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CATALYTIC CRACKING WITH POWDERED CATALYST IN LIQUID PHASE.

The disadvantages of discontinuous operation and high gas formation in cracking of paraffinic oils when operating the catalytic cracking process at atmospheric pressure and with a fixed catalyst bed led to experimental work on catalytic cracking under pressure in the liquid phase.

In order to avoid the difficulties and disadvantages encountered with the fixed-bed catalytic cracking process, the catalyst was suspended in the oil and the suspension was passed through the reactor space. This process has the advantage that the cracking stock is always in contact with fresh catalyst, whereas the spent catalyst is removed together with the reaction products, separated from them and regenerated in a special apparatus.

The reactor used in the experiments consisted of a high-pressure coil (length 10-16 feet, diameter 0.24 inches, capacity about 0.25 gallons) The rate of flow was chosen so that a mixture of oil and catalyst was maintained at all times. The coil was heated by means of a lead bath. Heating and cracking zones were not separated from each other.

Experimental Results.

1. Kogasin II.

Comparison of Cracking in Liquid Phase with and without Catalyst.

The first investigations were carried out with Kogasin (boiling range 446 - 680°F., API gravity 49.5, aniline point 201°F.) since this material seems to be especially suited because of its simple chemical structure. The results of comparative runs, with and without catalyst, at various temperatures are shown in Table 1. A natural clay (Frankonit H) was used as catalyst.

Table 1

Temp. °F.	Pressure psi	Space Velocity vol./vol./ hour	Catalyst	Yield % by wt.			Efficiency gals. gaso- line/gal. of catalyst/ hour	Gas*) Forma- tion	Octane**) No.
				gas	C ₃ /C ₄	gaso- line			
843	1470	2.61	-	1.0	1.9	21.5	0.62	11.9	41.5
874	1470	2.58	-	2.5	6.8	36.2	1.02	20.5	47.9
890	1470	2.47	-	5.1	12.2	45.1	1.23	27.7	52.5
858	1470	2.15	10% Frankonit (1. shipment)	1.7	4.7	32.5	0.76	16.4	58.5
874	1470	2.58	"	1.8	5.5	36.0	1.02	16.8	61.5
890	1470	2.37	"	2.5	7.8	41.4	1.08	20.0	66.0
874	1470	2.40	10% Frankonit (2. shipment)	1.8	8.0	35.9	0.95	21.4	60.5

*) % (by wt.) of gas + C₃/C₄ calculated from the sum of gas + C₃/C₄ + gasoline without consideration of the small amount of coke (<1%) formed.

**.) determined on stabilized gasoline, E. P. 392°F.

The differences become more pronounced on cracking at high temperatures with high throughput. This is indicated in Table 2:

Table 2

Temp. °F.	Pressure psi	Space Velocity vol./vol./ hour	Catalyst	Yield			Efficiency gals. gaso- line/gal. of catalyst/ hour	Gas*) Forma- tion	Octana** No.
				gas	C ₃ /C ₄	gaso- line			
912	1470	46.2	-	0.9	2.2	19.3	9.8	13.9	42.0
912	1470	43.7	7% Frankonit	0.8	3.7	23.3	11.2	16.2	64.0

Tables 1 and 2 indicate that in cracking of Kogasin under pressure in liquid phase without catalyst, at least the same amount of conversion is to be obtained as with a catalyst. In cracking at atmospheric pressure in the vapor phase, the cracking temperature is, as is well known, reduced by the effect of the catalyst and the conversion into lower-boiling hydrocarbons is increased. The product distribution also shows only slight differences for the 2 processes. In spite of that, the catalytic process is to be preferred since it gives considerably higher octane numbers. The octane number difference can amount up to 22 units at high space velocities and high temperatures. The effect of the catalyst is, therefore, mainly that of a modifier of the reaction, rather than of an accelerator.

Experiments were carried out with various catalysts in order to study the effect of the catalyst on conversion. The catalysts investigated comprise natural and synthetic aluminum hydrosilicates, magnesium silicates, bauxite and metal oxide catalysts. The results obtained are shown in Table 3.

