

INFORMATION DIVISION TRANSLATION T47-20

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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_{11} , and further cut in the laboratory. The different mixtures noted showed, according to the "Kettwinkel" 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 10° , 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 HgCl₂-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	C7,8,9,10,11 52% olefin 29.4 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 7.5% 36% olefin 5.8 OH value	9.6% V50=15.7 VPH=1.78 Iod.No.=80
2977	none	C5,6,9,10,11 56% olefin 33.6 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 3.3% 35% olefin 7.1 OH value	10.6% V50=16.1 VPH=1.78
2978	none	C12,13,14 44% olefin 22.7 OH value	4% AlCl ₃ 11 hrs. 80°	Cat.oil 5% 22% olefin 4.5 OH value	12.1% V50=9.6 VPH=1.42
2976/2	P ₂ O ₅ + Quartz sand, 4 hrs. 100°	C7,8,9,10,11	4% AlCl ₃ 11 hrs. 95°	Cat.oil 7% 18% olefin	18.2% V50=8.1 VPH=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

<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>
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 V _{FH} =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 200° distilling	to 200° 68 % olefin	4% AlCl ₃ 11 hrs. 95°	Cat. oil 8% 20% olefin	40.4% V ₅₀ =9.3 V _{FH} =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 V _{FH} =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 V _{FH} =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

<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.Ole fin</u>	<u>Resid.Oil</u>
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 VFR=1.75 Iod.No.=52
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 VFR=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 VFR=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 VFR=1.65 Iod.No.=49

Table 5

Oil Preparation from Products of the
Naphtha Synthesis Under Pressure

Furnace 10. 10¹ 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 =11.4 VPH=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 VPH=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 VPH=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 VPH=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 VPH=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 VPH=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 VPH=1.65 Iod.No.=32
2991/3	Soda lime to 140°F.	to 200° 75% olefin	4% AlCl ₃ 11 hrs. 80°	Cat.oil 0 56% olefin	30.7% V ₅₀ =26.4 VPH=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 VPH=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 11.0°	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 11.0°	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. 40°	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 cold, 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 cold, 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

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"Über, die Herstellung von Ölen
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