

The higher poly-fractions of an initial boiling of 220°C and boiling end point of 270° give the following constants:

$$d_{20} = 0.84 - 0.85$$

$$n_{D20} = 1.47 - 1.48$$

$$\text{olefins} = 86-88\%$$

Table IX

Compilation of several experiments with data on the octane number (research):

Exp.	Charge	Conditions			Fraction	Octane Number
		Temp.	Pressure	cc/hr		
4	Condensate-Naphtha	200°	5 atm.	400	to 200°	89.5
15	"	200	5 atm.	400	curde prod.	93.5
15	"	200	5 atm.	400	70-200°	94
23/I	"	200	100 atm.	250	70-200°	94.5
38/III	"	200	100 atm.	1000	to 200°	91.5
35/I	2 step polymer condensate naphtha	200	100 atm.	1000	to 200°	89.5
9	Condensate naphtha and gasol	200	5 atm.	250	to 200°	89
44/II	gasol	200	100 atm.	250	to 200°	96.5
44/III	gasol	200	100 atm.	500	to 200°	96

Table X

Residue gas analyses

- A) Polymerization of condensate naphtha: ng gas evolution
 B) Polymerization of gasol: Exp. 44/I (200, 100 atm., 250 cc/hr)

Gas Charge:		Exhaust Gas	
CO ₂	= 0.2%	CO ₂	= 0.4
C ₃ H ₆ + C ₄ H ₆	= 60.0%	C ₃ H ₆ + C ₄ H ₆	= 13.3
C ₂ H ₄	= 4.0%	C ₂ H ₄	= 3.4
C _n H _{2n+2}	= 35.0%	C _n H _{2n+2}	= 81.2
CO	= 0.0%	CO	= 0.1
H ₂	= 0.0%	H ₂	= 0.0
N ₂	= 0.8%	N ₂	= 1.7

L.G. = 2.1

L.G. = 2.2

(Trans: L.G. = Sp.gr. referred to air?)

The higher poly-fractions of an initial boiling of 220°C and boiling end point of 270° give the following constants:

$$d_{20} = 0.84 - 0.85$$

$$n_{D20} = 1.47 - 1.48$$

$$\text{olefins} = 86-88\%$$

Table IX

Compilation of several experiments with data on the octane number (research):

Exp.	Charge	Conditions			Fraction to 200°	Octane Number
		Temp.	Pressure	cc/hr		
4	Condensate-Naphtha	200°	5 atm.	400	to 200°	89.5
15	"	200	5 atm.	400	curde prod.	93.5
15	"	200	5 atm.	400	70-200°	94
23/I	"	200	100 atm.	250	70-200°	94.5
38/III	"	200	100 atm.	1000	to 200°	91.5
35/I	2 step polymer Condensate naphtha	200	100 atm.	1000	to 200°	89.5
9	Condensate naphtha and gasol	200	5 atm.	250	to 200°	89
44/II	gasol	200	100 atm.	250	to 200°	96.5
44/III	gasol	200	100 atm.	500	to 200°	96

Table X

Residue gas analyses

- A) Polymerization of condensate naphtha: ng gas evolution
 B) Polymerization of gasol: Exp. 44/I (200, 100 atm., 250 cc/hr)

Gas Charge:		Exhaust Gas	
CO ₂	0.2%	CO ₂	= 0.4
C ₂ H ₆ + C ₄ H ₆	60.0%	C ₂ H ₆ + C ₄ H ₆	= 13.3
C ₂ H ₄	4.0%	C ₂ H ₄	= 3.4
C _n H _{2n+2}	35.0%	C _n H _{2n+2}	= 81.2
CO	0.0%	CO	= 0.1
H ₂	0.0%	H ₂	= 0.0
N ₂	0.8%	N ₂	= 1.7

L.G. = 2.1

L.G. = 2.2

(Trans: L.G. = Sp.gr. referred to air?)

C) Polymerization of Condensate naphtha and gasol: Exp.: 49
(100°, 10 atm.)

Gas Charge	Exhaust gas: 49/I (250 cc/hr.)	(100°, 100 atm.) 49/V 250 cc/hr.
CO ₂ = 2.7%	CO ₂ = 3.3%	3.9%
C ₃ H ₆ = 43.0%	C ₃ H ₆ = 20.0% (67% polymerization)	5.4% (93% poly.)
C ₂ H ₄ = 0.5%	C ₂ H ₄ = 0.7% (no polymerization)	0.6% (45% poly.)
L.G. = 2.0	L.G. = 2.04	L.G. = 1.99

D) Polymerization of gasol and ethylene: Exp. 54
(200°, 50 atm.)

Gas Charge	Exhaust gas I. (200 cc/hr.)	200°, 50 atm. IV 250 cc/hr.
CO ₂ = 0.0%	CO ₂ = 0.0%	0.0%
C ₃ H ₆ = 29%	C ₃ H ₆ = 14.0% (60% C ₃ -poly.)	17.7% (47% poly.)
C ₂ H ₄ = 34.4%	C ₂ H ₄ = 34.5 (17% C ₂ -poly.)	38.6% (4% poly.)

200°, 5 atm.
II 250 cc/hr.
0.0%
14.1% (60% C₃ poly.)
36.5% (11% poly.)

Frames 44 - 50 are graphs

Translated by Dr. H. Cohen - 1/22 and 2/1/47

Checked by GGM - 2/4-5/47

Requested by R.F. Marachner

"Katalytische Polymerisation von ungesättigten Kohlenwasserstoffen".

(I. Teil)

Rohrchemie Aktiengesellschaft.

Oberhausen-Holten

March 29, 1939

20 pages, 7 graphs

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-10

API-TOM Reel 40, Frames 51-56
Oberhausen-Holten, June 12, 1939
To: Prof. Martin, et al
Polymerization of Gasol (Trans.: L.P.G.) with Increasing Charge
(Charge of Director Albert)

Summary

(1) By the utilization of narrow reaction tubes it was possible to increase five-fold the charges of gasol in comparison to the amounts which the U.O.P.C. described but that the polymerization fell below 90%, further to increase ten-fold whereupon the value of the polymerization, also by increase of the temperature to 240-250° declines only to 80-85%.

(2) The strongly exothermic reaction which proceeds caused no superheating; a good distribution of the temperature in the reaction tube occurs with the great rate of flow.

The apparatus utilized in these experiments is described in supplement I. It consists of a reaction tube (15 mm. i.d. 1300 mm. long, ca. 320 cc. capacity) which possesses an electric heater with 3 external temperature measuring positions. The feed of the gasol to the furnace occurs from a high pressure bomb by means of an iron tube which for the purpose of preheating of the gasol is wrapped about a small water-filled bomb, which is heated in an oil bath. (Wrapping ca. 6.8 m. long $F = 0.17 \text{ m}^2$). The addition of water was carried out in such a manner that, by means of a submerged tube, a determined amount of nitrogen was led into the bottom of the small water-filled bomb where it took along a portion of the water vapor (the amount was previously determined at different temperatures and pressures). The nitrogen laden with water vapor was introduced into the gasol conduit before the oil bath in order to obtain an intimate mixture between gasol and water vapors which were heated jointly in the oil bath in order to prevent a condensation of the water on the upper portion of the catalyst. The furnace is filled with the Ipatieff catalyst (275 cc.).

The Americans used a reaction furnace of 50-80 mm. i.d. for the polymerization and give the following polymerization conditions:

Temperature - 190°-205°
Pressure - 50-70 atm.
Charge - 1 l. liquid gasol = 0.5 kg on 0.5 l. catalyst
Original olefin content of the gasol - 30-40 vol. %
H₂O-addition - 1 mol. % calculated on gasol.

In the first experiments these conditions were accurately kept. Since there were 275 cc. of catalyst in the furnace, the previously-described amount of charge of gasol with 29.6% of C₃H₆ + C₄H₈ yielded 120 cc. of poly-naphtha/hr. in a 95-98% polymerization.

Since in the earlier experiments - without water addition - increasing charges have affected very favorably the boiling course of the products obtained, there should be established in these experiments how far the charge can be increased, in general, without sharply decreasing the polymerization, further how the reaction proceeding exothermally at high charges works out on the temperature of the several reaction zones in the narrow tube.

The following experiments were carried out with 200 cc., 400 cc. and 800 cc. of poly-naphtha formation per hour. At a rate of 200 cc./hr. the temperature of 200°C. suffices to get a 90-95% polymerization, at a 400 cc. hourly rate the temperature must be raised to 220-225°C. if a polymerization of 90-95% is to be obtained. Condensate of 400 cc/hr. corresponds to a charge of ca. 1.2 kg. of gasol or a space time yield of 1300 l. naphtha/m³ reaction space per hour or 1450 l. naphtha/m³ catalyst/hr.

In the further increase of the charge to 800 cc. condensate/hr., the polymerization decreased in spite of the increase of the temperature to 240-250°C. and reached an average value of 80-85%. About 2.4-2.6 kg. of gasol were necessary as charge. This corresponds approximately to ten-fold of the amount which the Americans stated for the charge.

The space-time yields in these experiments amount to 2600 l./m³ reaction space/hr. or 2900 l. naphtha/m³ catalyst/hr.

Since the polymerization decreased at a charge of 800 cc/hr. a further increase was omitted. These ratios all refer to a charge of utilized gasol of 29.6 vol.% C₂H₆ + C₄H₈. The space-time yields could be correspondingly raised at higher olefin content. On account of the resulting reaction heat a superheating in the narrow reaction tube could not also be established at the high charge of 2.5 kg. gasol/hr.

According to the view of Dir. Albert this should have its basis in that the cooling zones of the external wall (on account of the small diameter) can be more effective and make impossible a resulting peak temperature of the reaction in the interior of the tube, which by application of tubes with large diameters even at high charge cannot be prevented (see supplement I, figure 2).

From the weight calculation of several experiments can be concluded that a C-deposition in the shape of higher polymerization hardly takes place, since the experiments do not exceed a value of 1-2%.

Whether a rapid fatigue of the catalyst enters at high loads, cannot be stated, since the duration experiments in this direction have not yet been carried out.

In conclusion a table follows with data of several poly naphthas at increasing charge.

T A B L E

	I Charge 200 cc/hr. Distillate to 200° C.		II Charge 400 cc/hr. Distillate to 200° C.		III Charge 800 cc/hr. Distillate to 200° C.	
	Crude		Crude		Crude	
d ₂₀	0.725	0.735	0.725	0.735	0.718	0.727
n _D	1.4216	1.4226	1.4219	1.4225	1.4194	1.4172
Reid-pressure	0.47	0.24	0.71	0.24	0.46	0.15
Unsaturated % after Katwinkol	90	92	86	90	89	76
Octans Number	CFR Mot. 79.5	Mot. 80.2 Res. 95.0	CFR Mot. 78	Mot. 78 Res. 93.7	Mot. 78.8 Res. 93.7	Mot. 80.2 Res. 95.2
Boiling Initial	30° C.	34° C.	32° C.	33° C.	34° C.	49° C.
Boiling End	232° C.	194° C.	224° C.	196° C.	198° C.	195° C.
10%	-	93°	39°	88°	45°	95°
50%	127°	121°	122°	117°	114°	113°
95%	210°	187°	205°	184°	190°	182°
S.I.Z. °	137.5	126	134	122	128	122

° (Trans.: Boiling Characteristic Number?)

From the table is to be seen that the properties of the three naphthas are fairly equivalent. At greater charge (lesser polymerization) the boiling position (supplement 2) is most favorable and the specific gravity the lowest. Almost the whole fraction in all cases is to be used as motor naphtha. The portion of aviation naphtha (-165° C.) lies very favorable with 80%. The octane numbers of all also lie in the same range according to CFR motor at 78-80 octane number and according to Research at 93-95 octane number.

/s/ Spiske

Translated by H.J. Cohen, Feb. 8, 1947
Requested by R. F. Marachner
Checked by C. C. Miller, Feb. 13, 1947
Typed Feb. 24, 1947

Attachments in Original

Supplement 2

Boiling point plot of volume per cent versus temperature $^{\circ}$ C. for three investigations.

