# C-301

# FUEL MANUAL; THE RATING OF OTTO AND DIESEL FUELS

By Kadmer

# PREFACE

The "fuel manual" was written during long winter nights by candlelight, kerosene, or carbide illumination in trenches and field quarters in Soviet Russia. Many chapters of this booklet which is not even called a "book" and, therefore, merely will be called a fuel manual, has been written under interruptions by the enemy approaching in tanks and on snowshoes. This fact is not given at this point to present any excuses for the booklet but merely to indicate that the literature data are not complete, although the author was willing to give credit to any of his colleagues. No doubt, a book written under such circumstances can be supplemented by such an explanation.

The author is indebted to Colonel Luetzow for the interest shown in the work and its development.

Signed,

Eric Herwig Kadmer

Eastern Front 1942

## SYNOPSIS

The wide variety in the working process in an Otto-cycle engine and in a Diesel engine, requires fuels of a special type and justifies a subdivision of the subject into two main parts. Wherever correlations are to be shown, they will be properly mentioned. The working principle of an Otto-cycle engine consists in supplying the cylinder a correctly-adjusted fuel-air mixture. In this cylinder, the mixture is compressed to a certain degree and then burned after spark ignition. The fuel must meet definite requirements of this working method. At present, a large number of liquid substances are known which are used either singly or in a mixture, known as Otto fuels.

As known, in a Diesel engine air alone is taken in a measured amount and compressed. The fuel is then injected into the heated air in the engine cylinder and is burned without any separate ignition. The fact that ignition aids are used in special cases does not change the principle itself. Various liquid products of different origin can be used as Diesel fuels in addition to the "gas oils" of petroleum industry.

Since engines in motorized vehicles on land or in the air make extreme requirements on the engine dimensions and on the power increase per unit weight as far as material and fuel are concerned, the basic principles for evaluating Otto and Diesel fuels in motorized vehicles will be discussed in this pamphlet.

Of the Otto fuels the various benzines are of prime importance. For this reason, a short description of their production and of the characteristics during such manufacture will be discussed. A main component of many Otto fuels is the engine benzene, certain alcohols, and finally any substance used for regulating the combustion process and preventing engine knocking. In the discussion on Diesel fuels, tar oils and products of fuel synthesis will be discussed along with the products of petroleum industry.

The Benzines

"Benzines" include a large number of easily liquefiable and highly volatile hydrocarbons in which the aliphatic hydrocarbons, i.e., the normal and isomeric paraffins and olefins as well as the hydrogen-rich ring hydrocarbons (the naphthenes) prevail over the hydrogen-poor ring hydrocarbons (the aromatics). Benzines are obtained by simple distillation as the highest fraction of petroleum. Such products are known as distillate benzines or topped benzines or also as straight-run benzines. A further less clear concept is the designation "primary benzines". By dissociation distillation of heavy petroleum residues or other products, the so-called cracked benzines are obtained under very definite operating conditions. These benzines are of considerable quantitative importance along with the primary benzines but are generally used in mixtures with distillate benzines to cover the increased demand of carburetor fuels. Wet petroleums, i.e., petroleums containing easily liquefiable hydrocarbons in vapor form, are freed either by washing in heavy benzine, by compression, cooling, or adsorption with activated charcoal, silica gel, gray earth, etc. from these liquid hydrocarbons. These products according to their production, are known as gas benzine or natural gasolines. Dry petroleums and cracked gases are liquefied by polymerization under definite working conditions to result in the highly valuable polymeric benzines which generally are used as an admixture to Otto fuels for aircraft. Carburetion of lignite and bituminous shale were used for carbonizing benzines whose importance with respect to quantity is less than that of other types. The most important synthetic benzines are the benzines obtained by catalytic high-pressure hydrogenation according to the IG method or by catalytic reaction from water gas. Liquefaction under pressure of dry petroleum, cracked gases, and synthetic gases furnishes the so-called "liquid gases" representing benzines with the highest boiling point and used successfully as fuel in automobile engines if certain procedures are applied for their suitable reaction with combustion air.

Engine Benzene

A useful addition to benzines is the engine benzene (however, frequently not sufficiently resistant to low temperatures). This benzene is a product of high-temperature coking of anthracite. Chemically pure or technical benzene is less suitable than "engine benzene" which generally is a mixture of benzene, toluene, and xylene.

Alcohols

The alcohols, especially methyl alcohol (methanol), ethyl alcohol (ethanol), and isopropyl alcohol (or isopropyl ether) are valuable benzine additions for their antiknock characteristics. However, certain drawbacks such as hygroscopicity of the mixtures exist.

Antiknock Fuels

"Antiknock fuels" are additives to benzines or benzine mixtures which, even in a minute quantity, have the characteristic of increasing the compression resistance of Otto fuels. The most commonly used agent is tetraethyl lead or the same substance diluted with diethylene bromide and known under the name of "ethylfluid". Other substances of a similar effect will be discussed and evaluated later in the text.

Diesel Fuels

Diesel fuels are generally fractions of petroleum known as "gas oil", representing less volatile hydrocarbons in a boiling range between 150 - 360° C. Lignite-tar oils in the same boiling range have a lower amount in ignitable change-hydrocarbons than the petroleum products. However, subsequent hydrogenation or treatment with selective solution agents for removing the ignition-resistant aromatic compounds makes it possible to change these substances into useful Diesel fuels. A highly-inflamable product of the Fischer-Tropsch synthesis is known under the name of Kogasin II. Since its use without admixtures would be too expensive, it was attempted to cut it with anthracite-tar oils which generally are used only in stationary slowly-running Diesel engines, for producing fuels suitable for motorized-vehicle Diesel engines. The catalytic high-pressure hydrogenation according to the IG method furnishes a suitable Diesel fuel by distillation of the middle oil. Slight amounts of such a fuel are obtained also by polymerization of the unsaturated hydrocarbons of the hydration gas.

