

FILM STUDY GROUP

SUBJECT INDEX AND REPORT

T. O. M. REEL NO. 168

Prepared by

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INDEX OF TECHNICAL OIL MISSION MICROFILM

REEL NO.168

(Prepared by California
Research Corporation)

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Mr. L. L. Newman

**CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA**

**ABSTRACT OF TECHNICAL OIL MISSION
MICROFILM**

**REEL NO. 168
(Frame Nos. 1 - 579)**

(Prepared by California Research Corporation)

REEL NUMBER 168 (ABSTRACT)

I.

PAPERS ON LOW TEMPERATURE HYDROGENATION
(T.T.H. Process, files of Dr. Peters.)

May 31, 1944

Frame 1-2

1. WORKING WITH LIGNITE TAR AND FRACTIONS THEREFROM IN D.H.D. PLANTS

a. Working with low temperature distilled gasolines. Refining experiments proved that such products can be refined at 30-50 atm. hydrogen pressure. At about 425° increased hydrogenation occurs, at about 500° dehydrogenation and formation of aromatic products takes place.

The application of sulfur appeared of advantage, but inactivated the catalyst for other uses.

b. Working of medium oils. Such oils from Boehlen tar gave good results in refining experiments at pressures of 25 and 50 atm. respectively, with a catalyst 6434. The results are assembled in tables and discussed.

c. Working of the crude tar. Cracking experiments with the tar at 50 atm. hydrogen pressure were made. The results are compared to the results obtained in earlier cracking experiments with Boehlen tar and considered satisfactory.

Feb. 4, 1944

Frame 3-4

2. WORKING OF NAVY HEATING OIL

(File note regarding the discussion of a project)

Five varieties of bituminous or lignite oils are examined regarding their suitability to be worked into Navy Heating oil. They can be cracked individually at about 600 atm. of hydrogen pressure in the presence of fixed bed catalysts. The possible results of this cracking for these five oils are estimated. Plans are discussed to take up production at a plant suitable for this type of operations.

The alternative of treating these five oils in a single process is also discussed. Hydrogenation in either the gaseous phase up to 325° or at higher temperature in liquid phase are considered. This kind of operation, however, would call for previous pressure distillation, and difficulties might also result from the asphalt and paraffin components contained in the material.

March 23, 1943

Frame 5-10

3. WORKING OF HEAVY OIL IN THE GASEOUS PHASE AND IN THE PRESENCE OF FIXED-BED CATALYSTS.

(File note concerning the discussion of a project)

A hydrogenation process with the catalysts 7846W or 5058/7846W in the gaseous phase is discussed with special attention given to local plant conditions.

Two of the referees disagree on the activity of these fixed-bed catalysts. Other participants of the conference report on special experiments regarding the process in question from operations in their respective plants. Various details of plant construction and operational conditions are discussed including the project of installing a plant for the pressure distillation of heavy oils.

March 4, 1943

Frame 11-12

4. STABILITY OF CATALYSTS IN THE T. T. H. PROCESS.

T. T. H., i.e. low pressure hydrogenation experiments, in a 1 liter oven with tar from Zeitz at 230 atm. hydrogen pressure with catalysts 5058 and 8376 are briefly described and discussed. The results are assembled in a table (T.12) and special attention is given to the degree of stability or decomposition observed in the catalysts.

April 9, 1943

Frame 13-15

5. T.T.H. EXPERIMENTS WITH HEAVY OIL FROM PUERTOLANO SHALE OIL

This is a report on the possibility of producing lubricating oil from the shale oil in question. From data referring to the distillation of a sample (F-15) general figures for a possible full scale production are calculated. The individual fractions from such treatment are briefly discussed and suggestions are made to improve their quality.

The yield of lubricating oil for automobiles appears poor, unless the process can be modified, or the oil obtained be blended with other very viscous synthetic oils.

April 14, 1939

Frame 16-18

6. LUBRICATING OIL FROM VACUUM FRACTIONS OF LIGNITE EXTRACTS.

Fractions from the distillation of lignite "Concordia" were investigated and vacuum cracked at 30 mm pressure in the presence of catalyst 5058 and in other experiments without catalysts. The fractions obtained and their properties are listed in 3 tables. Further hydrogenation of some of these fractions gives a small amount of lubricating oil (7 to 9%) and paraffins. Treatment of these fractions at 230 atm. proceeded without difficulties.

Aug. 8, 1944

Frame 19-23

7. AUTOCLAVE EXPERIMENTS AIMED AT THE REMOVAL OF ARSENIC FROM BROEK TAR PRODUCTS.

Autoclave experiments to eliminate arsenic from medium oils, wash oils and heavy tars by hydrogenation at elevated pressure were successful. At 320 atm. the arsenic was removed completely and collected in concentration of about 10% in the benzene insoluble residue, which could easily be separated by filtration. The experimental results are listed in 3 tables. No catalysts were used.

June 19, 1944

Frame 23

8. EXPERIMENTS ON ARSENIC IN BRUEK TAR.

Some experiments aimed at removing arsenic from tars and medium oils by boiling them with absorbents such as activated charcoal, silica gel, etc., are briefly outlined. The results are described as unsatisfactory.

June 6, 1944

Frame 24-25

9. PROCESSING OF LIGNITE TAR FROM CENTRAL GERMANY AT 600 ATM.

Analysis data of the tar are given and a table illustrates the results of hydrogenation experiments at 250 atm. An iron catalyst was used. The table contains also estimated figures for full scale operations to be carried out at 600 atm. of pressure. The expectation is expressed that the material can be processed without difficulty.

June 1, 1944

Frame 26-28

10. FILE NOTE ON THE TREATMENT OF VARIOUS TARS IN THE PRESENCE OF A FIXED-BED CATALYST (8376).

Various tars were hydrogenated and cracked at 300 atm. The results obtained are listed in a table and briefly discussed, special attention is given to the ratio of the various fractions obtained from the individual raw materials. A fixed-bed catalyst 8376 was used.

Jan. 25, 1944

Frame 29-30

11. TREATMENT OF TAR FROM BOELEN AT 200 ATM. IN THE PRESENCE OF THE CATALYST 8376.

Cracking experiments at 200 atm. of hydrogen pressure are briefly described. The results are assembled in a table. The catalyst 8376 was used, possible improvement of the result is expected by the use of catalyst 6434 or a combination of 8376 with 6434.

Sept. 20, 1943

Frame 31

12. SEPARATION OF BENZENE INSOLUBLE SOLIDS ON PRESSURE HEATING OF TAR FROM BRUEK.

The tar was heated to about 300° in an autoclave at about 200 atm. of hydrogen pressure with various catalysts. The experimental results are listed in a table and briefly reviewed. Formation of benzene insoluble residues took place making it advisable to add the catalysts only after complete solution of the starting material.

Aug. 17, 1944

Frame 32-36

13. CRACKING OF TAR FROM KULKWITZ AT 200 ATM. IN THE PRESENCE OF CATALYST 8376.

Cracking experiments of this product are briefly described and discussed. The results are listed in 3 tables containing various data and characteristics.

With the catalyst 8376 cracking proceeded without difficulty at 250 atm. The fraction up to 350° yields a good medium oil from which gasoline of satisfactory quality could be obtained on further treatment.

APRIL 14, 1943

Frame 37-49

14. WORKING OF LURGI LOW TEMPERATURE CARBONIZATION TAR FROM PUERTOLANO OIL SHALE BY THE T. T. H. PROCESS.

This tar was subjected to the T. T. H. cracking process at 250 atm. with catalyst 5058. The results obtained are compared and assembled together in a table with results obtained from experiments with a similar product. The Lurgi shale oil serving as starting material is described, some analysis data are given.

Experimental details concerning pressure, temperature, ovens, yields, catalyst numbers, etc. are discussed with reference to some other tables with experimental results, included in the report.

Jan. 14, 1943

Frame 50-58

15. EXPERIMENTS ON THE DESTRUCTIVE HYDROGENATION OF BRUEX TAR AT 250 ATM. IN THE PRESENCE OF A FIXED-BED CATALYST 8376.

Filtered Bruex tar containing 11% of asphalt was cracked without difficulty in the presence of the alumina tungsten-nickel catalyst 8376. The cracking experiments are described and discussed in detail. Several tables and a chart illustrate the results which in general are favorable. Suggestions for improvement of details are made. The medium oil fraction obtained up to 350° was redistilled and cracked in the presence of catalyst 6434.

