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8. Conference on catalytic cracking and related process  
Minutes of first joint meeting November 30, 1938.

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I.G. Farbenindustrie Aktiengesellschaft  
Stickstoff-Direktion  
Ludwigshafen am Rhein

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Leitung Dr. Kersch*

Betr.: Katalytisches Kracken.

In der Anlage übersenden wir Ihnen drei Exemplare eines Protokolls über die am 30. November 1938 in den Esso Laboratories, Bayway, stattgefundenen erste Sitzung über katalytisches Kracken und verwandte Verfahren, an der Vertreter der Standard Oil Development Co., der M.W. Kellogg Co., der Standard Oil Co. of Indiana, der Anglo-Indiantan Oil Co. und der I.G. Farbenindustrie teilnahmen.

Wir begrüßen Sie

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Anlage.

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Conference on Catalytic Cracking and Related ProcessesMinutes of First Joint Meeting

A conference was held Wednesday, November 30, 1938 at the Esso Laboratories of the Standard Oil Development Company for the mutual exchange of information on catalytic cracking and related processes between representatives of the Standard Oil Development Company, The M. W. Kellogg Company, The Standard Oil Company of Indiana, The Anglo-Iranian Oil Company, and the I.G. Those in attendance were as follows:

Standard Oil Development Company

R. P. Russell  
 E. V. Murphy  
 N. E. Loomis  
 W. C. Asbury  
 G. H. B. Davis  
 W. J. Sweeney  
 H. G. H. Fischer  
 E. W. Luster  
 H. Sydnor  
 P. E. Kuhl  
 E. D. Reeves  
 E. J. Gohr  
 H. R. Poland  
 A. Voorhies, Jr.  
 J. R. Schonberg  
 C. E. Hemminger  
 R. B. Shepardson  
 G. C. Connolly  
 S. C. Fulton  
 B. G. Baldwin (Secretary)

M. W. Kellogg Company

P. C. Keith, Jr.  
 W. W. Gary  
 E. T. Layng  
 L. C. Rubin  
 L. H. Harvison  
 F. E. Johnson, Sr.  
 H. Dinsig  
 L. J. Kelly  
 H. H. Neely, Jr.  
 R. F. Ruthruff

Standard Oil Company of Indiana

W. B. Plummer  
 J. K. Roberts

Anglo-Iranian Oil Company

S. W. Adey

Chemanco (I.G.)

H. Heller

Mr. Russell of the Standard Oil Development Company served as chairman and suggested that each party take about one hour for a brief presentation of the reports to be followed by about one-half hour of discussion. The I.G. was not prepared to present any information at the present time and Mr. Adey explained that all Anglo-Iranian information was in the hands of Kellogg. It was suggested that the group have a technical meeting some time in December or after the first of the year.

Mr. Russell then presented a brief sketch of the Standard Oil Development Company work on catalytic cracking and related processes. Most of the work on catalytic cracking was on fixed catalysts since it was felt that a plant should be in operation at the earliest possible moment. Quite a number of small units were constructed in addition to a pilot plant at Baton Rouge charging about 100 B/D of gas oil. This plant may be converted to powdered catalyst operation. Sound design and operating data to serve as a basis for this alteration will be available some time in February. It will then be decided whether full scale commercial construction should be of the fixed catalyst or

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powdered catalyst type. The Jersey Company will be pushed a great deal for the production of aviation gasoline in the near future and could build now but prefers to wait about five months as explained above.

The Standard Oil Development Company reports were summarized as follows:

1. Catalytic Cracking - Fixed Bed Experimental Work
2. Catalytic Cracking with Powdered Catalysts
3. Combination Visbreaking and Catalytic Cracking of Reduced Crudes
4. Atmospheric Pressure Aromatization, Pressure Aromatization in the Presence of Hydrogen, and Low Pressure Hydrogenation
5. Cracking Catalyst Development - Synthetic Catalysts
6. Cracking Catalyst Development - Activated Clays

The reports on catalyst composition and catalyst preparation were not distributed and it was stated that the method of handling catalyst matters was to be decided at the next meeting.

The Standard Oil Development Company has been doing considerable plant scale work using powdered catalyst in small concentrations but the most successful work of that type has been carried out by the Imperial Oil Company. A preliminary, summarizing report of this work was distributed to various members of the conference. Mr. Russell stated that the operation is not yet well understood but that laboratory work is now in progress and it is hoped to have a complete story as early in 1939 as possible. The Imperial Oil Company is planning to go into full scale operation for cracked gasoline some time in 1939.

A large amount of work has been done in surveying the prior patent art. An average of four men has been working on patents for about a year and a half. Pertinent information on the prior art together with diagrams is being put out in the form of booklets, the first four of which were distributed to various representatives at the conference, representing approximately 40-50% of the information available. Additional booklets will be issued as rapidly as they can be formulated.

Mr. Russell then turned the discussion over to Mr. Murphree for a presentation of the Standard Oil Development Company results on catalytic cracking and related processes.

Mr. Murphree stated that the primary objectives in catalytic cracking were to make a higher yield of higher octane number gasoline than possible thermally, to make aviation gasoline of high octane number in high yields, and to find a better way of handling residual stocks. Several types of operation were considered as follows:

1. Fixed catalysts
2. Moving powdered catalysts
3. Moving piled or granular catalysts

Most of the work done thus far has been with fixed catalyst beds. An operation

involving moving catalyts which would be continuous would be preferable, however, and experimental work has been started on moving powdered catalyts. No work has been done on moving granular catalyts.

The Standard Oil Development Company work on fixed catalyts was presented first. Both activated clays and synthetic catalyts of the silica-alumina type have been investigated. Some clays, such as Super Filtrol, were satisfactory catalyts but, in general, the synthetics were found to be more active.

Nine cracking units of two-liters catalyst capacity were constructed at the Esso Laboratories and five units of similar type at Baton Rouge. In addition, two units of approximately one-cubic foot catalyst capacity were installed at Baton Rouge and a similar unit at the Process Laboratories. A pilot plant having a total of 42 cubic feet of catalyst in each of three reactors and charging approximately 100 B/D of oil was also constructed at Baton Rouge.

In the cracking operation, vaporized gas oil is passed over the catalyst mass. Due to formation of coke on the catalyst, it is necessary to stop and burn off the coke. The operation is thus intermittent in character. Steam or inert gas is blown along with air to burn off the coke. The catalyst is purged with steam or by vacuum prior to regeneration in order to remove adsorbed oil, and again prior to cracking in order to remove residual air. Two of the cubic foot units and some of the 2-liter units have been equipped with recirculating systems for regeneration so that the only material added to the system during regeneration is air. Steam or inert gas is added to limit the rate of oxidation.

Feed stocks employed in most of the work have been a 33 A.P.I. gravity East Texas gas oil or a 32 A.P.I. gravity West Texas gas oil, with mid-boiling points of 600° and 530°F., respectively. Catalyts employed in most of the work have been of two types, namely an activated clay catalyst (Super Filtrol) and a synthetic silica-alumina catalyst.

Using Super Filtrol catalyst, operations have been carried through approximately 950 cycles in experimental runs, equivalent to approximately two months actual life in a plant. The catalyst exhibits a gradual loss in activity with time. For example, at a feed rate of 0.6 volumes of liquid oil/volume of catalyst/hour with 1/2 hour cracking periods, the initial activity is somewhere in the neighborhood of 57% conversion to 400° E.P., 10 lb. R.V.P. gasoline, while after 500 cycles this conversion has dropped to about 47%, or after 1,000 cycles to about 43%. Other curves were shown for operations at the same feed rate with 1 and 2 hour cracking periods. Catalyst life is figured to be roughly six months. At this catalyst age, a feed rate of 0.5 volumes of liquid oil/volume of catalyst/hour with cracking periods of about 16-20 minutes is required to obtain 40% conversion to stable gasoline. Using the same volume of synthetic catalyst, an oil feed rate of 1.5 v/hr. has been figured, or using the same oil throughput, approximately 1/3 as much synthetic catalyst as natural catalyst would be required. This is due to the constant activity exhibited by the synthetic catalyts when regenerated in the absence of steam.

To determine the relative stability of synthetic and natural catalyts,

870 C  
 samples were heated for 48 hours in the presence of nitrogen or steam and their cracking activity then measured. With synthetic catalysts heated at 850°F. in the presence of nitrogen, a conversion of 51% was obtained. Super Filtrol clay gave 41%. At 1400°F., one type of synthetic catalyst exhibited no loss in activity while a second type exhibited a slight drop in activity. Super Filtrol, on the other hand, lost approximately 25% of its activity at 1400°F. When heated at 1600°F. in the presence of nitrogen, the synthetic lost activity to a small extent whereas that of the Super Filtrol was almost completely destroyed. Heating at 850°F. in the presence of steam had relatively small effect on the catalyst but at temperatures above 850°F. was extremely detrimental to activity.

450°C

760°C

Mr. Murphree then went on to discuss product distribution data obtained over a range of cracking cycle times at 3 different feed rates. It was pointed out that for a given conversion, the yield of other products was identical when using synthetic catalyst or clay catalyst. The synthetic catalyst, however, is more active than the clay catalyst and at any given temperature produces more gas and excess butane than the clay catalyst. Therefore, to get the same yields a lower cracking temperature is used with the synthetic catalyst, for example, in the neighborhood of 775-800°F. Curves were then shown for yields of gas, excess butane (above 10% R.V.P.), coke, and cycle gas oil plotted as functions of conversion to gasoline. This data were for atmospheric pressure operation. Coke, dry gas, and excess butane increase with conversion to gasoline. For example, at 40% conversion to 10% R.V.P. gasoline using light East Texas or West Texas gas oil, coke is 3.6 wt. % on feed; excess butane, 6% by vol.; and dry gas, 4% by wt. Gas oil bottoms is approximately 53.5% by vol. with an A.P.I. gravity of about 31.4 as compared to 33 on the feed.

Studies of the effect of pressure in cracking of the East Texas gas oil show that for a given gasoline conversion, coke formation at 45 lbs. pressure is much higher. For example, at 40% conversion to gasoline, coke increases from about 3.6% at atmospheric pressure to 8.6% by wt. at 45 lbs. Excess butane and dry gas also increase with a resultant decrease in the gas oil yield.

Mr. Russell explained that to fit Jersey's picture, it is calculated that a conversion of 40% gasoline/pass is necessary and that, therefore, product distributions are generally compared at 40% conversion.

In continuing the discussion, Mr. Murphree presented a figure to show the effect of cracking temperature using East Texas gas oil and Super Filtrol clay. With increasing temperature in the range of 750-900°F., the conversion to gasoline increases somewhat, excess butane and dry gas increase sharply, while coke remains essentially constant.

In addition to the extensive studies on the light East Texas and West Texas gas oil feed stocks, preliminary surveys have been made on several other feed stocks, some of which are as follows:

(Data on following page)



GOC12E Catalyst, 0.6 v/v/hr., 1/2 Hour, 850°F.

Feed	East Texas	West Texas	Coastal "B"	Mixed*
Source or Crude				
Position in Crude, %	51-89	35-84	20-90	54-83
Gravity, °A.P.I.	29.6	28.0	24.7	25.9
Aniline Point, °F.	188	161	154	185
5% - 95% of.	505+-950+	500-950+	465+-880+	620+-1000
50% at of.	725+	638	640+	785+
<u>Yields (Output Basis)</u>				
Vol. % 10 Lbs. Gasoline	39.0	38.5	47.8	37.1
Vol. % Gas Oil	55.7	55.1	48.5	56.5
Vol. % Excess C <sub>4</sub>	5.4	5.3	5.2	5.3
Wt. % Dry Gas	3.5	4.0	4.0	4.0
Wt. % Coke	3.7	4.8	2.9	4.9

\*A blend of 51% East Texas, 27% Van Zandt, and 22% Tanco.  
 +Extrapolated to atmospheric pressure from 10 mm. data.

In general, the higher boiling feed stocks crack as easily as the light ones, and in fact, yields for the heavier may be even slightly better than for the lighter. The amount of coke seems to be influenced by the cleanliness of the feed stock.

The gasolines produced from fixed catalyst operations using either synthetic or clay catalysts have a C.F.R.M.M. octane number of 78-81 and an S.O.D. L.T. octane number (similar to the C.F.R. research method) of 82-87. The gasolines require very little finishing. Likewise, the gas oils produced would require only caustic washing and sweetening for commercial products.