TABLE OF CONTENTS

Page

Part I: Otto Fuels

1. Distillate Benzines .......... 1
  a. Production of Distillate Benzines .......... 1
  b. Composition of Distillate Benzines .......... 1
  c. Refining of Distillate Benzines .......... 1
2. Cracked Benzines .......... 2
  a. Production of Cracked Benzines .......... 2
  b. Composition of Cracked Benzines .......... 2
  c. Resinification in Cracked Benzines .......... 2
  d. Refining of Cracked Benzines .......... 3
  e. Natural Aging of Cracked Benzines .......... 4
  f. Stabilization of Cracked Benzines .......... 4
  g. Reformed Benzine .......... 4
  h. Resinification and Engine .......... 4
3. Natural Gasolines ..........
  a. Natural Gasoline, Petroleum Benzene .......... 5
4. Polymeric Benzine .......... 5
  a. Starting Material .......... 5
  b. Method of Polymerization .......... 6
  c. Characteristics of Polymeric Benzines .......... 6
5. Liquid Gas .......... 7
  a. Composition of Liquid Gas .......... 7
  b. Use of Liquid Gas .......... 7
6. Carbonization Benzines .......... 7
  a. Carbonization Process .......... 7
  b. Characteristics of Carbonization Benzines .......... 8
7. Synthetic Benzines .......... 8
  a. The IG High-Pressure Synthesis .......... 8
  b. The Fischer-Tropsch Synthesis .......... 9
  c. Characteristics of Synthetic Benzines .......... 10
8. Engine Benzine .......... 10
  a. Coking of Anthracite .......... 10
  b. Characteristics of Benzene Hydrocarbons .......... 11
9. Methanol .......... 12
  a. Production of Methyl Alcohol .......... 12
  b. Characteristics of Methyl Alcohol .......... 13
10. Ethanol .......... 13

Page
a. Production of Ethyl Alcohol .......... 13
b. Characteristics of Ethyl Alcohol .......... 14
c. Azeotropic Mixtures .......... 16

11. Ethylfluid .......... 16

a. Tetraethyl Lead .......... 16
b. Ethylfluid .......... 16
c. Tetraethyl-Lead Effect and Leading .......... 17
d. Other Antiknock Agents .......... 20

12. Aviation Benzines .......... 20

a. Basic Benzine .......... 20
b. Aviation Benzines .......... 21
c. Components of Aviation Benzines .......... 21
d. Iso-Octane .......... 21
e. Polymeric Benzine .......... 22
f. Iso-Pentane .......... 22
g. Alcohols, Ethers, and Ketones .......... 23
h. Significance of Octane Rating in Aviation .......... 23
i. Specifications .......... 24
j. Additives and Octane Rating .......... 24
k. Color and Appearance .......... 24

13. Specific Gravity .......... 25

a. Hydrometer .......... 25
b. Pycnometer .......... 25
c. Specific Gravity of Otto Fuels .......... 25
d. Specific Gravity and API .......... 25

14. Distillation .......... 26

a. Characteristics of Pure Hydrocarbons .......... 26
b. Engler Distillation .......... 27
c. Boiling Coefficient .......... 28
d. Boiling Curves .......... 28
e. Evaporation Test .......... 29

15. Vapor Pressure .......... 30

a. Measuring Units of Vapor Pressure .......... 30
b. Vapor-Pressure Determination According to Reid .......... 30
c. Vapor-Pressure Curves, and Vapor-Pressure Values .......... 31
d. Vapor Lock .......... 31
e. Saturation Pressure .......... 32

16. Evaporation Residue .......... 33

a. Gum Test .......... 34
b. Resin Afterformation .......... 34

17. Viscosity .......... 35

18. Low-Temperature Resistance .......... 35

Page

a. Test for Low-Temperature Resistance .... 35

19. Calorific Value .... 35

a. Calculation of the Calorific Value .... 36
b. Calorific-Value and Density Relation .... 36
c. Mixed Calorific Value .... 37
d. Combustion Process and Energy Balance .... 37

20. Heat of Evaporation .... 38

a. Measurement of Heat of Evaporation .... 39

21. Water and Alcohol Content .... 40

a. Water Determination .... 40
b. Water-Miscible Benzine Additives .... 40

22. Sulfur Content and Corrosion .... 40

a. Active and Inactive Sulfur .... 40
b. Doctor Test .... 42
c. Quantitative Determination of Active Sulfur .... 42
d. Quantitative Determination of Total Sulfur .... 42
e. Corrosion Test .... 44

23. Flame Point and Ignition Point, Combustion Range .... 44

a. Flame Point .... 44
b. Ignition Point .... 44
c. Ignition-Value Tester .... 44
d. Explosion Range .... 45

24. Constitution .... 46

a. Unsaturated Hydrocarbons .... 46
b. Aromatic Hydrocarbons .... 46
c. Aniline Point .... 48
d. Naphthenes .... 49
e. Paraffins .... 49
f. Iodine Numbers .... 49
g. Differentiation of Distillates and Cracked Benzines .... 50
h. Peroxides .... 50
i. Refraction .... 50
j. Molecular Weight .... 53
k. Parachor .... 53

25. Engine Behavior .... 55

a. Compression Resistance and Nature of Hydrocarbons .... 55
b. Octane Number .... 55
c. Characteristic of Knocking .... 56
d. Knocking and Engine Design .... 57
e. Knocking and Operating Conditions of the Engine .... 58
f. Testing Engines .... 58
g. IG Testing Engine for Light Fuels .... 59
h. Measuring the Knock Intensity .... 60
i. Antiknock Test in Multicylinder Engine .... 62

