

FILM STUDY GROUP

SUBJECT INDEX AND REPORT

T. O. M. REEL NO. 141

Prepared by

STANDARD OIL DEVELOPMENT CO.

STANDARD OIL DEVELOPMENT COMPANY

Abstract and Index of Technical Oil Mission Microfilm

Reel No. 141

Index to Reel 141
Catalytic Cracking of Liquid Fuels

<u>Subject</u>	<u>Item #</u>	<u>Frames</u>
I. <u>Catalyst Activities</u>		
a). Weekly report of the High Pressure Experimental Section LU 558	1	1
b). Activity reports 10/37 - 1/38	3	3-12
c). Exploratory investigation for cracking catalysts	4	13-22
d). Activity reports 10/37 - 1/38	5	23-40
e). Catalytic cracking	8	47-52
f). Catalytic cracking of Kogasin in 3 litre retorts with magnesium silicate and superfiltrol	45	239-247
g). Catalytic cracking of paraffinic gas oils (East Texas) with superfiltrol and magnesium silicate in 3 litre retorts	46	248-256
h). Catalytic cracking with catalysts resulting in aromatization	48	260-261
i). Catalytic cracking of paraffin and similar products to middle oils.	49	262-264
j). Catalytic Cracking experiments with AlF_3 catalysts	57	308-310
k). Catalytic cracking in the 40 litre oven with catalysts 6108 and 6752 (Terrana and synthetic Al-silicate)	75	413-436
II. <u>Catalytic cracking with Synthetic $SiO_2-Al_2O_3$ catalyst</u>		
a). The position of catalytic cracking to date(2/22/38)	6	41-43
b). Activity report 4/20/38 - 5/4/38	14	79-90
c). Catalytic cracking, August 10 and 16, 1938	17	105-117
d). Catalytic cracking of "Kogasin II"	30	161-163
e). Remarks of Dr. Kaufmann on Catalytic cracking 11/26/41	71	403-404
f). Catalytic cracking in the 50 litre apparatus	74	407-412

III.	<u>Catalyst Preparation</u>		
	a). Catalytic cracking. Preparation of a synthetic aluminum silicate catalyst	7	44-46
	b). Influence of condition of precipitation upon the gasification of cracking catalysts	12	65-68
IV.	<u>Effect of Temperature upon Catalytic Cracking</u>		
	a). Catalytic cracking of Kogasin II (P1295) under varying operating conditions	13	69-78
	b). Catalytic cracking of Kogasin II at normal pressures. The effect of temperature and cycle duration.	33	174-183
	c). The composition of crack-benzines of petroleum middle oil which is rich in H ₂ and its dependence upon the cracking temperature.	64	368-381
V.	<u>Catalytic Cracking with SiO₂ - MgO Catalyst</u>		
	a). Cracking with SiO ₂ -MgO catalysts of various manufacture. Small-scale tests with Kogasin II.	10	55-61
	b). Catalytic cracking with an Si-Mg catalyst. First experiment in 400 ccm. retort with Elverath gas oil.	18	118-126
	c). Remarks on the position of cracking experiments of September 5, 1938	19	127
	d). Types of magnesium silicate catalysts	20	128-130
VI.	<u>Nitrogen Compounds</u>		
	a). Catalytic cracking June 20 and July 13, 1938	15	91-97
VII.	<u>Thermal vs. Catalytic Cracking</u>		
	a). The difference between thermal and catalytic cracking	16	98-104
	b). Comparison between thermal and catalytic cracking of Kogasin II	43	227-232
VIII.	<u>Lube Oil Fractions and Crudes</u>		
	a). The cracking of the lube oil fractions of Reitbrook petroleum.	21	131-134
	b). Catalytic cracking of Rumanian crude oil.	59	320-324

IX.

Cracking Catalyst Activators and Additives

a).	The effect of alkali on cleavage effectiveness of cracking catalysts.	22	135-136
b).	Experiments in catalytic cracking with the addition of sulfur.	31	164-168
c).	Zinc-containing catalysts for catalytic cracking	41	222-224

X.

Catalytic Cracking of Synthesis Products

a).	Catalytic cracking of CO-M synthesis product of Ka 502 (Dr. Michael).	23	137-139
b).	Cracking of propylene gas oil.	28	156-158
c).	Catalytic cracking of synthesis product (chamber 502) - Dr. Michael	32	169-173
d).	Catalytic cracking of the intermediate products of the lubricating oil synthesis	65	382-384

XI.

Catalytic Cracking Under Pressure

a).	Catalytic cracking of West Texas gas oil under high pressures.	29	159-160
b).	Treatment of benzines with SiO ₂ -containing catalysts both with and without pressure	56	294-307
c).	Cracking of benzines and gas oils under H ₂ pressure	61	327-343
d).	Cracking experiments with K 6108 (Terrana) and K 6109 (Terrana-HF) under various pressures	62	344-365
e).	Cracking of Kogasin II over Superfiltrol at different pressures	25	143-150

XII.