Sept. 24, 1942

Frame 59-62

16. COMPARATIVE T. T. H. EXPERIMENTS.

This is a supplementary report on destructive hydrogenation experiments previously conducted with two different catalysts 5058 and 7846W (8376). The results of the present and previous experiments are listed in two tables and are briefly discussed. The results obtained by use of catalyst 7846W are considered more favorable.

Jan. 30, 1942

Frame 63-68

17. WORKING OF BRUEX TAR.

Characteristics and analysis data of this tar are given. Destructive hydrogenation experiments with the tar at 600 and 300 atm. respectively are described. The results are listed in a table and discussed with emphasis on the ratio and properties of the fractions obtained and suggestions of improvement. The text relates also to distillation experiments and a project of a still construction at Bruex.

March 26, 1940

Frame 69-75

18. WORKING OF A PRESSURE DISTILLATE FROM DEUBEN TAR IN THE PRESENCE OF A CATALYST 6719 BY THE T.T.H. PROCESS.

These T.T.H. cracking experiments are described, the fractions obtained are considered satisfactory but the catalyst 6719 used was not found in satisfactory condition after the termination of the experiments. The experimental results are listed in tables and briefly reviewed.

Feb. 9, 1940

Frame 76-85

19. REPORT ON THE WORKING OF NATTAVAARA PEAT TAR.

Analysis data of this tar are given. T.T.H. cracking and vacuum distillation experiments with this tar are described. The resulting fractions including properties and analysis data are reviewed.

Jan. 27, 1940

Frame 86-99

20. WORKING OF TAR FROM BOEHLER PLUS A MEDIUM OIL FOR AUTOMOBILE AND AVIATION GASOLINE.

T.T.H. experiments with these materials are described. The fractions obtained are compared to corresponding results originating from operations with the same material in factories at Magdeburg and Ludwigshafen. The experimental results are listed in several tables. The review of these results gives special attention to the technical factors responsible for the variations, and to individual fractions, their properties and analytical data. The catalyst used was Terrana plus 20% ZnS @ 1% Mo O₃ and 6434.

Jan. 23, 1940

Frame 100-115

21. EXPERIMENTAL REPORT ON THE WORKING OF NATTAVAARA PEAT TAR.

This report relates to a series of T.T.H. experiments with this peat tar which can be worked into gasoline, Diesel oils and paraffins. Analytical data on the tar and the fractions obtained are given (tables) and also other characteristics of the cracked products (tables). The individual experiments are briefly discussed. Various catalysts and catalyst combinations were used, 5058-6434, 5935, 6612 plus granular coke from lignite and MoO₃ or FeSO₄.

Nov. 20, 1939

Frame 116-125

22. DEHYDROGENATING REFINING OF BOEHLER MIDDLE OIL WITH CATALYST 7360 AT 50 ATM.

A middle oil from Boehlen lignite tar was refined at 50 atm. with catalyst 7360 and 0.5 throughput. Hydrogenation occurred at 450° and decreased to an almost complete stop at 476°, at 510° dehydrogenation and cracking took place. After an eight day experiment the catalyst activity had decreased only slightly. The catalyst could be regenerated to its original activity for refining, dehydrogenation and cracking purposes.

In experiments at 25 atm. the catalyst activity decreased sooner and the phenol content of the product was 0.4% after 12 hours and 5% after 3 days as

compared to 0.01% in the experiments at 50 atm.

The report discusses the properties of the cracked products obtained and the experimental conditions. The results are listed in a table and compared to analogous results obtained with catalyst 6434 listed in another table. Some tables give supplementary data on the fractions obtained in the experiments. The catalyst 7360 is judged favorably.

May 19, 1938

Frame 126-129

23. WORKING OF SCOTCH SHALE OIL IN THE SUMP PHASE WITH A FIXED-BED CATALYST AND SUBSEQUENT CRACKING AT ELEVATED PRESSURE.

This shale oil was subjected to sump phase treatment with a fixed-bed catalyst 6719 (FeW) at 250 atm. In a second step (production of gasoline) the fractions obtained were subjected to catalytic hydrogenation at 600 atm. with a fixed-bed catalyst 6109 (HF Terrana). The experiments and results are briefly described and assembled in a table, and are not considered very favorable.

June 12, 1944

Frame 130-135

24. DESTRUCTIVE HYDROGENATION OF RUMANIAN PAOURA IN THE PRESENCE OF CATALYST 8376 AT 250 AND 600 ATM.

This Rumanian product was cracked at 300 atm. hydrogen pressure with catalyst 8376, and later at 600 atm. of pressure. The cracked products represent a good medium oil, suitable as Diesel oil, which could be hydrogenated to gasoline in the presence of catalyst 6434. The experimental results are listed in tables and described.

June 10, 1941

Frame 136-148

25. WORKING OF A CRUDE OIL PRESSURE DISTILLATE IN THE PRESENCE OF A FIXED-BED CATALYST (7878 AND 6434) FOR ENGINE FUEL WITH o.n.87.

Crude oil from Zisterdorf was cracked into gasoline, medium and heavy oils, the fractions except the gasoline fraction were distilled under pressure.

The pressure distillate was divided into a medium oil fraction up to 325° and a heavy oil fraction above 325°. The heavy oil fraction was subjected to destructive hydrogenation at 350 atm. in the presence of the catalyst 7878 (7846 sulfurated) with a throughput of 0.8 and recycling of the components boiling above 325°. The catalyst 7878 was very stable. The fraction up to 325° yielded 17% of gasoline of 150°C. end point. A good Diesel oil was also obtained.

The catalyst 6434 used in the pressure distillation of the low fraction (up to 325°) showed some decline of activity.

The experimental operations are represented in a flow sheet (F.148) which includes pressure refining of the middle oil of the pressure distillate, although this refining step was not carried out. A chart illustrates the cracking result obtained from the heavy oil fraction. The experiments and fractions as illustrated in several tables are discussed in detail, suggestions for future experiments are made.

March 1, 1941

Frame 149-162

26. WORKING OF CRUDE PETROLEUM OILS, PETROLEUM HEAVY OILS AND PETROLEUM PRESSURE DISTILLATES IN THE PRESENCE OF A FIXED-BED CATALYST.

Various German petroleums, petroleum pressure distillates and heavy oils were subjected to destructive hydrogenation (T.T.H. process) at 250 and 600 atm. with fixed-bed catalysts, mostly alumina-molybdenum.

Deposits forming during the treatment of petroleum and petroleum heavy oils interfered with these experiments so that they could not be completed, whereas treatment of redistilled and pressure distilled fractions presented no difficulties.

Suggestions for better methods of processing are made, providing pressure distillation and subsequent cracking with a fixed-bed catalyst in analogy of operations with Rumanian petroleum referred to in a flow scheme on frame 161.

The use of catalyst 6434 for the medium oils was not considered as favorable. Refining under pressure and washing with H_2SO_4 is suggested as a suitable treatment for the medium fraction.

The numerous experiments and cracked products as assembled in tables are described and discussed. Catalysts 7776, 7846, 7360, 7806, 5058, 7320, and 6434 were used.

Oct. 3, 1940

Frame 163-166

27. HYDROGENATION EXPERIMENTS WITH OIL FROM PECHELBRONN.

This filtered crude oil was cracked at 600 atm. hydrogen pressure at a temperature of 415-435^oJ. with a throughput of 0.6 in the presence of the catalyst 7360 (activated alumina + MnO_2).

Other cracking experiments at 600 atm. hydrogen pressure were made with a residue fraction above 350^o, a similar catalyst as before, but sulfurated, was used.

The middle oil fraction was worked to gasoline in the presence of the catalyst 6434 with satisfactory results.

Two tables illustrate the experimental results which are briefly reviewed.

July 25, 1940

Frame 167-169

28. LOW TEMPERATURE HYDROGENATION OF PETROLEUMS.
(Experiments by Dr. Kronig carried out in 1936)

These low temperature hydrogenation experiments were aimed at obtaining light colored lubricating oil and gas oil products from petroleum in analogy to similar experiments carried out with distilled lignite tars.

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The first experiment carried out at 250 atm. and 356° with a pressure sulfurized catalyst 3570 plus 2.4% of CS₂ yielded a low grade refining product of a dark green to brown color. Two other experiments carried out with slight variations of the experimental conditions gave no better results. Only an experiment with a catalyst 3510 was considered more favorable and produced less asphalt.