The recent Houdry paper presented at the A.P.I. meeting in Chicago describes the preparation of aviation gasoline by acid treating to 15° acid heat. The Standard Oil Development Company, however, has been able to get a gasoline of 7-9° acid heat in 30% yields directly from the unit. The feed stock was 17% Miranda Tops cracked with a synthetic catalyst at 725-750°F. and with feed rates of 0.3 and 0.6 v/v/hr., respectively, giving the following results:

Cracking 17% Miranda Tops with Synthetic Catalyst

Feed Rate, v/v/hr.	0.6	0.3
Cracking Period, Min.	30	30
Av. Cat. Temp.	750	725
<u>Yields</u>		
Vol. % Aviation Gasoline	29.2	30.8
Vol. % Gas Oil	60.0	62.5
Vol. % Excess C <sub>5</sub>	3.5	0.6
Vol. % Excess C <sub>4</sub>	11.3	8.1

(Data continued on following page)

Wt. % Dry Gas	2.3	2.1
Wt. % Coke	1.9	1.8
Acid Heat, °F.	9	5
Reid V.P., Lbs.	6.6	7.2
Oct. No. A.S.T.M.	79.1	79.2
Do + 3.0 cc. T.E.L.	92.2	89.5

The bottoms (practically a heavy naphtha) had an octane number of almost 75.

Mr. Murphree then proceeded to a discussion of the 100 B/D fixed catalyst cracking plant at Baton Rouge. Design of the reactors was shown. There are four catalyst beds 3 ft. deep through which the gas oil vapors pass in series during cracking, but which are regenerated in parallel by means of internal conduits and valves. The primary purpose of constructing the pilot plant was to get regeneration experience on a large scale. Reasonably good information on yields and operation variables in the cracking step could be obtained on small experimental units but it was felt that these units would not give regeneration data comparable to large scale operation. The 100 B/D unit is equipped with automatic, electrically operated valves to control the cracking cycle time, purging time, and regeneration time. The automatic equipment is extremely reliable and no trouble at all has been experienced in operating on an exact time schedule. Only one of the three reactors has been operated thus far but it is felt that experience gained in connection with one reactor could be readily applied to the use of three reactors. The plant has been in operation for about ten months.

Regeneration has been carried out to date at 45 lbs. ga. pressure. Two advantages are to be gained by the use of pressure: (a) for a given pressure drop, a larger amount of gas may be circulated, and (b) a somewhat lower ignition temperature can be obtained. The regeneration gas inlet temperature is 750°F. while the outlet temperature is regulated more or less by the maximum temperature allowable without destruction of catalyst activity. A 1000°F. maximum temperature, for example, is maintained with Super Filtrol catalyst. It is thus necessary to circulate large amounts of gas in order to control temperature and the amount circulated is fixed by the allowable temperature rise. A 3-4 ft. catalyst bed has been calculated for economic pressure drop. Pressures higher than 45 lbs. may provide further advantages and work is now being done on this problem.

A certain amount of yield information has also been obtained on the 100 B/D plant. Cracking activity is at least as good as in the smaller units. Life of the catalyst is also as good. On the other hand, somewhat poorer yields have been obtained on the 100 barrel plant than on the small experimental units. Somewhat more coke and more excess butane for a given conversion to gasoline are indicated on the larger unit. This may be due to inaccuracies of measurement and perhaps to some by-passing of the internal valves, which has been observed. While, in general, the temperature control during regeneration has been adequate in the 100 barrel plant, it is possible that temperatures higher than that recorded have been momentarily occurring. A certain amount of data on the small units indicate that heating a catalyst at too high a temperature gives higher yields of coke, gas, and butane even though the cracking activity is

measured by conversion to gasoline has not been seriously affected.

Designs were then shown for a commercial unit charging 20,000 B/D of oil to the cracking chambers. The plant is designed to operate with activated clay catalysts in six reactors of three beds each. The reactor design is essentially the same as that shown previously for the 100 barrel plant. The reactors are divided in pairs so that each pair is served by one waste heat boiler and one blower. The cycle for the reactor is planned so that when one of the two reactors is cracking, the other is being regenerated. Cracking is straight-through each reactor while regeneration is in parallel through the beds, the flow of gases being controlled by internal conduits and valves. Gas oil vapors received from a flash tower are superheated to 950°F. and after once-through cracking are delivered to the distillation equipment at 850°F. and about 5 lbs./sq.in. pressure. A general flow plan of the 20,000 B/D plant was thrown on the screen.

When employing synthetic catalysts, the above described reactors are too large. Smaller annular reactors have, therefore, been designed for a fixed catalyst plant using synthetic catalysts and also charging 20,000 B/D to the reactor. Each reactor contains one catalyst bed which is 3-4 ft. thick radially. Flow through the reactors is radial. Reactor height is about 21 ft. The annular bed is specially adapted to the more active synthetic catalyst because the cross-sectional flow rate of oil is much greater with the more active catalyst, and poor distribution of the oil through the catalyst due to stack effects resulting from the difference in density of the feed and the products is avoided. The feed rate for the synthetic catalyst is 1.5 v/v/hr. for 16 minutes cycle time as compared to a feed rate of 0.5 v/v/hr. for the clay catalyst. The flow plan for the synthetic catalyst cracking plant is essentially the same as that for the clay catalyst plant. To give steady operation, six reactors are employed, each two reactors being served by one regeneration system including waste heat boiler, blower, and compressor.

It was stated that the Standard Oil Development Company work on fixed catalysts is about completed. It is planned, however, to run the 100 B/D plant on fixed catalysts a little longer, to continue development work on catalysts, and to do more work on the production of aviation gasolines.

Mr. Murphree then proceeded with a discussion of the Standard Oil Development Company work on powdered catalyst cracking. Two types of moving catalyst processes were initially considered: (a) powdered catalyst injected directly into the gas oil stream, and (b) moving a granular catalyst through a gas oil stream. All the work to date, however, has been with powdered catalysts. Contacting of vaporized gas oil and powdered catalysts may be carried out in two ways as follows: (a) injection of the dried, preheated catalyst directly into the vaporized, preheated gas oil stream as carried out at the Esso Laboratories and the Baton Rouge Laboratories, and (b) mixture of the powdered catalyst with the cold oil and pumping as a slurry to the reaction coil as carried out at the Process Laboratories. Diagrams of these various units were then shown. The units at the Esso Laboratories and the Baton Rouge Laboratories feeding powdered catalyst into the vaporized gas oil stream consist essentially of a catalyst hopper, a screw feeder, an injector where the catalyst

is dispersed in steam, a gas oil injector, a pipe coil immersed in a lead bath, a cyclone separator for separating the coked catalyst from vaporized reaction products, a baffled tower for stripping catalysts with steam, a catalyst receiver, and condensing and distillation equipment for the cracked products. Regeneration is carried out in the same general type of equipment, injecting the coked, powdered catalyst directly into a preheated stream of oxygen-containing inert gases. A continuous unit feeding approximately 1 barrel/day of gas oil has now been constructed at the Esso Laboratories and is in initial stages of operation. For flexibility, the unit has been so designed that the cracking and regeneration sections may be operated either independently or in combination.

The powdered catalyst unit installed at the Process Laboratories consists essentially of hydraulic rams for feeding the catalyst/oil slurry through preheater coils and reaction coils, the coked catalyst being separated from the vaporized reaction products by means of a cyclone separator. The catalyst is stripped in the baffled tower and collected in an appropriate receiver. Reaction products are taken overhead, condensed, and carried to distillation equipment.

Both clay catalysts and synthetic catalysts have been used in experiments carried out on powdered catalyst operation. Synthetic catalysts may not have as great an advantage in powdered catalyst operations as in fixed catalyst operations. Due to the much smaller catalyst inventory in the powdered catalyst cracking process, it is possible to replace the catalysts more often without excessive cost. The advantages of powdered catalyst over fixed catalyst operation are several. In fixed catalyst operation, the gas oil vapors are brought over a fresh catalyst and in the early portions of every cycle overcracking occurs with excessive coke production. This overcracking is eliminated in the powdered catalyst process. Lower catalyst inventory, simplification of reactor design, and continuous operation are bound to result in a saving in the cost of the moving powdered catalyst plant as compared to the fixed catalyst plant. The fixed catalyst plant requires six reactors which must be piped up to provide for cracking, regenerating, and purging operations. In moving powdered catalysts, only one cracking reactor and one regeneration reactor are required. Rough cost estimates based on preliminary process designs for a powdered catalyst unit feeding 20,000 B/D of gas oil to the reactor indicate a difference of \$560,000 in favor of the powdered catalyst process as compared with a plant of similar capacity using activated clay catalysts in fixed beds. Both estimates are based on obtaining 4.3% by wt. of coke for a gasoline conversion of 40%. A further saving of \$650,000 is indicated for the powdered catalyst plant itself on reducing coke formation from 4.3% to 2.4 wt. % on feed at 40% conversion, the latter figure being indicated as the coke yield from present data on powdered catalyst operation.

East and West Texas light gas oils of approximately 33° A.P.I. gravity have thus far been cracked with powdered catalysts. Better yields have been observed with the powdered catalyst than with fixed catalysts. Product distribution curves were shown comparing powdered catalyst and stationary catalyst operation. Powdered catalyst gives somewhat less coke, gas, and excess butane and somewhat more cycle oil. Gasoline appears to have a lower volatility.

Cracking has been carried out at 0-45 lbs. coil outlet pressure and over a range of temperature from 850-950<sup>o</sup>F. 900<sup>o</sup>F. appears to be the best with a clay catalyst. Catalyst/oil wt. ratios in the range of 0.5 to 3.0 have thus far been studied and in this range conversion increases rapidly with catalyst/oil ratio for a given contact time and temperature. At a given temperature and a given catalyst/oil ratio, conversion also increases with increasing contact time in the range of 2-30 seconds thus far covered. Optimum conditions of clay/oil ratio or contact time have not as yet been determined, however. The effect of pressure in cracking with powdered catalyst has not been clearly established but it is indicated that the same general trends probably exist as were observed in fixed catalyst operation. Cracking at 45 lbs. pressure with powdered catalyst indicates that about the same product distribution would be obtained as cracking at atmospheric pressure with stationary catalysts.

A survey of the art in conveying solid materials indicates that there is nothing unfeasible about powdered catalyst operation. Mechanisms for conveying solids suspended in gas streams, for example, the Fuller-Kinyon type of pump, are well established. Many such devices now in commercial operation handle much larger concentrations of catalyst in the vapor stream than are contemplated in the present powdered catalyst cracking process. The matter of catalyst attrition is not felt to be serious. Some data are available, for example, on a gasoline recovery plant using silica gel which operated for a period of four months without a shutdown during which time the catalyst loss was only 0.014% of the catalyst circulation.

Preliminary designs for a commercial powdered catalyst unit feeding 20,000 B/D of gas oil to the reaction chamber were then presented. A baffled tower or other suitable reactor for the velocities employed may be used. For regeneration, the coked, powdered catalyst is injected into a recycle regeneration gas stream and the coke is burned out in a regenerator tower in four stages, at each of which fresh air is added. Various types of regeneration equipment might be used. Alternates now being considered, for example, are recycling of catalyst in the regeneration, and the removal of heat from regeneration gases between stages. The best type of regeneration equipment has not yet been determined.

Experimental work on the powdered catalyst cracking process is being continued on the four available units in the laboratories and conversion of the 100 B/D plant at Baton Rouge to powdered catalyst operation is contemplated as soon as the work on synthetic fixed catalysts has been completed (about six months).

Having concluded the discussion of powdered catalysts, Mr. Murphy then proceeded to a discussion of the Standard Oil Development Company work on the application of catalysts to cracking of reduced crudes. The work on catalytic cracking of heavy gas oils has shown that they may be cracked as easily as the light gas oils and a study of catalytic cracking was, therefore, extended to an investigation of methods for handling heavy residuals. The work to date has been carried out on Lake Venezuelan 92% reduced crude. The reduced crude together with steam is pumped through a preheater coil, downflow over the contact mass. First operations carried out with a Super Filtrol clay catalyst gave high coke figures. Further experiments using a pulvico contact mass indicated that the

operation should be carried out essentially as a mild coking operation with an inert adsorbent for coke to make as much gas oil as possible for subsequent catalytic cracking.

A new unit has now been installed to give totally distilled products for catalytic cracking. The reduced crude is introduced at the top of the unit while steam is introduced at the bottom and passes upflow. Volatile products are thus removed immediately from the reaction zone while the heavier products are allowed to flow down over the adsorbent for further cracking.

All the data presented, however, were for downflow operation with steam. Curves comparing catalytic and non-catalytic operation on the reduced crudes show considerably less gas oil and more coke with the Super Filtrol clay catalyst than with pumice. About the same gravity and viscosity on the products boiling above 400°F. were obtained with either pumice or clay. The viscosity breaking operation was carried out at 770-800°F. and atmospheric pressure with about 15 wt. % of steam and an oil feed rate of 1.2 v/v/hr. Essentially the same results can be obtained at higher feed rates by going to higher temperatures. For example, running at 3.0 v/v/hr. oil feed rate required a temperature increase of about 55°F. over that at 1.2 v/v/hr. Depending upon the temperature employed, about 90-95% of liquid products boiling above 400°F. are obtained with 1-4% by wt. of coke, about 2-10% by vol. of gasolins, and about 0.5-2% of dry gas. Conditions for producing the best feed stock for catalytic cracking have not yet been determined, however.