Hydrogenation

a).	Catalytic cracking of rehydrogenated "b ² " residual oils of catalytic cracking I.	34	184-192
b).	Behavior of cracked gasolines during hydrogenation	52	272-274

XIII.	<u>Dehydrogenation</u>		
	a). Refining and dehydrogenation of catalytically cracked benzins of P189 gas oil with contact 7360. 70		393-402
XIV.	<u>Aviation Fuel</u>		
	a). Manufacture of Aviation gasoline by catalytic cracking.	37	209-215
	b). Manufacture of aviation fuel by catalytic cracking.	42	225-226
XV.	<u>Stock Composition</u>		
	a). Effect of the composition of gas oils on the yield in catalytic cracking.	44	233-238
	b). Review of oils suitable for catalytic cracking and the yield to be anticipated in their processing.	51	268-271
	c). Catalytic cracking of the 150-200° fraction of Kogasin.	40	219-221
XVI.	<u>Isomerization</u>		
	a). Isomerization through cracking.	53	275-287
	b). Influence of the process and of the catalyst upon the degree of isomerization in catalytic cracking.	58	311-319

Item No.

1. Frame 1. Weekly report on Catalytic Cracking. Working at 450-470°C. with gas oil and a rate of 100 cc. oil/200 cc. catalyst/hour, the catalyst performances arranged themselves in the following order of decreasing effectiveness.

1. Untreated Terrana (34 wt.% benzene on oil input)
2. " Superfiltrol
3. Terrana treated with HF
4. Terrana + 10% WS₂
5. Superfiltrol treated with HF
6. Silica gel (11.5% by weight of benzene).

3. Frames 3-12. Progress Reports on Catalytic Cracking 10/13/37-1/14/38

These reports include the following observations:

- a. The iodine number increased with cracking temperature.
- b. The aniline point decreased with rising temperature.
- c. The highest unsaturated material was formed by HF-treated catalysts.
- d. Synthetic SiO₂-Al₂O₃ catalyst prepared from alkali-free silica gel (from SiF₄) gave no better yields than K379.
- e. After every regeneration of catalyst, that portion of the yield boiling up to 100°C. drops considerably.
- f. Tables are given comparing cracking of Kogassin and Scholven middle oil individually and in mixtures both on the Standard superfiltrol and the SiO₂-Al₂O₃ catalyst K 379. The latter gave more extensive gasification and a higher C₃ and C₄ content, the latter more cracking residues.

4. Frames 13-22. Exploratory Search for Cracking Catalysts.

A large number of substances were examined for catalytic cracking purposes. Designated as poor were those catalysts yielding less than 10% by volume of naphtha; fair were those yielding 10-20%; and good, those yielding over 20% by vol. Over 150 materials and catalyst mixtures are listed. Among those listed as good were: 1). Al₂O₃-WO₃; 2). SiO₂-Al₂O₃- 10% WS₂; 3). HF-treated Terrana. Many catalysts work well on a once-through operation, but on the first regeneration lose their effectiveness. Magnesium and titanium type catalysts are such.

5. Frames 23-40. Progress Reports on Catalytic Cracking. 10/37 - 1/38

The following observations are included in these reports:

- a. Catalyst K379 compared well with the best catalyst tried, with a yield of 29% naphtha on the oil run in, an iodine number of 49.7, and A.P.I. naphtha 33°. It had a constant naphtha yield even after 40 regenerations, and had a more satisfactory behavior than the Standard Superfiltrol GOC 12X. It also gave a higher yield of fraction boiling below 100°C.

6.

- b. Various stocks were tested on these catalysts and the results tabulated.
- c. Adding 10% CrO_3 to the $\text{SiO}_2 - \text{Al}_2\text{O}_3$ catalyst practically destroys the splitting action of the catalyst, and the dehydrogenating activity of the CrO_3 is apparent in the high iodine number of the naphtha. Iron and barium silicates are inferior; treating them with HCl raises the splitting and dehydrogenating activities of iron, lowers that of barium silicate.
- d. Activated clay + 10% CrO_3 , which dehydrogenates tetralin and decaline quantitatively to naphthalene, had no effect on the paraffinic gas oil.

6. Frames 41-43. Catalytic Cracking: Status as of 2/22/38

- a. Synthetic catalyst #379 showed the highest cracking capacity, the Houdry products were somewhat inferior.
- b. The best ratio seems to be $\text{SiO}_2 / \text{Al}_2\text{O}_3 = 3.5/1$
With increased cracking, $\text{C}_3 - \text{C}_4$ formation increases, also the low boiling fraction of naphtha.
- c. Cracking occurs at the ends of the paraffin chain.
- d. The residues on re cracking give no appreciable naphtha.
- e. Silica catalysts formed by leaching out Fe silicate with HCl cause splitting to occur in the middle of the chain, rather than at the ends, as in alumina.
- f. The naphthas are heavier and yields greater.
- g. Mixtures of oils of low cetane value (90%) with Kogasin II (10%) gave upon cracking products of higher octane number than the mixture.