Sept. 24, 1940

Frame 170-179

29. WORKING OF A RHEMANIA-OSSAG-PETROLEUM VACUUM DISTILLATE FOR AVIATION AND AUTOMOBILE GASOLINE

Two distillates, a light and a heavy one, were subjected to destructive hydrogenation at 260 atm. in the presence of catalyst 5058. The components above 325° were recycled. The catalyst activity did not decline.

Mixtures of these starting materials with equal volumes of a tar oil were subjected to the same treatment; however, the catalyst activity declined. It seemed advisable therefore, to treat the products in individual operations.

The experiments and cracked products obtained and comparative data are assembled in various tables and reviewed.

Feb. 2, 1940

Frame 180-187

30. WORKING OF SUMP PHASE MIDDLE OIL FROM CRACKING RESIDUES OF LAGUINILLAS CRUDE OIL FOR AUTOMOBILE AND AVIATION GASOLINE WITH CATALYSTS 6719 AND 6434.

These cracking residues were subjected to destructive hydrogenation at 250 atm. with catalyst 6719, yielding satisfactory results. The obtained fractions were redistilled under pressure with catalyst 6434. The results are listed in tables and reviewed.

Nov. 20, 1940

Frame 188-196

31. WORKING OF PETROLEUM FROM WIEZ WITH THE CATALYSTS 5058, 6434 OR 7019 AND 6434.

A medium oil fraction from this petroleum was subjected to destructive hydrogenation and subsequent redistillation with catalysts 5058 and 6434 or 7019 and 6434 respectively. The results obtained from a second series of experiments with catalyst 7019 were greatly inferior as compared to the first series with catalyst 5058.

The experiments and the various fractions from the cracking operations are assembled in comparative tables and reviewed.

II.

PHYSICAL PROPERTIES OF PURE HYDROCARBONS
(FILES OF DR. PETERS)

1941

Frame 197-207

1. KNOCK BEHAVIOUR AND POUR POINTS OF INDIVIDUAL HYDROCARBONS
IN DIESEL FUELS.

(A translation from "Bulletin de l'Academie des Sciences de U.S.S.R., Class des Sciences Chimiques, 1941 p. 145-155")

The paper gives the characteristics of the igniting properties (readiness to ignite) and the pour points of aliphatic and cyclic hydrocarbons of the composition C_{12} to C_{28} of various structural types (See tables).

The hydrocarbon components of gasoline, having mostly a C_5 to C_{10} structure, have all been investigated with respect to their knock behaviour as characterised by their octane numbers. The basic factors determining the relation between the structure and the knock rating are the following:

1. paraffinic hydrocarbons of normal structure knock more easily with increasing molecular weight. Only the first homologs of the benzene series form an exception to this general rule. The more widely branched their structures are and the nearer the branches are arranged to the center of the molecules, the less do hydrocarbons with an isostructure tend to knock.

2. Normal hydrocarbons of the olefinic series knock less easily than the corresponding paraffinic hydrocarbons. A branched structure reduces the tendency to knock. Diolefins, in particular when they contain conjugated double bonds, have a superior knock resistance.

3. Naphthenic hydrocarbons are more knock resistant than normal paraffins or paraffins with few branches and the same number of carbon atoms. Centralization of the molecules and rearrangement of long side chains into several short branches improves the knock resistance and so does the transition from naphthenic to unsaturated naphthenic hydrocarbons.

4. Aromatic hydrocarbons form a separate type of particularly knock resistant compounds. Hydrogenation of the benzene ring diminishes the knock resistance. The knowledge of the octane number has been the base for manufacturing over 100 industrial gasolines for automobiles and for the preparation of synthetic high class gasoline to be blended as knock resistant component with poorer gasolines.

The determination of the knock stability of Diesel fuel is a problem which is still not solved. Some Russian investigators carried out experiments to synthesize the paraffinic, aromatic and naphthenic hydrocarbons of a structure from C_{12} to C_{25} .

It could be expected that the ignition properties (readiness to ignite), as dependent upon the structure of these hydrocarbons, would be of approximately the reverse order as compared to the hydrocarbon components contained in gasoline. Determination and knowledge of the cetane numbers of the various classes and structures of hydrocarbons appears as an important and practical auxiliary for the evaluation of the knock stability.

For the choice of their experiments on synthesis the Russian investigators therefore gave attention not only to the igniting qualities, but also to the pour points of the synthetic hydrocarbons. In this latter respect the literature contains only an incomplete list of references.

About 30 synthetic hydrocarbons were prepared, many of them for the first time. The method of preparation will be dealt with in another paper to be published later.

The characteristics of these synthetic hydrocarbons are briefly described with reference to a series of tables. (Frames 203-207). The text of Frame 201-202 is so poorly legible that the content could not be abstracted.

1941

Frame 208-227

2. AN ABSTRACT FROM "OCTANE NUMBER RELATIONS OF ALIPHATIC, ALICYCLIC, MONOCYCLIC, AROMATIC HYDROCARBONS, ALCOHOLS, ETHERS AND KETONES" (FROM A PAPER BY EGLOFF AND ARDELL, IN J. INST. PETROL. TECHN. 27, 122 (1941))

A brief historical sketch of the development of octane rating of motor fuels is presented. Frame 209 illustrates methods of determining the octane rating of hydrocarbons in the boiling range of gasoline with a CFR engine. Several rules are derived concerning the relations between the octane number and the structure of the respective hydrocarbons. They are in essence:

1. The longer the carbon chain of the organic molecule, the lower the octane number.
2. Branched aliphatic compounds have a higher octane number than the corresponding normal hydrocarbons, so monomethyl isomers, and still more so dimethyl isomers have a higher octane rating. The isomers containing the methyl group in a central position have a higher octane number as compared to isomers in which the methyl group is allocated at the end of the chain.
3. A quaternary carbon atom increases the octane number when it is located at the end of the chain.
4. Methyl substitution in cyclic compounds with a definite number of carbon atoms lowers the octane number, whereas the introduction of methyl groups into chains with a definite number of C atoms increases the octane number, n-butane is an exception, the octane number of 2-methyl butane being lower.

5. In hydrocarbons of the cyclohexane group substitution in o-m-or p-position lowers the octane number, the more so the farther the substituents are removed from each other; whereas for the benzene series this rule applies in reverse.

6. With the exception of ethyl alcohol the increase of the length of the carbon chain lowers the octane number of alcohols. Up to butyl alcohol inclusive the OH group appears to lower the octane number as compared to normal hydrocarbons. The octane number of amyl alcohol, however, is higher than that of n-pentane. It has not yet been ascertained whether the reverse of this rule applied also to the next higher members in the boiling range of gasoline. The rule established for hydrocarbons, stating that branching of the chain increases the octane number, applies also to alcohols.

7. The thermal stability of pure normal paraffins is inversely proportional to the length of the carbon chain.

8. The higher the carbon content of the paraffin, the lower is the initial combustion temperature.

9. The critical compression ratio of pure normal paraffins is inversely proportional to the chain length, i.e. the lowest members of the chain have the highest critical compression ratio.

These rules are discussed with reference to the experimental material contained in the tables. Some pertinent literature references are quoted.

July 1, 1940

Frame 228

3. PHYSICAL DATA OF SOME HYDROCARBONS

This is an isolated table with physical data on hydrocarbons.

March 16, 1944

Frame 229-237

4. THE MOST IMPORTANT DATA AND METHODS FOR THE PREPARATION OF SOME ISOPARAFFINS WITH PARTICULAR REGARD TO THEIR USE AS MOTOR FUEL

These data are presented in several tables which contain also a scheme of the method of preparation, for example, chlorination, hydrogenation, etc. No other details are given in the text.

Sept. 1933

Frame 238-244

5. VAPOR PRESSURES OF SOME HYDROCARBONS AS A FUNCTION OF THE TEMPERATURE.

This is a series of charts and tables illustrating these relations without any other text than that contained in the tables.

June 1, 1941

Frame 245

6. SUPER-CHARGE KNOCK RESISTANCE OF VARIOUS AROMATICS.

This is a list of data assembled from experiments in the B.M.W. 132 1 cylinder test engine. The experimental conditions are very briefly discussed.

Feb. 1, 1941

Frame 246-249

7. THE DEPENDENCE OF THE MIXED OCTANE NUMBER OF THE BASIC GASOLINE.

Since the octane number of gasoline mixtures can not be represented as a linear function the concept of the "mixed octane number" was established which is variable according to the concentrations.