Page

j. Road-Antiknock Tests ... 63
k. Comparison of Antiknock Characteristics ... 63
l. Experiments for Calculating the Cetane Number ... 64

26. Determination of Additives ... 65

a. Determination of Tetraethyl Lead ... 65
b. Determination of Iron Carbonyl ... 67
c. Benzene and Other Additives ... 67

Part II: Diesel Fuels

1. Petroleum Diesel Fuels ... 67

a. Distillate Diesel Fuel ... 67
b. Kerosene ... 68
c. Cracked Diesel Oil ... 68
d. Characteristics of Petroleum and Petroleum Diesel Fuels ... 68

2. Lignite Diesel Oil ... 68

a. Carbonization Tar Oil ... 68
b. Hydrogenated Tar Oil ... 69
c. Characteristics of Lignite Diesel Fuels ... 69

3. Anthracite Carbonization Tar Oil ... 69

4. Shale Tar Oil ... 70

5. Kogasin II ... 70

6. Color, Odor, Appearance ... 70

7. Specific Gravity ... 71

a. Specific Gravity and API ... 71
b. Specific Gravity and Hydrogen Content ... 71
c. Specific Gravity and Calorific Value ... 72

8. Distillation ... 72

a. Boiling Curves of Petroleum and Gas Oil, Boiling Points of Hydrocarbons ... 72
b. Temperature Correction and Vacuum Distillation ... 73
c. Boiling Point/Density Constant ... 73

9. Viscosity ... 74

a. Viscosimeter ... 74
b. Viscosity/Density Constant ... 74

10. Low-Temperature Resistance ... 75

a. Pour Point ... 75
b. Filterability at Low Temperatures ... 76

11. Asphalt and Coking Test ... 77

Page
a. Asphalt Test .......... 77
b. Coking Test .......... 78

12. Ash and Water Content .......... 78

13. Calorific Value .......... 79

14. Sulfur Content .......... 79

15. Corrosion .......... 79

a. Neutralization Number .......... 80

16. Storage Property and Miscibility .......... 80

17. Flame Point .......... 81

18. Constitution .......... 81

a. Hydrocarbon Groups .......... 82
b. Aniline Point .......... 82
c. Elementary Analysis .......... 83
d. Molecular Weight .......... 83
e. Surface Tension .......... 84
f. Parachor .......... 84
g. Refraction .......... 84
h. Ring Analysis .......... 85
i. Diesel Index .......... 85

19. Engine Behavior .......... 85

a. Ignition Lag .......... 85
b. Ignition Quality and Nature of Hydrocarbons .......... 87
c. Cetane and Cetene Number .......... 87
d. Ignition Quality, Engine Type, and Operating Conditions .......... 88
e. Testing Engines and Testing Method .......... 89
f. The IG Testing Engine for Heavy Fuels .......... 90
g. Laboratory Methods for Determining Ignition Quality .......... 91

20. Ignition Accelerators .......... 93

21. Appendix: Energy Distribution in Engine and Motorized Vehicle .......... 94

22. Bibliography .......... 95

Author Index .......... 102
Subject Index .......... 104

## LIST OF ILLUSTRATIONS

Fig. 1 Mixed Octane Numbers
Fig. 2 Boiling Curve of Alcohol-Free and Alcohol-Containing Benzine
Fig. 3 C-Fluid Addition to Knocking Benzines
Fig. 4a Oppau Alignment Chart
Fig. 4b Mathematical Lead Sensitivity
Fig. 5 Power Increase and Fuel Consumption in Aircraft Engines
Fig. 6
Fig. 7 Evaporation Curves of Several Light Fuels
Fig. 8 Vapor-Pressure Curves of Several Liquid Substances
Fig. 9 Vapor-Pressure Curves of Several Fuels
Fig. 10 Apparatus for Determining the Saturation Pressure
Fig. 11 Apparatus According to Stelling
Fig. 12 Sulfur Determination According to Grote and Krekeler
Fig. 13a Aniline Point and Boiling Points or Boiling Cross Sections of Hydrocarbons and Their Mixtures
Fig. 13b Diagram by Garner for Determining the Naphthene Content of Benzines
Fig. 14 Boiling Level and Refraction of Hydrocarbons and Automobile Benzine
Fig. 15a Combustion Course at Knock-Free and Knocking Combustion
Fig. 15b Pressure-Time Diagram of Knocking and Knock-Free Combustion in the Otto-Cycle Engine
Fig. 16 Influence of Mixture Preheating on Power of the Otto-Cycle Engine
Fig. 17 Influence of Operating Conditions on Engine Knocking
Fig. 18 Bouncing-Pin Apparatus with Adjustable Bar Spring
Fig. 19a Knock Indication by Cathode-Ray Oscillograph
Fig. 19b Oscillogram (According to Wawrziniok)
Fig. 20a Oscillogram
Fig. 20b Oscillogram (According to Schmidt and Generlich)
Fig. 21 Knock Intensity and Boost
Fig. 22 Critical Values for Knocking

Fig. 23 $n_D$ of Benzine and Pure Benzene Blends

Fig. 24 Boiling Curves of Petroleum and Gas Oil

Fig. 25 Nomogram by Beale and Docksey

Fig. 26a Filterability of Diesel Oils at Low Temperatures

Fig. 26b Filterability of Diesel Fuels

Fig. 27 Conradson Coking Test

Fig. 28 Heat Value (cal/l or cal/kg) of Heavy Fuels

Fig. 29 Relations Between Boiling Cross Section, Aniline Point, Refraction, Density, and Cetane Rating