7. Frames 44-46. Production of a Synthetic Aluminum Silicate Catalyst.

A molecular mixture of aluminum oxide and SiO_2 is prepared by adding $\text{Al}(\text{NO}_3)_3$ to freshly prepared SiO_2 . In effect, this material was superior to superfiltrol in cracking of paraffins. Replacing SiO_2 with B_2O_3 gave also good results. ($\text{Al}_2\text{O}_3 : \text{H}_3\text{BO}_3 = 1:1$). For Fischer synthesis oil, $\text{SiO}_2 - \text{MgO}$ was superior, giving no C_3 or C_4 ; it could also be regenerated without activity loss.

8. Frames 47-52. Catalytic Cracking

Compares the Houdry superfiltrol catalyst with the synthetic aluminum silicate catalyst developed in Germany on Elwerather gas oil and Fischer oil (H_2 -rich). The latter in particular gives high yields of low boiling hydrocarbons. Methods were investigated to prevent this gasification.

Item No.

10. Frames 55-61. Cracking with SiO₂-MgO Catalysts of Various Manufacture. Small Scale Tests with Kogasin

- a. A Si-Mg cracking catalyst showed itself to form less gasification products than the hitherto used Si-Al catalysts, and was also found to be regeneratable.
- b. These new catalysts also attained naphtha yields equal to that of the usual catalyst.
- c. Adding traces of Zn considerably changes the properties of the Mg-Si catalyst, repressing gasification even further.
- d. Adding Ca and Ti gave no increase or decrease of yield of gas.

12. Frames 65-68. Influence of the Conditions of Precipitation upon the Gasification of Cracking Catalysts of Si-Mg.

Investigated were the effect of temperature of precipitation, treatment on boiling, and influence of alkali. Catalyst precipitated in the cold had higher gasification but was more efficient than that precipitated hot. When the precipitation is effected by KOH instead of NH₃, gasification is low even when precipitation is done in the cold. The catalyst is chalky instead of glossy.

13. Frames 69-78. Catalytic Cracking of Kogasin II (F1295) Under Varying Working Conditions

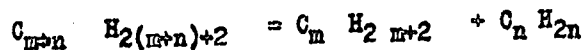
As catalysts, Superfiltrol and #379 were used. The operating temperature lay between 350-500°C., the oil rate 0.5 vol./vol.catalyst/ hour.

- a. At equal naphtha concentration of the product, the #379 catalyst shows considerable more C₃O₄ gasification than superfiltrol.
- b. Benzene formation depends on cracking temperature.
- c. At 500°C. the specific weight of the naphtha drops.
- d. With rising temperatures, iodine numbers increase, aniline point decreases.
- e. The octane nos. of the naphthas are between 57.5 and 64.3.
- f. Superfiltrol product is more unsaturated than the K379 product. Data are also given on solvent extraction - cracking of Kogasin, dehydration of Kogasin by active alumina + 10% CrO₃ at 460°C. In the latter case, the products are quite different from those of the splitting catalyst; the naphtha is heavier and more saturated. Two curves are appended.

Item No.

14. Frames 79-90. Activity Reports 4/20/38 - 5/4/38

- a. Pressureless experiments with Kogasin II show that benzine yield increases only in the range 350°C. to 460°C. (10.8-20.5% naphtha) and that gasification also increases in the same range. Under pressure, however, one may operate at higher temperatures, obtain more benzine of higher octane rating, and only slightly greater gas formation.
- b. The influence of different oil throughputs upon the yield and quality of naphtha were examined in the presence of synthetic $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst (#6752). With F189,
- 1) increasing the rate from 1 to 2.5 did not decrease the octane rating; a further increase to 5 did decrease it.
 - 2) at a throughput of 5, corresponding to a contact time of 0.05 seconds, catalytic splitting of the paraffin yielded only paraffinic and olefinic fragments:



- 3) increasing contact time or decreasing rate caused an increasing amount of H_2 to be split off; whereby at a throughput of 1.66 (corresponding to 0.15 seconds contact) there occurred isomerization, and increasing contact time to 0.25 seconds, aromatization of the naphtha.

Five curves are appended and described.