Catalytic cracking studies on the products boiling above 400°F. from the above type coking or viscosity breaking operations on Lago reduced crudes have shown that it is essential to completely vaporize in the catalytic cracking step. Curves were shown to indicate that with more complete vaporization, a much lower coke yield is obtained in cracking. Steam is introduced with the feed stock in order to insure complete vaporization at temperatures suitable for catalytic cracking. The effect of temperature and other operating variables in catalytic cracking of the visbroken reduced crudes is essentially the same as that in cracking of gas oil. The following yields based on crude were obtained by the Standard Oil Development Company on combined viscosity breaking and catalytic cracking of Lago crude in comparison to data reported by Houdry for similar operation also on a Lago crude.

Yields Based on Crude

	<u>S.O.D. Co.</u>	<u>Houdry (A.P.I. Meeting)</u>
Wt. % Dry Gas	5.5	4.3
Vol. % Gasoline	48.3	44.9 (11.0 R.V.P.)
Vol. % Excess C <sub>2</sub>	3.2	-
Vol. % Cycle Oil	46.2	50.0
Wt. % Coke	8.2	11.9
Cycle Oil Gravity	21.3	21.5

In general, the Standard Oil Development Company data are somewhat better than the Houdry data.

further work of this nature is to be continued and further improvement is expected with the new unit now installed.

The meeting then adjourned for lunch, following which Mr. Murphree continued to a presentation of the Standard Oil Development Company work on low pressure hydrogenation. Experimental investigations of low pressure hydrogenation (750 lbs./sq.in.) were instigated in an effort to reduce the cost of hydrogenation and to produce high octane number gasoline. Early work indicated that the high pressure (3,000 lbs./sq.in.) hydrogenation catalysts for gasoline production would not be satisfactory for 750 lbs./sq.in. operation due to an excessive catalyst degradation rate. Data were shown comparing the 3,000 lb. and 750 lb. operations feeding a virgin gas oil cut from either East Texas or Van Zandt crude over 6104 catalyst at about 700°F. The gas rate was 12,000 cu. ft./barrel. A gasoline yield of 60% with 63.5 A.S.T.M. octane number was obtained at 2 v/v/hr. oil feed rate at 3,000 lbs. as compared to a yield of 27% gasoline with 71.9 A.S.T.M. octane number at 0.3 v/v/hr. at 750 lbs./sq.in. Although giving octane number improvement, the low pressure operation gave very low conversion even at low feed rates and high operating temperatures, and catalyst degradation rates were excessively high, amounting to as much as 30°F./day.

Further attempts to improve the hydrogenation process were then directed toward a reduction in hydrogen partial pressures in the 3,000 lb. operation. For example, operations were carried out with 25% hydrogen as compared to the normal 85% hydrogen. While some octane number improvement over the normal high pressure operation was obtained, an excessive rate of degradation amounting to 100°F/day resulted and yields were low. The operation does not, therefore, appear too attractive but is probably tied up with the proper catalyst to use and investigations of this nature will be carried out.

To evaluate the effect of feed stock characteristics on the quality of gasolines produced by hydrogenation at 750 lbs./sq.in. pressure over catalyst 6104, Quiriquire kerosene (naphthenic base) and 17% tops from Mirando crudes (aromatic base) were investigated. These stocks had been shown to give high octane number gasoline by hydrogenation at high pressure over 6104. As compared to the 3,000 lb. operation, the 750 lb. operation at lower feed rates and considerably increased temperature gave a slight improvement in octane number of the aviation gasoline but also increased the acid heat. Yield was slightly lower in the low pressure operation. Catalyst degradation rate was again high.

Mr. Murphree then went on to discuss Standard Oil Development Company work on the catalytic aromatization or reforming of naphthas. Virgin naphthas were treated with catalysts of the alumina-chromia type in the same general types of equipment and operations as used in catalytic cracking with fixed beds. Powdered catalyst in this operation would probably be superior to stationary catalyst. Data were presented on 85% bottoms from East Texas total naphtha and on Baton Rouge heavy cracked naphtha showing octane number improvement of 15-20 points with very little change in volatility. Yields obtained in this preliminary work were quite low, however, for the octane number obtained. In general, yield-octane number relationships were not as good as obtained by thermal reforming. Catalyst activity dropped rapidly due to deposition of coke on the catalyst surface and frequent regenerations would thus be necessitated. It was conceivable that operations in the

presence of hydrogen might decrease coke formation and give better yields. The same general type of catalytic reforming reaction with alumina-chromia catalyst was, therefore, carried out in the presence of hydrogen. Conditions were about 200 lbs./sq. in. pressure feeding normal debutanizer bottoms with varying amounts of hydrogen at temperatures of 900-950°F. Runs were made with 80% hydrogen, 80% nitrogen, and with no gas added. On a total  $O_4$  recovery basis, yields in the presence of hydrogen were slightly higher while on the basis of 4.6 lbs. R.V.P. gasoline, yields were slightly lower. The highest octane number improvement, however, was obtained when hydrogen was used and the load susceptibility was considerably higher when hydrogen was used. Color and stability of the gasoline were also much better in the presence of hydrogen and acid heat was considerably lower.

The above work was followed by some work on reforming of West Texas naphtha, which was presented by Mr. Fischer. Best results up to the present time were obtained at a catalyst temperature of 904°F. with a liquid feed rate of 1 v/v/hr. and a hydrogen concentration of 70 mol %. The West Texas heavy naphtha of 45.4 A.S.T.M. octane number was reformed to give an 87% yield of 77.8 octane number product. In another case, an 82% yield of 82.4 octane number reformed product was obtained. Acid heat was about 14°F. It was emphasized that in all cases more hydrogen was produced from the unit than was fed to the unit.

The above discussion completed the presentation of the Standard Oil Development Company work and the floor was turned over to Mr. Keith for presentation of the Kellogg work.

Mr. Keith suggested that since the previous discussions were on the subject of catalytic reforming of naphthas, that the Kellogg work on this subject be presented first, to be followed later by the work on catalytic cracking. The sole object of the Kellogg work on catalytic reforming has been to find a method for reforming of straight-run and cracked naphthas to produce gasolines competitive with catalytically cracked naphthas, while utilizing existing thermal equipment. Work has been done on various feed stocks such as light virgin naphthas and cracked naphthas but the discussion is to be limited to East Texas heavy naphtha. Dr. Layng was designated to present the Kellogg work on catalytic reforming of naphthas.

Apparatus employed was of the continuous, moving catalyst type using a granular catalyst. The reactor consisted of a 7 ft. length of 2 in. pipe surrounded by a lead bath. Catalyst is introduced from a hopper at the top of the unit through a plug valve. The rate of flow of catalyst through the reactor is controlled by a rotary valve at the bottom of the tube where the catalyst is withdrawn through a series of hoppers and plug valves. The tube contains about one gallon of catalyst and is full at all times. The reaction is carried out in the presence of hydrogen, the amount added depending on the naphtha feed rate employed. The hydrogen and naphtha are mixed and preheated in a coil and passed either concurrently or countercurrently to the catalyst. Present operation, however, is concurrent and the naphtha-hydrogen mixture enters the tube at the top and is withdrawn from the bottom through a cooler, gas absorber, etc. In this operation, there are five variables as follows: (a) temperature, (b) pressure, (c) naphtha feed rate, (d) catalyst feed rate, and (e) hydrogen feed rate.



Temperatures studied have been in the range from 850-1000°F.; pressures from atmospheric to 200 lbs./sq.in.; naphtha feed rates from 250-2000 cc./hr.; catalyst feed rates from 200-800 cc./hr.; and hydrogen feed rates depending on the feed rate of naphtha. Feed stock has been an East Texas heavy naphtha of the following inspections:

A.P.I. gravity	50.3
Initial boiling point	248°F.
50%	319°F.
Final boiling point	396°F.
C.F.R.M.M. octane number	42.3

Dr. Layng then presented a series of curves showing the effect of the various operating variables on yield, octane numbers, and other properties of the gasoline. Copies of these curves are appended.

Plotting the weight per cent liquid product versus octane numbers showed a considerable advantage for operations in the presence of hydrogen over those in the absence of hydrogen. In the most favorable case as regards octane number, a 91 octane number C.F.R.M.M. product was obtained in 79-80 wt. % yields (76-76 vol. %) when using hydrogen. In the absence of hydrogen, it was not possible to reach this high octane number.

Plotting weight per cent coke against octane numbers, a considerable advantage was again shown for operation in the presence of hydrogen. For example, when reforming to 91 octane number in the presence of hydrogen, approximately 2-1/2 to 3% coke was obtained, while extrapolation of data for operation without hydrogen indicated about 10% coke. Gas formation increases rapidly with increase in octane number and, taking the case of 91 octane number product, the wt. % gas loss was in the neighborhood of 15%, 60% of which was hydrogen. Mr. Keith emphasized that far more hydrogen was produced in the operation than was consumed. Dr. Layng elaborated on Mr. Keith's statement by saying that 24-26 cu. ft. of  $C_4$  free gas/gallon of naphtha was produced, 60% of which was hydrogen when reforming to 91 octane number. At lower octane numbers, the hydrogen may be as high as 88-90%.

Gravity of the reformed product decreases with increasing octane number. Gravity of the feed was 50.3 and when reforming to 91 octane number, a gravity of approximately 37° A.P.I. was obtained. Aniline point decreased from 124°F. on the charge to an estimated figure of -37°F. on the product of 91 octane number. The volume % aromatics in the product increased sharply with octane number. Aromatics estimated by Kuttinkel (corrected for olefins) were 10% on the charge and were increased to 73% in single-pass operation to 91 octane number. Olefins which were not present in the charge increased to a maximum of about 17% at 70 octane number and decreased again to about 5% on reforming to 91 octane number. Mr. Keith suggested that the process might have possibilities for the preparation of high solvency naphthas. Dr. Layng stated that other than hydrogen, the gas contained mostly methane.

Dr. Layng then went on to illustrate with curves the effect of various

operating variables on yields and octane numbers. A temperature range of 850-1000°F. was surveyed when holding other variables constant as follows:

Pressure	100 lbs./sq.in.
Naphtha feed rate	1000 cc./hr.
Catalyst feed rate	400 cc./hr.
Hydrogen feed rate	11.2 cu.ft./hr.

The yields of liquid products decreased from 90% at 850° to about 78% at 1000°. Octane numbers increased from approximately 60 at 850° to 86 at 1000°. Coke increased from somewhat less than 1% at 850° up to 5% at 1000°. In reply to a question as to the length of runs, Dr. Layng stated that most runs were carried out for at least 12 hours after reaching equilibrium conditions and some were as long as 24 hours. In answer to Mr. Russell's question, it was decided that the above conditions were equivalent to 0.25 v/v/hr. feed rate of naphtha when expressed in Standard Oil Development Company's customary terminology, since the volume of the reactor is about 4 liters.

Dr. Layng then presented curves to show the effect of pressure when reforming at 950°F. and holding all other variables constant as above. Wt. % liquid products ranged from about 87% at 50 lbs. pressure to 81% at 200 lbs. pressure. Gas formation increases while coke decreases up to 100 lbs. pressure and then levels off at higher pressures (approximately 2% at 200 lbs. pressure). Octane number increases from approximately 78 to 50 lbs. pressure to approximately 85 at 200 lbs. pressure.

Operating at 100 lbs./sq.in., 950°F., 11.2 cu. ft. of hydrogen/hr., and 400 cc. of catalyst/hr., an increase in liquid throughput in cc./hr. from 250-2000 increases the liquid yield from approximately 78% to 91%, and decreases octane number from approximately 91 to 74. Coke is essentially constant at about 2%. Gas decreases markedly with increased feed rate.

The effect of hydrogen added was determined when operating at 100 lbs. pressure, 950°F., 1000 cc. liquid/hr. and 400 cc. of catalyst/hr. A maximum octane number increase was obtained when 3 mols of hydrogen were added per mol of naphtha. With 1 mol of hydrogen/mol of naphtha, octane number was approximately 78, increasing to a maximum of approximately 83 at 3 mols of hydrogen and decreasing thereafter. Gas, likewise, passed through a maximum of approximately 12% at 3 mols of hydrogen while the wt. % yield of liquid products passed through a minimum of approximately 87% when using 3 mols of hydrogen. Coke decreased steadily from approximately 3% with 1 mol of hydrogen to about 1% with 4 mols of hydrogen.