Starting from the hypothesis that two basic gasolines with the same octane number give a gasoline mixture which have the same octane number, it has been experimentally proved that the octane number of a gasoline mixture depends on the concentration and the octane number of the basic gasolines which constitute the mixture. By calculation of the octane number for the constituting components it is possible to calculate the octane number for mixtures of 3 and more gasolines. Some charts illustrate such octane number relations of various mixtures and are briefly discussed.

Jan. 6, 1941

Frame 250

8. THE TEMPERATURE DEPENDENCE OF NAPHTHENES.

This relation is illustrated by a table without additional text.

Dec. 7, 1940

Frame 251

9. KNOCK BEHAVIOUR OF FUEL MIXTURES

The influence of mixing pure hydrocarbons on the octane rating of the mixture has not yet been studied extensively. It can be said that the knock resistance is not an additive function of the two knock resistances of the components of a binary mixture, it cannot be derived from the mixing rule. For example mixtures of pure benzene, which in itself is very knock resistant, are less knock resistant than corresponding mixtures with iso-octane or dicyclopentadiene unless the percentage of benzene used is more than 80%.

20% of cyclopentadiene added to iso-octane result in a knock rating equivalent to that of pure dicyclopentadiene.

Paraffins behave differently in pure state as compared to their state in solutions. 2,2,3- and 2,2,4-trimethylpentanes in spite of their very similar structure have a different octane number in pure state, but have the same octane number in molar solution.

The saturated naphthenes can be compared to the paraffins. The unsaturated pure naphthenes have a low octane number which increases by 3 to 4 times in mixtures. The mixing properties of hydrocarbons derived from benzene

are not as characteristic as those of paraffins and naphthenes.

Dec. 5, 1940

Frame 252-261

10. OCTANE NUMBERS OF AROMATICS.

As illustrated by some curve charts the octane number of benzene homologs increases with increasing atomic weight, reaches a maximum and then declines again. With the number of side chains the octane number rises, and decreases as the length of the chain increases, at least starting from propyl benzene. The decrease is more noticeable for n-homologs than for iso compounds. The mixed octane numbers are higher than the pure octane numbers, and the more so the higher the octane number.

When examining hydrocarbons with an equal number of C atoms concerning the position of their side chains and their relation to the benzene nucleus (see curve in chart), it can be seen that the octane number decreases from the o-position over the m- to the p-position. With three side chains the 1.3.5.-position gives a higher octane number than the 1.3.4.-position. The more C atoms are contained in the side chain, the lower are the octane ratings of the o-m- and p-positions, unbranched chains have lower octane ratings than branched chains with exception of isopropylbenzene as compared to n-propylbenzene. When the C atoms are evenly distributed over two side chains the octane number is higher as compared to two chains of different length. The text is illustrated by a table with mixed octane numbers and several charts.

Dec. 5, 1940

Frame 262-274

11. OCTANE NUMBER OF NAPHTHENES.

When naphthenes are examined in the order of their increasing molecular weight (see chart) it can be seen that the mixed octane number decreases greatly with increasing size of the ring. With one unbranched side chain the octane numbers of the 5 and 6 membered ring decrease and are higher for 6 ring compounds than for 5 ring compounds having the same number of C atoms. Up to tert-butylbenzene (this probably should read tert.but.cyclohexane) increased branching of the side chain increases the octane number, whereas it decreases it for the higher homologs. This behaviour is analogous to that observed in aromatic compounds. However, in contrast the increase of the side chains from 1 to 2 or 3 side chains does not increase the octane number but reduces it.

Nevertheless, in analogy with the aromatics the octane number for compounds with equal molecular weight and a larger number of side chains is higher as compared to those with fewer but longer side chains. In contrast with the aromatics no increase of the octane number occurs when the C atoms are evenly distributed over the side chains instead of forming side chains of varying length.

Changing of the side chain from the o-over to the m-to the p-position

causes in general a decrease of the octane number, whereas the reverse applies to aromatics with exception of 1.4-dimethylcyclohexane whose octane number is higher as compared to that of 1.3-compounds. As in the aromatics the octane number is the lower, the more C-atoms are contained in one of the side chains.

The octane number of unsaturated naphthenes are higher than those of saturated naphthenes, but not as high as those of the aromatics with exception of toluene (see curve chart). A table illustrates the effects of changes in the side chain on the octane number of aromatics and naphthenes, several charts with curves illustrate the general relations as discussed above.

Dec. 3, 1940

Frame 275-285

12. OCTANE NUMBERS OF PARAFFINS.

As shown by the chart the octane number decreases in general as the molecular weight increases, with exception of 2.2 dimethylpropane as compared to 2.2-dimethylbutane for which the octane number is higher. The octane numbers of paraffins with branched side chains are higher as compared to such with straight side chains having the same number of C atoms.

The mixed octane number of n-paraffins are higher than the pure octane numbers of the lower members of the series, but they decrease more rapidly than the pure octane numbers on increase of the molecular weights, so that for the higher paraffins the mixed octane numbers are by far lower than the octane numbers of the pure components, and more so, the more the side chain is branched. These relations are illustrated by a number of tables and charts.

June 28, 1940

Frame 286-299

13. COMPOUNDS CONTAINED IN THE LIGHT FRACTIONS OF COAL TARS.

These compounds obtained from high and low temperature coal tars are subdivided into aromatic hydrocarbons, naphthenes, olefins and diolefins, oxygen containing, nitrogen containing, and sulfur containing compounds and are listed in tables giving their name, their structural formulae and boiling points.

June 29, 1940

Frame 299-304

13B. COMPOUNDS OBTAINED FROM CRACKED PETROLEUM.

A list of compounds obtained from fractions up to 200° divided into aromatic hydrocarbons, naphthenes, olefins, oxygen, nitrogen and sulfur containing and cyclic compounds is presented with the names of the compounds, their formulae and boiling points. Frame 304 contains another list of aromatic compounds from fractions up to 200° obtained from coal tars and petroleum and its cracked products.

June 28, 1940

Frame 305-313

14. COMPOUNDS CONTAINED IN THE GASOLINE FRACTIONS OF PETROLEUM.

A table of aromatic compounds of the gasoline fractions up to 150° from

petroleums of various origins is presented, second table of aromatic compounds contained in the gasoline fraction up to 200°, and a third table containing naphthenes in the fraction up to 200°. The tables give the names, structural formulae and boiling points of the substances.

June 17, 1940

Frame 314-321

15. ON THE BEHAVIOUR OF AROMATIC ENGINE FUELS IN THE ENGINE.

1. Behaviour of aromatic fuel with respect to ring sticking. Experience showed that when aromatic fuel or fuel mixtures are used ring sticking can be considerably reduced by special refining. Such refining leads to the development of the aviation benzene V.H.T., 308.

Experiments showed also that on use of benzene fuels the temperatures in the combustion chamber and surrounding parts (pistons, valves, cylinder heads) were much higher as compared to the use of imported gasolines. Moreover benzene tends to form more deposit of soot than gasolines which are richer in hydrogen. These two factors contribute greatly to ring sticking.

Experiments proved that pure toluene had particularly favorable characteristics with respect to ring sticking. Engine experiments in the BMW 132 1 cylinder test engine showed that the combustion temperature of higher aromatic fuels are much lower than those of aviation benzene because the higher aromatics are much richer in hydrogen than benzene.

Comparative engine endurance tests with various fuels in various test engines were made. The results with aromatics which were particularly rich in hydrogen proved very favorable.

2. Knock behaviour of aromatic engine fuel (octane numbers). Whereas up to about four years ago the knock resistance of aviation fuels in Germany was evaluated almost exclusively by the CFR motor method, it has been seen in the meantime that the result obtained by this method were unduly unfavorable for temperature sensitive fuels such as aromatics and alcohols, and that the results obtained by the use of the research method apparently produced more adequate figures. The supercharge method, however, appears to be the best for so-called pressure sensitive fuels. By this method the pressure limits at which finally knocking occurs are determined and form the base of the knock rating.

Since pure aromatics could not be directly investigated in the existing test engines mixed octane numbers of test gasoline mixtures with 50% of various aromatics were determined by calculation. The thus obtained octane numbers however, proved to be an insufficient characteristic for the knock behaviour of aromatic fuels so that only the supercharge limits is a reliable knock rating characteristic.