15. Frames 91-97. Catalytic Cracking. 6/20/38 and 7/13/38

- a. Influence of Nitrogen compounds on cracking catalysts.
- 1) HF-treated Terrana (K6109) was most affected by aniline, least affected were the natural untreated catalysts (Superfiltral Terrana) and those catalysts of Al and Si which were obtained from N-free starting materials. Decrease in benzine formation was always tied up with a lessening of the fraction boiling up to 100°C.
- b. With a synthetic Al-Si catalyst, and recycling, catalytic cracking with recycling gave the following:
- | | | | |
|----|----------|--------------------|-------------------------------------|
| 55 | weight % | naphtha | (stabilized) |
| 7 | " | " | $\text{C}_3\text{-C}_4$ |
| 3 | " | " | $\text{C}_1\text{-C}_2, \text{H}_2$ |
| 28 | % | Cracked middle oil | |
| 7 | % | cols | |
- c. Catalytic cracking under pressure appeared promising, giving more saturated hydrocarbons in the naphtha, more highly branched and readily susceptible to lead addition.

Item No.

16. Frames 98-104. Difference Between Thermal and Catalytic Cracking

1. Thermal cracking yields more aliphatics.
2. Catalytic cracking yields naphthas with higher octane numbers.
3. Octane number of cat. cracked naphtha is independent of length of cycle and origin of the stock; this is the contrary for thermal cracking.
4. Data and curves are given for cracking West-Texas gas oil at 470°C. over 3 liters of a synthetic Si-Al catalyst (K379) at a rate of 3 liters oil/hour; the whole cycle being 2 hours.

17. Frames 105-117. Progress Reports on Catalytic Cracking 8/10/38-2/18/38

- a. Gives data on cracking West-Texas gas oil, Elwerath gas oil, and Kogasin II over superfiltrol COC 1,2X, the cracking temperature being 460°C., and throughput of oil 0.5 or 1.0 Vol./vol cat./hour, and cycles of 2 or 1 hour. Kogasin-II gave highest benzine yields (55%) and most constant behavior under recycling.
- b. The following was ascertained about synthetic $Al_2O_3-SiO_2$ catalyst (1:2)
 - 1) optimum pH for precipitating the catalyst by ammonia (from a cat. cracking point of view) is 5-5.5. Optimum temperature of precipitation is at 90°C.
 - 2) susceptibility towards aniline was slight, and could be restified by addition of 2% boric acid to the catalyst.
- c. Data are given on the cracking of residues of polymer benzines and deasphalted lubricating fractions, and cracking of West-Texas gas oil catalytically at pressures of 20-100 atmospheres. In the latter case, increased benzine yields were obtained with increasing pressure, and also increased coke losses. Lead susceptibility was better.

18. Frames 118-126. Catalytic Cracking with an Si-Mg catalyst

- a. Cracking Elwerath gas oil under the usual conditions gave 38% benzine of octane number 74 (motor) with 40% = 100°C. Gasification: 8-9% C_3-C_4 , 2.5 - 3% $C_1 + C_2$ coke formation was 5-7% of the oil charged.
- b. After 20 cycles, there was no change in catalyst activity.
- c. Catalyst treated at 750°C. gave less coking than untreated catalyst.

19. Frame 127. Cracking. 9/5/38

Deasphalted lube oil fraction on cracking with Si-Mg catalyst (Temp. 460°C.) for 1 hour gave, for 100 kg. oil:

1 kg.	Fluid gas (C_3-C_4)
11 "	Benzine -195°C.
32 "	Middle Oil -325°C.
45.5 "	residual oil -325°C.
10.5 "	coke, gas and losses

Item No.

20. Frames 128-130. Types of Magnesium Silicate Catalysts

Comparison of catalysts obtained by

- 1) cold precipitation
- 2) precipitated cold, then immediately heated to boiling.
- 3) precipitated boiling.

<u>Catalyst</u>	(1)	(2)	(3)
<u>Cracking Activity:</u>	very good	less gasification but also less cleavage.	
<u>Analysis:</u>	SiO ₂ 67.4 MgO 31.0 Na ₂ O 1.1	SiO ₂ 60.0 MgO 36.2 Na ₂ O 2.3	SiO ₂ 55.0 MgO 36.0 Na ₂ O 1.5
<u>X-Ray:</u>	Like Terrana	Like Terrana	Absorption @ 68° & 690
<u>High Press. Activity</u>	doubtful	untested	positive

21. Frames 131-134. Cracking of Lube Oil Fractions of Reitbrook Petroleum

Catalytic cracking of this deasphalted lube oil over superfiltrol gave:

10% Benzine (O.N. 64.0 (Motor))
28% Middle Oil - cetane No. 48
1% Gas C₃ C₄
2% " C₁-C₂, H₂
48% cracking residue
11% coke.

The solid point of the middle oil (-2 to -12°C.) was still too high for diesel oil, though the rest of the data fulfilled diesel requirements.

22. Frames 135-136. Effect of Alkali on the Cleavage of Cracking Catalysts.

Earlier experiments indicated that cleavage by cracking catalysts tended to production of higher boiling products by addition of small quantities of alkali. To prove this, up to 3% Na₂O was added to magnesium silicate catalyst (in the form of NaOH solution). Adding alkali equivalent to less than 1% Na₂O immediately suppressed formation of low boilers (C₃-C₄) and increased benzine formation. Larger quantities decreased yield.