Fig. 30 Pressure Curve and Ignition Lag in a Diesel Engine

Fig. 31 Decrease of Ignition Lag with Increase in Compression

Fig. 32 Engine Octane Rating and Cetane Rating

Fig. 33 Ratio of Suction Subpressure and Cetene Number in IG Test Diesel

Fig. 34 Calibration Diagram IG Test Diesel

Fig. 35 Density of Cetene Number of Diesel Oils

Fig. 36 Cetone-Number Nomogram by Tannenberger

Fig. 37 Family of Curves of the Boiling Characteristic

Fig. 38 Nomogram by Best

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# FUEL MANUAL; THE RATING OF OTTO AND DIESEL FUELS

## PART I: OTTO FUELS

## 1. DISTILLATE BENZINES

### a. Production of Distillate Benzines

Simple distillation of purified petroleum from stills or pipes without use of vacuum furnishes the distillate or straight-run benzine as the lowest boiling fraction (approximately in the range between 35 and 220°C). Since the removal of benzine hydrocarbons from petroleum is known as "topping", benzine obtained in this manner is marketed under the name "topped benzine". Other expressions used are "primary benzine" or "first-run benzine". To obtain "automobile benzines" from these distillate benzines, the product frequently is redistilled and freed of any components of a high boiling point. In addition, the heavy benzine is removed so that a more narrow distillation sector is obtained. Generally, "light benzines" have a boiling point between 35 and 150°C, while "medium benzines" boil between 40 and 190°C. Aircraft fuels are synthetized on the basis of degased light benzines, while automobile fuels generally are produced from medium benzines. Special benzines represent certain distillation sectors of distillate benzines; for example, extraction benzines in two stages between 60 and 110°C and 80 and 130°C, kerosene 60 - 120°C (with 75% to 100°C), white spirits 120 - 200°C, P & V M Naphtha, (Ligroin) 150 - 210°C, test benzine 130 - 200°C, petroleum ether DAB 40 - 60°C, gasoline 30 - 80°C, surgical benzine DAB at least 80% between 50 - 75°C, and ordinary benzine 65 - 95°C.

### b. Composition of Distillate Benzines

Composition of the distillate benzines differs widely, depending on the origin of the petroleum. It will be completely insufficient to give preliminary data on this item, since the composition of crude petroleums or benzines varies widely even in closely-limited natural sources. For example, in Rumania paraffinic and aromatic benzines are available. In Oklahoma all imaginable compositions occur and the Pennsylvania types and Mid-Continent products have a more paraffinic character only in a general description than the oils and benzines of California, the Gold Coast, and Mexico.

Paraffinic benzines are benzines with a 50 - 75% content of paraffins, 20 - 30% naphthenes, and 5 - 10% aromatic compounds. Naphthenic benzines are benzines with 30 - 40% paraffins, 40 - 60% naphthenes, and 5 - 30% aromatic compounds. In benzines rich in aromatic compounds, the relation shifts to approximately 20 - 40% paraffins, 10 - 30% naphthenes, and 30 - 50% aromatic compounds. Since the antiknock characteristic of benzines increases with the isoparaffin, the aromatic, and the naphthene content while it is rather poor if normal paraffins prevail; the suitability of unblended distillate benzines for Otto fuels to be used in motorized vehicles fluctuates within wide limits. Distillate benzines rich in n-paraffins and low in aromatic and naphthene content, produce considerable knocking and have octane numbers between 45 and 60 in many cases. On the average, distillate benzines have octane ratings between 55 and 65. Only a small number of these benzines, which are rich in isoparaffins or naphthenes or aromatic compounds, can be used in high-quality Otto-cycle engines as distillate benzines with an octane rating between 70 and 76 without requiring compression-increasing additives. An extensive literature on the analyses of straight-run benzines of different origin is given in the "Science of Petroleum", Volume 2.

### c. Refining of Distillate Benzines

In most cases, a redistillation is sufficient for purifying distillate benzines. Only in benzines rich in sulfur of various origin, a washing with lye, or with a small amount of sulfuric acid and lye or else with a so-called "doctor solution" (sodium-lead solution) is used.

## 2. CRACKED BENZINES

### a. Production of Cracked Benzines

The supply of distillate benzines, disregarding their frequently completely insufficient antiknock characteristics, does not cover the demand of motorized vehicles. For this reason, various methods for "cracking" of reflux oils in petroleum industry were developed with the purpose of producing benzines of a special type from a rather poor residue oil. These residue oils or crude oils, which are too poor in quality to be directly converted, are subjected to dissociation distillation in cracking furnaces in a system of superheated pipes at temperatures between 400 and 600°C under a certain pressure. In most cracking methods, the "liquid phase" is used. The distillation is so conducted that a correspondingly high pressure prevents evaporation of the liquid which generally would take place under the given temperature in the oil in question. In cracking in the "vapor phase", the oil to be cracked is first evaporated and the oil vapors are then dissociated. In addition, the cracking process can be catalytically accelerated by using aluminum chloride. In all cases, the cracking process is so controlled that a large amount of benzine along with slight quantities of a carbon-rich oil is obtained. This oil is used as heavy fuel oil. In the cracking distillation, the long-chain molecules of the reflux oils are cracked into short-chain or shorter-chain molecules of a benzine character, and into molecules which can be polymerized, forming a residue with oxygen and sulfur-containing compounds.