The catalysts which had been found suitable for fixed-bed cracking at atmospheric pressure were found to be the least favorable ones in these experiments; for the same conversion they produced less gasoline but more C₃/C₄ and gas. On the other hand, with those catalysts which are fairly inactive in cracking at atmospheric pressure, e. g., bauxite or Fullers earth, the same conversion is obtained as with the other catalysts. This again proves that the cracking reaction in this case is a thermal reaction and is not accelerated by the catalyst. On the other hand, the product distribution and the octane number is affected by the choice of the catalyst.

The results of these cracking tests can be summarized as follows:

- a) The conversion obtained with various catalysts is practically the same.

Temperature of.	Pressure psi	Space Velocity vol./vol./hour	Catalyst 10%	Yield % by wt. gas C ₃ /C ₄ line	Efficiency gals. of gasoline per gal. of catalyst per hour	Gas Formation % of conversion	Octane No.
874	1470	2.58	Frankonit (1. shipment)	1.8 5.5 36.0	1.02	16.8	61.5
874	1470	2.40	Frankonit (2. shipment)	1.8 8.0 35.9	0.94	21.4	60.5
874	1470	2.74	Terrana A	2.1 6.6 34.5	1.04	20.1	58.0
874	1470	2.39	Terrana spec.	2.7 8.0 35.9	0.94	23.0	57.0
874	1470	2.60	Clay 16	2.0 5.9 33.8	0.96	18.9	
874	1470	2.35	Fullers Earth	3.0 7.6 35.9	0.93	22.8	
890	1470	2.39	1247 synth. Al hydrosilicate	2.9 10.6 37.5	0.99	26.5	67.5
890	1470	2.38	1384 Mg silicate	2.6 7.1 42.5	1.11	18.3	63.0
874	1470	2.84	Baurite	2.5 5.2 33.7	1.06	18.6	58.0
890	1470	2.52	3510	3.9 7.4 40.0	1.10	22.0	59.0
874	1470	2.57	Terrana with W03 6434 ignited	2.9 7.7 39.4	1.11	21.2	63.5
874	1470	2.12	Baurite - Cr ₂ O ₃	2.9 5.5 42.8	1.00	16.4	54.0

- b) The highest octane numbers are obtained with natural and synthetic aluminum hydrosilicates.
- c) Frankonit H (1st shipment) and magnesium silicate are found to be the best catalysts for cracking of Kogasin in the presence of finely-divided, suspended catalysts since these catalysts give the best product distribution and the highest octane numbers.

Effect of Temperature, Pressure and Space Velocity on the Cracking Process.

The effect of the temperature has been shown in Table 1 and it was found that with increasing temperature the gasoline yield and the yield of C₃ and C₄, as well as gas, is increased. The yield of gasoline can hardly be raised above 40%, but the amount of C₃ and C₄ formed increases considerably so that further increase of the conversion by raising the temperature would be undesirable.

Conversion, product distribution and octane number are even more affected by changes in pressure. Table 4 shows cracking experiments at various pressures:

Table 4

T C	Pressure psi	Space Velocity vol./vol./ hour	Catalyst	Yield % by wt.		Ef- ficiency	Octane No.	Total Con- version % by wt.	Gas C ₃ /C ₄ % of total conversion		
				gas C ₃ /C ₄	gasoline						
858	590	2.26	10% Frankonit	1.1	6.7	25.4	0.64	66.0	33.2	3.3	20.2
858	1030	2.25	"	1.9	8.0	30.1	0.75	60.0	40.0	4.8	20.0
858	1470	2.08	"	3.0	11.5	37.1	0.85	58.0	51.6	5.8	22.3
858	2940	2.18	"	3.5	11.1	40.7	0.98	59.5	55.3	6.3	21.0
858	8820	2.09	"	5.0	11.6	42.6	0.99	55.5	60.2	8.3	19.3

The data indicate that the conversion is considerably increased with increasing pressure and that the greatest increase takes place when the pressure is raised from 590 to 1470 psi. The amount of C₃/C₄ formed increases parallel with the conversion but the amount of gas formed increases 2 - 3 times as much, which has an adverse effect on the product distribution, especially at a pressure above 1470 pounds. If it is furthermore considered that the octane number is lowered when the pressure is raised, it can be seen that it is disadvantageous to operate the cracking process at a pressure exceeding 1470 psi.