The effect of catalyst feed rate up to 1000 cc./hr. was also determined when operating at 100 lbs./sq.in., 950°F., 1000 cc./hr. liquid feed rate, and 11.2 cu.ft./hr. of hydrogen. Octane number increases rapidly to about 82 up to 400 cc. of catalyst/hr. but tapers off thereafter. Coke and gas increase steadily with increased catalyst feed rate while yields of liquid products drop steadily from about 89% at 200 cc./hr. of catalyst to 85% at 1000 cc./hr.

In comparing operations at 200 lb. pressure as compared to 100 lb.

pressure, Mr. Keith stated that to get the same octane number at 200 lbs. required more hydrogen circulation but, on the other hand, the amount of coke is correspondingly less. Dr. Layng stated that Kellogg has carried out successful catalytic reforming operations also on a cracked California naphtha, on a light naphtha, and on East Texas total virgin naphtha. A comparison of the Kellogg results on East Texas heavy naphtha and the Standard Oil Development Company results on West Texas heavy naphtha was then put on the board as follows:

	S.O.D. Co.		Kellogg	
	West Texas Heavy		East Texas Heavy	
Feed Naphtha				
O.N. Feed Naphtha	42		42	
Temperature, °F.	90 1/4		950	
Pressure, Lbs./Sq.In.	200		100	
Naphtha Feed Rate:				
cc./hr.			2000	1000
v/v/hr.	1.0		0.5	0.25
Catalyst Feed Rate, cc./hr.	(Stationary)		1000	
Hydrogen Feed Rate, cu.ft./bbl.	3400		1750	
Vol. % Reformed Naphtha	89	84	89.1	85.3
O.N. Reformed Naphtha	77.8	82.4	79.5	81

It was agreed that the Kellogg and the Standard Oil Development Company results were essential checks. Standard Oil Development Company operations were carried out with stationary catalyst at 1.0 v/v/hr. at 200 lbs. pressure and 3400 cu.ft./barrel of hydrogen. Runs were continued as long as 96 hours but the data reported by Mr. Fischer represented the 6-12 hour period. Mr. Keith stated that the Kellogg conditions were the same regardless of time and emphasized that Kellogg felt that they had to use a moving catalyst for political reasons.

Dr. Layng then presented some data on blending various octane number reformed East Texas heavy naphthas in 50-50 proportions with the light East Texas virgin naphtha of 69 octane number.

50-50 Blends of Catalytically Reformed Heavy  
East Texas Naphthas with 69 Octane Number Light East Texas  
Virgin Naphtha (8.8 to 9.5 R.V.P. Blends)

O.N. Reformed (Aromatic) Product	O.N. Blending Value	Overall O.N. of the Blend
77.9	78.4	73.7
82.3	85.2	77.1
86.9	92.2	80.6
90.0	94.8	81.9

Mr. Keith commented that from the above data, Kellogg feels that they can compete with catalytically cracked naphthas by catalytic reforming of straight run or thermally cracked naphthas. He also added that the catalyst is an excellent desulfurization catalyst for high sulfur feeds.

Mr. Russell inquired whether Kellogg had investigated the economics of the process. Mr. Keith replied that they are now trying to evaluate the process. Mr. Keith asked Mr. Russell if he did not agree that the catalytically reformed naphthas could not be used for aviation gasoline. Mr. Russell replied that he did not know since the reformed naphthas were too high boiling but pointed out that acid heats were in the neighborhood of 12-14°F., however.

This concluded the discussion on catalytic reforming of naphthas and Mr. Keith proceeded to a discussion of Kellogg's results on catalytic cracking.

It was stated that from a survey of the patents on catalytic cracking, the Kellogg Company was more or less forced to accept the following point of view:

1. That fixed catalysts would lead to patent difficulties and that, therefore, Kellogg should consider only a moving catalyst.
2. Powdered catalysts have been considered but patents of this nature were found, and therefore the only path open was to use a moving granular catalyst.
3. From the standpoint of catalyst composition, it would be necessary to stay below a 3.5-1 ratio of silica to alumina or well above an 8-1 ratio of silica to alumina. The best way to accomplish this was through the use of synthetic catalysts.

Two types of apparatus have been employed in the laboratory. The first apparatus was a 4-inch tube about 4-feet long while the present apparatus is a 2-inch tube about 14-feet long. Operation may be either countercurrent or concurrent. Feed stocks employed have been as follows: (a) Mid-Continent gas oil, 35° A.P.I. gravity, 482° I.B.P., and 736° F.B.P., (b) a heavy Abadan cut over 6-8% pitch from Iranian crude, 25.5° A.P.I., 612° I.B.P., and 737° mid-boiling point; (c) cycle stocks, (d) wax distillates, and (e) visbreaker gas oil. Design of the laboratory units is essentially that given by Dr. Layng above, with rotary valves at the top and bottom of the units to control catalyst feed rate.

Data were then presented on the Mid-Continent gas oil feed operating at 900°F. with gasoline yields determined on a 100% C<sub>4</sub> recovery basis and calculated to a 10% R.V.P. basis.

Operating variables investigated in the moving catalyst pilot plant were (1) oil feed rate, (2) catalyst feed rate, and (3) catalyst volume in the reactor. In order to evaluate the effect of the first two of the above variables, the oil rate was varied from 750 to 6,465 cc./hr. and the catalyst feed rate from 175 to 1,040 cc./hr. This corresponded to a catalyst time in the reactor of approximately 2 to 56 hours. Catalyst volume in the reactor was varied from 2.0 to 10.1 liters. Considering only the data obtained with 4.5 liters or more of catalyst in the reactor, a curve was shown for a plot of the ratio of gas oil feed to catalyst feed rates vs. the volume per cent gasoline on a 100% C<sub>4</sub> recovery basis. A single line resulted, indicating that within this range catalyst volume in the reactor has no effect on the gasoline yield. Gasoline yield is

thus purely a function of the ratio of oil to catalyst feed rates. For example, at 40% cracking/pass the ratio of gas oil feed to catalyst feed was approximately 6, or in other words, 6 barrels of oil were being circulated/barrel of catalyst circulated. At 20% conversion/pass, the gas oil to catalyst feed ratio was approximately 34, or in other words, 34 barrels of gas oil were being circulated to 1 barrel of catalyst. (Note: Feed rates expressed as volume of oil/volume of catalyst in the reactor/hr. are customarily employed in the Standard Oil Development Company work; range from 0.1 to 1.0 in the above Kellogg work.) The single curve referred to above means that within catalyst volume ranges studied (4.5-10 liters) the volume of catalyst in the reactor has no effect on the gasoline yield. However, it is obvious that with no bed of catalyst in the reactor, gasoline yields will be approximately zero since the catalyst would have practically zero contact time with the oil. In order to show the effects of catalyst volume, a chart was shown plotting the volume per cent gasoline on 100% C<sub>4</sub> recovery basis vs. the ratio of volume of catalyst in the reactor to volume of gas oil feed/hour. A series of curves was thus drawn to represent the gasoline yields at various volumes of gas oil/volume of catalyst fed/hour. It is indicated that with a given oil/catalyst feed ratio, maximum conversion to gasoline is obtained when the catalyst volume is such as to give a ratio of catalyst volume in the reactor to oil feed rate of about 1.0-1.3 (Notes: 0.77 to 1.0 v/v/hr. in S.O.D. Co.'s customary terminology.) Increasing the catalyst volume beyond this point does not give an increased gasoline yield. (Note: The data showing a rapid increase in gasoline yields with increase in catalyst volume correspond to feed rates of approximately 2.0 to 3.0 v/v/hr. as customarily employed by the Standard Oil Development Company.)

Contrary to Standard Oil Development Company's experience, Kellogg has found that heavier stocks are considerably more difficult to crack in once-through operation. For example, on a heavy Abadan wax distillate a 36% yield was obtained at conditions which on Mid-Continent gas oil gave 40% conversion. Mr. Keith pointed out, however, that their feed stocks had been stored for quite a long time and were not cleaned up or preflashed and that a cleaning up operation of the type described above by Mr. Murphree might give better yields on catalytic cracking. Petrolatum cracked more easily than any of the other feed stocks investigated.

High yields of excess butane are produced in the Kellogg cracking process. For example, at 40% conversion with Mid-Continent gas oil, the excess butane amounts to 16-17% by vol. based on the feed. As conversion is lowered, the excess butane decreases. At 35% conversion to 10% R.V.P. gasoline, coke is approximately 4% by wt. on the feed, which is somewhat higher than the Standard Oil Development Company results. At 40% conversion to 10% gasoline, coke would be about 6%. Dry gas at 35% conversion to 10% gasoline is about 7% by wt. and gas oil is about 47.5% by vol. The above data are for operations at 900°F. Coke and gas increase rapidly with temperature.

With the synthetic catalyst, it is not advisable to go above 1200°F. in regeneration and in the Llandarcy plant, maximum temperatures are being limited to 1100°F. Ignition temperature is approximately 800°F.

The effect of pressure in the cracking step as determined by Kellogg

has been identical with the Standard Oil Development Company results, namely, an increase in coke and excess butane with somewhat lower conversion to gasoline. Concurrent or countercurrent operations show no essential differences in yields. There is some indication, however, that upflow operation in a long, narrow tube provides essentially a vapor phase treating in the upper portions of the catalyst bed. Good color, low gum, and good stability have been observed on the catalytic gasolines prepared thus far. The Llandarcy plant is equipped to run either upflow or downflow.

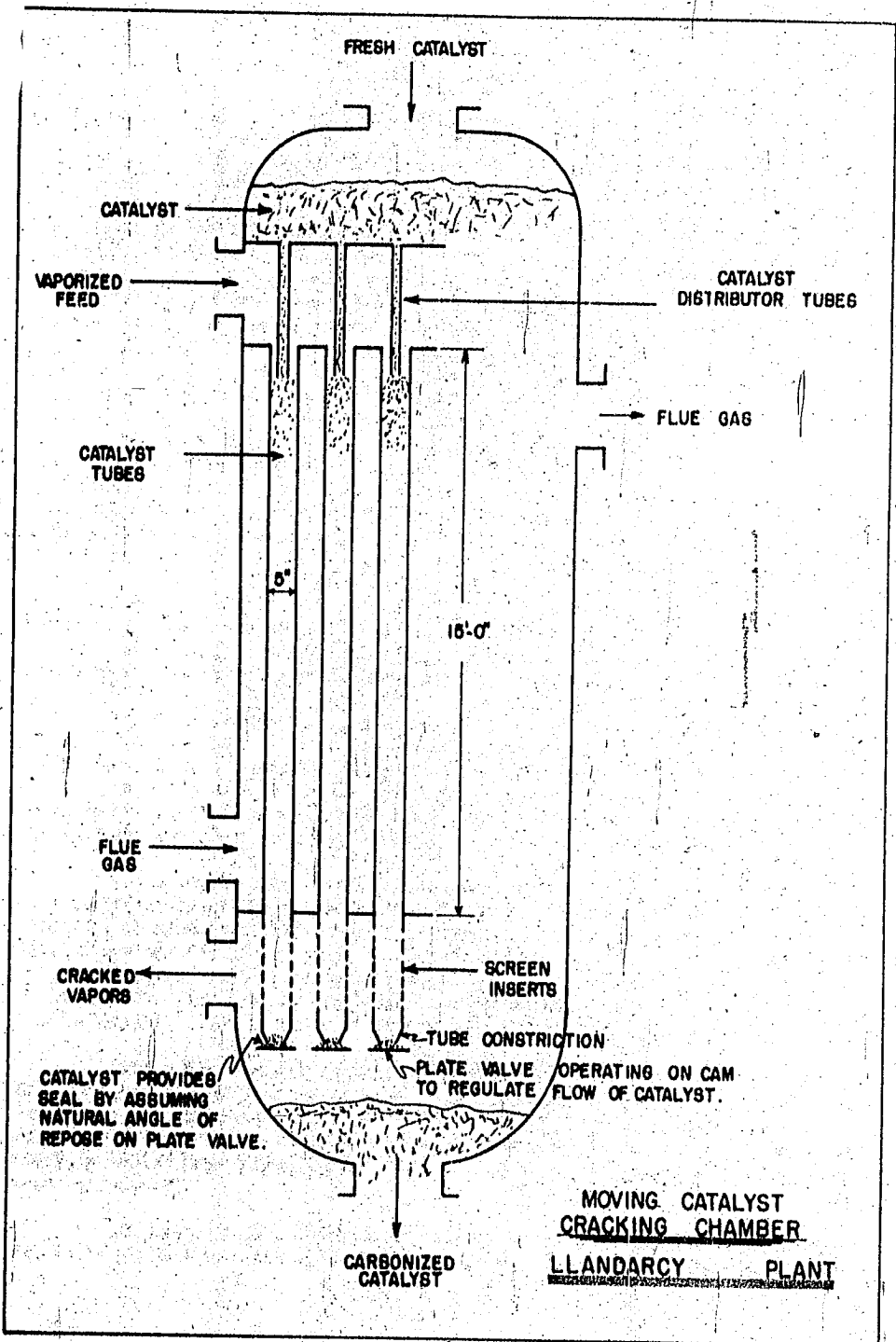
Kellogg has only recently considered this process for the production of aviation gasolines, and practically no data are available on this phase of the work. 78-80 octane number motor fuels have been prepared.