### b. Composition of Cracked Benzines

The crude cracked benzines have a much higher content of unsaturated hydrocarbons than the distillate benzines which is a typical characteristic of the fact that cracking has taken place previously. Consequently, such products can be changed chemically. In cracking processes in the "liquid phase", only single unsaturated olefins are formed while diolefins highly reactive as to resinification are formed in cracking processes in the vapor phase. While the olefin content in straight-run benzines generally is not more than 1 - 6%, this amount increases to 15 - 30% in cracked benzines. In addition, the content in aromatic compounds of 15 - 40% is rather high while the naphthenes and paraffins are present in lower percentage. The high content in aromatic and unsaturated compounds results in a higher specific gravity than that of straight-run benzines. Distillate benzines for motorized vehicles generally show a specific gravity of d/20 = 0.720 to 0.760 while cracked benzines of the same boiling point have a gravity of d/20 = 0.755 to 0.780. Naturally, the high content of antiknock components keeps the octane rating of cracked benzines between 60 and 80 and rarely results in an octane number lower than 60. However, the chemical variability of the cracked benzines constitutes a drawback which may be reduced by skilled refining or by additives known as "inhibitors" or "antioxidants". The most unfavorable characteristic of cracked benzines is their tendency to aging under resin formation.

### c. Resinification in Cracked Benzines

The types of resins occurring in cracked benzines can be differentiated as follows:

a) Benzine-insoluble resins;
b) Benzine-soluble or "preformed" resin;
c) Forming or "potential" resins.

Resins no longer soluble in benzine appear in form of voluminous rust-brown floccules in stored or in unrefined or poorly refined cracked benzines. It has never been accurately defined whether the insoluble resins of this type represent a last polymerization stage of the diolefins or a last condensation stage of olefins with organic sulfur and oxygen compounds or whether they are formed by colloid mechanics through coagulation. In any case, these insoluble resins are still readily soluble in alcohol, acetic acid, or acetone and their elementary analysis (according to Sachanen) gives the approximate composition of 70% C, 7% $H_2$, 21% $O_2$, and up to 2% S.

The benzine-dissolved resins in cracked benzines presumably are mixtures of high-molecular acids and other condensation products. The process of resinification until formation of these substances can be grouped into three stages representing the unstable end of a succession of chain reactions. In the first stage, unsaturated hydrocarbons will form peroxides under oxygen addition. These peroxides are decomposed in the second stage into aldehydes and ketones which, in turn, condense in the third stage to "preformed" resins. Gruse gives the composition of such gum resins (actual gums) as follows:

| | %C | %$H_2$ | %$O_2$ | %S | Mol. Weight | Fusion Point |
|---|---|---|---|---|---|---|
| Liquid gum resin | 65 | 8.56 | 26.08 | 0.22 | 172 | - |
| Oily-drying gum | 72 | 8.00 | 19.48 | 0.33 | 338 | 68/71°C |

The potential resins, i.e., the resins in the process of formation, are not real resins but rather unstable hydrocarbons or even different similar compounds. That means, these products are resin formers mainly represented by olefins with aromatic radicals and by diolefins, and hydrocarbons with two double bonds (bibl. 1).

In all cracked benzines, the fraction between 70 and 140°C is especially rich in resin producers. Within this distillation fraction the unstable and, therefore, reactive cracking fractions are located, as shown on investigating the process of cracking. Table 1 shows a general survey on the distribution of these fractions of cracking distillation over the individual fractions, according to indications given by Morell and Egloff (bibl. 2). These fraction components are represented by the unsaturated hydrocarbons (% U) along with a number of other hydrocarbon groups (% A, N, P). For comparison, the relations in a straight-run benzines are shown.

### d. Refining of Cracked Benzines

Since treatment of cracked benzines with sulfuric acid for refining produces considerable losses especially of valuable antiknock components, fuel manufacturers in the USA have developed a process known as the Gray process in which the cracked-benzine vapors are conducted through a dephlegmator after slight acidulation. This dephlegmator is filled with lumps of natural fuller's earth. Naturally-active earths are preferred to synthetic acid-activated earths since the traces of acid in this latter type may produce increased resin formation in the purified benzines. The autocatalysis of acids on unsaturated compounds will be discussed later in the text. The extremely disagreeable penetrant odor of crude cracked benzines generally is due to organic sulfur compounds (mercaptanes, thiophenes). However, it should be mentioned that the lower naphthenic acids, similarly to the lower fatty acids, are extremely disagreeable in odor. Sulfur-rich cracked benzines are successfully treated with sodium plumbite $Na_2PbO_2$ known as a "doctor solution". The reaction mechanism is as follows:

$$2\ NaOH + PbO \rightarrow Na_2PbO + H_2O$$

$$2\ RHS\ (\text{mercaptane}) + Na_2PbO_2 \rightarrow (RS)_2Pb + 2\ NaOH$$

$$(RS)_2Pb + S \rightarrow RS\text{-}SR + PbS$$

If this refining process is used, the products should first be washed with a 1% plumbite solution for removing the sulfur compounds. Then, afterwashing with water, pretreatment with a slight amount of sulfuric acid for removing all humidity, and finally refining with 1 - 3% sulfuric acid at 66° Beaumé with a final washing in lye and redistillation with water vapor should be used. In using sulfuric acid, the reaction should be kept to a moderate rate. It may be possible that sulfonium or other addition compounds are formed which (since they are soluble in acid) enter the acid sludge but are decomposed on washing with water. This causes formation of sulfuric-acid esters (generally with a boiling point between 200 and 220°C) mainly by addition to the double bonds. These $OSO_3H$ additions are soluble partly in acid and partly in benzine and cannot be completely removed by washing with alkali, resulting in a decomposition during the required redistillation under formation of sulfur dioxide. This produces aging of the crack benzines. The fact that the sulfuric acid finally produces a condensation of unsaturated compounds with sulfur and oxygen-containing substances is in itself of no disadvantage on the benzine refining product as far as stability is concerned. However, the loss in yield may become high and the antiknock characteristic of the product may decrease considerably.