3. Knock rating of aromatic fuels (supercharge knock rating). Supercharge experiments with various aromatic fuels were conducted and the results were assembled in tables. The supercharge knock rating of aromatics in the

boiling range from 175-200° was lower than for those in the boiling range of 150-175°. Refining with AlCl₃ appeared to have a favorable influence on the supercharge limits. Several comparative tables and charts illustrate the report and many details.

March 30, 1940

Frame 322-323

16. INFLUENCE OF THE LOW BOILING COMPONENTS (BELOW 100°) ON THE KNOCK BEHAVIOUR OF RESIDUAL GASOLINES.

This influence is shown in a comparative table and a chart without other text than contained in the illustrations.

Feb. 15, 1940

Frame 324-326

17. 2,2,3-TRIMETHYLBUTANE AND OTHER BRANCHED HYDROCARBONS OBTAINED BY HYDROGENATION OF TRIALKYLACETIC ACID.

According to literature references isopropylketones (isobutyron) after introduction of a Cl atom (monochloro isobutyron) can be converted into mono-hydroxydiisopropyl ketone or dimethylisopropyl acetic acid by treatment with alkali. When working with aqueous concentrated alkali mainly oxyisobutyron is obtained from the process in addition to some dimethylisopropyl acetic acid, whereas when water is excluded as strictly as possible (by working with powdered caustic soda suspended in dry benzene) dimethylisopropyl acetic acid can be obtained in almost quantitative yield with only some oxyketone as a side product. By this method all the ketones which contain an alkyl radical with a secondary C atom and also a second alkyl radical of any kind whatsoever can be converted into oxyketones or homologs of the trimethyl acetic acid.

Moreover it was ascertained that the oxyketone can be completely converted into trialkyl acetic acid by a second treatment with alkali suspended in benzene in strict absence of water, although the yield of acid is less than from hydrolysis of the chloroketone in absence of water. More details are given on the probable mechanism of the chemical reactions involved. When the process is applied to diisopropylketone (isobutyron) dimethylisopropyl acetic acid is obtained, whose C-structure corresponds to that of the hydrocarbon 2,2,3-trimethylbutane. Since isobutyron is obtained in the process of making butyl oil either directly or as an oxidation product of one of the alcohol fractions and since it is a product of the CO reduction, it might possibly constitute an interesting base for the making of trimethylbutane.

The steps of chlorination of isobutyron and subsequent hydrolysis and conversion into 2,2,3-trimethylbutane and finally the catalytic hydrogenation of the latter are described (catalyst 5058). The unsuitability of other catalysts (7360, 8367) and the possibility of finding other suitable catalysts are discussed and hope is expressed that triptane (2,2,3-trimethylbutane) can thus be obtained from dimethylisopropyl acetic acid (Ni-W catalyst 6718).

Oct. 22, 1946

Frame 327-329

18. PREPARATION OF ISOPARAFFINS, IN PARTICULAR ISOOCTANES.

The excellent knock resistance of multi-branched paraffinic hydrocarbons, particularly of isopentane and iso-octane with an octane rating of 100, lead in U.S.A. to the use of such components for blending aviation gasoline. In Germany, great efforts were made to obtain these hydrocarbons in quantity which is possible since hydrogenated gasoline contains from 65 to 90% of isopentane.

The general method of preparation of iso-octane is by polymerization of unsaturated gases, in particular isobutylene into diisobutylene, for example with phosphoric acid as a catalyst, and subsequent hydrogenation of this unsaturated compound to iso-octane or else by alkylation of isoparaffins in particular of isobutane together with an olefin, preferably n-butylene, to form iso-octanes, with sulfuric acid as a catalyst.

Hydrogenation-, polymerization- and alkylation processes of this type as in operation at Ludwigshafen and Oppau are briefly described and the technical types of product obtained are summarized.

Oct. 30, 1940

Frame 330-338

19. EXPERIMENTS AIMED AT THE PREPARATION OF TRIPTANE AND OTHER ALKYLPARAFFINS.

Triptane or 2.2.3-trimethylbutane is of interest as a substitute for isooctane in aviation gasolines. It has thus far been available only in small quantities by a Grignard reaction, of tertiary butyl chloride and conversion of the resulting butylene magnesium chloride with acetone, which is a reaction of only scientific but not of technical application. Therefore, simpler methods of preparation were studied.

1. Conversion of the hydrocarbon by the Grignard reaction, conversion of the resulting 2.2-trimethyl-butynol to trimethylbutane (alumina catalyst) or hydrogenation of the alcohol with a sulfide catalyst (5058 and 6718) directly to triptane. Trimethylbutene could also be quantitatively hydrogenated to triptane.

2. Alkylation of isobutane and propylene with sulfuric acid. Autoclave experiments yielded triptane, the scheme of the reaction and the results are described.

3. Alkylation of isobutane and propylene in the presence of $AlCl_3$ and $AlCl_3 \cdot NaCl$ (complex salt). Autoclave experiments to this purpose gave no definite results, but are being continued, in particular the use of the complex salt catalyst appears to be promising.

4. Hydrogenation of dimethylvaleraldehyde and dimethylol and butylaldehyde. Condensation of isovaleraldehyde with two moles of formaldehyde gives

2,2 dimethylisovaleraldehyde. Although the latter could not be directly converted to triptane, other useful reactions are described leading to 2,3-dimethylbutane and isohexane.

5. Oxonization of isobutylene to isovaleraldehyde, condensation with 1 mole of formaldehyde to isopropyl acrolein with subsequent hydrogenation to 2,3-dimethylbutanol-1 (Co catalyst). This alcohol is converted to 2,3-dimethylbutane with an alumina catalyst at 300°. Variations of these methods are also discussed.

6. Hydrocarbon synthesis by aldolization of aldehydes with subsequent hydrogenation of the aldol. 2 moles of aldehyde are aldolized to 1 mole of aldol by treatment with weak alkalies (NaOH, K₂CO₃). The trimethyl acetaldehyde obtained by oxonization of isobutylene in the presence of catalytic quantities of K₂CO₃ was aldolized with i-butyraldehyde by refluxing for several hours. The resulting aldol is hydrogenated; variations of this process and schemes of reaction are described.

March 13, 1940

Frame 339-350

20. RARELY ENCOUNTERED COMPONENTS OF COAL TAR

(On the results of coal tar research of the last 30 years, Angew. Chem. 53, 69).

A list of compounds - evidently taken from the German paper quoted - which are sometimes contained in coal tar is presented, giving the names, structural formulae, melting and boiling points of these compounds without further description.

July 7, 1943

Frame 351-352

21. SOME CONDENSATION REACTIONS OCCURRING IN HYDROGENATION PROCESSES AT NORMAL AND ELEVATED PRESSURE.

In some hydrogenation - and dehydrogenation processes - a side reaction takes place with condensation of small molecules to large molecules. Among such side reactions condensed ring system may be formed according to the following scheme: isomerization on conversion of hydrogenated 6 rings into 5 rings with subsequent condensation to aromatic hydrocarbons.

Some possible schemes of such reactions and examples are briefly outlined.

III.

LABORATORY FOR HIGH PRESSURE EXPERIMENTS, FILES OF DR. PETERS, PAPERS ON MOTOR FUELS

Nov. 23, 1942

Frame 353-365

1. SOME SUGGESTIONS FOR AVIATION ENGINE DESIGN BY THE FUEL MANUFACTURER.

This is the rough draft of a lecture, so to speak an answer to a lecture given previously in 1939 on "Suggestions of the engine designer to the fuel manufacturer".

The author reviews the development of the quality and octane rating of motor fuels and points out that in many respects the efficiency of the engine can be greatly improved by relatively small constructional changes which are often much simpler than changes in the fuel composition which are limited by the natural properties of the fuels. The efficient and uniform cooling of the engine constitutes a major problem, overheating of certain engine parts or points, for example at the outlet valves, is often responsible for engine failure and should be avoided. Attention should be given to the further development of engines with slide valves, which had good success in England and avoid much of the overheating trouble of the valves occurring in ordinary engines. It may also help to cool the super-charge air because this would help to lower the combustion temperature in the engine. This appears important for example with respect to lead corrosion, which becomes dangerous at combustion temperatures at above 700°C, high combustion temperatures also reduce the knock stability of fuels to a great extent. The right timing of the ignition and injection processes also requires due attention, and possibly cooling of the pistons might be advisable. Many relations between fuel properties and engine operations in general are dealt with.