Supplement 1

Polymerization apparatus.

"Polymerisation von Gasol mit steigenden Durchsätzen"

Oberhausen-Holten
June 12, 1939

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION 747-12

API-TOM Reel 40, Frames 92-3 (Item 14)

Target 3453-30/5.01-14

To: Prof. Martin et.al.

Concerns: Addition of U.O.P. Inhibitors into our Foly Naphthas

For the execution of the experiment a fresh polymer-naphtha was used. Since ordinary daylight causes a real increase of the peroxide number during the passage of the naphtha through the condenser, the effect of the light was prevented by painting the glass apparatus black. The average naphtha had the following properties:

d_{20}^{20}	0.729
n_{D20}^{20}	1.4208
Reid pressure	0.20
Olefin, according to Kattwinkel	62%
Octane Number(CFR Motor)	80.5
Octane Number (CFR Motor) + Pb	85.0
Boiling initial °C	15°
Boiling end °C	206°

The distillation was carried out on the day of production of the poly-naphtha. The inhibitor was added at once at the beginning of the distillation of the naphtha in the prescribed manner and amount, whereby was tested at first the influence of the smallest added amount which was prescribed:

Test 1 was without inhibitor,
Test 2 contained 0.01 weight % U.O.P.
inhibitor 1 calculated on naphtha,
Test 3 contained 0.003 weight % U.O.P.
inhibitor 4 calculated on naphtha,
Test 4 contained 0.0015 weight % cresol,
calculated on naphtha

The four tests were investigated in the division of Dr. Velde in the oxygen bomb at 70° in the customary manner, and moreover in the tests which lasted an induction time of 240 minutes the total induction time was determined.

The results were the following:

Test	Peroxide	Induction Time	Bomb Test	Total Ind. Time
1	165 mg/l.	65	338	65 min.
2	20 mg/l.	240	3	9.5 hrs.
3	20 mg/l.	240	8	9.5 hrs.
4	145 mg/l.	120	261	120 min.

The two tests 2 and 3, which were treated with U.O.P. inhibitor, are to be labelled as good, while the influence of cresol in the applied amount (test 4) is very slight in comparison with the naphtha without inhibitor.

For the next four tests was used the same poly-naphtha which was preserved in crude form for 14 days in aluminum flasks and afterwards first distilled to 200°, whereby also the inhibitor was added at the beginning of the distillation of the naphtha and indeed this time in its greatest prescribed concentration.

Test	Inhibitor	Amount Wt. %	Peroxide mg/l.	Ind. Time Min.	Bomb Test mg	Total Ind. Time	Octane No. (CFR Motor)
5	-	-	8	200	103	200	83.2
6	U.O.P. 1	0.06	-	210	1	ca. 10 hrs.	83.7
7	U.O.P. 4	0.012	1	210	1	ca. 10 hrs.	82.7
8	O-cresol	0.06	6	210	3	ca. 10 hrs.	82.2

These results signify that the peroxide and gum formation proceeds very rapidly at the beginning, but that by a distillation which is carried out after several days' storage, new peroxide and gum formation are strongly repressed. The octane numbers of these products lie between 82-83, also a proof that the peroxide formation must be slight. It is true, these results do not agree with the previous experience in the field of aging and must be further investigated by systematic experiments.

However, it can already be said that the U.O.P. inhibitors can be used well in our polymer-naphtha, since they have already yielded good results in small dosages.

/s/ Spiske

"Zusatz von U.O.P. Inhibitoren bei
Unsere Poly.-Benzinen". (Ruhchemie
Aktiengesellschaft?) Oberhausen-
Holt, June 13, 1939
2 pages, no illust.

Translated Feb. 8, 1947 by H.J. Cohen
Requested by R.F. Marschner
Checked by CCM - Feb. 13, 1947

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-11

API-TOM Reel No. 40, Frames 207-210

Target 3453 - 30/501-22

To: Dr. Hagemann

Concerns: Case 8

Bases for Auto-Naphtha Qualities

Octane number of mixtures of polymer naphtha with residue naphtha from oil syntheses which were carried out with previously treated primary naphtha prepared under pressure.

1) Component Mixture Polymer Naphtha to 200° Vapor*

A crude polymer naphtha prepared in Spiske's division was distilled to 200° (vapor). The yield of this distillate from 6000 kg.* amounted to 5354 g* = 89.2 weight %. $d_{20} = 0.715$.

2) Component Mixture Residue Naphtha from Oil Syntheses.

In several series of experiments, primary naphtha which stems from the pressure syntheses was pre-treated in various ways for the removal of alcohol, for example, with PCl_5 or ZnCl_2 or other suitable materials, and then worked up to an oil with AlCl_3 . The chlorine-containing mixture of the resulting residue naphtha in these oil syntheses was de-chlorinated in the autoclave in the customary manner and after filtration distilled to 200° (vapor).

The analytical data of this naphtha portion to 200° was:

$d_{20} = 0.707$

Neutralization No. = 0.01

Saponification No. = 0.05

Olefin after Kattwinkel = 10%

The materials 1) and 2), whose Engler analysis is to be seen from appendix 1, were mixed in various proportions and the octane number investigated. Thereby was obtained (compare curve page appendix 2):

<u>Mixture 1) and 2)</u>		<u>Octane Number</u>
100 vol. 1 polymer naphtha	+ 0 vol. 2 residue naphtha	95.6
80 " " " "	+ 20 " " " "	87.5
70 " " " "	+ 30 " " " "	80.1
50 " " " "	+ 50 " " " "	61.7

* Trans... One is evidently in error. It is probably 6000 g not Kg.

Appendix 1

Engler Analysis of Mixture Components

<u>Vol.% boiling</u>	<u>Polymer-Naphtha to 200° 32°C</u>	<u>Residus Naphtha to 200° 65°C</u>
5	low condensate	86°C
10	"	93
15	71°C	98
20	92	103
25	106	108
30	114	113
35	118	118
40	121	125
45	125	131
50	128	136
55	131	141
60	135	146
65	140	150
70	145	155
75	153	160
80	165	167
85	175	174
90	183	183
95	194	202
4.5%	residue	residue
0.5%	loss	loss

Attachments in Original

Supplement 2 (Frame 210) Octane numbers of mixtures of polymer naphtha and residue naphtha, versus weight per cent components (Graph)

"Unterlagen für Auto-Benzin Qualitäten"
Ruhrohemia Aktiengesellschaft.
Oberhausen-Holteln. Dec. 27, 1940
3 pages, 1 graph

Translated Feb. 8, 1947 - H.C. Cohen
Requested by R.F. Marschner
Checked Feb. 13, 1947 - GCM

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION TL7-13

API-TOM Reel 40, Frames 212-215

Target 3453-30/501-23 Item 23

To: Prof. Martin et.al.

Concerns: Purification of Primary Naphtha from Alcoholic Constituents by Passage of the Vapor Over Alumina and Jointly the Preparation of Oils.

In connection with the report of Diplom.-Ing. Glar of June 1, 1942 concerning the preparation of oil from primary products of the naphtha - pressure synthesis by pretreatment over aluminum hydroxide, I present attached a sketch for the execution of the technical arrangements. At full charge of 25000 t. cycle naphtha per year = 3 t/hr = 4.2 cbm, a catalyst space of 4.2 cbm is required. The temperature in the catalyst space must be regulable between 240 and 320°C. As catalyst an aluminum hydroxide comes into question. The preparation of the catalyst could be undertaken in the catalyst works of the LT-plant, since the aluminum oxide must have the same nature as the aluminum oxide for the hydration, in any case: as far as measurements have been carried out until now. The charging of the product should appropriately flow by way of a heat exchanger. The product can then be drawn off by way of a cooler and water separator. 40-50 l. of water per hour fall into the water separator. One should figure on a settling time of ca. 2 hours in the separator since the naphtha must be used very dry for the oil synthesis. Since the catalyst chamber standing available in practice is intrinsically larger than is required for the process, one will fill it approximately with only about 4-5 cbm. According to the existing determinations, a longer stay in the empty space does not harm the naphtha, since the temperature here amounts to only 300°. The catalyst chambers can go for about 10 to 15 days without requiring to be burnt out. After this time about 5 to 6% of carbon calculated on the catalyst have deposited. With this carbon formation, the catalyst becomes inactive. A certain difficulty exists in the burning out of the catalyst. If the catalyst were burned with air without further ado, there would be obtained (mathematically) a temperature increase of about 1900°, thus up to 2200°C. It therefore becomes expedient to carry away the resulting heat with large amounts of flue gas. For this reason I propose the following arrangements:

The flue gas is conducted through catalyst chamber ,2, by the ventilator, 1, while catalyst chamber, 3, is in operation for the dealcoholization. The flue gas leaving chamber 2 goes through an after-burning chamber,4, in which incompletely burned portions of the catalyst coating are after-burned, whereby an additional firing with gas is provided. The gas, so purified of tarry constituents goes through the automatically adjustable throttle damper 5 to the ventilator 1. A branch stream goes before the throttle damper to the spray cooler, 6, and is here cooled with direct-sprayed water. The amount conducted through 6 is controlled by means of a temperature regulator to the adjustable throttle damper. The open air suction nipple 7 sits in front of the ventilator. Here a certain amount of fresh air is sucked in, which serves to supplement the combustion air. The amount of fresh air is controlled through the temperature in the catalyst chamber, in that this temperature opens the exhaust valve 8, out of which the combustion

gas can escape. This arrangement should provide every desired safety. If one counts upon a permissible temperature rise of 80°C , the necessary amount of air is obtained from the following considerations:

There is 4.2 cbm of catalyst in the oven. At a pouring density of about 0.5 that corresponds to 2.1 tonnes catalyst. At 6% carbon deposit the amount of carbon eliminated amounts to about 120 kg. If one figures the amount of carbon with a heat of combustion of 9000 heat units, one gets a total heat of combustion of 1,080,000 heat units, which have to be carried away with air. At the permissible temperature rise of 80°C , one cubic meter of air can transport $0.35 \times 80 = 28$ heat units, consequently about 40,000 cbm of air are required for 1,080,000 heat units. If one calculates 50 hours regeneration time, $40,000:50 = 800$ cbm air per hour are to be circulated. The circulatory oxygen concentration results automatically in this arrangement by means of the temperature detector built into the reaction chamber.

(In original two rough flow diagrams follow.)

"Reinigung des Primärbenzins
von alkoholischen
Bestandteilen durch Überleiten der Dämpfe
über Tonerde und anschliessend die
Herstellung von Ulen".
Ruhrochemie Aktiengesellschaft
Oberhausen-Holten
June 4, 1942
2 pages, 2 illustrations.

Requested by R.F. Marachner
Translated by H.J. Cohen and C.C. Miller -
Feb. 8-13, 1947

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-20

API-TOM Reel No. 40, Frames 313-328, Oct. 31, 1940

To: Prof. Martin et.al.

Concerning: The Preparation of Oils from Primary Products of the Naphtha Pressure Synthesis

After the question had already been treated a long time ago in our works by Dr. Goethel (see report of August 29, 1940), in which way a useful oil is obtained by means of $AlCl_3$ polymerization from olefin-rich primary products of the corresponding synthesis carried out (iron catalyst cycle) without cracking, the main laboratory was also introduced into the working up of this problem since July 1940. Two problems were considered to be solved by this question.

- 1) To obtain a high oil yield and so extensively transform the introduced olefin; its concentration in the separated residue naphtha served as a measure.
- 2) To form a thin fluid catalyst oil so that the repeated utilization of the catalyst appeared possible.

If necessary, the naphtha must undergo, as far as possible, a simple and economically productive pretreatment, two means in this direction were proposed previously by Dr. Goethel: 1) calcium chloride, which not only dries but oftentimes also forms addition compounds with the alcohols formed in the pressure synthesis, 2) soda lime, which as basic material binds the acids present.

The submitted report brings a review of the mode of action of the naphtha pretreatment carried out by us and the synthesis connected with it. Concerning the extensive investigations of the initial naphtha by crude and precision distillation shall be reported separately.