### e. Natural Aging of Cracked Benzines

Natural aging of cracked benzines shows in the storage property of these products. After a prolonged storage of reactive benzines, not only the quantity of gum resins increases but also the "frontal distillation tail" of such fuels, which shows that the main component of the reactive unsaturated hydrocarbons is contained in the lower distillation fraction as mentioned in the chapter on "Resinification". The compression resistance of these benzines decreases gradually with this natural aging and reductions in octane numbers up to 10 units have been measured frequently. This shows that exactly the unsaturated fractions have high antiknock characteristics in fresh cracked benzines. As known, resin formation is rather low at the beginning of storage of cracked benzines. However, as soon as peroxides or acids have formed, in which case the acids act as catalysts, aging progresses rapidly. In one example, the aging of a refined cracked benzine was only 1 mg resin after the first two months, 3 mg resin after two additional months, and then increased to 26 mg after a total of six months. This value rose to 64 mg after eight months and to 100 mg resin per 100 cc cracked benzine after months.

### f. Stabilization of Cracked Benzines

To improve the storage property of refined cracked benzines, small amounts of "inhibitors" should be added. Such inhibitors are mainly represented by aminophenol, phenylhydrazine, monobenzyl-para-aminophenol, alpha-naphthol, pyrocatechin, and other substances. In large-scale industry, these substances actually are added with the effect that the resin formation is practically suppressed over a long period of time. In one experimental case, full stabilization was obtained with an addition of 0.01% naphthol on a cracked benzine which had shown an increase in resin content from 4 - 53 mg within six months without any addition. After adding the naphthol, no change was observed in the resin test for the same period of time.

### g. Reformed Benzine

"Reforming" is a cracking at a slightly reduced pressure and temperature. The process consists in production of "reformed" benzines of satisfactory antiknock characteristics and storage property by suitable selection of the raw materials and working conditions. The starting material generally are straight-run benzines of poor antiknock characteristics.

### h. Resinification and Engine

While the resin formation merely characterizes and influences the storage property, ready-formed resins, depending on their amount, have an unfavorable effect on the engine since they form deposits on the intake valves, especially in winter operation of motorized vehicles. The valves can then no longer close as required by the firing order of the engine. In addition, disturbances in the carburetor and gasoline supply become especially noticeable.

### 3. NATURAL GASOLINE

#### a. Natural Gasoline, Petroleum Benzine

Natural gasoline or petrolene are obtained directly from wet petroleums in petroleum fields, i.e., from the exhalation of drillings which contain sufficient benzine-like vapors that 1/2 - 2 l light benzine can be precipitated per cc of gas. Benzine removal from such wet petroleum is generally done by washing in heavy petroleum (mineral seal oil) or by compression or cooling. One other method is an adsorption in silica gel, activated charcoal, and activated earths. Natural gasoline has a high antiknock characteristic and is very suitable for starting in low temperatures but tends to form vapor locks during the warm seasons, resulting in disturbance in the gasoline feeder lines. Consequently, it is not always desirable to have a very high addition of gasoline in regular automobile benzines, such as frequently is done in petroleum districts, or to "improve" heavy benzines in this manner. Natural gas benzines mainly contain saturated hydrocarbons of low boiling point. Analysis of typical commercial natural-gas benzines shows a specific gravity d/20 of 0.640 - 0.670, $nD_{20}$ of 1.365 - 1.380, distillation start at 20 - 30°C, 10% over at a boiling point of 30 - 45°C, 50% at a boiling point of 45 - 70°C, 90% at 75 - 105°C, and end of distillation at 110 - 150°C. The Reid vapor pressure is 0.8 - 2.0 kg/cm², n-butane content 15 - 30%, n-pentane content 20 - 25%, i-pentane 15 - 25%, and higher hydrocarbons 10 - 20%. The octane number generally is between 70 - 85, and the antiknock characteristics increase with the volatility of the gasoline.

### 4. POLYMER BENZINES

#### a. Starting Material

Initial substances for polymerization are gaseous hydrocarbons rich in unsaturated components. Consequently, cracked gases are easily polymerized, i.e., the gases which are obtained in rather large quantities during the above-described cracking process. In addition, dry natural gases and hydrogenation gases can be used for polymerization but must be subjected first to a gas splitting (pyrolysis) because of the content in saturated hydrocarbons.

In the cracking process, paraffins are dissociated into shorter-chain paraffins and olefins. At lower temperatures, cracking takes place approximately at the center of the chain while only side chains and hydrogen are separated at higher temperatures. The olefins polymerize partly in their formation state and then are split again. For this reason, residue products which run several times through the cracking equipment, are more difficult to crack and will finally form the residue. At higher pressures and temperatures the content in olefins decreases and the formation of aromatic compounds and naphthenes increases. Naphthenes split mainly side chains and are only then dehydrated into aromatic compounds. These aromatic compounds resist the cracking which makes it easier for the side chains to be split off on increasing length, while the methyl groups will adhere. Cracking may produce an intermediary formation of $CH_3$ and $CH_2$ radicals in any case. In addition, the possible chain reactions during the cracking process are innumerous and cannot be estimated.

The possibility for cracking a certain material can be defined as the activation energy required for a first dissociation of the molecules which, according to Waltner (bibl. 3), is 64,500 cal for hexane and octane and 33,000 cal for dimethyl hexane. The heat of separation for aliphatic C-C bonds is 71 cal and for aromatic-aliphatic C-C bonds 80 cal, while the heat of separation for CH bonds is 92 cal per mole. According to Buchan (bibl. 4), the relation between free energy and specific heat is so clear that this specific heat can be used for determining the cracking characteristic and for defining the above-indicated succession of splitting: paraffins, naphthenes, aromatic compounds.