Feb. 18, 1943

Frame 366-373

2. SUGGESTION FOR THE COMPOSITION OF SYNTHETIC ENGINE FUEL MIXTURES AS STANDARD TEST FUEL FOR SUPERCHARGE ENGINE TEST.

In connection with a D.V.L. conference in Berlin on June 16-17 1941 and with a suggestion by Dr. Pier to use a Standard Test Fuel for super-charge tests, some suggestions for the composition of such a Standard fuel are made which must be tested and corrected as far as necessary by practical test engine experiments.

The test gasolines previously used are briefly reviewed. Most of them are characterized by their trade mark and octane ratings. The components for the new mixtures are also described by their trade marks or octane numbers.

Among others a special mixture of aromatics containing 15% by weight of benzene, 40% of toluene, 30% of xylene and ethylbenzene and 15% of higher aromatics is recommended.

Oct. 31, 1941

Frame 374-390

3. INVESTIGATIONS OF THE COMPOSITIONS OF GASOLINES.
(Literature review)

Whereas no systematic treatise on the composition of gasoline exists many papers have been published dealing with special problems, such as the determination of chemical and physical characteristics of hydrocarbons, the determination of aromatics by refractive measurements and spectrographic method, etc. The various hydrocarbons occurring in the various temperature fractions are summarized with literature references. The special literature dealing with some pertinent problems and characteristics is cited.

Feb. 8, 1941

Frame 391-395

4. KNOCK RATING CURVES OF MIXTURES OF ALCOHOL AND GASOLINE.

The knock ratings of mixtures of gasolines and alcohol in various ratios were checked because they were lower than expected. A brief description of the method applied to the theoretical calculation of the knock rating of these mixtures is given and the possible reasons for the deviation of the experimentally obtained octane numbers from the theoretically knock ratings are pointed out.

Jan. 23, 1941

Frame 396-400

5. EVALUATION OF THE C.V.L. METHOD FOR SUPER-CHARGE TESTS WITH VARIABLE AND CONSTANT IGNITION.

The method for the determination of knock ratings in the test engine was originally designed for experiments with variable ignition. The ignition was adjusted to the fuel so as to give the engine its optimum efficiency, taking into consideration the combustion time necessary for the flame to pass from the ignition point to the upper dead point. Different adjustment of the ignition was necessary for the faster burning rich mixtures in contrast to poorer mixtures with a slower rate of combustion.

In order to simplify the measurements recent test experiments were made for the determination of knock ratings with fixed ignition. This method worked satisfactorily for the richer mixtures because the ignition was approximately adjusted correctly for the combustion time required by rich mixtures for the passage of the flame from the ignition point to the upper dead point. For poorer mixtures however the ignition was by far too late and produced a distorted and unduly unfavorable result. Consequently it was concluded advisable to return to the former method of testing with variable ignition.

Jan. 20, 1941

Frame 401-405

6. THE EVALUATION OF SUPER CHARGE KNOCK-RATING CURVES AND THE ERROR LIMITS OF THEIR DETERMINATION.

The theoretical error limits of the determination of super charge knock ratings are outlined, consisting in the possible errors concerning the octane number of the individual fuel components in addition to some operational factors which might distort the test result, such as hot points in the engine leading to premature ignition, etc.

The conclusion is stressed, that this method of evaluation can only give indications of the fuel properties, but never furnish definite proof in this respect.

Dec. 12, 1940

Frame 406-416

7. CALCULATION OF THE COMPRESSION AND COMBUSTION TEMPERATURE OF BENZENE AND ISO OCTANE-AIR MIXTURES AS DEPENDENT ON THE EXCESS AIR.

Exact knowledge of the compression and the combustion temperatures is required for the calculation of the theoretical super-charge knock ratings and knock rating curves of fuels. The method and formulae for such calculations are developed and the results obtained are assembled in several tables and charts.

Dec. 6, 1940

Frame 417-428

8. THE THEORETICAL EVALUATION OF SUPER-CHARGE KNOCK RATING CURVES.

Compression and combustion temperatures and compression and combustion pressures for iso-octane and benzene were calculated, assuming the compression ratio $\lambda = 8$, a super-charge pressure of 1.4 atm. and super-charge air temperatures of 80° and 130°C. With both substances the compression temperature and accordingly also the final compression pressures increase almost in proportion to the increase of excess air. The combustion temperatures (in agreement with the combustion pressures) exhibit a maximum in the range of $\lambda = 0.8-1.0$. This maximum is different for the two substances under investigation and varied for both when the temperature of the super-charge air was raised from 80 to 130°. Super-charge curves were plotted for benzene and iso-octane for super-charge air temperature of 80 and 130° respectively, using the figures calculated by Jost for spontaneous ignition as dependent on the temperature. The resulting picture of the curves gives of course only a relative and not an absolute picture. A scale proportional to the charge pressure was chosen as ordinate. Several simplifying assumptions were made for the calculation, for example the heat of conductance was neglected. Nevertheless some characteristics could be read from the resulting curves.

IV.

LABORATORY FOR HIGH PRESSURE EXPERIMENTS, FILES OF DR. PETERS, PAPERS ON GASES FORMED ON HYDROGENATION OF COAL

Feb. 5, 1944

Frame 429-432

1. GASEOUS PRODUCTS FROM THE HYDROGENATION OF COAL.

Some tables and charts are presented listing the properties of some coals cracked at 600 atm. hydrogen pressure in a 10 liter oven in the presence of iron catalysts. Regarding the formation of gaseous products (carbon gasification)

the following relation is established: the ratio of the hydrocarbon gasification as compared to the total gasification increases with the increase of the C numbers of the pure coal. Values of lignite corresponded approximately to the figures extrapolated from coal, but as only 2 lignites were investigated no general conclusions can be drawn.

Oxygen gasification (percentage of O in CO and CO₂ referred to pure coal). The O oxygen gasification decreases with increasing C content of the pure coal. Represented in a curve the curvature of this curve-only in the opposite sense-is the same as for the hydrocarbon gasification so that decrease of the gasification (increase for hydrogen gasification) diminishes steadily with rising C content. This clear dependence of the oxygen gasification on the C content of the pure coal does not exist for mineral coal. Calculated values for mineral coal from Silesia indicated a decrease of the oxygen gasification with rising C content of the pure coal, the high values found for lignite appeared to indicate the general existence of such a relation because up to 70% of the oxygen is eliminated from lignite in the form of CO and CO₂, whereas the corresponding figure for mineral coal is about 25%.

Oct. 19, 1942

Frame 433-435

2. ON HYDROGENATION GASES.

In addition to the utilization of the gaseous products of the catalytic hydrogenation under extreme pressure for the production of hydrogen by further cracking, the gaseous hydrocarbons and the use of propane and butane for heating gases, the preparation of iso-octane and alkyl-octane from the butene components of these gases has become of particular importance during the war, so that the quantity and composition of the hydrogenation gases deserve renewed interest. The report contains a table of various starting materials and the respective gaseous products resulting from hydrogenation either in the liquid (slump) phase or the gaseous phase.

The liquid phase process is generally used for 3 types of raw material, mineral coal, lignite and petroleum residues. The quantity of gaseous products obtained increases from the petroleum residues over the lignite to mineral coal, for which it is largest, in accordance with the difficulty of hydrogenation. A large portion of the gaseous products from the liquid phase process consists of hydrocarbons containing 1-3 C atoms, whereas the butane component is comparatively small.

The products resulting from the liquid phase cracking are subjected to various processes of hydrogenation in the gaseous phase and accordingly yield varying amounts of gaseous products in addition to the main products. The smallest amounts of gaseous by-products is obtained in the process of making motor gasolines and Diesel oils. In the process of making merely motor gasoline from medium oils and liquid phase gasolines an amount of about 10% of gaseous products is obtained. In the process of making aviation benzene the cutting point is lowered from 185° to 146°, 4% of butane which are tolerable in motor gasolines are eliminated by distillation, so that the yield of gaseous by-product

is almost twice that resulting from the making of motor gasoline.

As compared with the liquid phase process the gaseous products from the gaseous phase (with a dilute bleaching earth Tungsten catalyst 6434) consist mostly of C₄ hydrocarbons, whereas only comparatively small amounts of methane, ethane and propane, are obtained, so that the composition shows almost the reverse ratio of components.