It is anticipated that the submitted problem is to be regarded as, if not concluded, yet as fundamentally solved.

Following are discussed six different furnace products (Tables 1-6). The portion of the naphtha boiling up to $200^\circ C$ were mainly charged, along with it also fractions as: to 150° , 150 to 220° , 220 to 275° and others.

1. Furnace 10. 9 Packing. Water gas straight passage. 7. Atm. Absolute July 27-28, 1940 (Table 1)

This furnace product was separated in the Jantzen column according to single hydrocarbons C_5 -----to C_{14} and further cut in the laboratory. The different mixtures noted showed, according to the "Katwinkler" method, a higher olefin content than calculated from the ascertained iodine numbers. These analytical differences often determined in this kind of naphtha could not completely be explained. There lacks an exact method for the determination of olefins. With 1% $AlCl_3$ the different naphthas noted, characterized by a

high OH number yield, indeed, some catalyst oil but very low yields of lubricating oil, the pole heights lie at 1.78. This value reaches 1.42 when the initial material consists of C_{12,13,14}. By pretreatment of the naphtha at 100°C with P₂O₅ to which quartz powder was added for better dispersion the yield rises from 9.6% to 18.2% and the iodine number falls from 80 to 10. Further experiments at temperatures higher than 100°C must yet be tried. Worthy of note here is the deterioration of the viscosity pole height from 1.78 to 1.97.

2. Furnace 2. 8 Packing. Low pressure water gas cycle 1+3.
Aug. 25-26, 1940 (Table 2).

As the low OH value of 10.6 signifies here the hydrocarbons are mixed with small amounts of alcohols; the yields of oils are correspondingly greater (ca. 37%) after polymerization with 4% AlCl₃. Also catalyst oil (2980/1) is abundantly formed. If one uses, besides about 2.5% AlCl₃, several times of this separated catalyst oil, the yield of the oil so falls to 28.6 and 23.2%, or the concentration of the unreacted olefins in the residual naphtha rises to 28 and 36% (2980/4 to 6). Since the furnace product becomes poorer in olefins with increasing boiling range, the attack on the oil accordingly goes backward (2980/7 to 9).

A pretreatment with soda lime up to 140° brings no improvement. Remarkable in all experiments of this series is the low viscosity of the formed n-oils = 4.5 to 8°E.

3. Furnace 11. 5 Packing. Water gas cycle 1+3. Fe catalyst. Gas pressure. 11 atm.abs. April 1940 (Table 3).

Naphtha and condensate oil were separately worked up. The first produces small amounts of oil which is permeated with paraffin, the latter a peculiar paste. The picture changes quite essentially if the naphtha portion boiling to 200°C is treated with sodium bisulfite for removal of the aldehydes and then with sodium metal in open vessels to 200°C for binding the alcohol as alcoholates. On addition of the metal brisk gases are evolved, a deposit is formed. By qualitative test, the naphtha was found free of aldehydes and acids. By formation of 8% catalyst oil arises 40.4% oil with AlCl₃, to be sure of poor pole height = 2.2 (2968). This value is specific for the naphtha and not to be traced back somewhat to an injurious influence of the metal because if one treats a normal cracked naphtha in a similar fashion with bisulfite and distills over sodium, yields and analytical values of the n-oil, also the pole height remain unchanged (exp. 2993/1 against 2).

4. Furnace 11. 7 Packing. Water gas cycle 1+2.7. Fe Catalyst Gas Pressure. 20 atm.absolute Sept. 11-19, 1940 (Table 4).

The portion boiling to 200°C was mixed for the synthesis with 5% AlCl₃ or 2.5% AlCl₃ + catalyst oil from a similar sort of conversion. Since a pretreatment with sodium appeared to be slightly suited for the operation, other means must be investigated. Naphtha pretreated in the cold solely with CaCl₂ yielded even in an AlCl₃ addition increased to 5%, only 10% oil yield without catalyst oil formation.

Astonishingly, no improvement also appeared when one vaporized the naphtha shaken with CaCl_2 and slowly led it with admixture of small amounts of HCl as a gas at 200°C over aluminum shavings. Hereby indeed entered an essential increase of the reactivity in contrast with AlCl_3 : 20 cc. naphtha are heated about 1.5°C within 10 minutes by addition of 1 g. AlCl_3 , after pretreatment only with CaCl_2 , about 10°C within 10 minutes after pretreatment only with HCl and Al . In spite of that the expected improvement in experiment 2995/4 failed to appear. The oil formation rose only from 10 to 16%; the concentration of the olefins in the residual naphtha fell only to about from 75 to 70%.

Excellent in comparison proved a pretreatment of the naphtha either with silicon tetrachloride to 200°C or with activated aluminum to 200°C .

SiCl_4 is an easily mobile liquid boiling at 56.9°C ; it reacts very energetically with water and transforms, for example, acetic acid into acetyl chloride. If one adds this material to naphtha, the liquid becomes turbid by the separation of gelatinous silicic acid and a gas is formed. When this is complete, (the material) is distilled up to 200° from the formed precipitate. The naphtha thus purified gives with 5% AlCl_3 54.2% oil of $V_{50} = 11^\circ$ and viscosity pole height ≈ 1.70 along with formation of much catalyst oil. The concentration of olefins in the residual naphtha drops now to about 13% (2995/3). The low boiling point and also the preventing of toxicity stands in the way of the practical utilization of SiCl_4 .

Further progress was made for the operational utilization of the other way which we found, to use activated aluminum. According to Kaufmann the metal after etching by means of strong sodium hydroxide was moistened with a dilute solution of HgCl_2 . The drying of this exceedingly rapidly oxidizing material in the air remains bothersome. If one heats the naphtha with activated aluminum at 40° , there appear here also brisk gases; after two hours action one distills to 200° .

The synthesis with 2.5% AlCl_3 and the catalyst oil separated in the analogous experiment 2994/2 gave the excellent yield of 63.2% oil, whereby the olefin content of the residual naphtha returned to 5% (1). Corresponding to this far-reaching conversion the V_{PH} lay at 1.65 (exp. 2995/2).

5. Furnace 10. 10 Packing. Medium pressure. Water Gas Cycle 1-3
Sept. 1-2, 1940 (Table 5).

This furnace product is of especial interest, and forms the subject of further, not yet concluded investigations. The series 2991 presented here yields, summarized in brief, the following: without pretreatment no catalyst oil is formed with 4, 5 and 7% AlCl_3 ; the yield of oil rises indeed with the amount of catalyst up until about 55%. Low-boiling naphtha portions react better (2991/5 and 4). With high-boiling fractions the yield of oil declines (2991/6 and 7). High OH values!

CaCl_2 drying has just as little effect as heating with soda lime to 140°C , whereby indeed the organic acids are neutralized to neutralization number = 0.01 (2991/9). The treatment with BaO or CaO works out absolutely injurious (2991/10 and 11).

Also useless is the increased introduction of hydrogen chloride gas into the naphtha, increasing of itself the activity of the naphtha (2991/13), likewise the effect of the first impact with 3% AlCl_3 at 65°C (No.14).

The best results are brought again by application of

NaHSO_3 and Na to 200°C (No. 12 and 17)

SiCl_4 " 200° (No. 18)

activated aluminum to 200° (No.16)

Catalyst oil formation yields and pole height of the oils are good. While in the other experiments the concentration of olefins in residue naphtha amounts to 53 to 65%, it has now fallen to 1 to 2%. The activated aluminum fails to work when it is brought to action only at 40°C on the naphtha (experiment No.15).

The low iodine values 21 in No. 18 and 15 in No.16 caused us to investigate the aging stability of both oils:

<u>Aging 6 hrs. 160°O_2</u>	<u>No.18 SiCl_4</u>	<u>No.16 activ.Al.</u>
Thickening + "V50"	63%	76%
Neutralization No.	16.5	15.6
Saponification No.	39.3	43.5
+ DK	0.75	0.73
water separated	12.9 cc	12.6 cc

In spite of the low iodine value these oils are not oxygen-stable compare hydrogenated oils.

6. Furnace 10. 10 Packing. Medium Pressure. Water gas cycle 1 + 3
Sept. 1-11, 1940 (Table 6).

Therefore, the question is as to the same type as in 5, i.e. regarding a later production from the same furnace packing. The olefin content of the naphtha had fallen within this period from about 75 to about 62%. The experiments 2, 3, 4 substantiate anew the good results in the pre-treatment with activated aluminum, NaHSO_3 + Na , SiCl_4 , namely, in regard to catalyst oil formation and practically complete reaction of the olefins in the synthesis.

The introduction of HCl fails, in spite of the application of 5% AlCl₃ (experiment 2994/5).

Summary

The experiments show that the pretreatment of naphtha from the pressure synthesis before polymerization to oil is unconditionally necessary. As a new method is proven.

- a) NaHSO₃ then sodium
- b) silicon tetrachloride
- c) with H₂Cl₂-activated aluminum

Further experiments are to be tried with other, if necessary activated, metals as Cu, Fe, Zn, Mg, with oxide compounds as Sr(OH)₂, P₂O₅, chlorides as FeCl₃, ZnCl₂, SbCl₃, PCl₃.

/s/ Clar

Table 1

Oil Preparation from Products of the Naphtha Synthesis Under Pressure.

Furnace 10. 9 Packing. Water gas straight passage. 7 atm.abs. July 27-28, 1940

Exp. No.	Pretreatment of Naphtha	Boiling range starting olef.	Synthesis AlCl ₃ cat.oil heating	Cat.Oil Form. Resid.Olef.	Resid.Oil
2976/1	none	C _{7,8,9,10,11} 52% olefin 29.4 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 7.5% 36% olefin 5.8 OH value	9.6% V ₅₀ =15.7 VFH=1.78 Iod.No.=80
2977	none	C _{7,8,9,10,11} 56% olefin 33.6 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 3.3% 35% olefin 7.1 OH value	10.6% V ₅₀ =16.1 VFH=1.78
2978	none	C _{12,13,14} 44% olefin 22.7 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 5% 22% olefin 4.5 OH value	12.1% V ₅₀ =9.6 VFH=1.42
2976/2	P ₂ O ₅ + Quartz sand, 4 hrs. 100°	C _{7,8,9,10,11}	4% AlCl ₃ 11 hrs. 95°	Cat.oil 7% 18% olefin	18.2% V ₅₀ =8.1 VFH=1.97 Iod.No.=10

Table 2

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 2. 8. Packing. Low pressure water gas cycle 1+3. Aug. 25-26, 1940

<u>Exp. No.</u>	<u>Pretreatment of Naphtha</u>	<u>Boiling range starting olef.</u>	<u>Synthesis AlCl₃ cat.oil heating</u>	<u>Cat.Oil Form. Resid.Olefin</u>	<u>Resid.Oil</u>
2980/1	None	to 200° 69% olefin 10.6 OH value	4% AlCl ₃ 11 hrs. 95°	Cat.oil 6.2% 18 % olefin	37.4% V ₅₀ =6.7 VPH=1.97
2980/2	Soda lime 80 to 140°	to 200° 70% olefin	4% AlCl ₃ 11 hrs. 95°	Cat.oil 5.9% 18% olefin	37.4% V ₅₀ =6.7 VPH=1.90
2980/3	none	to 275° 62% olefin 11.2 OH value	4% AlCl ₃ 11 hrs. 95°	Cat.oil 6.7% 18% olefin	32% V ₅₀ =7.5 VPH=1.89
2980/4	"	"	2.5% AlCl ₃ Cat.oil 2980/3 11 hrs. 95°	Cat.oil 0.3% 27% olefin	32.6% V ₅₀ =4.6 VPH=1.70
2980/5	"	"	2.5% AlCl ₃ Cat.oil 2980/4 11 hrs. 95°	Cat.oil 0.6% 28% olefin	28.6% V ₅₀ =4.5 VPH=1.77
2980/6	"	"	2.5% AlCl ₃ Cat.oil 2980/5 11 hrs. 95°	Cat.oil 3% 36% olefin	23.2% V ₅₀ =4.8 VPH=1.74
2980/7	"	to 150° 72% olefin	4% AlCl ₃ 11 hrs. 80°	Cat.oil 4.5% 25% olefin	33.1% V ₅₀ =6.6 VPH=2.08
2980/8	"	150 to 220° 63% olefin	4% AlCl ₃ 11 hrs. 95°	Cat.oil 3.9% 21% olefin	28.1% V ₅₀ =6.8 VPH=1.69
2980/9	"	220 to 275° 49% olefin	4% AlCl ₃ 11 hrs. 95°	Cat.oil 10.3% 20% olefin	21.7% V ₅₀ =6.8 VPH=1.53