The composition of cracked gases which can be determined by low-temperature distillation according to Podbielniak, is approximately as follows: small amounts of noncondensable gases, ethylene next to ethane, propylen next to propane, butylene next to butane, low amounts of higher chain hydrocarbons, and traces of benzene vapors.

b. Method of Polymerization

In the technique of polymerization three different methods are differentiated:

1) The low-temperature high-pressure method;

2) The high-temperature low-pressure method;

3) The catalytic method.

The low-temperature high-pressure method operating with temperatures between 480 and 540°C and pressures between 42 and 56 atm, is suitable mainly for cracked gases having a high content of unsaturated hydrocarbons. The polymeric benzine, at satisfactory yields, will be rich in isoparaffins of octane numbers as high as 80 - 100. The second method requires the high temperatures for treating of natural gases in which case at least one part of the saturated hydrocarbon is split off and made more reactive. However, in that case the reaction has more the character of an aromatization, resulting in polymer benzines with a content of aromatic and unsaturated compounds as high as 95% at octane numbers between 80 and 100 with a simultaneous production of naphthene-containing tar. The catalytic method generally operates at medium temperatures between 230 and 260°C and medium pressures between 7 and 13 atm. The catalyst used is orthophosphoric acid on a carrier substance. In this method, the cracked gases are first brought to the desired temperature in heating coils and are then conducted through two or more contact chambers at the desired pressure. The phosphoric acid is exhausted by adhesion of the polymers and must be renewed from time to time. The resultant polymer benzines are still rich in unsaturated hydrocarbons and have an octane rating of 80 - 85. The third method is most important for practical application. If the hydrogen-sulfide of the cracked gases is not removed by washing in caustic-soda solution or plumbite solution, mercaptans will be found in the polymerized benzine. A longer contact period will raise the distillation curve of the polymer benzines. Ipatieff and Egloff (bibl. 5) showed that the 90% boiling point of the polybenzine is kept below 200°C up to contact periods of 50 sec but increases to 240°C at contact periods of as much as 3 min.

c. Characteristics of Polymeric Benzines

Table 2 gives various coefficients for typical polymeric benzines. One of the main characteristics of polymeric benzines is the fact that the widely differing rather steep boiling curve hardly influences the antiknock characteristics. The fact that polymeric benzines with octane numbers between 80 and 82 in a mixture with knocking straight-run benzines decrease this knocking tendency considerably more than indicated by the octane rating, is of high interest. General conditions are so that an octane rating between 100 and 125 would be obtained mathematically for the effect of polymeric benzines in such mixtures. Table 3 shows this characteristic effect of polymeric benzines when cut with primary benzines in the octane-rating stages of 45, 50, 55, 60, 65, and 70 (see also Fig. 1).

Depending on the content of polymeric benzine in unsaturated hydrocarbons, inhibitors will have to be used. A subsequent hydrogenation has the same effect and has the additional advantage that polymeric benzines become more sensitive to lead since it is known that lead sensitivity of benzines rich in unsaturated and aromatic compounds is relatively low.

## 5. LIQUID GAS

### a. Composition of Liquid Gas

When first using compressed gases in motorized vehicles (1934), a mixture of propylene with propane and butylene with butane was put on the market under the name of "Ruhrgasol". The IGF and Deurag Company market a liquid gas in which propane and butane are the main components. The most important characteristics of these two components are as follows:

| | Density d/20 | Critical Pressure atm abs | Critical Temperature °C | Air Requirement cc/cc | Cal. Value | | Vapor Press in kg/cm$^2$ at | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Upper | Lower | -30°C | 0°C | +20°C | +40°C |
| Propane | 0.511 | 45 | 95.6 | 23.8 | 12,000 | 11,050 | 2.3 | 5.7 | 9.7 | 16.5 |
| Butane | 0.584 | 35.7 | 153.2 | 31 | 11,850 | 10,900 | 0.6 | 1.4 | 2.8 | 5.4 |

The antiknock characteristic of liquid gas is expressed by an octane rating of 100 - 110.

### b. Use of Liquid Gas

Operation of motorized vehicles with liquid gas eliminates the carburetor of standard Otto-cycle engines. Despite this fact, the combustion principle is rather similar. The liquid propane-butane mixture is carried under a pressure of 25 atm in light-metal bottles of 15 - 40 kg capacity. For evaporation, the gas whose flow is controlled, is supplied to a preheater which is heated by the cooling water or by the exhaust gases. Then, the gas is conducted through an automatically-controlled expansion valve (pressure control) and finally supplied with the necessary addition of combustion air in a mixing valve. With respect to benzine, the fuel consumption is lowered by 12 - 15% at equal power which may be traced to a better mixture and more complete combustion of the charge. The excess air should be 2 - 5% and the preignition must be increased by 5° since the gas burns slightly less rapidly in the engine. The main advantage is the good starting property at low temperatures, easy operation, satisfactory gear changing, and good climbing ability. Propane can still be kept liquid under pressure even at extremely low temperatures while in the case of butane, the pressure in the bottle may drop to atmospheric pressure which then will prevent the correct fuel-air mixture from reaching the engine. In addition, icing of the governor may occur by incomplete expansion of the bottled gas.

## 6. CARBONIZATION BENZINES

### a. Carbonization Process

Carbonization is a dry distillation of coal and bituminous shale at temperatures between 500 and 600°C. As soon as higher temperatures are used, the process is known as coking. At lower temperatures of the dry distillation of these fuels, certain finished products of the treatment of tar and carbonization gases will have a benzine-like character. This is logical, since chain hydrocarbons are split at higher temperatures and since the unsaturated cracking components produce a formation of aromatic hydrocarbons. The best material for carbonization are coal and shale since their content in bitumen and tar formers exceeds 6%. Carbonization in large-scale manufacture is done by two methods, either by external heating (Rolle and Geissen furnaces) or by heating with scavenging gases (Lurgi method). In carbonization, water vapors will evaporate since the water content in a non-predried coal will be as high as 50%;

development of tar vapors takes place between 300 and 600°C.

