243
95% distilled °F.	385	369	383
Octane No.			
I G Research	78.5	78.5	82.0
Motor Method	-	76.5	-
Data of Recycle Stock			
API Gravity	31.7	37.2	33.7
Pour Point	-37	45	37
5% distilled °F.	455	475	465
50% distilled °F.	609	647	632
95% distilled °F.	689	716	687

0.45 GAL. UNIT





CONTROL PANEL