Table 3

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 11. 5 Packing. Water gas cycle 1:3. Fe-catalyst, gas pressure 20 at. abs. 4/1940

Exp. No.	Pretreatment of Naphtha	Boiling range starting olef.	Synthesis AlCl ₃ cat. oil heating	Cat. Oil Form. Resid. Olefin	Resid. Oil
2962/1	None	to 310° 66% olefin	4% AlCl ₃ 11 hrs. 80°	Cat. oil 0 52% olefin	16.4% paraffin containing V ₅₀ =6.3 VPH=1.98
2962/2	"	110 to 186°* 50% olefin	4% AlCl ₃ 11 hrs. 95°	Cat. oil 0 50% olefin	paraffin V ₅₀ =3.5
2968	NaHSO ₃ cold, Na until 2000° distilling	to 200° 68 % olefin	4% AlCl ₃ 11 hrs. 95°	Cat. oil 8% 20% olefin	40.4% V ₅₀ =9.3 VPH=2.2

Comparison normal cracked naphtha from gas oil RB

2993/1	None	to 200° 74% olefin	4% AlCl ₃ 11 hrs. 95°	Cat. oil 14.7% 6% olefin	51.4% V ₅₀ =15.8 VPH=1.69
2993/2	NaHSO ₃ cold Na to 200° distilling	to 200° 76% olefin	4% AlCl ₃ 11 hrs. 95°	Cat. oil 14.6% 5% olefin	61.1% V ₅₀ =17.6 VPH=1.63

* (Tr.: might be 286°)

Table 4

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 11. 7 Packing. Water gas cycle 1+2.7, Fe-catalyst, Gas Pressure 20 at.
Sept. 11-19, 1940

Exp. No.	Pretreatment of Naphtha	Boiling range starting olef.	Synthesis AlCl ₃ cat.oil heating	Cat.Oil Form. Resid.Olefin	Resid.Oil
2995/1	CaCl ₂ drying	to 200° 78% olefin	5% AlCl ₃ 11 hrs. 85°	Cat.oil 0 75% olefin	10.3% V ₅₀ =29 VPH=1.75 Iod.No.=62
2995/4	CaCl ₂ drying gas phase + HCl cover Al 200°	to 200° 75% olefin	2.5% AlCl ₃ Cat.oil 2994/5 10 hrs. 85°	Cat.oil 0 70% olefin	16.1% V ₅₀ =24.1 VPH=1.72 Iod.No.=66
2995/5	CaCl ₂ drying SiCl ₄ cold to 200° distilled, washing, drying	to 200° 74% olefin	5% AlCl ₃ 10 hrs. 95°	Cat.oil 9% 13% olefin	54.2% V ₅₀ =11 VPH=1.72 Iod.No.=50
2995/2	CaCl ₂ drying Act.Al to 200° distill	to 200° 74% olefin	2.5% AlCl ₃ Cat.oil 2994/2 10 hrs. 95°	Cat.oil 1% 5% olefin	63.2% V ₅₀ =13.1 VPH=1.65 Iod.No.=49

Table 5

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 10. 10' Packing. Medium pressure. Water gas cycle 1-3. Sept. 1-2, 1940

Exp. No.	Pretreatment of Naphtha	Boiling range starting olef.	Synthesis $AlCl_3$ cat.oil heating	Cat.oil Form. Resid.Olefin	Resid.Oil
2991/1	None	to 200° 75% olefin 33 OH value	4% $AlCl_3$ 11 hrs. 60°	Cat.oil 0 Olefin 61%	22.1% $V_{50}=14.4$ $V_{FH}=1.63$
2991/2	"	to 200° 75% olefin	4% $AlCl_3$ 11 hrs. 80°	Cat.oil 0 60% olefin	23.1% $V_{50}=33.6$ $V_{FH}=1.62$ Iod.No.=37
2991/5	"	to 150° 74% olefin 25 OH value	5% $AlCl_3$ 11 hrs. 80°	Cat.oil 1% 54% olefin	43.5% $V_{50}=8.4$ $V_{FH}=1.48$
2991/6	"	150 to 200° 70% olefin 44 OH value	5% $AlCl_3$ 11 hrs. 95°	Cat.oil 0 22% olefin	28.3% $V_{50}=8.4$ $V_{FH}=1.48$
2991/7	"	220 to 275° 61% olefin	5% $AlCl_3$ 11 hrs. 95°	Cat.oil 0 26% olefin	19.8% $V_{50}=12.4$ $V_{FH}=1.37$
2991/4	$CaCl_2$ dried	to 200° 75% olefin	5% $AlCl_3$ 11 hrs. 95°	Cat. oil-0 42% olefin	40.5% $V_{50}=26.6$ $V_{FH}=1.64$ Iod.No.=42
2991/8	$CaCl_2$ drying	to 200° 75% olefin	7% $AlCl_3$ 11 hrs. 95°	Cat.Oil 0 19% olefin	ca. 55% $V_{50}=31.8$ $V_{FH}=1.65$ Iod.No.=32
2991/3	Soda lime to 140°F.	to 200° 75% olefin	4% $AlCl_3$ 11 hrs. 30°	Cat.oil 0 56% olefin	30.7% $V_{50}=26.4$ $V_{FH}=1.63$
2991/9	Soda lime to 140°	to 200° N.N.=0.01 S.N.=0.10	4% $AlCl_3$ 11 hrs. 80°	Cat.oil 0 65% olefin	18.2% $V_{50}=30.4$ $V_{FH}=1.60$ Iod.No.=39

Table 5 (Continuation 1)

Exp. No.	Pretreatment of Naptha	Boiling range starting olef.	Synthesis AlCl ₃ cat.oil heating	Cat.oil Form. Resid.Olefin	Resid.Oil
2991/10	BaO to 1140°	to 200° SN = 0.07	4% AlCl ₃ 11 hrs. 80°	Cat.oil 0 67% olefin	8.8% V ₅₀ =28.9 VPH=1.61
2991/11	CaO to 1140°	to 200° SN = 0.56 72% olefin	4% AlCl ₃ 11 hrs. 80°	Cat.oil 0 66% olefin	12.1% V ₅₀ =28.4 VPH=1.62
2991/13	HCl gas cold tonsil	to 200° SN = 1.58 72% olefin	4% AlCl ₃ 11 hrs. 95° upper phase decomposed	Cat.oil 0 53% olefin	31.5% V ₅₀ =33.8 VPH=1.58 Iod.No.=38
2991/14	3% AlCl ₃ , 65% H ₂ O, soda tonsil	to 200° SN = 0.84 64% olefin	4% AlCl ₃ 11 hrs. 95° upper phase decomposed	Cat.oil 0 56% olefin	29.5% V ₅₀ =30.7 VPH=1.59 Iod.No.=21
2991/12	NaHSO ₃ cold Na to 200° (D)	to 200° SN = 0.03 74% olefin	4% AlCl ₃ 11 hrs. 80-95 brisk reaction upper phase decomposed	Much cat. oil boiled over	? V ₅₀ =22.2 VPH=1.58
2991/17	NaHSO ₃ cold Na 70° to 125°	to 200° 72% olefin	5% AlCl ₃ 9½ hrs. 95° upper phase decomposed	Cat.oil 22.4% 1% olefin	53.2% V ₅₀ =24.2 VPH=1.68 Iod.No.=16
2991/18	SiCl ₄ cold to 200° distilled	to 200° 69% olefin	5% AlCl ₃ 9½ hrs. 95° upper phase decomposed	Cat.oil 2.1% 2% olefin	61% V ₅₀ =22.6 VPH=1.60 Iod.No.=21
2991/15	Act.Al. 400°	to 200° SN = 0.01 74% olefin	4% AlCl ₃ 11 hrs. 95° upper phase decomposed	Cat.oil 1.2% 62% olefin	26.1% V ₅₀ =31.1 VPH=1.58
2991/16	Act.Al. distilled to 200°	to 200° 69% olefin	5% AlCl ₃ 9½ hrs. 95° upper phase decomposed	Cat.oil 19.8% 2% olefin	55.8% V ₅₀ =22 VPH=1.58 Iod.No.=15

Table 6

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 10. 10 Packing. Medium Pressure, Water gas cycle 1+3. Sept. 1-11, 1940

Exp. No.	Pretreatment of Naphtha	Boiling range starting olef.	Synthesis AlCl ₃ cat.oil heating	Cat.oil Form. Resid.Olefin	Resid. Oil
2994/1	CaCl ₂ drying	to 200° 61% olefin V OH No. = 22.5 n " = 18.2	5% AlCl ₃ 11 hrs. 95°	Cat.oil 0 35% olefin	39.3% V ₅₀ =25.6 Iod.No.=41
2994/5	Gas phase +1+Cl over Al 200°	to 200° 61% olefin	5% AlCl ₃ 10 hrs. 95°	Cat.oil 2.7% 39% olefin	25% V ₅₀ =13.9 Iod.No.=63
2994/4	SiCl ₄ col.d. to 200° distilled, Tonsil	to 200° 64% olefin OH value = 2.8	5% AlCl ₃ 9½ hrs. 95°	Cat.oil 10.9% 2% olefin	46.2% V ₅₀ =17.9 Iod.No.=19
2994/3	NaHSO ₃ col.d., Na 60-180°	to 200° 62% olefin OH value = 1.1	2.5% AlCl ₃ + cat.oil 2991/17 9½ hrs. 95°	cat.oil 5.2% 2% olefin	48.2% V ₅₀ =15.1 Iod.No.=31
2994/2	Act.Al. to 200° distilled	to 200° 64% olefin OH value = 0	2.5% AlCl ₃ + cat.oil 2991/16 10 hrs. 95°	cat.oil 6.2% 1% olefin	48.9% V ₅₀ =13.2 Iod.No.=36

Requested by R.F. Marachner
Translated March 7, 1947 - by H.G. Cohen
Checked March 6, 1947, by C.C. Miller

"Über die Herstellung von Ölen
als Primärprodukten der Benzin
Drucksynthese".
Führchemie Aktengesellschaft
Oberhausen-Holten
Oct. 31, 1940
16 pages, no illus.

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-26

API-TQM Reel 46, Frames 877-888
(Construction priority explanation)
Construction of an Aviation Oil Plant with a Capacity of 11050 Tonnes per Year of Aircraft Motor Oil.

A) **Builder:** Ruhrchemie Aktiengesellschaft
Location: Oberhausen-Holten
Telephone: Oberhausen 60242
Director of Building Project: Dr. Dipl.-Ing. Alberts

B) **Explanation of Building Purposes**
The Holten plant of the Ruhrchemie Aktiengesellschaft has up-to-date already produced synthetic lubrication oils in quantities of about 1000 tonnes per month, which have been used particularly for unit engine oil of the "Wehrmacht."

Upon request of the R.L.M., aircraft motor oil is now to be produced as well. Trial quantities which Holten made available to R.L.M. for testing purposes, were found suitable according to dispatches from the R.L.M. dept. general-aircraft-head of February 18-42. R.L.M. has assured the Ruhrchemie Aktiengesellschaft of their acceptance of such a type of aircraft motor oil in quantities of 8000-12000 tonnes per year. Discussions concerning this order and their documentations are still in process.

In the interest of assuring the supply of aircraft motor oil, expansion of the Holten plant should take place as soon as possible. The expansion is confirmed to be particularly urgent in the communication of the R.L.M. mentioned earlier. The capacity is planned to be 11050 tonnes per year with a working year of 330 days.