23. Frames 137-139. Catalytic Cracking of CO-N-synthesis Product over Catalyst 502.

The synthesis product from Catalyst 502 was cracked to give a greater conversion and better benzine than the corresponding fraction of Fischer-Kogasin II. The yields were 39% benzine as against 25.8%. Oxygenated products in the starting material were converted to H₂O quantitatively.

Item No.

25. Frames 143-150. Cracking of Kogasin II at various Pressures over Superfiltrol

The following data were obtained on pressure cracking a fraction boiling at 200-325°C.

A. Expansion at Constant Pressure.

1. Increased yield over the atmospheric process at 20 atmospheres, 33.5%, at atmospheric, 18.5% benzine.
2. Increase in isoparaffins and decrease in olefins with pressures up to 12 1/2 atmospheres. No aromatics or naphthenes.
3. Constancy of O.N. up to 12 1/2 atmospheres. Above this, the octane numbers decreased. (From 66 down).
4. The iodine number of the cracking residue increased with increased pressure, and the aniline point decreased more sharply than with atmospheric cracking.
5. For gasification, conditions were at an optimum between 5 and 12.5 atmospheres.
6. Losses in coke and uncondensable gases (C₁, C₂, H₂) were greater than by atmospheric cracking.
7. The C₄ fraction consisted almost entirely of isobutane.
8. Lead susceptibility was greater for the pressure cracking process. (13 points as against 12)

B. Expansion with increasing pressure showed somewhat the same results.

28. Frames 156-158. Cracking of Propylene Gas Oil

The starting product, a polymerization product of isoparaffins, was cracked with a yield of 62.7% benzine in a once-through operation at a temperature of only 370°C. The cracked benzine consisted entirely of olefins, had an octane No. of 80 (motor) and little losses to coke or gas formation occurred. A table compares the data of various cracking temperatures.

29. Frames 159-160. Catalytic Cracking of West Texas Gas Oil at High Pressures

This gas oil did not give as good results with high pressure catalytic cracking as was experienced with Kogasin II. A table of data shows this.

30. Frames 161-163. Catalytic Cracking of Kogasin II.

The fraction boiling between 206-240°C. which, in petroleum middle oils, has catalytic cracking difficulties, was cracked more readily than the higher Kogasin fractions. A table of comparative data gives results of cracking Kogasin II at various temperature ranges over an Si-Al catalyst.

31. Frames 164-168. Catalytic Cracking with Addition of Sulfur.

The octane number was increased by adding sulfur, but the yields were the same, save somewhat more coking. The mode of sulfur addition was not very effective, most of it being lost to coke and H₂S before vaporization. One table of data.

Item No.

32. Frames 169-173. Catalytic Cracking of Synthesis Product (Dr. Michael)
- It was desired to find a way of cracking catalytically crude benzene and diesel oil to give satisfactory yields of isobutylene. The products from the synthesis under normal conditions formed little condensable gas. Raising temperature to 500°-530°C. increased the C₅ yield and also C₁, C₂ yield with slight effect on the C₃-C₄ fraction; much coking resulted. The isobutylene content of one run was about 2% by weight.
 - Further experiments increased the i-C₄ yield to 7.9 weight %, leaving it still unsatisfactory. Pressure also was ineffective.
33. Frames 174-183. Catalytic Cracking of Kogasin II at Normal Pressures. The Influence of Temperature and Cycle Duration.
- Between 400-460°C. the benzene yield at atmospheric pressure was independent of temperature or duration of cycle.
 - Strongly temperature dependent were the yields of condensable gases and C₅. Uncondensable gas yields increased slightly.
 - The aniline point of the benzene fell with increasing temperature, while the iodine number rose.
 - Short cycles (under 30 minutes) gave, at 400° and 430°, naphthas with poor octane numbers.
 - The height of the octane number was given by the low boiling fractions and the olefin content in the pressure-less process.
34. Frames 184-192. Catalytic Cracking of Rehydrogenated "b" residual Oils of Catalytic Cracking I.
- The b-cracking residual oils, obtained from cat. cracking of fresh oils, cleaved poorly.
 - Hydrogenation of these residues gave more effective cracking behavior than the unhydrogenated materials. Five tables of comparative data give results for experiments with Elwerath gas oil, West Texas gas oil and Fischer Kogasin II.
37. Frames 209-215. Manufacture of Aviation Gasoline by Catalytic Cracking.
- Only oils giving saturated cracking products were suitable.
 - This was brought about by low cracking temperatures and short cycles. Naphthenic and mixed base stock was most suitable.
 - The octane number of the crude benzene was independent of olefin content except when the base had been refined with acid.
 - Cracking temperatures should be maintained at 400-430°C. and cycles of about 15 minutes.
 - Stocks with low final boiling points should be used, to insure complete vapor phase cracking, no higher than 400°C., and they should be topped to 250°C. Best range, 250-350°C.