There is some indication that the high excess butane is the result of too much coke on the catalyst. An increase in the feed rate of catalyst to decrease the amount of coke deposited on the catalyst would probably result in a better gas/gasoline ratio. The catalyst stays in the cracking chamber about 4-6 hours before revivification.

All the above data were for atmospheric pressure cracking in once-through operation. In order to reduce gas losses, a two-pass operation has been set up on paper. Reactor volume is increased somewhat less than two-fold and the additional catalyst moved is relatively small. In two passes, the excess butane for 41.6 conversion to gasoline is 13.4% by volume as against 17% for single-pass operation. Cycle gas oil is approximately 41% by volume. At 37% conversion, excess butane is 7% with 52% gas oil. At 31.4% conversion, excess butane is 3.6% with approximately 62.4% gas oil.

As yet, not enough work has been done on catalyst development. It has been found, however, that when water is introduced with the feed the catalyst can be regenerated at temperatures above 1200°F. without loss in activity. If no water is introduced, however, some loss in activity is experienced on revivification.

Mr. Koith then went on to describe the cracking plant now being constructed for the Anglo-Iranian Oil Company at Llandarcy. A rough diagram of the cracking chamber as presented by Mr. Koith was copied by the writer as shown in Figure 1. The cracking chamber consists of a bed of tubular reactors, each tube being approximately 5 inches in diameter and about 14 feet long. Catalyst is introduced into the tubes at the top of the chamber through smaller distribution tubes leading directly into the top of the reactor tubes. The catalyst flows either wet or dry without any difficulty and no trouble has been experienced with catalyst distribution although a levelling device has been provided. The catalyst bed is 8 feet in height but can be increased to 14 feet. A screen is inserted at the bottom of the tubes to allow the cracked oil vapors to escape. At the bottom of the screen, the tube is constricted somewhat and a plate valve is placed just below the constriction with sufficient clearance for removal of catalyst. Catalyst provides a seal on this plate by assuming a natural angle of repose. The plate moves on a cam to regulate the catalyst flow at any desired rate. The catalyst is withdrawn from the bottom of the chamber and its steam



stripped. Using shallow beds and superheated vapors, it is thought that no heat will have to be supplied to the units. On the present experimental unit, however, it was thought advisable to provide for iso-thermal operation which might possibly decrease coko formation. Flue gases, therefore, circulate around the reactor tubes. The plant is equipped to operate either concurrently or counter-currently, and the gas oil may be recycled. 360 cu. ft. of oil vapors is circulated/hour/tube.

Catalyst is taken from the reactor to the regenerator by means of conveyors. Water-gas type of regeneration was considered but due to the large amounts of gas which had to be circulated, the blowers were large and expensive. It was, therefore, decided to go to a wedge type furnace. Extra precautions were therefore taken to prevent an excessive rate of burning. Catalyst is fed downward over a series of hearths maintained at a temperature of about 1100°F. and provided with steam tubes underneath each hearth for cooling the gases. The gases are passed in parallel across the hearths. From laboratory experience, it is indicated that the first 20% of the coko burns rapidly but that the remainder burns with difficulty. Not all the oxygen is used up. It is, therefore, proposed to burn off the first 20% under carefully controlled conditions, then blast off the rest of the coko by regeneration of the water-gas type.

Kellogg was considerably worried about catalyst losses due to the production of fines. Experiments in a small, wedge type furnace at Jersey City, however, indicate that after the initial breakdown, the catalyst reaches an equilibrium size and thereafter forms little or no fines.

With an average catalyst mesh of 17 and 360 cu. ft. of vapor/hour, pressure drop amounts to about 1 lb./cu.ft. The flow, originally designed to be countercurrent, was therefore changed to concurrent in the Llandarcy plant. At 10 mesh, pressure drop is not an important factor and Kellogg has, therefore, tried to make synthetic catalysts of approximately 10 mesh by binding, for example, with clays such as Super Filtrol.

In studying clay cracking catalysts, Kellogg was surprised to find that the activity of the clays can be a function of the amount of acid used for treating. Maximum activity occurs at a very narrow peak for clays such as Wyoming bentonites, Horden clay, and Super Filtrol. From analyses at the University of Michigan, most clays were found to be about 3.5 silica/alumina weight ratio or less. The Kellogg synthetic catalyst is approximately 200:1 silica/alumina weight ratio. A range of composition has not yet been tried.

The power cost for mechanical conveying of the catalyst in a 10,000 B/D plant has been calculated at 5-6¢/hour. Assuming a two-year payout on equipment, this cost represents 0.02-0.03¢/gallon of gasoline for mechanical conveying as compared to 0.07¢/gallon on pneumatic conveying systems. At Llandarcy, a Redlor type conveying system is used and no production of fines has been encountered.

In answer to Mr. Murphree's question as to the regeneration technique, Mr. Koith replied that the gases were recycled and that oxygen could be added



at each hearth in the wedge furnace. Steam cooler tubes are placed above each hearth to provide for temperature control in the experimental plant. Mr. Murphree inquired as to how many hours the catalyst was in the furnace and Mr. Keith replied that he did not know exactly although it would probably be in the range of 4-8 hours. It is necessary to burn completely to maintain activity.

Kellogg has not investigated variables such as shape of reactors or how much catalyst should be circulated or what depth of bed should be used for optimum cracking yields. Mr. Keith emphasized that since the Llandarcy plant is largely experimental, it has been made extremely flexible and many extra precautions have been taken. The Llandarcy plant is now designed for a capacity of about 500 B/D but can run up to 1500 B/D. Up to 3600 lbs. of catalyst/hour can be circulated and burned. No extensive catalyst studies have been carried out as yet since it is felt that if the process can be worked out a catalyst can be found to fit the process. Mr. Murphree asked if wedge type furnaces were not too expensive and whether Kellogg had considered any other way to regenerate the catalyst. Mr. Keith replied that a wedge type furnace was installed at Llandarcy largely as a precautionary measure in the experimental plant. Burning has been carried out at Sunbury with a rotary kiln which may be a better way to regenerate. After the catalyst has reached an equilibrium size, no more fines are produced in the rotary kiln. Mr. Kelly remarked that for a 10,000 B/D plant operating at 35-40% conversion, a wedge type furnace would cost \$40,000-\$50,000 for material only. The 10-hearth furnace burning up to 4000 lbs. of catalyst/hour at the Llandarcy plant was contracted for \$18,000.

Large quantities of  $C_3$  and  $C_4$  olefins are produced in the Kellogg moving catalyst process, which can be polymerized to increase yield and to improve the gas/gasoline ratio. At 35% conversion, the following is a typical gas analysis on a 100%  $C_4$  basis:

Hydrogen	18.9 vol. %
Methane	8.1
Ethylene	3.8
Ethane	5.3
Propylene	13.9
Propane	7.0
Isobutylene	5.7
Normal Butylene	12.9
Butane	19.4
Total	100.0

The butylenes thus amount to 20% of the  $C_4$  cut while propylenes represent 70% of the  $C_3$  cut.

Mr. Hemminger inquired as to the nature of the seal between the regeneration and cracking chambers, and Mr. Keith replied that they were using a steam seal.

This completed the discussion of the Kellogg work and Mr. Roberts was asked to summarize the catalytic cracking work of the Standard Oil Company of Indiana.

Mr. Roberts stated that catalytic cracking work had been carried out in Indiana for two reasons: (a) to find out what catalytic cracking is, and (b) to determine what possibilities it offers for Indiana. The type of work has been such the same as that of the Standard Oil Development Company but considerably less complete. Super Filtrol and synthetic catalysts have been used and results have been very similar to those presented by the Standard Oil Development Company. Variables such as temperature, time and frequency of regeneration have been investigated. Some consideration has also been given to cracking of the cycle stocks and Indiana has come to the conclusion that not more than two passes are justified. For example, with a first pass yield of 33 vol. % producing 6.7 wt. % of dry gas and 62.4% cycle gas oil plus butane, the second pass yield was only 13 vol. %. Octane numbers were 79 or better. In general, the temperatures have been higher than those reported by the Standard Oil Development Company.

To get data for economic evaluation, a number of stocks have been run which could have to be processed in the various Indiana refineries. Some work has been done on other catalysts and also some work on ignition temperature and regeneration variables. No work has been done experimentally on an actual installation. Indiana is now constructing a moving catalyst pilot plant for comparison with fixed catalyst operation.

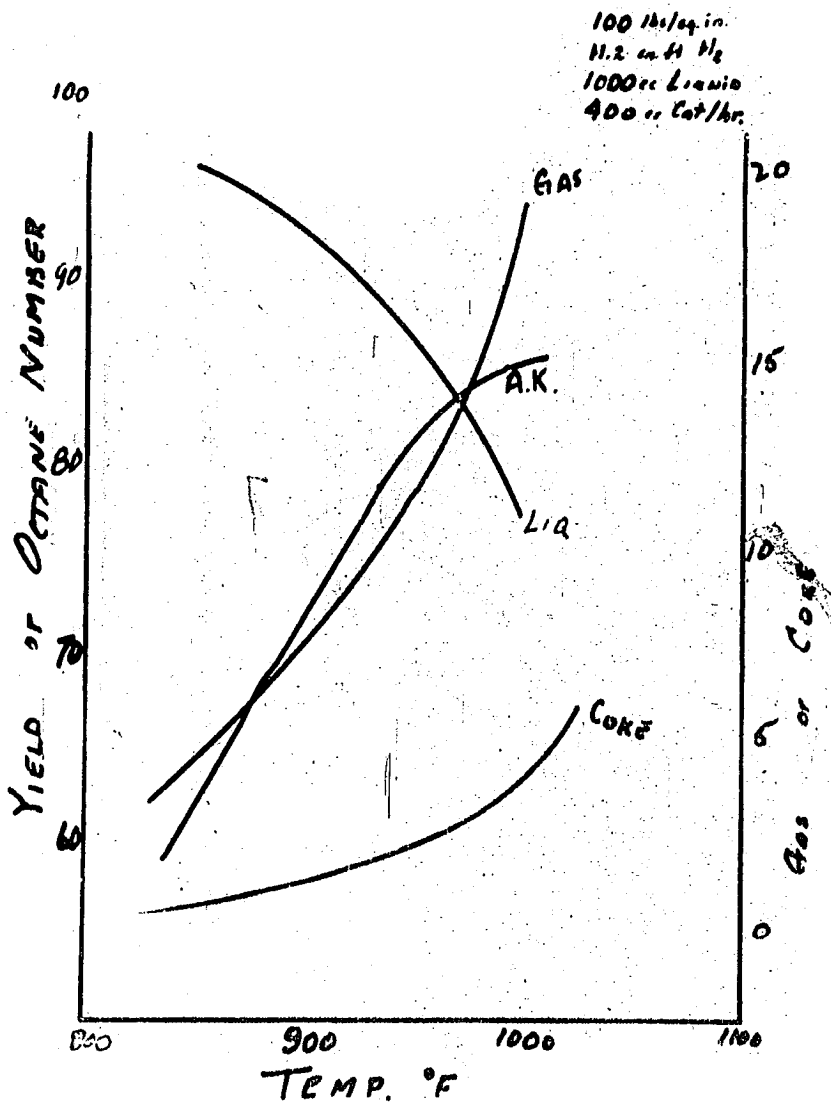
Some work has been done at Indiana on catalytic dehydrogenation although without the presence of hydrogen. Yield-octane number relationships are no better than for thermal reforming. Some work has also been done on the isomerization of paraffins with aluminum chloride and although the results are interesting, no immediate significance can be seen. Isomerization of olefins (cracked gasoline) has been carried out with 3-4 octane numbers improvement and without loss of yield. Complete information will be given in the Indiana reports which will be prepared.