C) **The Procedure**
After completion of the erection of the synthetic plant which is now in process, there will take place a change in the procedure for the manufacture of aircraft naphtha. The following building plans for the production plant have been set into motion:

- 1) Enlargement of the lubricating oil plant to 12,000 tonnes per year, building permission of March 5, 1941.
- 2) Erection of an oxo-plant, building permission of March 11, 1941.

The Ruhrchemie Aktiengesellschaft makes the proposal to take on the manufacture of aircraft motor oil under expansion of the Holten plant. The following production can be expected

(the data are given for 3 cases): see pp. 4 & 5 original

- Case 1 - Our own normal production
- Case 2 - Our own maximum production of liquid primary product.
- Case 3 - Our own maximum production and purchase of primary product.

The building permission concerns the maximum aviation oil production which was specified in more detail for case 3.

The manufacture in Holten will take place in such a manner that the unsaturated portions of the primary production boiling from C_8-C_{10} are used for the oil synthesis, and those from $C_{11(?)}$ - C_{18} are used for the oxo-synthesis.

Furthermore, for the oil production, products boiling above $250^{\circ}C$, partly from the primary synthesis and partly paraffinic portions from the oxo-synthesis, are introduced by means of a special thermal cracking.

For the automobile oil production the hydrocarbons boiling from C_8-C_9 are derived from both sources, for the aviation oil production the hydrocarbons boiling from C_8-C_{18} are used. The C_5 hydrocarbons produced in the cracking plant and in the primary synthesis go to the plant for manufacture of aviation naphtha. For the production of high performance aviation naphtha the polymerization products of C_4-C_5 olefins which have been obtained from the Diesel oils (C_9-C_{13} , C_{17} and above) by catalytic cracking, can further be used as starting materials. The waste materials from the paraffin factory as well as distillates from the precision fractionation of olefins for oxo products serve as starting material for the Dubbs-cracking plant. The cracked products from this last are put into the oil synthesis, or added to the gas oil.

Frame 881: summary

D.) Data from documents concerning the permission of the construction.
Regulations for air-raid protection.

E.) Technical Construction Data

For the aircraft motor oil production the following are to be newly erected:

Building Parts	Oven	Receivers	Building		
			length m	width m	stories
Fractionation	1		42	12	1
Distillation	1		18	12	1
Refining	1		-	-	1
Synthesis Dechlorination		16	45	7	3

Frame 882: summary

Building Parts	Oven	Tanks	Building		
			length m	width m	stories
Pressure distillation			8.5	7	1
Foam extinguishing plant			24	9	1
Tank plant		8			
Oil distillation	1		18	12	1
Filtration			32	15	3

The area of the Ruhrchemie Aktiengesellschaft (incl. synthetic-, oxo- and lubricating oil plants) is 397,000 m². The buildings, incl. the aviation oil plant, cover 20% of this area.

Data on time, manpower, costs, and material to be used.

Frame 883: summary

- Data on distribution of material and manpower
- Data on electrical energy requirements
- Data on steam energy requirements
- Data on water energy requirements
- Data on traffic and transportation

Translated by E. Rothstein, March 4, 1947

Checked by CCM March 6, 1947

Requested by R. F. Marschner

Information Division Translation T47-26

"Errichtung einer Flugolanlage mit einer Kapazität von 11050 jato Flugmotorenabfl."

Ruhrchemie Aktiengesellschaft

Oberhausen-Holten

October 20, 1942 7 pages, no illustration

Primary Products include Gasol 6540 tonnes/month 8410 tonnes/month 8410-1250 tonnes/month

Completed Products:
Gasol
Ethylene

1140 t
120 t
1360 t
165 t

Automobile naphtha
(unleaded)
boiling range
octane no.
density d20

1640 t
appr. 35-2000
appr. 66.0
0.69-0.7

2330 t
appr. 35-2000
appr. 66.0
0.69-0.7

2500 t
appr. 35-2000
appr. 66.0
0.69 - 0.7

Lubricating oil I
pole height
viscosity
solid pt.

885 t
1.80
appr. 8E°/50
-35°C

1100 t
1.80
appr. 8E°/50
-35°C

1145
1.80
appr. 8E°/50
-35°C

Lubricating oil II
(aviation oil)
pole height
viscosity
viscosity index
solid point

490 t
1.55
appr. 8E°/50
-35°

600 t
1.55
appr. 8E°/50
-35°

990 t
1.55
appr. 8E°/50
-35°

Aviation naphtha
boiling range
octane no. with 1.2% lead
superchargability
density

825 t
50-165°
100
analog
0.71

1070 t
50-165°
100
C3
0.71

1235 t
50-165°
100
motor fuel
0.71

Oxo-products
Table paraffin
Extra-hard paraffin

565 t
185 t
375 t

630 t
220 t
460 t

630 t
220 t
460 t

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-28

API-TOM Reel 47, Frames 994-995, Bag 3446, Target 30/5.01, Item 86

To: Professor Martin, et. al.

Preparation of Adipic Acid from Cyclohexane

The purification of hydrocarbons of the naphtha and benzene series as well as its transformation into valuable products possesses as usual a great significance. In spite of other submitted tasks we have been sporadically engaged on this problem for a long time. It shall be reported below, concerning a new process for the preparation of the important adipic acid as starting material for technical material e.g. nylon fibers.

On the basis of the experiences which were obtained in the dehydrogenation of high molecular weight and low molecular weight hydrocarbons with chlorine and bromine, it was investigated how the dehydrogenation of cyclohexane or methylcyclohexane would proceed to the corresponding mono-olefin, i.e. cyclohexene or methylcyclohexene under analogous conditions.

We found that fundamentally similar proportions and conditions are decisive as concerned the dehydrogenation of paraffins by means of halogens. Naphthenes also require the presence of catalysts in the transformation by means of halogen, likewise proportionately short reaction times, as well as the application of vacuum and temperatures above 450°C, especially above 600°C. For example, at 650°C, 15 mm. absolute and reaction times between 15 and 30 minutes there was reached an olefin yield, i.e. the change to cyclohexene, of about 20%. Pumice stone was used as catalyst, and the charge per 350 cc. catalyst amounted to 250 cc. cyclohexane and 50 cc. bromine, corresponding to an amount theoretically necessary for about a 40% conversion into mono-olefin. If the catalyst supply is doubled as well proportionate cyclohexane and also bromine and retention of the other conditions, so could be obtained only 18% olefins in the liquid product. Only at a further doubling, therefore four times the amount of charge compared with normal conditions, did the olefin yield drop to 12.6% whereby the density in the reaction product simultaneously rose sharply which signifies the presence of larger amounts of brominated products. Similar observations were made also in the dehydrogenation of paraffin hydrocarbons by means of halogen.

An increase of the amount of bromine alone to twice against the normal charge raised the olefin yields only from 20 to about 24%. Also here, the increase in density was quite appreciable, also to be traced back to the presence of brominated products. The working out of all problems still to be clarified concerning the dehydrogenation of naphthenes by means of bromine or chlorine could not be completed in consequence of the submission of more pressing work. It can be mentioned, in short, that orienting experiments for the dehydrogenation of methyl cyclohexane to methylcyclohexene for the present remained without success, and indeed because it was established that halogens in the presence of side chains preponderantly attached to them. There therefore arose from methylcyclohexane almost exclusively α -methylcyclohexyl-chloride or bromide. Methylcyclohexene was practically not formed. It was however conceivable that a

further treatment could still find out conditions under which a conversion into methylcyclohexanes would take place. Perhaps even a general method for the preparation of monoclefins of the naphthene series would be developed in this way. Complete experiments, to prepare mono-olefins from naphthenes in a catalytic method (by means of pure dehydrogenation catalysts) can be seen as wrecked at this time, since in all cases the catalytic dehydrogenation penetrates directly into the aromatics.

The cyclohexane used was obtained from benzene by hydrogenation over Fischer catalyst at 300° and 25 atm. hydrogen. It has zero iodine number, and a density of 0.768.

The further working up of the reaction product after the dehalogenation into adipic acid shapes itself relatively easy. The mixture cyclohexane-cyclohexene was separated by simple distillation from the likewise existing mono- and poly-cyclohexylhalogens. The opening of the ring followed by application of nitric acid, chiefly of density 1.35 corresponding to a 56% nitric acid, although the concentration can be varied within from 46-60%. As oxidation accelerators, small amounts of vanadic acid found application, its presence is not unconditionally necessary. The reaction is finished after 3-4 hours of slow boiling. We chose in our experiments, of which only three charges were carried out, a nitric acid excess of 100%. Obviously, this amount can yet be reduced.

The non-reacted cyclohexane is separated after completion of the reaction and returned to the dehydrogenation cycle. After cooling of the nitric acid the adipic acid formed crystallized out, relatively pure. To obtain further quantities, we completely evaporated the nitric acid and thereby obtained the last remains of the acid formed. In manufacture one could increase the concentration of the nitric acid after the reaction by introduction of nitrous gases and again utilize in the oxidation.

The adipic acid obtained was completely pure after two crystallizations from hot water and possessed the theoretical neutralization number and the melting point in the literature.

The separated cyclohexane possessed an iodine number of 0, so it contained no more olefin. The yield of adipic acid, calculated on the original existing amount of cyclohexane, amounted to over 80 weight %.

/s/ Rottig

Translated March 8, 1947 by H. G. Cohen
Checked by CCM March 13, 1947
Requested by C.F. Leydig, Jr.

"Betrifft: Herstellung von Adipinsäure aus Cyclohexan"
Oberhausen-Holtrop February 26, 1944
2 pages, no illustration

INFORMATION DIVISION TRANSLATION T47-26

API-TOM Reel 48, Frames 740-741

Preparation of the cobalt-thorium catalyst

(Cobalt-Normal catalyst: 100 Co; 15 ThO₂; 200 Kg.)
Laboratory charge with 25 g cobalt.

1) Starting Materials:

- a) 124 g cobalt-nitrate (Co (NO₃)₂ 6 H₂O), corresponding to 25 g Co-metal
- b) 7.85 g thorium nitrate (Th(NO₃)₄ 4H₂O), corresponding to 3.75 g thorium oxide (15%Co).
- c) 59 g H₂O-free soda.
- d) 50 g kieselguhr (200 %/Co)
- e) 3 liters distilled water heated to boiling

2) Precipitation

- a) Cobalt-nitrate and thorium-nitrate together are dissolved in water, diluted to 500 cc, and heated to boiling. 59 g of soda are dissolved in 750 cc of distilled water and heated to boiling in the precipitation vessel of $\sqrt{2}$ a-steel. The flame is removed and the precipitation is carried out by quickly pouring the cobalt-thorium solution into the soda solution, stirring constantly. Immediately after the precipitation, 50 g of kieselguhr are mixed in. The total precipitation time should be less than 1 minute.
- b) In place of the solid salts of cobalt nitrate and thorium nitrate, one can also use solutions of cobalt nitrate and thorium nitrate, i.e. those which can be obtained by dissolving cobalt metal and thorium hydrocarbonate in nitric acid, or by other means. Since the cobalt-thorium solutions usually contain varying amounts of free nitric acid, one needs a large amount of soda for the precipitation, as indicated above.

One then proceeds as follows:

5 cc of the cobalt-thorium solution diluted to 500 cc are titrated with a diluted soda solution which contains 100 g soda in 1 liter:

- i) to the beginning of a constant cloudiness. The amount of soda solution

is then the g of soda which have to be added

to 59 g of soda in order to obtain complete precipitation.

- ii) to the complete precipitation, i.e. until the solution above the precipitate is colorless and clear. The cc soda solution used then indicates how much soda is necessary for the complete precipitation.

3) Filtration

After the precipitation the mother liquor is filtered by suction,

INFORMATION DIVISION TRANSLATION T47-26

API-TCM Reel 48, Frames 740-741

Preparation of the cobalt-thorium catalyst

(Cobalt-Normal catalyst: 100 Co; 15 ThO₂; 200 Kg.)
Laboratory charge with 25 g cobalt.