Table 5 shows the effect of space velocity under otherwise constant conditions:

Table 5

Temp of.	Pressure psi	Space-Velocity vol./vol./hour	Catalyst	Yield % by wt.			Efficiency	Gas Forma- tion % of con- version	Octane No.
				gas	C ₃ /C ₄	gaso- line			
874	1470	2.44	10% Frankonit	2.7	8.3	34.5	0.93	24.2	63.0
874	1470	3.60	"	2.5	8.0	32.7	1.30	24.3	62.5
874	1470	4.18	"	1.6	6.0	25.7	1.19	22.8	64.5
874	1470	8.74	"	1.3	3.5	20.2	1.94	19.2	62.5

At higher space velocity and constant temperature the conversion decreases but the reactor efficiency is increased that much more. Changing the space velocity from 2.44 to 8.74 decreases the gasoline yield by 41% but the efficiency is increased by 108%. At higher space velocity and lower gasoline concentration the product distribution is improved, whereas the octane number remains approximately constant.

The favorable effect of cracking at high space velocity can be further improved by simultaneously raising the temperature. The results of experiments in this direction are shown in Table 6:

Table 6

Temp. of.	Pressure psi	Space Velocity vol./ vol./hour	Catalyst	Yield % by wt.			Ef- ficiency	Gas Forma- tion % of con- version	Octane No.	Bromine No.	Carbon Deposit % by wt.
				gas	C ₃ /C ₄	gaso- line					
858	1470	2.34	10% Frankonit	1.8	8.0	35.9	0.92	21.4	60.5	55.0	1.1
905	1470	22.2	"	1.5	5.6	25.8	6.4	21.6	62.4	53.9	1.6
912	1470	44.2	"	0.8	4.1	22.3	10.85	18.0	64.5	54.0	0.5
912	1470	42.4	"	0.7	3.6	20.1	9.35	17.6	67.5	60.3	0.6

The table shows that at very high space velocities and a gasoline yield of 20 - 22% by weight, a better product distribution, a higher octane number and a reactor efficiency which is 10 times as great as at a space velocity of 2.57 volumes per volume per hour can be obtained. Without catalyst, the same amount of conversion can be obtained at the same space velocity but the octane number, in this case, is even lower than for thermal cracking at lower space velocity and high gasoline concentration. In the presence of a catalyst, the high temperature results in an increase in the octane number. At lower pressure, high reactor efficiencies can be obtained by high space velocities and high temperatures. Table 7 shows a comparison of cracking experiments at different pressures and high space velocities:

Table 7

Temp. of.	Pressure psi	Space Velocity	Catalyst	Yield			Gas Forme- tion	Ef- ficiency	Octane No.	Bromine No.
				gas	% by wt. C ₃ /C ₄	gasoline				
920	590	19.8	10% Frankonit	0.9	3.7	19.2	19.3	4.19	66.5	67.6
920	880	24.3	"	1.2	5.9	27.2	20.6	7.27	66.5	63.0
912	1470	44.2	"	0.8	4.1	22.3	18.0	10.84	64.5	54.0

Assuming that the recycle stock can be cracked approximately as well as the fresh feed, this method of operation at high temperature, high space velocity and a gasoline yield of 20 - 25% should be considered most advantageous because of the low gas formation and high octane number of the finished product.

Cracking of Recycle Stock.

The cracking of recycle stock is especially important because of the low gasoline concentration obtained at high space velocities. The recycle stock obtained by cracking of the fresh feed at a space velocity of 44.7 and at 912°F. was cracked at the same space velocity, the gasoline was distilled off and this was repeated twice with the recycle stock obtained in each experiment. The results of the second and third pass are shown in the following Table 8:

Table 8

Temp. of.	Pressure psi	Space Velocity	Catalyst	Yield			Ef- ficiency	Gas Forma- tion	Octane No.	Residue	
				gas	% by wt. C ₃ /C ₄	gasoline				API Gravity	Aniline Point, °F.
Recycle stock from 2. pass											
920	1470	43.6	10% Frankonit	1.2	4.5	20.1	9.7	22.0	65.5	48.8	193
Recycle stock from 3. pass											
933	1470	44.1	10% Frankonit	1.5	4.0	23.3	11.3	19.1	68.0	47.9	187

It can be seen that the recycle stock can be equally well cracked. The gasoline yield and the quality of the gasoline are the same but the gas formation is somewhat higher than with the fresh feed.