This contrast illustrates the selective activity of the catalysts present in the gaseous phase in high concentration, whereas in the liquid phase much smaller concentrations of less active catalysts are used.

The ratio of normal butane to iso-butane in the C₄ component from the gaseous phase is much more favorable than from the liquid phase, because the butane from the gasoline step (gaseous phase) contains three quarters of the iso-butane needed for the production of iso-octane.

The formerly applied preparation of iso-octane by dehydrogenation of iso-butane, polymerization of iso-butylene to di-isobutylene and hydrogenation to iso-octane will be increasingly substituted by the much simpler alkylation of iso-butane with normal butylene which requires merely dehydrogenation of the normal butane.

Dec. 1941

Frame 436-446

3. GAS HYDRATES.

Starting from data obtained from various hydrogenation plants calculations of the possible formation of gas hydrates in the liquid phase and gaseous phase processes were made. The details of this calculation are described and the results are assembled in tables and charts. The question was studied with respect to possible clogging of pipes by forming hydrates.

April 10, 1940

Frame 447-459

4. COMPOSITION OF GASES RESULTING FROM MANUFACTURING PROCESSES OF GASOLINE AND AROMATICS.

A series of 123 experiments, gas analyses with a Podielnak column, was examined in order to find rules for the composition of the hydrogenation gas. The experiments were divided into five groups according to the end products and the pressures applied; the results of each group were studied separately and the ratios of the various components contained in the hydrogenation gaseous are discussed and illustrated by tables and charts.

Jan. 3, 1941

Frame 460-467

5. TOTAL BUTANE AND ISO-BUTANE CONTENT IN THE GASEOUS PRODUCTS FROM CATALYTIC HYDROGENATION UNDER PRESSURE AS DEPENDENT OF THE OPERATING CONDITIONS.

These relations were investigated, but the material available is termed insufficient for definite conclusions. Some preliminarily established relations

are discussed. They appear to be dependent on the variations of temperature, the degree of cracking, the pressure, the nature of the catalyst used and the nature of the product obtained.

Nov. 23, 1940

Frame 468-470

6. RATIO OF THE HYDROCARBON COMPONENTS IN THE GASIFICATION PRODUCTS OF HYDROGENATION IN THE LIQUID PHASE AND IN THE GASEOUS PHASE.

These ratios are given in a series of tables without explanatory text.

April 10, 1942

Frame 471-475

7. REPORT ON A CONFERENCE OF THE HYDROCARBON COMMITTEE AT LUDWIGSHAFEN FROM MARCH 16-18, 1942.

Very brief and concentrated reports are given on various subjects.

1. The dehydrogenation of iso-butane as conducted in the plants at Leuna, Scholven and Poelitz are outlined and the technical differences are pointed out and evaluated.

The dehydrogenation of n-butane in pilot plant experiments with a fixed bed catalyst at Leuna are described. A brief sketch of the method and of the catalyst preparation is given. From the results obtained data and conclusions are derived for future large scale operations.

Other laboratory experiments of a similar nature are described which were made at Oppau with catalysts obtained from Leuna. The results are assembled in a table. In connection with these dehydrogenation experiments a wash process with a solution of $AgNO_3$ was tried out, aimed at improving the octane rating of the gasoline obtained. The result was considered favorable, but commercial scale operation of the process which is briefly described appears too expensive.

April 15, 1943

Frame 475

8. TUNGSTEN SULFIDE AS AN ISOMERIZATION CATALYST FOR BUTANE.

This is a note describing the operating conditions with this catalyst WS_2 , 5058, which is said to be the most active of a series of catalyst investigated such as 6434, WS_2 precipitated on bleaching earth pretreated with HF, which gave no isomerization results. Next to the WS_2 catalyst WO_3 plus Cu are mentioned as good catalysts.

Jan. 24, 1941

Frame 477-480

9. YIELD OF HY-GAS FROM HYDROGENATION OF RUHR COAL TO GASOLINE OR HEATING OIL PLUS GASOLINE.

These are tables illustrating the percentage and quantities of the various hydrocarbon constituents in the gases. Another table lists auxiliary factors useful for the calculation of the hourly hydrocarbon production from the data in table 2 and other comparative tables.

Dec. 18, 1940

Frame 481-489

10. ISOMERIZATION OF n-BUTANE AND n-PENTANE.

For this type of isomerization mostly halogen salts of aluminum such as $AlCl_3$ and $AlBr_3$ were used as catalysts, the catalyst activity could be increased by traces of hydro halogen acids, water or addition of halogen alkyls. The use of the latter leads to the splitting of hydrohalogen acids from Al halogen salts. The catalyst activity is illustrated by a comparative table, the activity and effect of the catalyst is discussed in some details, particular attention is given to their isomerization effect for n-butane and n-pentane. The text gives some literature references and contains also some general outlines on the mechanism of the reactions involved and remarks on the use of other catalysts (table 481-489).

Jan. 6, 1942

Frame 490-495

11. DEHYDROGENATION OF n-BUTANE WITH GAS CIRCULATION AT ATMOSPHERIC PRESSURE.

n-Butane was dehydrogenated at atmospheric pressure and 540° in a 1 liter oven, using a catalyst $Al_2O_3-K_2Cr_2O_7$. The negative heat of reaction was produced by heat circulation of about the 20-40 fold amount of the fresh gas throughput through the contact space.

The butane conversion was 36.8% or 31.8% respectively (after deduction of 5% of butylene in the fresh butane). The selectivity was 87-96.6%. In order to obtain the same ratio of conversion the throughput of fresh gas should be somewhat smaller as compared to operation without gas circulation, the difference is probably due to a drop of temperature in the catalyst.

A table with comparative figures for a variety of operating conditions is given. These figures are given for cost calculation purposes. The details of the experiments are described and discussed and the results are assembled in two other tables. A sketch of the oven is given in Frame 494.

Sept. 12, 1941

Frame 496-500

12. DEHYDROGENATION OF n-BUTANE AT ATMOSPHERIC PRESSURE WITH A CATALYST FROM OPPAU.

These experiments were made with a fixed bed catalyst identified as 8417, being an alumina bichromate combination, in a 100 cc oven in order to study the selectivity and some other data, such as the ratio of conversion, etc. The experiments and results are described and assembled in a table and a chart.

April 5, 1940

Frame 501-522

13. ADSORPTION AND DESORPTION.

A general description of this method of very effective separation of mixtures of various gases is given. It was used and developed first for the inert gases which are adsorbed at temperatures near their critical temperature

by absorbing agents as for example activated charcoal, and which are later successfully desorbed at rising temperatures. The desorption temperatures are sufficiently different for the various gases to allow a very fine separation. The adsorption is strong enough to exclude any desorption in the intermediate temperature ranges between the adsorption and desorption temperatures.

Whereas the laws governing adsorption and desorption of the inert gases are rather simple, they are much more complicated for other gas mixtures, in particular hydrocarbons, as the adsorbing forces of the adsorbing agent and the chemical forces of the contacting molecules tend to interact. However, the principles of adsorption and desorption have been developed and can be successfully applied for the separation of all kinds of gases. It is possible to increase the selectivity of an adsorbing agent, for example by precharging it with a certain gas. Another method to increase the selectivity is for example the use of wash gases, resulting in a lower partial pressure of the gas to be adsorbed.

Finally the use of various adsorbing agents of different selectivity constitutes a valuable auxiliary of this method.

The author quotes a series of interesting examples and discusses some theoretical problems of the adsorption and desorption technique.

Frames 521-522 contain literature references pertinent to the problem.

V.

LABORATORY FOR HIGH PRESSURE EXPERIMENTS, FILES OF DR. PETERS,
PAPERS ON CATALYTIC THEORIES AND GAS PHASE CATALYSTS

May 27, 1943

Frame 523-524

1. MOLYBDENUM AS AN ACCELERATOR (Abstracts from "Abhandlungen Zur Kenntnis d. Kohle" 11 No. 24, 25, 26, p. 216-245 and 12 No. 18 and 19, p. 183-204).

The first paper by A. J. Patrick gives references on the problem and deals with the reduction of phenol. The catalysts used are divided into two main groups, one for hydrogenation the other for dehydration. The first group includes the oxides and sulfides of Ni, Co, Fe, Cu, the second group comprises AlO_3 , ThO_2 , ZnO and the oxides of the 6th group of the periodic system, Cr, Mo, and U and some of their sulfides.