Item No.

40. Frames 219-221. Catalytic Cracking of the 150-200° Fraction of Kogasin

A light, highly unsaturated but high octane benzene was obtained from this stock. The naphtha, boiling at 130°C. was obtained in 20-25% yield, and had an octane No. 76.5-78.8 (motor); it was 65-75% unsaturated. Temperature of cracking was 490°C. Its low boiling point indicates its possible use for blending purposes.

41. Frames 222-224. Zinc-containing Contacts for Catalytic Cracking.

Zn(OH)₂ was added to a magnesium silicate catalyst. The material had a strong dehydrogenating activity, but showed little cracking property.

42. Frames 225-226. Aviation Fuel by Catalytic Cracking

A West Texas fraction (225-310°C.) was cracked over a Mg silicate catalyst. A once-through operation gave a 35% yield based on charge, 74% based on oil consumed. The unrefined benzene contained 8% unsaturates, an O. N. of 77.5 (motor). After light refining and Pb addition, O.N. was 88.5.

43. Frames 227-232. Thermal and Catalytic Cracking of Kogasin

For working up the gas oil fraction, catalytic cracking was superior to thermal in respect to benzene yields, octane ratings, less residue. For working up the heavy benzene fraction, comparison was difficult, since catalytic cracking forms a good octane but somewhat too light a benzene, requiring polymerization to obtain a better boiling range. (This is possible because of its unsaturated character).

44. Frames 233-238. Influence of Gas Oil Composition on Yield in Catalytic Cracking.

a. Virgin gas oil, catalytic cycle stock, and thermal cycle stock were examined and compared in aniline point, gasoline and coke yields on catalytic cracking. The gas and coke yields of the two latter were greater than that of the former. To determine the reason each of these stocks was solvent extracted into narrow fractions. The first 25% of the extracts of the cycle stocks were particularly poor in hydrogen and contained condensed aromatic rings. Thereafter the aniline points rose quickly and approached those of the virgin oil.

45. Frames 239-247. Catalytic Cracking of Kogasin with Mg silicate and Superfiltrol.

Kogasin II yielded an olefin-poor, high octane benzene with the Mg silicate catalyst at 480°C. It was similar to the best benzene obtained heretofore by catalytic cracking under pressure, with the same coke formation also. Superfiltrol did not give nearly as good results.

46. Frames 248-256. Catalytic Cracking of Gas Oil with a Paraffin Base (E. Texas) with Superfiltrol and Mg Silicate

a. A good Mg silicate catalyst - Kr 690 - had, at 15°C. lower temperature, 150% of the capacity of superfiltrol. The corresponding benzene had a lower % at 100°C. (42 instead of 51), higher aniline point, lower iodine number. Its knock rating with lead was higher (88 against 87.2), without lead it was lower (75 against 76.5), indicating stronger isomerization.

Item No.

48. Frames 260-261. Catalytic Cracking with Catalysts that Resemble Those Used as Carrier in Aromatization

In the series, superfiltrol, Terrana, Terana HF-MgO, uncondensable gas formation increased in the ratio 1:1.5:3.5 (while cleavage decreased). The higher value of Terrana is connected with its increased iron content, the latter was activated in Terrana HF-MgO, for the first cycle, thereafter it cleaved the same as the plain Terrana.

49. Frames 262-264. Catalytic Cracking of Paraffin and Similar Products to Middle Oils.

For cracking to middle oils, active alumina was particularly suitable; siliceous catalysts yielded benzine. Adding steam was favorable to middle oil formation. The middle oils obtained from active alumina were highly unsaturated, particularly when water vapor had been added in the cracking process.

51. Frames 268-271. Review of Oils Suitable for Catalytic Cracking and the Yields Anticipated in their Processing.

Curves are given for the following:

- a. That group of oils which can be catalytically cracked.
- b. Coke and gas losses ($C_1 - C_4$) from oils of (a).
- c. Average yield of cracked naphtha ($T=200^\circ C.$) with octane No. 75-80 (motor) of the individual members.
- d. Olefin contents of the naphthas from the various oils.

52. Frames 272-274. The Behavior of Cracked Benzines in Hydrogenation.

- a. Catalytic cracked benzines of high olefin content can be hydrogenated over Ni-W to saturated naphthas.
- b. Hydrogenation lowered the octane numbers of cracked benzines from natural middle oil fractions about 2-3 points, while the octane value of synthetic stock cracked benzines (propylene gas oil) dropped over 20 points.
- c. Lead susceptibility of hydrogenated benzines improved considerably.

53. Frames 275-287. Isomerization Through Cracking

- a. It was not possible to produce isomerization without cleavage into smaller molecules.
- b. Catalytically cracked benzines were so strongly isomerized in their fractions boiling under $70^\circ C.$ that the octane number of these fractions rose after separation of the cracking olefins. On the other hand, the O.N. of the fractions above $70^\circ C.$ fell after separation of the olefins.