The recycle oil was also blended with the fresh feed and the mixture

was cracked; the results indicate that product distribution and properties of the gasoline are the same as when fresh Kogasin was cracked. The experiments indicate that cracking of Kogasin with recycling will be possible for prolonged cracking periods.

Catalyst Concentration.

The results of experiments with various amounts of catalyst are shown in Table 9:

Table 9

Temp. °F.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency	Gas Forma- tion	Octane No.	Carbon Deposit
				gas	C ₃ /C ₄	gaso- line				
874	1470	2.52	10% Frankonit	3.0	6.6	37.5	1.05	20.4	58.0	0.1
874	1470	2.36	3% "	2.7	8.0	35.1	0.92	23.3	63.0	0.45
874	1470	2.25	7% "	2.3	7.5	36.8	0.91	21.2	61.5	0.75
874	1470	2.49	10% "	2.7	8.3	34.5	0.93	24.4	63.0	1.1
874	1470	50.8	3% "	1.0	2.1	20.3	11.38	13.2	67.5	0.2
912	1470	43.6	7% "	0.8	3.7	23.3	11.20	16.2	64.0	0.3
912	1470	44.2	10% "	0.8	4.1	22.3	10.85	18.0	64.5	0.5

When the gasoline is cut to an end point of 365°F., the octane number can be raised by about 3 units.

The octane number by the motor method is about 2 - 3 units lower than that obtained by the research method. The research octane number is 67, whereas the motor method octane number is 65.5. On addition of 1.1 cc. of TEL per gallon of gasoline, the research octane number is raised to 78.0, on addition of 2.2 cc. of TEL the octane number is raised to 82.0, and addition of 3.4 cc. of TEL brings the octane number to 85.5. The octane number of the gasoline increases proportionally with the olefin content. A gasoline with an octane number of 64 - 70 has a bromine number of 60 - 70, which corresponds approximately to an olefin content of 40%. The untreated cracked gasoline is not stable to storage, which is probably due to its high olefin content.

The recycle stock which boils above 392°F. has a higher gravity, a lower aniline point, and about the same boiling range as the feed stock; the octane number after 1 pass is 100 or higher.

Comparison of Catalytic Cracking under Pressure with Suspended Catalyst and Catalytic Cracking at Atmospheric Pressure using a Fixed-Bed Catalyst.

The 2 processes are compared in the following table:

Cracking at Atmospheric Pressure

Temp. OF.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency	Gas Forma- tion	API Gravity	Octane No.	
				gas	C ₃ /C ₄	gaso- line					
851	-	0.60	1308 SiO ₂ .MgO	2.3	8.6	28.2	1.5	9.9 (in- cluding regenera- tion).	27.9	68.6	73.0

Cracking at Elevated Pressure

914	1470	50.8	3% Frankonit	1.0	2.1	20.3	0.2	11.35	13.2	68.9	67.5
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The data indicate clearly that the pressure process is far superior to the atmospheric pressure process with respect to product distribution and efficiency. It must also be considered that it is difficult to process the recycle stock at atmospheric pressure, whereas using pressure it can be recycled at least 3 times, which results in a final yield of 60 - 70% of gasoline without increasing the gas production beyond 20%.

Another advantage of the process lies in the fact that it permits to use commercial activated clays without further treatment.

Reforming of Heavy Naphtha from Kogasin.

Heavy naphtha from Kogasin was blended with a middle oil (naphtha) in the ratio of 1 : 1 and cracked under the usual conditions in the presence of catalyst. The middle oil was added to maintain the liquid phase and should not participate in the reaction. Consequently, a middle oil was used which originated in the sump phase hydrogenation of coal tar and was predominantly aromatic. The heavy naphtha had an API gravity of 66.1, an aniline point of 145°F., a boiling range of 226 - 383°F., and an octane number of about 16.5. The middle oil had an API gravity of 7.5 and a boiling range of 538 - 648°F. The results of the experiments are shown in the following Table 10:

Table 10

Temp. OF.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency	Property of Gasoline		
				gas	C ₃ /C ₄	gaso- line		API Gravity	Aniline Point OF.	Octane No.
889	1470	2.43	10% Frankonit	3.5	3.7	70.0	105	69.2	145	32.5

The data of the reformed gasoline indicate that partial cracking of the gasoline has occurred. The improvement in octane number, however, is low. Since the temperature could not be raised much more without sacrificing liquid phase operation, there does not seem to be much hope to improve the octane number by this method. A special disadvantage consists in the comparatively large losses (22.8%) resulting from the formation of higher-boiling hydrocarbons. It was, consequently, attempted to crack the heavy naphtha together with Kogasin middle oil boiling from 284°F. to 752°F. The results are shown in Table 11:

Table 11

Temp. °F.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency gasoline E.P. 365°	Octane No. gasoline		
				gas	C ₃ /C ₄	gasoline E.P. 365°F.		gasoline E.P. 392°F.	E.P. 365	E.P. 392°F
30% fraction 284 - 752°F. + 70% recycle stock										
920	1470	23.1	5%	1.1	4.3	22.3	24.7	5.66	58.5	54.0
920	884	23.1	Frankonit	1.2	4.1	25.2	29.4	6.4	63.0	55.5
20% fraction 284 - 752°F. + 80% recycle stock										
910	1470	46.2	"	0.9	2.5	18.6	-	9.5	61.5	-
25% fraction 284 - 752°F. + 75% recycle stock										
920	1470	40.0	"	0.9	3.3	20.5	-	9.1	57.5	-

Comparison of Catalytic and Thermal Cracking of Natural Petroleum Fractions.

The first experiments were carried out at low space velocity which, as had been previously found, is not the best operating practice. However, in order to have a complete picture of the reaction, the results are given in the following Table 12:

Table 12

Temp. °F.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Efficiency	Gas Formation	Octane No.
				gas	C ₃ /C ₄	gasoline			
874	1470	2.44	-	2.0	5.3	29.6	0.86	19.8	71.5
874	1470	2.26	10%	1.6	4.4	31.7	0.86	15.9	74.0
889	1470	1.93	Frankonit	1.6	5.9	41.0	0.95	15.5	76.0

The runs were carried out with a diesel oil of API gravity 35.6, an aniline point 144°F., and boiling range of 446 - 721°F. In accordance with the previous experiments, cracking in the presence of catalyst is not different from cracking without catalyst. The slight improvement in octane number is probably due to the rapid loss of activity of the catalyst due to the

large carbon deposit. The increased carbon deposition as compared to that observed with Kogasin is explained by the high percentage of non-paraffinic hydrocarbons in the oil which promote carbon formation. The sulfur compounds present might also effect the carbon formation.

Further experiments with respect to catalyst activity, effect of pressure, and study of the optimum processing conditions were carried out on a diesel oil from German crude with an API gravity of 33.6, an aniline point of 150°F., and a boiling range of 464--734°F. With this oil a greater improvement in octane number could be obtained in the presence of catalyst. The octane number increased from 65 of the thermally-cracked gasoline to 75 for the cracked gasoline when cracking was carried out at 1470 pounds and 874°F. Since it is assumed that the improvement in octane number by catalytic cracking is mainly due to isomerization, it is reasonable that this oil, which is more paraffinic than the previously-used diesel oil, should give a greater improvement in octane number.

The results of experiments with different catalysts are given in Table 13:

Table 13

Temp. °F.	Pressure psi	Space Velocity	Catalyst	Yield			Ef- ficiency	Gas Forma- tion	Carbon Deposit % by wt.	API Gravity	Gasoline Ani- line- Point °F.	Octane No.
				gas	C ₃ /C ₄	gaso- line						
			10%									
874	1470	2.32	Frankonit	1.2	3.7	30.0	0.84	15.5	1.9	59.0	111	71.0
889	1470	2.36	"	2.1	5.7	32.0	0.92	19.6	1.7	58.4	106	73.0
874	1470	2.32	10% 3510	2.1	4.1	29.1	0.82	17.3	0.0	58.2	104	68.0
889	1470	2.36	"	3.1	5.3	30.9	0.89	21.4	0.0	58.2	83	70.0
889	1470	2.08	10% 1804*	1.8	4.3	32.5	0.82	15.8	1.3	58.7	114	74.5
889	1470	2.26	10% 1444**	1.7	3.9	35.2	0.96	15.8	1.9	58.2	108	72.5

* Bauxite + Cr₂O₃

** activated Frankonit.

In this case, also, only very slight differences can be detected between the various catalysts. The most favorable results are given by Frankonit, a natural clay which is activated with sulfuric acid. The amount of carbon deposited on the catalyst is about twice as large as that obtained with Kogasin. Raising of the octane number by increasing the amount of catalyst to 20% was not found to be feasible.