The second paper by F. Fischer, T. B. Bahr and A. J. Patrick on the catalytic reduction of tarphenols to benzene hydrocarbons deals with the formation of toluene from cresol with MoO_3 as a catalyst at 330° and normal pressure.

The third paper gives a more detailed description of the experiments and substances discussed in the second paper.

The fourth paper deals with the same subject as paper two, but fused MoO_3 was used as a catalyst in the experiments. This catalyst is said to be superior to the powdered MoO_3 used in the experiments described in paper two and three.

The fifth paper on the preparation of pure benzene hydrocarbons from phenols by Bahr reports on experiment with the same fused MoO_3 catalyst and describes the good results obtained.

Frame 525-530

2. HYDROGENATION, DEHYDROGENATION AND CRACKING WITH
Ni, Pt, Pd, Fe, Co AND Cu.

Comparative experimental results are assembled and presented in a series of tables without further description.

June 26, 1943

Frame 531-536

3. TUNGSTEN OXIDES.

This is a report on the preparation and the treatment of various tungsten catalysts, particularly tungsten oxides. The tungsten oxides are listed in a table (Frame 534) with their chemical formulae, X-ray characteristics and electric resistances. These latter were measured with a special apparatus sketched and described on Frame 533. Some details of the report are illegible.

June 24, 1943

Frame 537-538

4. MECHANISM OF THE ACTIVATION OF THE CATALYTIC SURFACES.

This is an abstract from a paper on this subject by Taylor in Proc. Roy. Soc. (A.) 113 (1926) p. 77.

The author explains that the surface of a catalyst does not participate uniformly in chemical reactions and that its activity may to a large extent be influenced by the chemical energy and action of special atom groups located at particularly activated places of the catalyst surface.

The effect of a promoter on the surface of a nickel catalyst is described as an example, another example describes the poisoning effect of hydrogen atoms accumulated on the surface of a hydrogenation catalyst. Equations for the calculation of the so-called real and apparent activation heat are derived.

May 23, 1943

Frame 539-540

5. A THEORY OF THE CATALYTIC SURFACES.

This is an abstract from a paper on this subject by Taylor in Proc. Roy. Soc. (A) 108 (1925) p.103.

According to a theory developed by Langmuir catalyst surfaces contain certain regions with adsorbed atoms or molecules which are of particular influence on the catalyst activity. In general the activity of a catalyst is

determined by the arrangement and distances of the surface atoms. The theory on the activity of catalyst surfaces is described in some detail.

1943

Frame 541-547

5A. HETEROGENOUS CATALYSTS.

This is an abstract from a treatise by Schwab on "Katalyse von Standpunkt der Chemischen Kinetik". The theory of adsorption is developed and equations for the state of equilibrium and the heat of adsorption, based on principles put forth by Langmuir, are derived.

The more complicated kinetics of heterogenous catalytic reactions are discussed and explained by examples, the theoretical processes (equations) are developed.

Some special cases, such as a decrease of catalyst activity due to reaction products and the simultaneous adsorption of two different gases, are discussed.

Other sections of the paper refer to the reduction of the heat of activation, to the selectivity, the properties and behaviour of catalysts and of some catalyst combinations.

March 19, 1943

Frame 548-549

6. COMPOUND CATALYSTS.

This is a short review of this subject with reference to the pertinent literature. Various definitions and examples for compound catalyst actions are given, and the problems involved are briefly outlined.

May 10, 1943

Frame 550

6A. LITERATURE REFERENCES TO A LECTURE ON CATALYSTS.

(An abstract from "Les Grands Problemes De La Chimie de la houille, p. 178-179" by E. Mertens and J. Massionn, Liege 1941)

Molybdenum and tungsten are mentioned as very resistant catalysts in gaseous phase operations, particularly in the presence of sulfur, which far from poisoning the catalyst, acts even as an activator for molybdenum oxide.

Molybdenum trisulfide is even more active than the disulfide or the oxide, but is not always stable under the conditions of destructive dehydrogenation, unless in the presence of a certain partial pressure of H_2S . To this end a certain percentage of S or H_2S may be added either to the hydrogenation product or to the hydrogen used for dehydrogenation.

X-ray investigation on molybdenum trisulfide showed that conversion to the disulfide is accompanied by basic structural changes. The former compound has a micro crystalline structure, whereas the latter obtained from it by heating has a perfect crystalline structure. Since this crystallization diminishes the catalyst activity, experiments were made aimed at inhibiting the formation of

crystals by the addition of various additives, such as chromium-and aluminum oxide and silica. These additives, however, proved ineffective, whereas the addition of phosphorus ammonia molybdate increased the catalyst activity considerably.

Jan. 21, 1941

Frame 551-552

7. DRYING OF CV₂b WITH SILICA GEL, (File note on a discussion concerning silica gel at Oppau 299)

Dr. Urban reported on a project to dry CV₂g, because it caused corrosion in the tank cars and storage tanks when transported and stored without drying. The projected drying process provides drying of the material while it is filled into the tank cars, which requires about 8 minutes per carload of 15 tons. It is intended to pass the material alternately through two towers of 1-1.5 m³ each, packed with silica gel, so that one tower is in action for drying, while the other is being regenerated. The regeneration (drying) is effected by blowing out at 100-180°. The slight browning of the silica gel by polymerization as it was observed in laboratory experiments is not supposed to affect its absorbing power for water. After 10 or more regenerations reactivation of the gel by blowing with air at 400-500° and burning of the polymerization products becomes necessary. More details are discussed with respect to other plants and the possibility of using activated alumina instead of silica gel. Experiments in this latter direction are planned.

Nov. 27, 1940

Frame 553-561

8. SURVEY OF THE LITERATURE ON THE OXIDATION OF HYDROCARBONS IN THE PRESENCE OF CATALYSTS.

The pertinent literature references are assembled in some tables which list also the type of substances oxidized, the catalyst used and the experimental conditions as well as the resulting products.

Some principles of oxidation as developed by the various authors are described.

Nov. 22, 1940

Frame 562-564

9. STUDY OF CATALYSTS SUITABLE FOR THE CONVERSION OF HYDROCARBONS.

These catalyst studies cover four main groups on fields of activity, cracking, dehydrogenation, cyclization and isomerization or polymerization.

1. The chief catalysts of the first group are silicon oxide, SiO₂, and carbon, they can be used as such or activated with Al or Mg, which increases their cracking activity, thus allowing either to reduce the reaction time or to increase the rate of conversion. Since the catalysts when activated with Al or Mg act also as polymerizing catalysts for olefins, their use changes also the composition of the cracked products.

Bleaching earth and iron catalysts are also suitable for cracking, use of the latter leads to formation of large quantities of gaseous products.

2. The chief catalyst of the second group for the purpose of dehydrogenation is Al_2O_3 , combinations with Fe_2O_3 or MgO did not give satisfactory results.

3. The best catalyst for cyclization is a combination of Al_2O_3 with Cr.

4. The good effects of SiO_2 and Al_2O_3 for polymerization have already been mentioned under group 1. They can be used also for the polymerization of gaseous olefins instead of other catalysts such as phosphorus catalysts, used in some industries.

Nov. 22, 1940

Frame 565-566

10. OBSERVATIONS ON CATALYSTS, IN PARTICULAR ON CRACKING CATALYSTS.

These are a few isolated remarks on some metal catalysts for cracking when used under certain operational conditions, and the resulting effects on the composition of the cracked products.

Jan. 13, 1944

Frame 567-571

11. ON THE ATOMIC STRUCTURE OF TUNGSTEN-AND MOLYBDENUM SULFIDES

Physical investigations of the lattice structure of these compounds have been made, the results of which are assembled in a series of tables and pictures and briefly discussed.

Dec. 17, 1943

Frame 572-574

12. ELECTRON INTERFEROMETRIC INVESTIGATIONS ON ALUMINA CATALYSTS.

These investigations were intended to clarify the relations between the activity of these catalysts and their crystalline structure. X-ray and electron interferometric experiments were carried out and described, including the equipment used. The very technical physical results obtained are discussed and evaluated but considered incomplete because the experimental apparatus was destroyed.

Sept. 7, 1943

Frame 575-579

13. NEW RESULTS ON THE LATTICE DISTURBANCES IN ACTIVE TUNGSTEN SULFIDE.

This is a report on very technical details concerning a series of X-ray photographs of tungsten sulfide and the evaluation of these details regarding the arrangement of the crystal layers within the lattice. The report is illustrated by some figures.