Item No.

56. Frames 294-307. Treatment of Benzines with Catalysts Containing SiO₂.
With and Without Pressure.

- a. Pressure-less work up of benzines over silicate catalysts yielded only small quantities of fluid cleavage and polymerization products.
- b. Condensable gas yields (C₃C₄) were high.
- c. The isobutane, comprising 80-90% of the total C₄, was very high.
- d. Benzine quality, increased splitting and polymerization were attained by working under H₂ pressure in silicate catalysts.
- e. Working with H₂ pressure, it was possible to prepare aviation naphtha from heavy benzine, but no aromatic high duty fuels.
- f. The higher boiling fractions formed by polymerization of cleavage products were highly aromatized. This showed that aromatization brought about by silicate catalysts was the consequence of polymerization of olefins.
- g. The benzine fractions boiling under 150°C. were most suitable for aromatic polymerization.
- h. Under these conditions the cleavage action of synthetic Al silicates was much greater than that of natural fullers earth. As a consequence, using synthetic Al silicate under H₂ pressure gave greater gasification, higher cracked benzine and stronger aromatization of the polymerizate with paraffinic and naphthenic stocks than by the use of fullers earth.

57. Frames 308-310. Catalytic Cracking Experiments with AlF₃ catalysts.

- a. The catalysts had medium activity.
- b. The products were similar to those obtained by the use of Si-Al or Si-Mg catalysts.
- c. Best values were obtained by a pure AlF₃ catalyst and one activated with 10% MgCl₂.

58. Frames 311-319. Influence of the Process and the Catalyst upon the Extent
of Isomerization in Catalytic Cracking.

A prehydrogenated middle oil (Scholvan) was catalytically cracked over Terrana (K6108) under atmospheric and under 15 atmospheres pressures, with the following results:

- a. The i-C₄ content of both processes was the same.
- b. The pressure (debutanized) light naphtha (E-113°C.) was, for the same boiling curve, of higher octane value and greater lead susceptibility than the pressure-less, olefin-rich light benzine.
- c. The heavy benzine of the pressure process was richer in aromatics.
- d. Catalytic cracking of East Texas gas oil over Terrana and over Si-Al catalysts (K6752) showed the latter synthetic catalyst to yield far more i-C₄ (88% i-C₄) as against 58%.
- e. The i-C₄ content of the C₄ fraction increased even somewhat with increased temperature.
- f. The olefine content of the condensable gas increased with increasing cracking temperatures.

59. Frames 320-324. Treatment of Rumanian Crude Oil by Catalytic Cracking.

- a. Aviation naphtha and gas oil could be obtained from Rumanian crude oil by catalytic cracking, but no premium fuel.
- b. The gas oil from this paraffinic crude was a good diesel fuel (cetane#55) but did not meet aviation gas oil specification due to low viscosity.

Item No.

61. Frames 327-343. Benzine and Gas Oil Cracking under H₂ Pressure.

Different benzines and gas oils were cracked over Al-silicate and Mg-silicate in 8 hour cycles under H₂ pressures of 10, 25 and 50 atm. and temperatures of 459 and 476°C. The following were the observations:

- a. The aromatic-poor heavy benzine was readily split over Al-silicate, the i-C₄ content was 30% of the total C₄; the octane number of the cracked material was 4 points higher than the stock.
- b. The aromatic-rich benzine was more difficult to crack, and splitting increased only slowly with increasing pressure. The isobutane content was greater than above. The octane number of the residual benzine was not improved over stock.
- c. P 189 gas oil after cracking over silica catalyst yielded 5.1-9.8% gas and coke, 15-22% benzine -150°C., 12-16% heavy benzine and 55-63% middle oil. The benzine had an exceptionally high octane number of 76-77.2 (motor) and, with 0.12 cc. lead, 90-92.5. It was highly unsaturated.

62. Frames 344-365. Cracking Experiments with K6108 (Terrana) and K6109 (Terrana HF) Under Different Pressures

With increasing H₂ pressure, cleavage increased when fullers earth was used as cracking catalysts. This pressure dependence was more marked with HF-treated clay than with untreated clay.

- a. In the absence of H₂, 6109 gave greater gasification.
- b. Addition of CS₂ in the presence of H₂ in lower pressure ranges decreased benzine yields and increased gasification. In higher pressure ranges (over 40 with 6108, over 30 atm. with 6109) CS₂ and H₂S improved cleavage.
- c. With K6109 and Elverath Diesel Oil, at 45 atmospheres pressure (H₂ partial pressure = 42.8 atm.) without CS₂ a benzine efficiency of 0.25 was attained (up to 190°C.); with 1% CS₂ addition to the oil, the value became 0.31.
- d. Gasification and coke accounted for 30%.
- e. From 0-45 atmospheres pressure, no H₂ consumption could be determined. 9 tables and 8 sheets of curves.