Experiments at High Space Velocity.

By increasing the throughput and the temperature, the octane number and the reactor efficiency can be considerably increased. This is shown in Table 14.

Table 14

Temp. of.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency	Octane No.	Gas Forma- tion	Carbon Deposit
				gas	C ₃ /C ₄	gasoline				
920	1470	18.3	10%	0.9	2.2	18.6	4.2	77.5	14.3	0.8
952	1470	19.9	Frankonit	1.8	3.7	25.0	6.0	79.5	18.0	0.5

However, in this case the bromine no. of the gasoline is raised from 35-40 to 50-55 which corresponds to an increase of the olefin content by about 10%.

Results obtained by cracking at lower pressures are shown in Table 15:

Table 15

Temp. of.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Efficiency	Octane No.	Gas Formation
				gas	C ₃ /C ₄	gasoline			
936	589	13.2	{ 10% 1444	1.7	2.4	23.6	3.76	82.0	14.8
	883	19.2		1.0	2.6	19.4	4.50	76.5	16.4

Similarly favorable results could be obtained by cracking of a fraction from Austrian crude; the fraction had an API gravity of 31.9; aniline point 164°F., and a boiling range of 446 - 770°F. The results are shown in Table 16:

Table 16

Temp. of.	Pressure psi	Space Velocity	Catalyst	Yield % by wt.			Ef- ficiency	Gas Forma- tion	Octane No.	Carbon Deposit
				gas	C ₃ /C ₄	gasoline				
936	1470	18.3	10% 1444	1.3	3.5	24.0	5.4	16.6	78.5	1.6
920	1470	17.7	10% Frankonit	1.1	2.7	21.8	4.7	14.8	77.5	1.6
936	1030	16.2	10% 1444	1.1	2.7	22.1	4.4	14.7	81.0	1.5
968	735	14.1	10% 1444	1.0	3.8	22.7	3.9	17.4	84.5	1.35
936	735	9.4	10% 1444	1.0	2.5	21.1	2.4	14.2	82.0	0.4

Cracking of Recycle Stock.

The recycle stock was found difficult to crack but at somewhat lower space velocity and higher temperature it could be cracked to yield 24% gasoline. The results of the pertaining experiments are given in Table 17:

Table 17

<u>Temp.</u> °F.	<u>Pressure</u> psi	<u>Space</u> <u>Velocity</u>	<u>Catalyst</u>	<u>Yield</u> % by wt.			<u>Efficiency</u>	<u>Octane</u> <u>No.</u>	<u>Gas</u> <u>Formation</u>	<u>Carbon</u> <u>Deposit</u>
				gas	C ₃ /C ₄	gasoline				
<u>Recycle stock from German crude</u>										
952	1470	14.5	10% 1444	0.9	4.1	23.5	4.2	74.5	17.3	2.3
<u>Recycle stock from Austrian crude</u>										
952	1470	12.7	10% 1444	1.3	2.4	23.8	3.7	78.0	13.4	1.7

Quality of Gasoline.

The raw cracked gasoline is colorless and has an agreeable odor. As compared to thermally-cracked gasoline, it contains a smaller proportion of products boiling up to 212°F. (about 30%) and has, at higher octane numbers, a considerably higher bromine number. The octane number of the gasoline can be raised by 2 - 3 units by lowering the end point to 365°F. The octane number by the motor method is 5 - 6 units lower than that found by the research method. The storage stability of the gasoline seems to be considerably better than that of the cracked gasoline made from Kogasin. Gasoline with a very high bromine number can be made stable to storage by mild hydrogenation. The raw cracked gasoline had API gravity 59.7; aniline point 90°F.; bromine number 61.9, and octane number 84, induction period 240 minutes and a gum content of 146.4 mg. After mild hydrogenation the same gasoline had API gravity 59.2; aniline point 98°F.; bromine number 56.8; octane number 80; induction period 240 minutes, and a gum content of 14 mg. It contained 85.66% carbon, 13.99% hydrogen, 0.1% nitrogen, and 0.015% sulfur. The starting material had 86.39% carbon, 13.20% hydrogen, 0.13% nitrogen, and 0.279% sulfur.