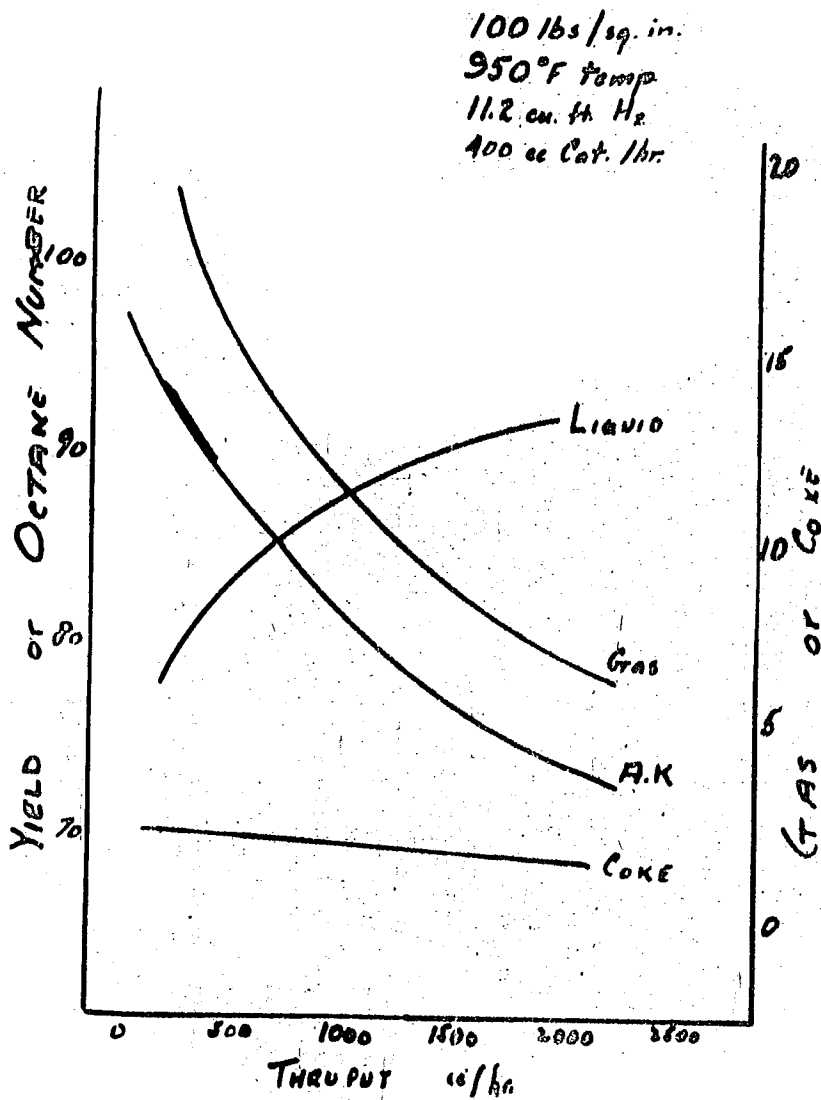
Mr. Plummer asked what was to be done about the distribution of reports. Mr. Russell suggested that each group contact Mr. Murphree to let him know how many copies of which reports are wanted. The Standard Oil Development Company will then take care of the distribution.

At Mr. Russell's suggestion, it was agreed that the group should convene again as soon as possible after the first of the year.

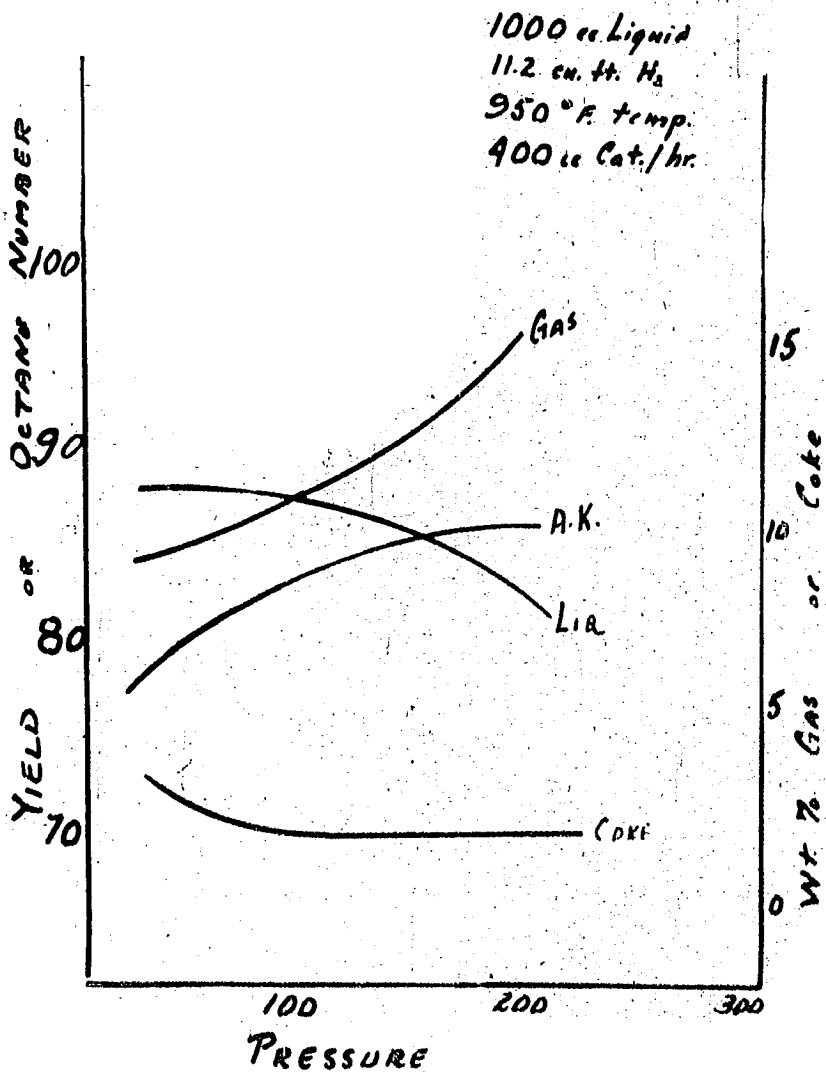
The meeting then adjourned for an inspection of the experimental powdered catalyst units at the Esso Laboratories and the Process Laboratories.

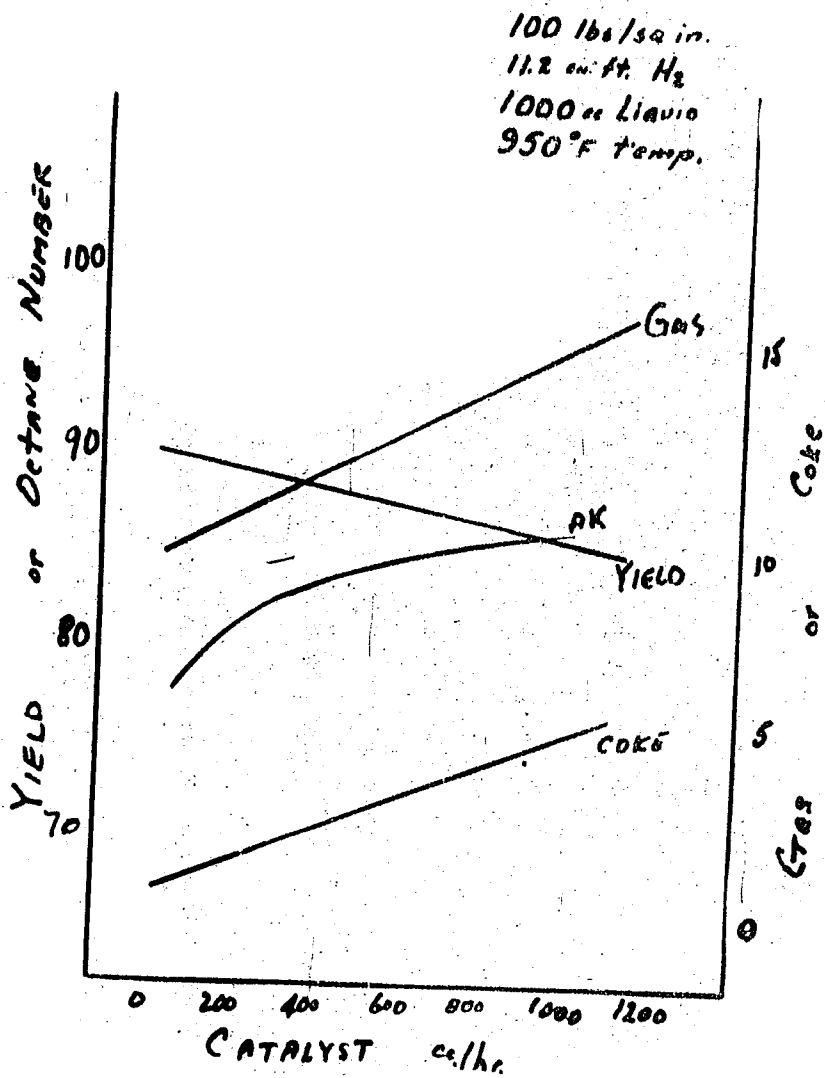
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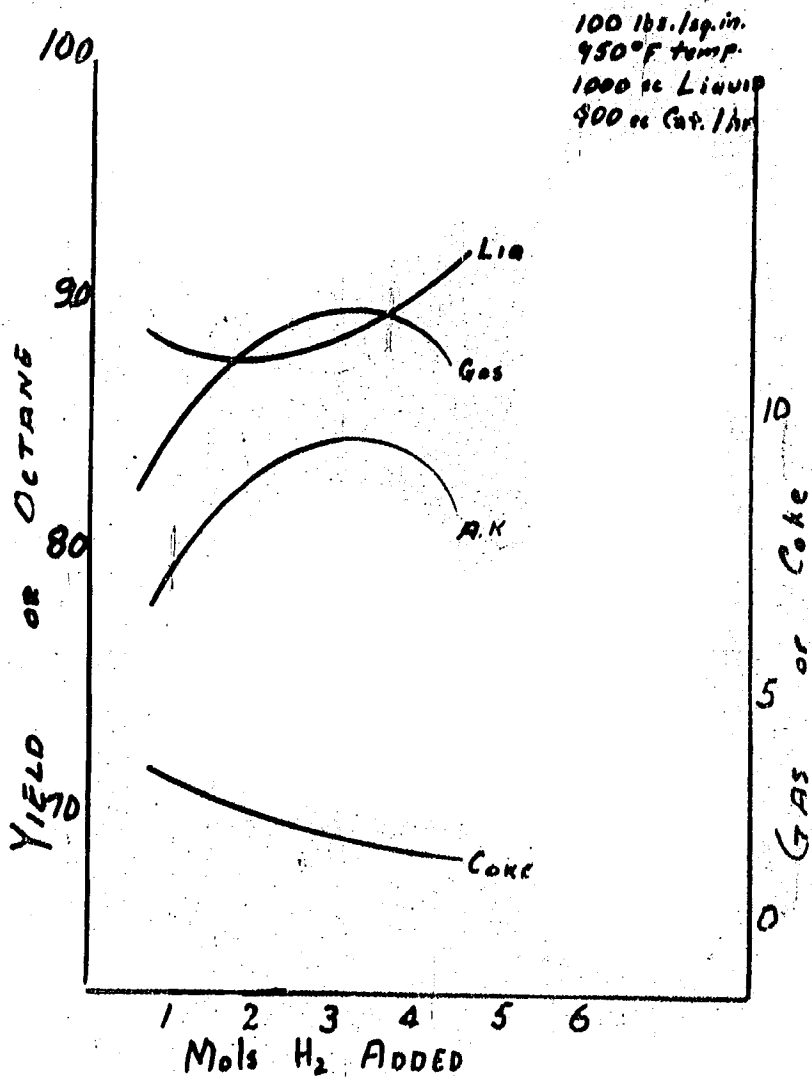