64. Frames 368-81. Composition of Cracked Benzines of H₂-rich Petroleum Middle Oil in Relation to the Cracking Temperature.

- a. In the temperature range 420-480°C., increased temperature caused increased aromatization of the heavy fraction (150°-200°C.) of cracked benzine. This was accompanied by an increased octane number. The aniline point of the heavy naphtha was not influenced by the cracking temperature.

Item No.

- b. In the light benzine fraction the olefin content increased with the cracking temperature when the throughput rate was 1.2; when this value was 0.6, increase of the temperature from 420-450°C. decreased the olefin content.
- c. Since aromatization is accompanied by decrease in olefin, it is probably a case of cause and effect.
- d. Changing temperature and throughput rates enables one to improve the knock characteristics of the above benzine fractions. 3 tables, 5 pages of curves.

65. Frames 382-384. Catalytic Cracking of the Intermediate Products of Lubricating Oil Synthesis

Gas oil fractions resulting from the polymerization of propylene, butylene or mixtures of these may be catalytically cracked (once-through) readily and with very high yields (50-75% by weight) and low gasification. The cracked naphthas were practically purely olefinic and had an octane number (motor) 80-82. Hydrogenation decreased this value by 20 points.

70. Frames 393-402. Refining and Dehydrogenation of Catalytically Cracked Benzines of F189 Gas Oil with Catalyst #7360.

A benzine, produced by cracking a F189 Diesel Oil Fraction (BP 237-345°C.) over aluminum silicate, with a 190°C. end point, was refined over a D.H.D. dehydrogenation catalyst at 25 atmospheres pressure and 340°C. The octane number of the fraction boiling over 100°C. dropped 2 points. A benzine from the same source, having an end point of 170°C. was then divided into fractions boiling below and above 85°C., and the heavy benzine dehydrogenated at 20 atmospheres pressure at 50°C. There was obtained then from the cracked benzine a premium naphtha in 85.8% yield, containing 42.5% aromatics. From the same stock there could be obtained a premium naphtha with 50 vol. % aromatics by injecting into the refining oven of the D.H.D. chamber only a part of the light benzine together with the dehydrogenated heavy benzine. As by-product there was obtained (from 1000 kg. stock) 728 kg. premium naphtha and 130 kg. unrefined light benzine.

71. Frames 403-404. Remarks of Dr. Kaufmann on Catalytic Cracking 11/26/41.

Experiments on catalytic cracking were carried out in Leuna with synthetic aluminum silicate. A middle oil fraction (to 400°C.) was cracked both with and without pressure.

- a. Coke yield was 3-5% of charge, considerably higher than the 1-1.5% with HF.
- b. The regeneration period was 2-4 times as long as the cracking period.
- c. Yield and quality were dependent on the charging stock. The best were naphthenic, paraffinic, being less suitable.

Naphtha -165°C.	25-30 wt. % (with 25-30% aromatics)
C ₃ C ₄	10-15 " "
H ₂ , CH ₄	2-3 " "
Coke	3-5 " "
Rest is diesel oil.	

Item No.

- d. In spite of the low aromatic content, the naphtha was of aviation grade. The olefins were all of the harmless mono-olefin type. The octane number was 70-80, with lead it was 90.
- e. The cracked products were highly branched, and much $i-C_4$ was present, making them, together with the high olefin content, suitable material for alkylation.

74. Frames 407-412. Catalytic Cracking in the 50-litre Apparatus.

A Bruchsal gas oil fraction (F1203) was cracked with the following result.

	<u>Conditions</u>
39.3% Raw benzine-165° (unstabilized)	Catalyst: Synthetic Al-silicate
44.2% Cracked & middle oil	Temperature: 415°C.
0.7% Distillation losses	Throughput: 0.46 vol/vol.cat.
11.9% Gas (containing C_5)	Cycle: 15 minutes
3.9% Coke	Pressure: None.

After adding the C_5 fraction to the benzine from the gas, and after stabilization, there remained:

38.7% stabilized benzine(165°C.)
12.5% gas.

The O.N. of the unstabilized benzine was 78.5 and the iodine number 16.4.

75. Frames 413-436. Catalytic Cracking in the 40 litre oven with Catalysts 6108 and 6752.

A series of cracking experiments were carried out in a D.H.D. oven consisting of 4 single 10 litre ovens. Cycles were 20 and 60 minutes, throughputs 0.5 and 1.0 kg./litre catalyst/hour. The catalysts were Terrana (K6108) and synthetic Al-silicate (6752). The oils were a coal base pre-hydrogenated middle oil and 2 petroleum middle oils. The products were divided into benzine-150°C., heavy benzine 150-180°C. and residues >180°C. and the properties of these fractions were compared in relation to catalyst, stock, and reaction conditions; both tabular and graphically. The exact gas composition and its change in the course of a 20 minute cycle was also discussed. 13 Tables, 10 pages of curves.