Catalytic Cracking under Pressure of Recycle Stock from Catalytic Cracking at Atmospheric Pressure.

2 recycle stocks obtained by catalytic cracking at atmospheric pressure were processed under pressure. Recycle stock #1 was obtained from diesel oil (API gravity 33.2; aniline point 144°F.; boiling range 452 - 716°F.) and #2 was obtained from East Texas gas oil (API gravity 32; aniline point 145°F.; boiling range 455 - 698°F.). They were cracked under the same conditions as the fresh feed stock. Table 18 shows a comparison of the results obtained by catalytic cracking according to the 2 processes:

Table B

Op. No.	Pressure psi	Space Velocity	Catalyst	Yield % by wt. gas C ₃ /C ₄ gaso- line			Ef- ficiency	Gas Formation	Octane No.	Carbon Deposit
Recycle stock #1 - pressure cracking										
952	1470	16.3	10% Frankonit	1.6	4.8	23.3	4.7	20.8	72.0	2.0
Recycle stock #1 - atmospheric pressure cracking										
796	-	1.17	1726	2.7	7.1	21.0	0.21	31.2	86	2.5
Recycle stock #2 - pressure cracking										
945	1470	18.5	10% Frankonit	1.8	3.5	21.5	4.5	19.8	73.0	1.7
Recycle stock #2 - atmospheric pressure cracking										
765	-	1.6	1726	3.0	5.9	18.2	0.18	32.7	85.0	3.4

Cracking of recycle oil from the cracking process operating at atmospheric pressure shows, at first, the same picture as presented by the cracking of recycle oil from cracking under pressure. At high space velocity and high temperature the same gasoline yields can be obtained. The gas and carbon formation, however, is greater than for fresh feed. As compared to catalytic cracking at atmospheric pressure, the pressure process has the advantage for cracking of recycle stock that the efficiency is considerably higher, carbon formation is lower, and the product distribution is more favorable. The octane numbers are surprisingly low as compared to cracking at atmospheric pressure and no explanation can be offered for this phenomenon.

Processing of High-Boiling Petroleum Residual Oil.

Experiments were carried out to obtain a maximum yield of naphtha by pressure cracking residual oils boiling above 752°F. In order to safeguard continuous operation, 5% of finely-ground Grude coke were added to the residue in order to absorb the carbon formed during the reaction and thereby prevent clogging of the cracking coil.

A residue from West Texas crude which contained 44% of material boiling up to 932°F. was cracked at 858°F. with a space velocity of 19.5 volumes per volume per hour and a pressure of 735 psi. The following yield was obtained: Fraction boiling up to 752°F. 35%; fraction from 752° - 932°F. 33%; fraction boiling higher than 932°F. 29%.

By distillation of the fraction boiling up to 752°F. and cracking of the residue, the yield of naphtha can be further increased. This is shown by experiments in which a residue from Austrian crude was processed in 2 passes at

889°F., 735 psi. pressure and a space velocity of 42.6. The following yields were obtained: Fraction boiling up to 752°F. 45%; fraction 752° - 932°F. 32%; fraction higher than 932°F. 23%. The fractions boiling from 392° - 752°F. could be cracked without pressure at 759°F. and a space velocity of 1.9 volumes of oil per volume of catalyst per hour and a cracking time of 30 minutes, using catalyst 1726. The yield was 35% by volume (29.6% by weight) of gasoline, (octane no. 81.0) 5.1% by volume, (4% by weight) of C₃C₄, 2.5% gas, 1.1% coke, 58.3% by volume (59% by weight), recycle stock. Finally, the ~~fraction 752° - 932°F. together with the material distilled from the residue~~ can be converted to gasoline by catalytic cracking under pressure or catalytic cracking at atmospheric pressure in the presence of steam.