1) Starting Materials:

- a) 124 g cobalt-nitrate (Co (NO₃)₂ · 6 H₂O), corresponding to 25 g Co-metal
- b) 7.85 g thorium nitrate (Th(NO₃)₄ · 4H₂O), corresponding to 3.75 g thorium oxide (15% Co).
- c) 59 g H₂O-free soda.
- d) 50 g kieselguhr (200 % Co)
- e) 3 liters distilled water heated to boiling

2) Precipitation

- a) Cobalt-nitrate and thorium-nitrate together are dissolved in water, diluted to 500 cc, and heated to boiling. 59 g of soda are dissolved in 750 cc of distilled water and heated to boiling in the precipitation vessel of $\sqrt{2}$ a-steel. The flame is removed and the precipitation is carried out by quickly pouring the cobalt-thorium solution into the soda solution, stirring constantly. Immediately after the precipitation, 50 g of kieselguhr are mixed in. The total precipitation time should be less than 1 minute.
- b) In place of the solid salts of cobalt nitrate and thorium nitrate, one can also use solutions of cobalt nitrate and thorium nitrate, i.e. those which can be obtained by dissolving cobalt metal and thorium hydrocarbonate in nitric acid, or by other means. Since the cobalt-thorium solutions usually contain varying amounts of free nitric acid, one needs a large amount of soda for the precipitation, as indicated above.

One then proceeds as follows:

5 cc of the cobalt-thorium solution diluted to 500 cc are titrated with a diluted soda solution which contains 100 g soda in 1 liter:

i) to the beginning of a constant cloudiness. The amount
cc soda solution

$\frac{10}{10}$ is then the g of soda which have to be added to 59 g of soda in order to obtain complete precipitation.

ii) to the complete precipitation, i.e. until the solution above the precipitate is colorless and clear. The cc soda solution used then indicates how much soda is necessary for the complete precipitation.

3) Filtration

After the precipitation the mother liquor is filtered by suction,

as quickly as possible, through a funnel (diameter 190 mm) using S. & S. filter paper II 589³, so that there are no cracks in the filter-cake. (The time from the beginning of the precipitation to the removal of the mother liquor should not be more than 2 minutes.) Then one washes 6 times with 500 cc of hot distilled water each, always being careful not to let any cracks appear in the filter-cake. Finally the funnel is sucked as dry as possible and the cake is pressed down with the help of a spatula.

4) Drying and Breaking Up

The catalyst is placed in a dish, separated into small pieces, and dried evenly in the drying oven at 110-120°. This requires up to 12 hours. The dry catalyst is weighed and is then broken up on a sieve. The particles between 1-3 mm are sifted.

From the weight of the dry catalyst one can calculate the cobalt content. However, it is advisable to have the composition of the catalyst tested analytically from time to time.

/s/ Roelen

Translated by E. Rothstein, March 4, 1947
Information Division Translation T47-26
Checked March 6, 1947, by CCM

"Herstellung des Kobalt-Thorium-Katalysators."
Ruhrbenzin Aktiengesellschaft
Oberhausen-Holten
January 4, 1938
2 pages, no illustration

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-23

API-TQM Reel 48, Frames 742-743

Reduction of the Cobalt Catalyst

1) General

The reduction is carried out outside the synthesis oven in a special reduction oven. This is done for several reasons:

- a) By the separate carrying out of the reduction and the synthesis each in a special oven, the oven-temperatures and the flow-rates of the gases can be more easily kept constant. Thus the reduction and the synthesis-conditions can be easily duplicated.
- b) Because of the larger diameter of the reduction tube (21 mm) the length of the layer of grains to be reduced is decreased to about $\frac{1}{3}$ of the length of the layer in the synthesis tube. Thus the decline in the reduction value in the length of the layer is considerably less. Therefore one obtains a more constant reduction value.
- c) The time until a test with a synthetic gas can be incorporated is considerably reduced.

2) Apparatus

- a) An aluminum block-oven with a block-length of 1 m. Temperature regulators are attached on both sides in order to maintain uniform temperatures.
- b) Supremax glass tube with inside diameter of 21 mm and approximate length of 1.5 m.

3) Execution

The desired amount of the catalyst is separated, i.e. as much as corresponds to 4 g Co (appr. 15-20g) or of a definite volumetric amount.

~~This amount is filled into the Supremax glass tube in such a manner that the layer comes to lie in the last part of the oven (in the direction of the gas.) The catalyst is held fast on both sides by a plug of glass wool which is as even as possible.~~

After rinsing with hydrogen, the glass tube is pushed into the reduction oven which has been heated to constant temperature.

We now differentiate between two types of reduction,

- 1) normal reduction
½ hour at 350°C and 300 l. H₂/hour
- 2) intensified reduction
2 hours at 400° and 300 l. H₂/hour

After the reduction is completed, the glass tube is taken from the oven and left to cool in a stream of H₂. The normal reduction leads to a reduction value of approximately 75%, the intensified reduction to a reduction value of 100%.

The normal reduction is used for all normal laboratory tests, the intensified reduction for all operating tests.

In cases of intensified reduction, catalysts with weak catalytic effect show the decline earlier in contraction measurements and oil yield, thus reducing the testing-time. Good catalysts show no difference between normal and intensified reduction in up to 500 operating hours.

/s/ Roelen

Translated by E. Rothstein, March 4, 1947
Checked by C.C.M., March 6, 1947
Information Division Translation T47-23

"Reduktion des Kobalt-Katalysators"
Ruhrbenzin Aktiengesellschaft
Oberhausen Holten
January 4, 1938
2 pages, no illustration

INFORMATION DIVISION TRANSLATION T47-24

Determination of the Free Metal-Content in Catalysts

(Acid-vacuum method)

API-TOM Reel 48, Frames 744-749

1) General

The reduction of the Co catalysts is generally not carried to completion. Therefore, there is found aside from metallic Co, still unreduced oxide and carbonate. The determination of the portion of reduced metal rests on the following reaction:



On dissolving in acid, the oxide forms water. Only the reduced metal, on treatment with H_2SO_4 , forms an equivalent amount of hydrogen, which is measured. Through determination of the total amount of cobalt used it is possible to calculate the portion of reduced metal.

In the practical carrying out of this determination, various possibilities for errors should be watched for:

- a) Nitrogen to be used for transfer of the catalyst is to be tested for oxygen. Even small amounts of oxygen in nitrogen can cause a noticeable oxidation of the catalyst after longer contact.
- b) Saturated catalysts have usually come in contact with air. They are then no longer to be brought in contact with hydrogen, i.e. for the rinsing of vessels. For then a strong heating takes place, while the oxygen of the air attached to the catalyst burns with the hydrogen. This causes the possibility of a further reduction.
- c) The hydrogen adsorbed on the catalyst has to be previously sucked off in vacuo, since otherwise the reduction values found are too high. In order to remove all but small remnants of oxygen it is sufficient to suck for 1-2 minutes with the full vacuum of a water aspirator pump. In cases of saturated catalysts it is further necessary to heat, since at times the saturating oil prevents the sucking off of the hydrogen.
- d) Hydrochloric acid should not be used for the examination of the catalyst since it sometimes contains chlorine which combines with a corresponding amount of Co-metal without formation of H_2 .

2) Apparatus

The apparatus is to be seen on the enclosed sketch. (frame 749)
The stoppering of the reaction flask can be accomplished with ground-glass or with rubber stoppers.

3) Filling

Into the reaction flask one fills an amount of catalyst to contain appr. 0.5 - 0.6 g Co.

- a) Unsaturated catalyst is brought into the reaction flask with constant addition of hydrogen into the reaction flask through the sidearm and simultaneous passing of hydrogen through the storage vessel from which the catalyst is to be transferred. Then the apparatus is put together and 20-30 cc of 50% sulfuric acid is put into the dropping funnel. The stream of hydrogen is cut off by means of a clamp and simultaneously the hydrogen in the flask is sucked off as completely as possible through the 3-way stopcock* by means of a water aspirator pump. Particularly it should be seen to it that the apparatus is completely tight.
- b) Catalyst saturated with oil can be brought into the clean and dry reaction flask as such. Then the air is replaced by oxygen-free nitrogen. The flask is put into a bowl of boiling water and sucked for about 15 minutes with the aid of a water aspirator pump. It is better yet to heat in a hollowed aluminum block at 200° for five minutes during the sucking. The heating of the catalyst is necessary in order to be able to suck off the hydrogen adsorbed on the catalyst. The aluminum block is removed and the flask is cooled.
- c) With CO₂-saturated catalyst one proceeds as under 3a.

4) Dissolving

The connection between the reaction flask and the gas burette is completed by turning the 3-way stopcock. The check-valve prohibits the backflow of the sealing water from the gas burette. Then one slowly adds the sulfuric acid to the catalyst, being careful not to let any gas escape or air seep in through the dropping funnel. Depending on the type of catalyst, there immediately evolves a sufficient amount of gas to close the check-valve; otherwise one heats carefully with a small burner. The gas evolved rises in the gas burette by replacement of the sealing water. The adjustment vessel had best stand low, so that even a slight gas pressure can open the check-valve. One heats until the gas-evolution is completed and the steam formed has driven over all the gas in the burette.

The flame is removed and the 3-way stopcock turned so that the reaction flask is in contact with the outside air. Gas volume, temperature, and barometer are read. The contents of the reaction flask is transferred quantitatively to a flask, diluted, heated until all the cobalt sulfate is dissolved, and after being brought to room temperature is filtered by suction to separate the kieselguhr and the thorium sulfate. The cobalt content is then determined by the following method:

5) Determination of the Cobalt

- a) The indirect method of determining the amount of cobalt by
- * Stopcock with an outlet through the end of the key.

weighing of the kieselgahr, leads to completely unsatisfactory values which do not always correspond to the composition of the catalyst.

b) The titration method with cyanide does not lead to exact values either, since in this definite concentrations have to be kept and the endpoint is difficult to recognize.

c) The titration method with soda lye gives perfect values in the absence of impurities which have a pH value similar to that of cobalt.

d) The photometric method is the quickest. With filtered solutions that are completely clear it gives values which are accurate enough. (Filter cold)

e) The electrolytic method gives perfect results.

6) Determination of the hydrogen

In the volume of gas obtained, it is best to determine the percentage of hydrogen in an Orsat-apparatus attached to the rest of the apparatus. Since the constituents which are present aside from the hydrogen do not affect this determination, one can simply burn the hydrogen over copper oxide at 290° by the known method. It is superfluous to cool the small steel tube with copper oxide between determinations. From 5-7 determinations can be made without oxidizing or cooling.

7) Calculation

58.9 g Co give 22.40 l H₂

1 g Co give 380 cc H₂

Then if y cc of H₂ are developed from x g of total cobalt,

$$\text{Cobalt value } (\%) = \frac{y \cdot 100}{x \cdot 380}$$

8) Example

One catalyst gives: .150 cc gas at 20° and 762 mm pressure

Under normal conditions: 162 cc gas at 0° and 760 mm pressure

The analysis shows: 96.9% H₂

Obtained: 157 cc H₂

0.590 g Co photometrically

$$\text{Cobalt value } (\%) = \frac{157 \cdot 100}{0.590 \cdot 380} = 70\% \text{ metal}$$

9) Accuracy

With accurate determinations of cobalt, the limit of error amounts to 2-3 units of the reduction value in either direction.

/s/ Roelen

Translated by E. Rothstein, March 5, 1947
Checked By C.C.M. March 6, 1947
Information Division Translation T47- 24

"Bestimmung des freien Metall-Gehaltes in Katalysatoren."
Ruhrbenzin Aktiengesellschaft
Oberhausen-Höfen
January 5, 1936
5 pages, 1 illustration

API-TOM Reel 48, Frames 819-827

Polymerization

To Professor Martin, et. al.

- I. Plans and descriptions of the technical polymerization catalyst plant.
- II. Operation of the plant, production of 4000 kg. of H_2PO_4 catalyst.
- III. Duration test on a representative sample of this catalyst.