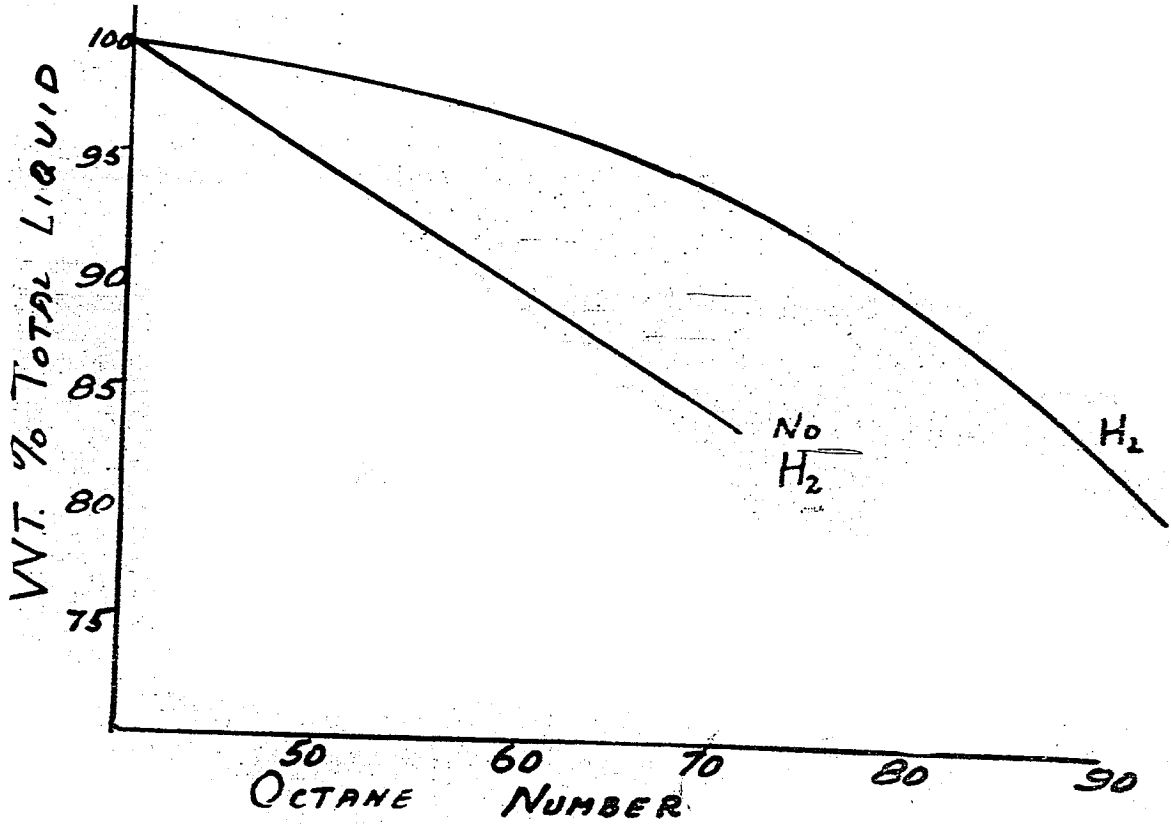
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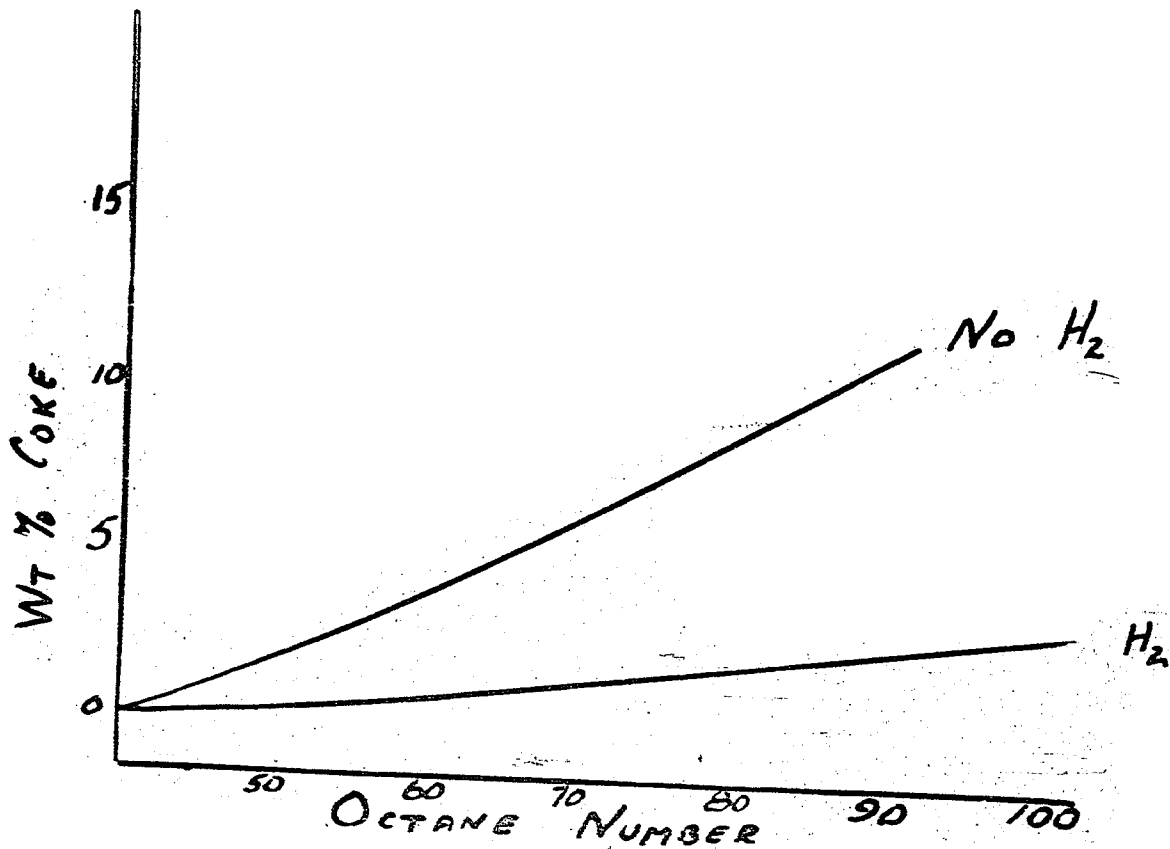


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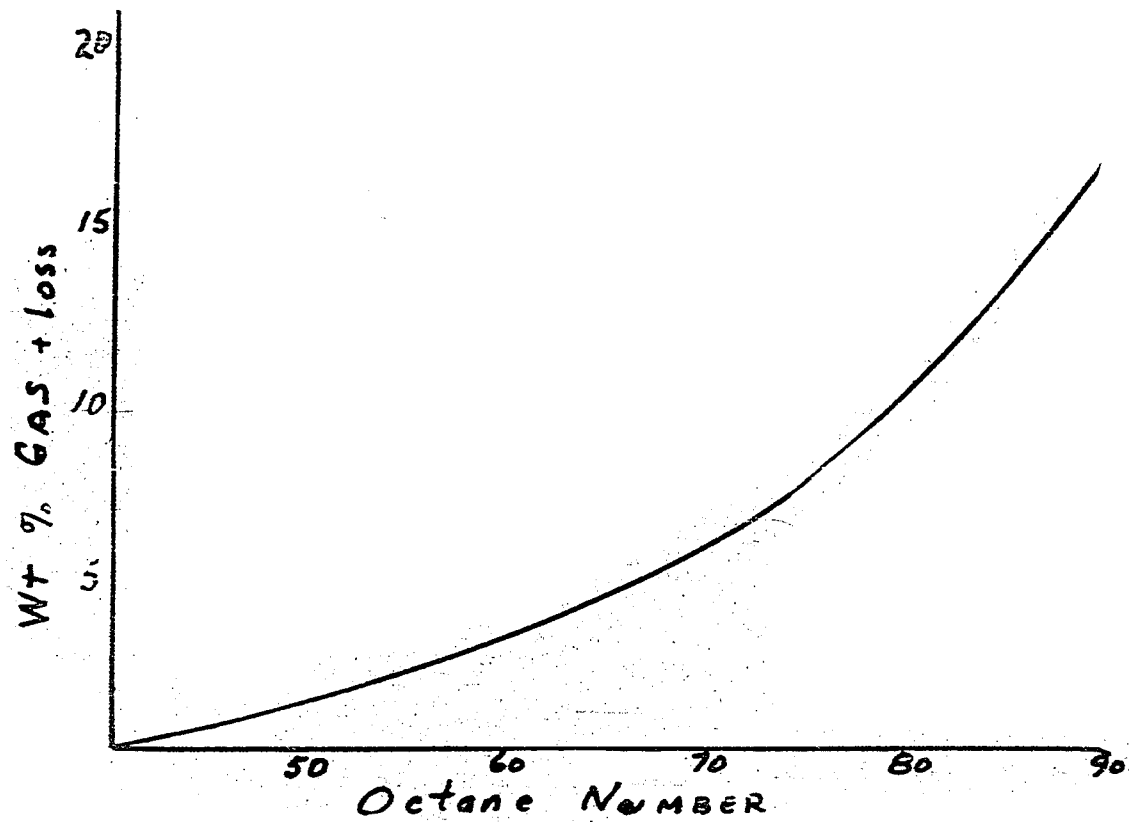


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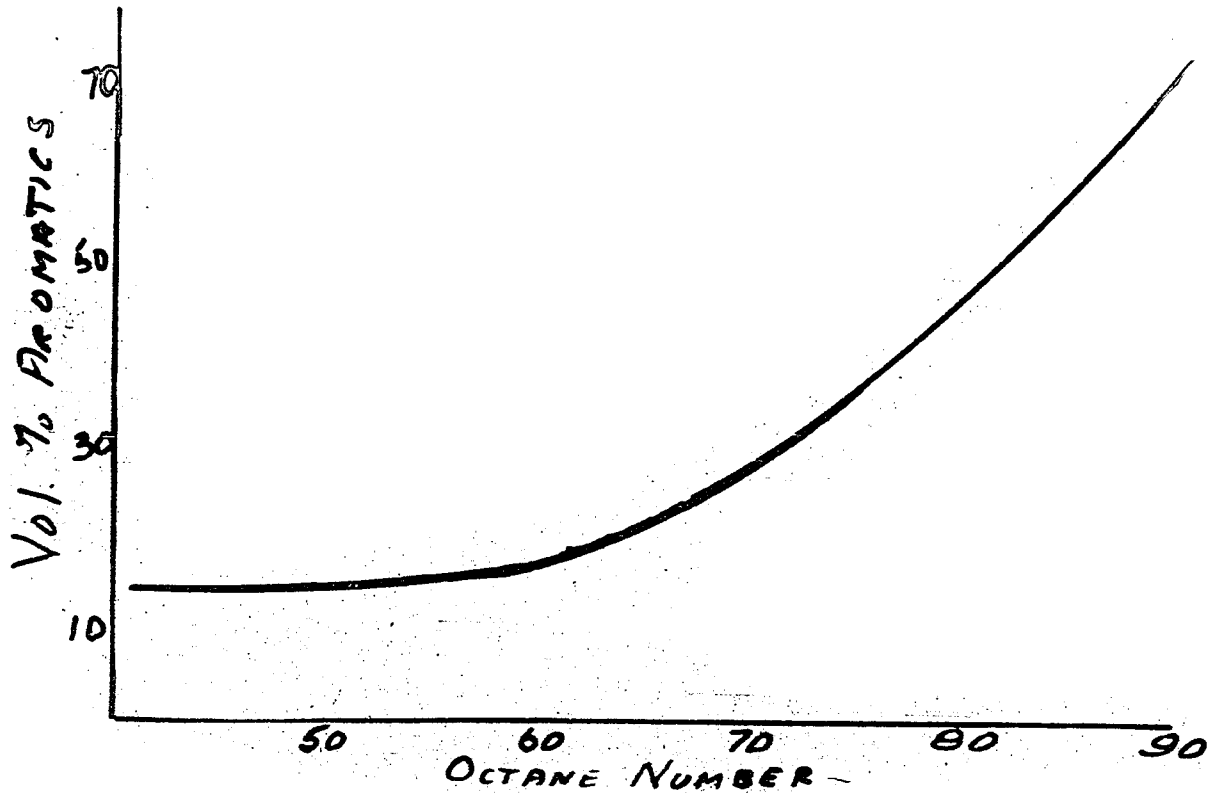