Before the plans and description of the technical polymerization catalyst plant are gone into in more detail, the present working procedure is to be outlined here. The procedure, up to the present time, was the following: 63% H_2PO_4 and kieselguhr in the weight proportion of 4:1 were mixed in a kneader and dried at 170-180°C. For this purpose the viscous catalyst-mass was poured into dishes and placed in the drying oven for 12 hours. To prevent a crusting of the mass, they had to be deposited in thick layers (at least 30 mm) and had to be rearranged into layers several times during the drying process. After this preliminary drying, the catalyst material was worked up in a heatable kneader of V₂A, during which process it again became rather soft. (Temperature of the material 150°C) The desired plasticity was reached by addition of dust. This required 30-50 wt. % of dust, an amount which accumulated naturally in the process of crushing and sieving the molded materials. This highly plastic material was shaped into cords in an extruder with a punch. The cords were led on tin plates and subsequently came into a drying oven at 230-240°C. After a drying period of about 24 hours, the cords were broken and sifted. (2-4 mm.). The undersize grains were ground (less than 0.5 mm.) and used for the next plastification.

I. The plant was laid out for 50 tonnes per year, i.e. the plant is sufficient for 35,000 tonnes of poly-naphtha with use of 1 kg. catalyst/700 kg. poly-naphtha. In this it was calculated that, according to need, the plant would be in operation perhaps four times a year for one month. Under these conditions, the daily output-to-be is 0.5 tonnes, i.e. the charge would have to be approximately 600 kg. H_2PO_4 and 125 kg. kieselguhr per day (8 hours), amounting to about 60 kg. H_2PO_4 and 15.0 kg. kieselguhr per hour.

The individual pieces of apparatus are described with the help of a graph (Frame 827). The following pieces are here described in detail: Supply container, measuring equipment, kneading machines, air circulation chamber dryer, preliminary dryer, main dryer, hydraulic cordpress, wooden plate-belt with worm-gear, crusher, high-capacity-vibration-sieve, micro-hammer mill.....

II. The operation of the plant was held up by a number of technical difficulties, the most important of which are discussed in the paper.

Frans 623

The final production process in the technical plant was the following: 60.0 kg. of 89% H_3PO_4 and 15.0 kg. of kieselguhr were charged into the mixer, mixed for 20 minutes and then placed into the sheet metal cups of the preliminary dryer. The mass is a rather thin liquid and can be poured out of the tilted mixer in this condition. The drying period in the preliminary dryer is about 15 hours. A frequent stirring of the mass at the critical stage of hardening speeds the drying and makes the material more homogeneous. In the beginning we took the preliminary drying so far that no addition of dust was necessary. However, this requires very careful work and heating of the second mixer. Since dust is formed as the procedure is continued, the mass later was pre-dried until the irregular clump looked dry, were of a crumbling firmness and yet were easily ground. When this hot product was placed into the second mixer, 50% of dust still had to be added in order to obtain a solid highly plastic material which could be cut. (Kneading time for one charge - approximately 80 kg. - one hour). Since only 30% of dust accumulated in the comminuting process, finished grains had to be ground. This had to be prevented. Since further drying caused the formation of small, hard grains, we took the following route: The H_3PO_4 was mixed with only 10% kieselguhr and put to dry. This mixture did not form hard crusts at the surface and therefore did not need to be stirred. The pre-dried, completely homogeneous material was now treated with the remaining 10% kieselguhr in the second mixer. This procedure required only 25-30% dust to be added in order to reach the desired consistency, without the mixer having to be heated. This material came into the cord-press and required a pressure of about 220 atm. abs. to be pressed through the punch. The pressure later became a criterion of consistency and quality of the grain. For example, at 120 atm. abs. the dust accumulation in the comminuting was 60%. About 120 kg. of material could be put through the press per hour. The cylindrically shaped cords (diameter 6 mm.) did not cling together; they were led onto tins from the press and were pushed into the main dryer where they remained about 12 hours. On tilting the tins, they fell into containers where they were cooled. By means of a bucket conveyor they were later led to the comminuting plant where the main outfits, crusher, sieve, and mill were arranged on top of each other. The molded materials, which were led into the crusher by the bucket conveyor and there crushed, fell on the sieve where the three fractions - finished product, oversize, and undersize grains, were separated. While the finished product was caught up in iron barrels, the oversize grains were led to the conveyor and re-charged. The undersize grains were simultaneously converted to dust (0.5 to 1 mm.) in the hammer-mill and used for the next plastification. The output of the comminuting plant was about 200 kg. finished grain per hour

III. A representative sample was taken from the first ten iron barrels of finished catalyst. The catalyst was white, very hard, and showed practically no grinding at smooth surfaces. It had a pouring density of 0.9. It was charged into our laboratory experimental oven for the purpose of testing its activity. The 30 mm. i.d. oven was filled with 240 g. of catalyst. The

activity test was carried out with a high-olefin cracked gas. The catalyst was started at 150°C and 60 atm. abs. and in spite of an increasing load from 0.6 to 2.5 it showed a polymerization of more than 95%. At a temperature of 170°C, 600 l of poly-naphtha were produced per kg. of catalyst in about 400 hours. The conversion always was above 90% with a load of 1:2. Only after the production of 800 l of poly-naphtha the activity of the catalyst decreased in spite of slowly rising temperatures. The decrease is relatively slow at first. At the output of 1,200 l poly-naphtha per kg. of catalyst, the conversion was still greater than 70%, although the temperature had to be raised to 220°C. A further increase in temperature or decrease in load do not produce any special effects at this stage. The experiment was discontinued after the catalyst brought about only a 50% conversion. The catalyst had produced 1,285 l. poly-naphtha per kg. of catalyst in 918 reaction hours. (38 days).

At the end, the load had sunk to 1:1, i.e. 100 g of catalyst were supplied with 100 g. of gas. The conversions were carried out in one pass in the standing reactor. The American guaranteed amount (1 kg. poly-catalyst = 700 kg. poly-naphtha) thus was not only reached with our catalyst but exceeded by approximately 35%.

Frame 827: Diagram of the polymerization-catalyst plant.

/s. Spiske

Translated by E. Rothstein, March 10, 1947
Checked March 12, 1947 by C.C.M.
Requested by R. F. Marschner
Information Division Translation T47-29

- I. Planung und Beschreibung der techn. Polykontakanlage.
- II. Inbetriebsetzung der Anlage, Erzeugung von 4000 kg H_2PO_4 Kontakt.
- III. Dauerversuch mit einer Durchschnittsprobe dieser Kontakte.

Ruhrochemie Aktiengesellschaft
Oberhausen-Holten, March 10, 1942
8 pages, 1 illustration.

HUMBLE OIL & REFINING COMPANY

REFINING DEPARTMENT
TECHNICAL AND RESEARCH DIVISION

LABORATORY
BAYTOWN, TEXAS

July 18, 1946

Translation by:
M. S. Baer

File No. LQ 6.1-1518

Method for Determining the Location of Double Bonds in Olefins

The following analytical method was translated from Technical Oil Mission Microfilm, Reel No. 50, Pages 361 to 366.

1. Principle

Boiling 55 to 60 per cent nitric acid will not attack saturated hydrocarbons, regardless of degree of branching, but will oxidize olefins at the double bond such that cleavage takes place, forming two acids, each having the same carbon number as the corresponding fragment. Terminal olefins do not produce a molecule of formic acid as would be expected but produce one molecule of CO₂ instead.

The acids will be distributed between the aqueous and gasoline phase. Acetic-, propionic-, butyric-, and caprylic acids remain in the aqueous phase; and the higher, water-insoluble acids, in the gasoline phase. The phases are analyzed separately. The gasoline phase analysis consists of extraction with potassium hydroxide, acidification of the hydroxide with sulfuric acid, and removal of the liberated organic acids. Remaining acids are removed by means of ether. The aqueous phase is extracted with chloroform and the chloroform distilled off. The acids are separated by fractionation, and for each fraction the neutralization number and the silver content of the silver salts prepared from the fraction are used to determine the carbon number.

Attention is called to the fact that it is very necessary to have clean separation of the hydrocarbon fractions used in the analysis. The fraction should contain only hydrocarbons of a single carbon number.

2. Procedure

The olefins of the fraction to be analyzed are first determined (by bromine number, iodine number, or other methods). Nitric acid of $d_{20} = 1.35$ (= 57 per cent) is placed in a 300 cc. flask provided with reflux condenser. The amount of nitric acid used is 200 per cent of the amount required for complete oxidation of the olefins to acid as determined by the equation:



Copies to: WDS(2), JHK, AEM(25), DFB(2), ELB(2)

One gram of ammonium vanadate is added to the nitric acid as oxidation accelerator. Twenty to 25 cc. of the sample to be analyzed is placed in a dropping funnel atop the reflux condenser and slowly dropped in the nitric acid while the acid is being heated to 98° to 100° C. The gasoline is added over a period of $\frac{1}{2}$ hour. The nitric acid is kept at 90° to 100° for one hour after gasoline addition is complete and then vigorously boiled three hours. The gasoline phase is then separated from the aqueous phase in a separatory funnel, and both are analyzed separately.

To avoid emulsion formation, an equal volume of ether is added to the gasoline phase and it is then shaken vigorously three times with portions of 50 per cent potassium hydroxide. The total amount of KOH used is twice that required for neutralization of the acids. To determine the acid concentration, a neutralization number is run before the KOH treat. It is recommended that 120 per cent of the calculated amount of KOH be used in the first treat, 60 per cent in the second, and 20 per cent in the third. A neutralization number must then be run on the extracted gasoline to make certain that all the acids have been removed. If they are not completely removed, more shaking with KOH is required. The three alkali extracts are combined and carefully neutralized with excess 50 per cent sulfuric acid under cooling. The acids separate almost quantitatively from the potassium sulfate solution so that ether extraction is practically unnecessary. The acids are then distilled. In general, a long-neck 15 cc. distilling flask is used. The fractions are taken over separately as follows:

Acetic Acid	108°-129°
Propionic Acid	129°-151°
Butyric Acid	151°-175°
Valeric Acid	175°-195°
Caproic Acid	195°-214°
Heptanoic Acid	214°-230°
Caprylic Acid	230°-245°

This means they are separated with the cut point exactly between the boiling points of two successive fractions. The neutralization number is determined on each fraction, the silver salts are prepared, and the silver content is determined. The silver salts are prepared as follows: One cc. of the fraction is dissolved in 20 cc. of 50-50 ether-methanol and the solution neutralized with alcoholic 4N potassium hydroxide until neutral to one drop of phenolphthalein. If salts are precipitated, sufficient water is added (about 20 cc.) to redissolve them. The solution is placed in a separatory funnel and the aqueous separated from the ether phase which contains any gasoline that might still be present. If the phase separation is not perfect, a small amount of ether might have to be added. The aqueous phase is now very weakly acidified (to turn litmus red) with very dilute nitric acid (one part of 1.20 gravity nitric acid to 10 parts of water); cloudiness in this step indicates a separation of small amounts of fatty acids. These are redissolved by addition of several cc.'s of methyl-alcohol. The acids are precipitated by addition of about 10 cc. of saturated silver nitrate solution. After a brief period of settling, the mixture is filtered through a suction funnel. It is washed four to six times with small amounts of 50 per cent aqueous methanol and then dried one and one-half to two hours at 110° C. The precipitate is transferred to a porcelain crucible which has previously been ignited and weighed, and is ashed until all the carbon is burned and only the silver residue remains. The crucible is allowed to cool in a desiccator and the weight of the silver residue determined. This permits immediate calculation of the carbon number of the acids which had been present.

To determine the acids in the aqueous phase, 50 cc. of chloroform are added and it is extracted in a continuous extraction apparatus. The determination of the acids is identical to that just described.

It is not always necessary to analyze the aqueous phase since the long chain acids from the gasoline phase often permit estimation of the lighter acids in the aqueous phase.