22900

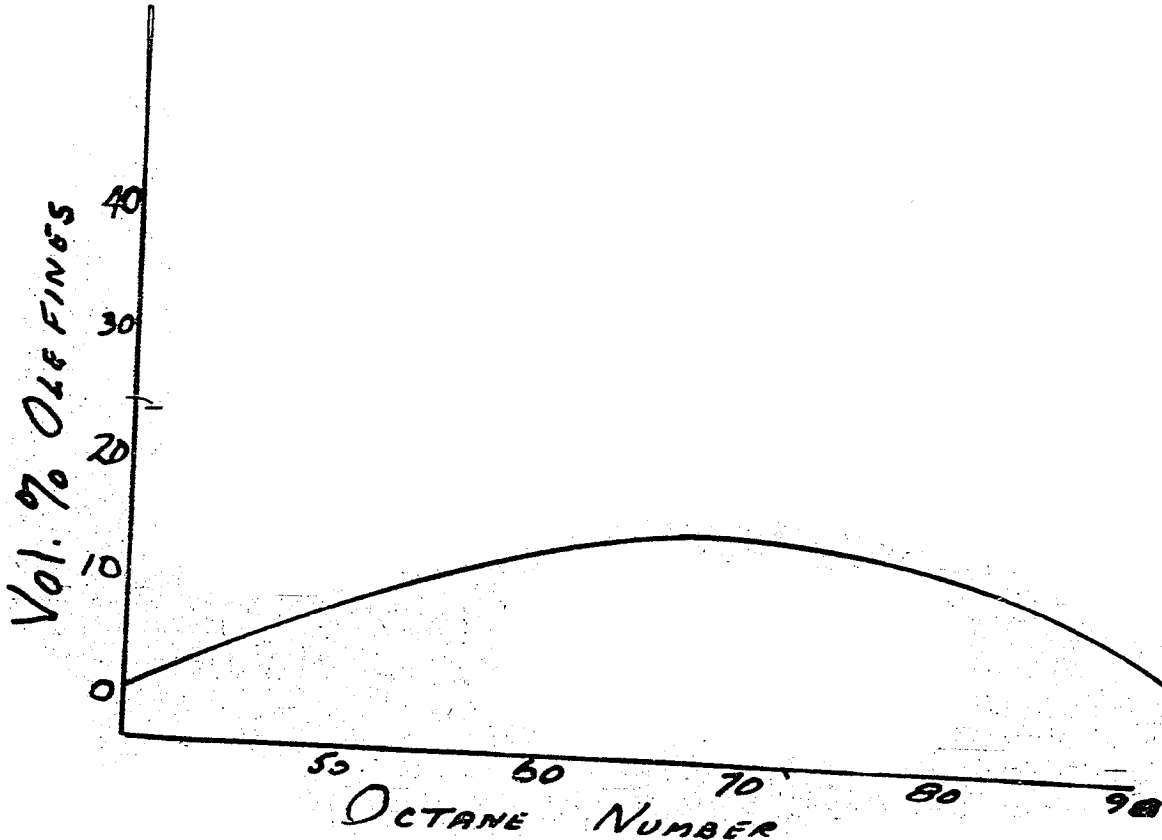


000426

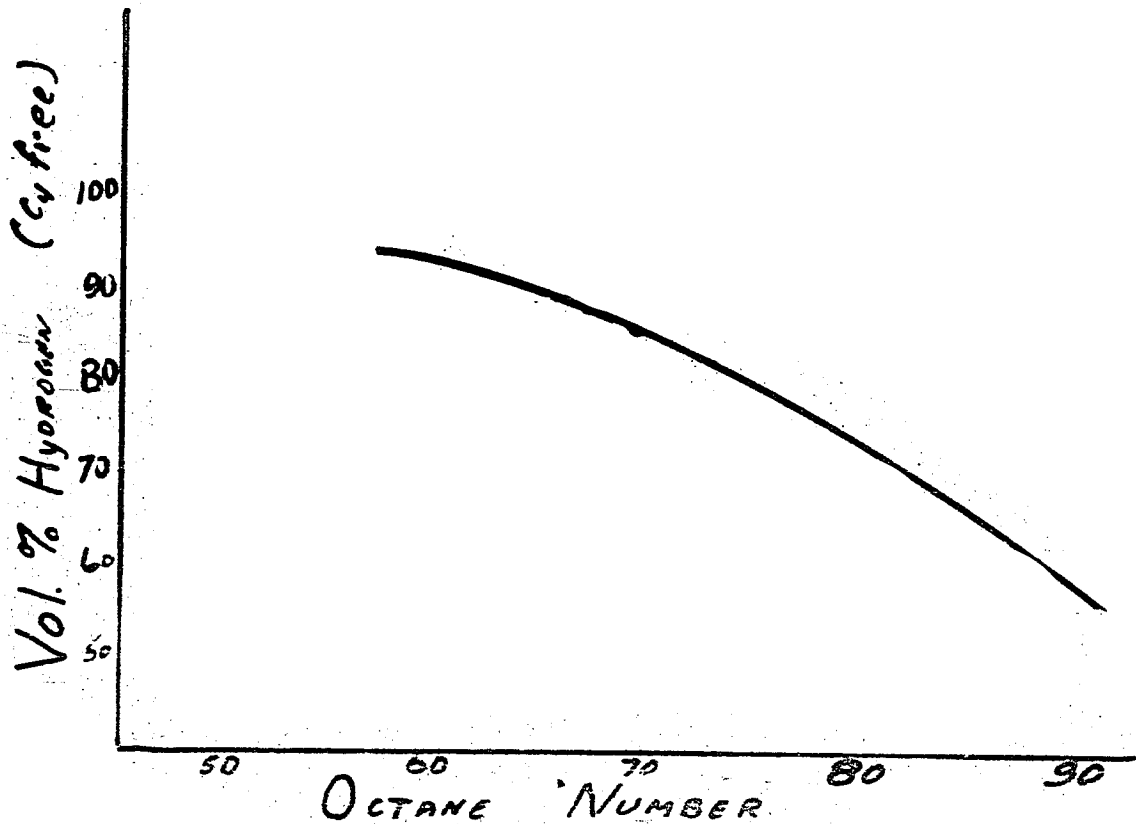


625000

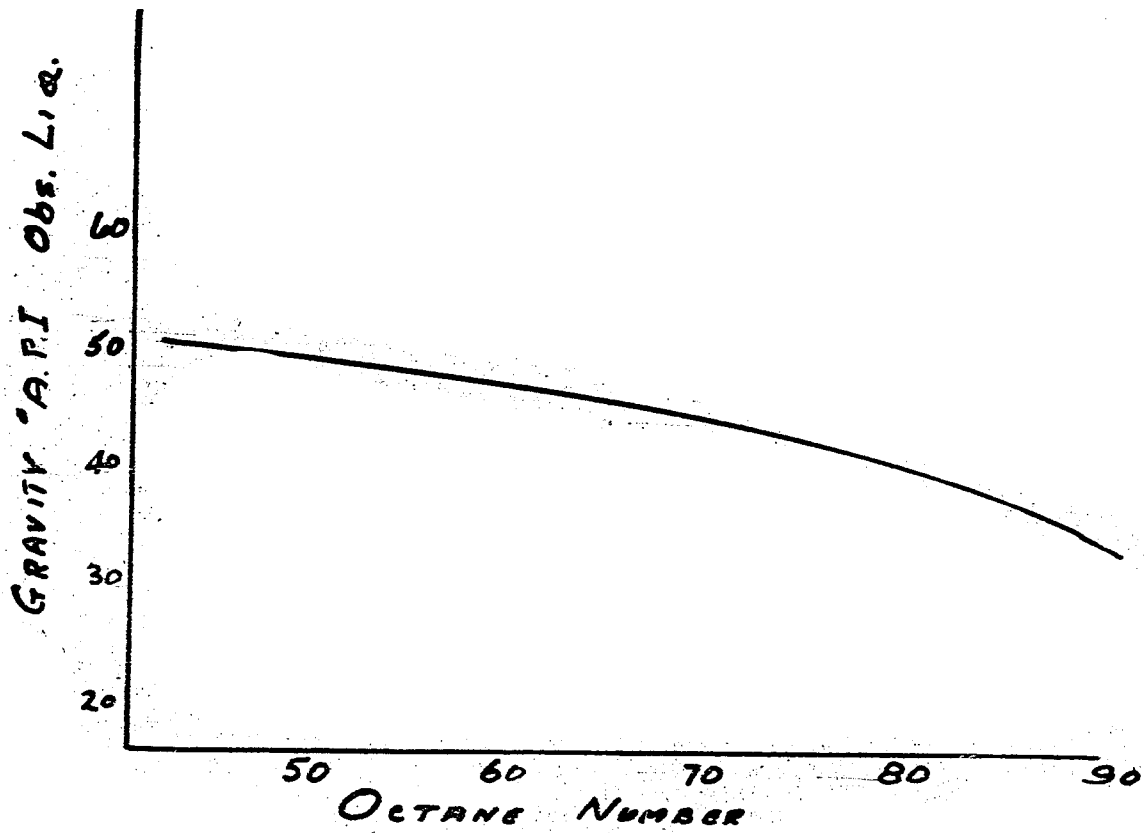
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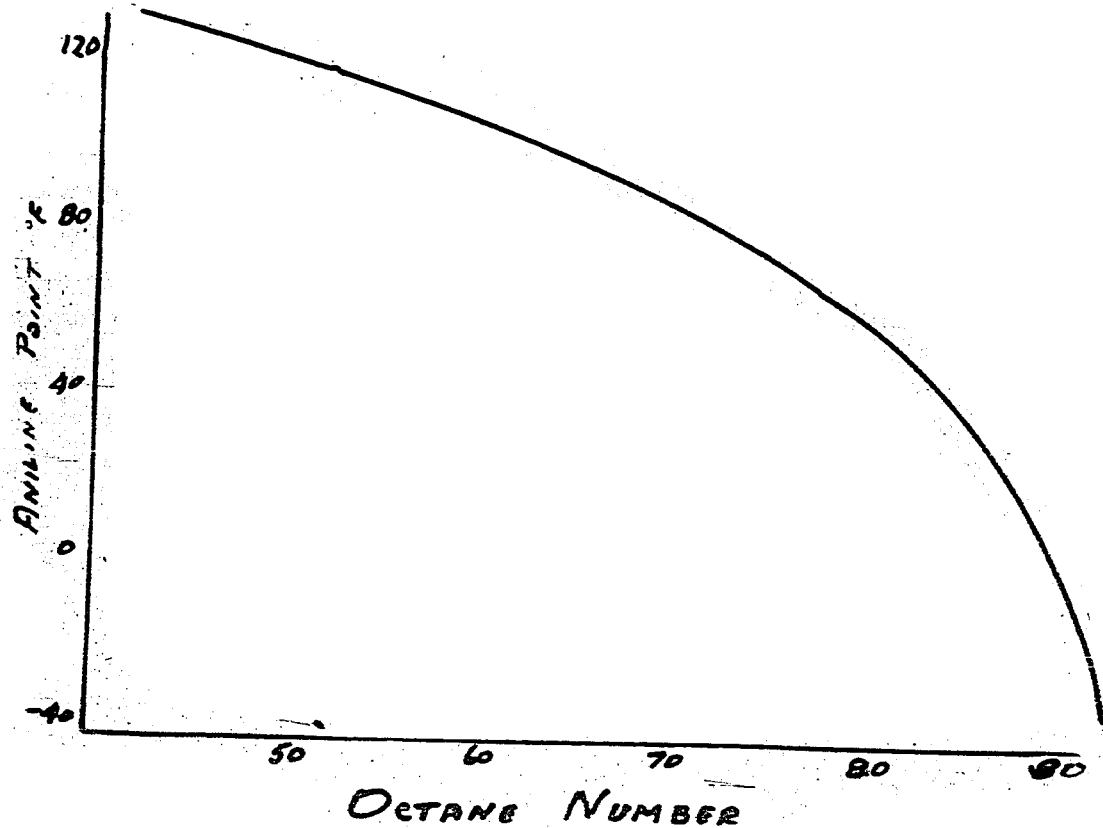
000430



000431

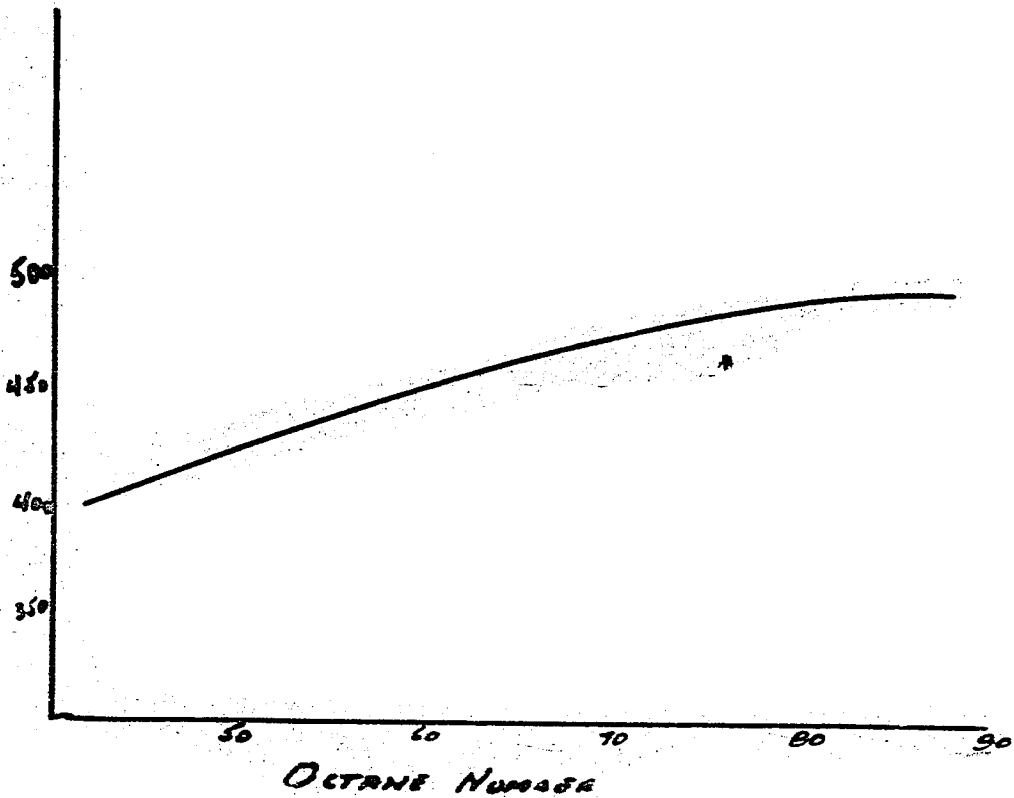


000432



000638

End Point Obs. L.i.a. (A.S.T.M)



000700