A special modification of this method permits determination of terminal olefins. In this case, CO_2 is formed instead of the expected formic acid. To determine the amount of terminal olefins, therefore, it would be sufficient to treat a known quantity of gasoline, which need not even be sharply fractionated, with nitric acid and determine the amount of CO_2 formed. With unbranched gasolines this process has proven quite feasible. Unfortunately it was observed, however, that resinous components of the gasoline and branched olefins are also decomposed to form CO_2 , if the branching is at the double bond, so that in such cases high values are obtained, particularly since the branched olefins decompose to form several molecules of CO_2 . For example, 2,2,4-trimethylpentene-3 forms three mols of CO_2 per branched double bond. However, the method seems to be particularly suitable for Fischer-Tropsch products, since branching at the double bond has never been observed in these products provided there was no aftertreatment. For example, pure C_7 , C_8 , and C_9 terminal olefin fractions prepared by precision fractionation were analyzed by CO_2 determination with almost 100 per cent accuracy. At the same time the gasoline phase was analyzed and the C_6 , C_7 , and C_8 acids, respectively, were found to be the only ones present. The procedure for determination of terminal olefins is as follows:

Two to five grams (depending on the olefin content of the product) are weighed accurately. Five times the theoretical amount of nitric acid ($d_{20} = 1.20$; 33 per cent) is added. The reaction takes place in a small Erlenmeyer flask with ground glass connection to a reflux condenser, on top of which is a gas takeoff tube. Through a side arm of the Erlenmeyer a weak CO_2 -free stream of nitrogen is added during the reaction. The gas takeoff is connected to a three-way stopcock to permit changing the receiver of 1/2N barium hydroxide.

A fritted-glass absorber filled with sulfuric acid is suitably inserted between the three-way stopcock and the barium hydroxide receiver to remove any entrained nitric acid. The reaction is started by heating the gasoline-nitric acid mixture until it boils mildly, the nitrogen stream being started at the same time. The barium hydroxide solution begins to cloud shortly after boiling has begun. A second barium hydroxide-filled receiver is used in series with the first and when it begins to cloud, receivers are changed. After the reaction is completed the barium carbonate precipitates are combined and filtered and the carbonate determination is carried out as usual. It is not absolutely necessary to add ammonium vanadate to accelerate the reaction.

Lately, a modification of this procedure has been used which makes the sulfuric acid scrubber unnecessary and makes use of alkaline barium hydroxide solution which is prepared as follows: About 120 per cent of the amount of barium oxide required to make a saturated solution at room temperature is weighed and dissolved in three liters of hot water. The solution is diluted with five liters of cool

File No. IQ 6.1-1518

water, 200 to 300 cc. of 50 per cent potassium hydroxide are added, and the solution is made up to ten liters. After 24 hours of standing, the precipitated barium carbonate is filtered off. The saturated barium hydroxide solution is then immediately ready for use and is used in place of the above-mentioned 1/2N barium hydroxide. The excess of free caustic is sufficient to take care of any entrained nitric acid.

After the combined barium carbonate precipitates (from the analysis) are filtered, they must, of course, be washed several times with hot water to remove the free alkali. Subsequently the precipitate is dissolved in excess 1N hydrochloric acid and back titrated with 1N sodium hydroxide.

MSB: tnr

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-30

API-TOM Reel 50, Frame 378 (Page 33)

The catalytic cracking of cracked gas oil.

In reply to your letter of July 20, 1943, we wish to report that we began the tests only during the past few weeks, due to the late arrival of the samples. Dr. Meyerling is probably interested in the question, originally discussed by him and Dr. Tramm, as to what extent it is possible to improve the naphthas produced at the cracking plant of the Concordia Vega, Floesti by inserting a catalytic cracking chamber into the process of the thermal cracking plant.

The cracked gas oil sent to us had the following characteristic data according to Concordia:

d_{45}	0.9258	up to 250°	5%
flash point	32°	up to 280°	10%
viscosity at 20°C	4.9°E	up to 300°	20%
solid point	+20°	up to 350°	66%
start of boiling	196°	up to 380°	72%

The oil was cracked in a single pass under a catalyst load of 50, respectively 100%, i.e. $\frac{1}{2}$ l, respectively 1 l of cracked gas oil were charged per hour per liter catalyst. The temperature was 460°. Under 50% load, a cracking of 30-40% by weight was obtained, while under 100% load the cracking was found to be 20-25% by weight. The composition of the cracked products was the following: Carbon-3-5%, gases, i.e. C_2 and low-boiling cracking products-approximately 10%, C_3 approximately 10% with an olefin content of 75-85%, C_4 -also about 10% with the same olefin content as the C_3 hydrocarbon. The unsaturated portion of the C_4 hydrocarbon contained about 25% of isohydrocarbons. There was obtained 60-65% of naphtha boiling up to 200°C. The quality of the naphtha is still not known, since the amount is not sufficient for an engine test. Compared with the catalytic cracking of a normal gas oil it can be said that the cracked gas oil is more difficult to crack, so that about 35% conversion takes place rather than 50% conversion. Of course the difference can be overcome by a change in temperature, but in that case the technical possibilities have to be tested carefully. The high olefin content of the C_3 and C_4 hydrocarbons seems worthy of mention. A synthetic catalyst of high activity was used for the tests. The total yield of completely stabilized naphtha is 74-80%. The naphtha should contain 0.45% lead and have a motor octane number between 80 and 90 when stabilized at 0.7 atm.

Translated by E. Rothstein, March 7, 1947

Information Division Translation T47-30

Checked by CCM March 12, 1947

Requested by R. F. Marechner

Letter, no legible title
Ruhrchemie Aktiengesellschaft
Oberhausen-Holtan, August 1943
1 page, no illustration

INFORMATION DIVISION TRANSLATION T47-27

API-TQM Reel 50, Frames 846-854 (Item 93)
To: Professor Martin et. al.

Polymerization in the Technical Experimental Plant.

A technical experimental plant for polymerization was built for the purpose of working up more quickly the gas quantities accumulating in the catalytic cracking (IR-plant), and also for testing the conditions for polymerization of the high olefinic, strongly isomeric catalytically cracked products of the C_4 - C_6 -fraction on a large scale. The purpose of this report is to be a description of the plant and of the first trial runs, including the experiences gained therein.

Description of the plant:

The plan of the set-up is reproduced on the enclosed drawing (Frame 854). There are in all 3 set-ups, in order to be able to carry out the polymerization of the C_3 - C_4 - and C_6 fraction separately and yet at the same time. The path of the product is the following: The C_3 - C_4 - and C_6 product separated in the distillation of the cracked naphtha reaches the pressure tank designed for this purpose. The liquid gasol is transferred from there to a mixer with the aid of a cog-wheel pump, and from there to a special Bosch-pump by way of a small cooler and a filter. The pump presses the liquid gas into the reactor by way of a preheater and an oil receiver. In a stabilizer there then takes place the separation into the poly-naphtha which flows into a tank by way of a cooler, and into a paraffinic residual gas which reaches a receiver by way of a cooler. From there it can either be fed again to the mixers or lead off in residual-gas bottles.

(Tr: Frames 847-849 give the dimensions and further descriptions of the following pieces of apparatus:

- 1) Pressure tank 2) Pump 3) Mixer 4) Cooler 5) Filter 6) Bosch pump 7) Preheater 8) Reactor 9) Stabilizer 10)-12) Cooler 13) Receiver)

Operation of the Plant.

The reactor, the preheater, and the stabilizer are brought to the desired temperature. The gas in the pressure tank is analysed in order to calculate its ratio of the paraffinic product. Then the two mixers are filled consecutively with product from the pressure tank up to a certain height, after which the olefin-lean product from the receiver is permitted to flow in. The ratio depends on the initial olefin content of the gas put in. It should be mixed in such a way that the olefin content equals from 40 to 50%. From experience, the initial pressure in the mixers should be approximately 8 atm. abs. for the C_6 fraction to obtain an undisturbed running of the naphtha Bosch-pump. By heating of the water-bath in which the

mixers stand this pressure is easily kept constant. The path from a mixer to the bosch pump is opened and the material is pressed into the reactor by way of a preheater at a temperature of 195-200°C. The exit valve of the reactor remains closed until the reactor is at the desired reaction pressure. A pressure of 60 atm. abs. was used for all trials, while the temperature varied from 110-200°, depending on the starting material. Once the pressure of 60 atm. abs. is reached, the exit valve is adjusted so that the pressure in the reactor remains constant. Since the naphtha bosch pump feeds very smoothly, the regulation is extremely simple. The naphtha-gas mixture flows from the reactor into the stabilizer. In order to obtain a naphtha with a Reid-pressure of 0.4 atm. abs., the bottom temperature of the stabilizer must be kept at 120°C, and at a pressure of 3-4 atm. abs. The head temperature then is 30-40°C. The back-flow of the stabilizer was completely open in all cases. A definite height of the poly-naphtha was kept in the glass-gauge of the boiler, while the excess flowed over into the tank continually. In the same manner, the gas at the head of the column was continually forced into the receiver. After one mixer is empty, one switches to the other. At any time, one can determine the degree of polymerization from the residual gas examination, or the quality of the poly-naphtha formed from the naphtha test.

Carrying out of the trial runs.

1st. Trial Run

In order to obtain a quicker control over the apparatus, it was started with ordinary gasol with an olefin content of 32-34%. The reactor was filled with 7.2 kg. of self-manufactured H_2PO_4 catalyst. The reaction conditions were the following: 195-200°C, 60 atm. abs., with a load of 1:1 in the naphtha bosch pump fed appr. 15 l of liquid gasol into the reactor every hour. Up to the 200 th hour the polymerization constantly amounted to 80-95% and then decreased within a shorter time (15 hours) to 30%. Since at the same time a new gasol with only a 25% olefin content was being used, the assumption lay at hand that some impurities which may have been in the gasol had poisoned the catalyst. However, neither impurities such as Cl_2 , S_2 , etc. nor higher hydrocarbons were found in the gasol. The temperature was raised to 220°, a high olefin product was put in, and the time of retention was doubled. Yet it was impossible to raise the polymerization above 50%. For that reason the reactor was exhausted. It was found that one reaction tube was empty except for about 10-15 cm. The catalyst was rather soft, (strongly saturated with naphtha) and had probably pressed through the sieve. Therefore several Raschig rings (10 mm) were put into the reaction tubes in the 2nd trial run whereupon the process was not repeated. The removal of the catalyst was comparatively easy; the catalyst was light grey, the top and still all white at the bottom, a sign that it must still have been unused and highly active. The total duration of the first run was 309 hours, and 1,350 l of poly-naphtha were produced in this time (188 l per kg. of catalyst).

2nd. Trial Run

Since each reaction tube was filled at the bottom with a layer

of Raschig rings, the amount of catalyst this time was only 6.7 kg. The apparatus was again started with gasol, this time for about 150 hours without any disturbance. Then there was an interruption of about 6 weeks before we were able to continue the trial run of the polymerisation of the distilled catalytically cracked product. Since the paraffinic products of the gasol products, had by mistake been carried off with other gasol bottles, we had to fill the apparatus with the high-olefinic product. This was done at first at a temperature of 140-150°C, which later could be lowered to 110-120°C. The pressure was again 60 atm. abs. and the output 12-14 l of liquid product per hour. Table I gives a summary of the 2nd trial run regarding time, starting materials, conditions, and percent polymerisation. It lasted 322 hours. In this time 2,456 l of poly-naphtha were produced, i.e. 367 l per kg of catalyst. After that time the reactor became plugged. The cause was of a purely technical nature: The suction line to the pump had become plugged, and therefore the reactor was run through a whole night with reduced output. (Appr. 2 l per hour.) Because of the long period of obstruction, an over-polymerization set in, which led to the plugging of the reaction tubes.

3rd. Trial Run

This run is not yet completed. Again 6.6 kg. of catalyst were filled in. Up to this moment, 1,770 l of poly-naphtha were produced in 260 hours, i.e. about 270 l per kg. of catalyst.

With a load of 1:1, for example, one apparatus for the polymerization of C_6 -product from a catalytic cracking with appr. 80% olefins and a 80% polymerization, can produce appr. 180 l poly-naphtha per day.

/S/ SPISE

Translated by E. Rothstein, March 5, 1947
Checked by CCM March 7, 1947
Requested by R. F. Marschner
Information Division Translation T47-27

"Polymerisation in der technischen Versuchsanlage."
Rohrchemie Aktiengesellschaft Oberhausen-Holten
July 7, 1941
8 pages, 1 drawing