In lignite carbonization, approximately 7 - 8% crude tar or approximately 0.3% carbonization benzine over tar formation is obtained. Further treatment of the carbonization gases will result in a precipitation of an additional 0.4% benzine, so that the yield in carbonization benzine from lignite processes is approximately 0.7%. Maximum tar yield is 40%. In anthracite carbonization within the same temperature range, similar yield ratios are obtained in direct distillation. If the tar and paraffin oils of the crude tar (approximately 3 - 5% of the coal) are treated by cracking distillation, a corresponding increase in benzine yield will be obtained. Generally (all volumetric data refer to tar), 5% of benzine rich in aromatic compounds is obtained in anthracite carbonization, 35% gas oil, 20% heavy fuel oil, and 30% tar pitch at a 10% gas yield and loss. Simple lignite carbonization will furnish 6% benzine, 30% gas oil, 35% fuel oil, 10% paraffin, and 20% coke, pitch, gas, and residue. If lignite tar is subjected to a careful pressure distillation (semicracking), as much as 12% benzine, 50% gas oil, and 10% fuel oil can be obtained while the remainder will consist of pitch, gas, and residue. At complete cracking of lignite low-temperature tar a yield of as much as 35% benzine rich in aromatic compounds, and 20% fuel oil can be obtained. In this process, 30% will be pitch and 10 - 15% gas and residue. Much better results are obtained by high-pressure hydrogenation for these tars. In treating carbonizable shale which mainly is found in Estonia, dry distillation will furnish 8 - 10% tar. The crude shale oil is treated by means of the Dubbs cracking method, resulting in a yield of as much as 65% crude benzine (related to tar) with a small amount of fuel oil and 20% of coke.

### b. Characteristic of Carbonization Benzines

Carbonization benzines have the characteristic of a high aging tendency since they are rich in unstable hydrocarbons. The crude benzines have a very disagreeable odor and can hardly be used in engines since they deposit pitch on the valves. Along with unsaturated hydrocarbons, the content in organic oxygen and sulfur compounds may become rather high. Consequently, considerable difficulties occur in refining and any thorough refining will produce high losses. The undesirable diolefins (diene) are condensated and eliminated by an addition of 70% sulfuric acid. As known, the sulfuric acid used in refining of carbonization benzines does not exceed 60° Be. In acids of higher baume, the yield losses would even be 50% and, in addition, condensation products of aromatic and aliphatic compounds would be formed. In this case, any compounds such as $C_6H_5-C_8H_{17}$ and $C_6H_5-C_5H_{10}$ were already isolated.

Since development of the IG high-pressure hydrogenation, production of refined carbonization benzines as Otto fuels has only a minor or local significance. The refining hydrogenation of carbonization benzines is uneconomical and merely has a scientific interest. The only suitable method is high-pressure hydrogenation of a coal paste according to the IG method, described below. Additional data are given in Table 4.

## 7. SYNTHETIC BENZINES

### a. The IG High-Pressure Synthesis

Bergius attempted "coal liquefaction" in 1910 - 1930 by reacting coal with hydrogen at a pressure of 200 atm and at a temperature between 400 and 500°C. In cooperation with the Goldschmidt Company in Essen the well-known Bergin method was developed. In 1925, Pier and Krauch, in Leuna, in cooperation with the steel industry, were able to eliminate the various material drawbacks, especially the hydrogen "sickening" of steels occurring in reaction cylinders used under high pressure. In addition, these inventors were able to discover suitable nontoxic catalysts for accelerating the process and for increasing the desire benzine yield.

The IG method of high-pressure hydrogenation which is used in Leuna, Scholven, Stettin, and in the plants of the Brabag, for producing synthetic benzine in amounts which exceed 1 million tons per year, uses either lignite and anthracite or the tars of lignite and anthracite as well as topped petroleum as raw material. In hydrogenation of coal, mainly lignite, this coal is made into a paste in the dry and ground state with a cheap catalyst (iron oxides) and heavy oils (intermediary product of this synthesis). The components are then mixed in heat exchangers with hydrogen of at least 300 atm by means of pulp pumps and brought to a temperature 400°C. The retorts are 30-m high steel cylinders in which the temperature is increased to 460°C and in which the main process, i.e., a splitting of the coal molecule and a hydrogenation of the fraction components takes place. This first part of high-pressure hydrogenation is known as the "sludge phase" or "liquid phase" in which middle oil is produced. The heavy-oil residue with the distillation residue of the middle oil returns to the initial material after removing solid substances and then is used for "pasting" the coal. In the second stage, known as the "gas phase", the middle oil (unless it is to be used as Diesel fuel) is reacted in benzine retorts with fixed lump catalysts (molybdenum or tungsten sulfides on aluminum hydroxide, etc.) at a temperature of 400°C and 300 atm hydrogen. The product is then cracked and refined in the individual cracking components by hydrogen addition to hydrogenation benzines. In this manner, liquid products of as much as 50% of the lignite and 30% of hydrogenated benzine are obtained. If lignite tar is used for hydrogenation, this tar is treated separately in sludge furnaces at 450°C with 200 atm hydrogen (or after removing the middle oil by distillation). The combined middle oils then are again hydrogenated in benzine retorts under similar conditions in which case the benzine yield is up to 97% of the tar. The hydrogenation benzines, after redistillation and washing with sulfuric acid or lye, represent the Otto fuel, while the hydrogenation gases are compressed into liquid gases.

For hydrogenating one ton of coal (anthracite or lignite) approximately 1200 cc hydrogen are required and approximately 820 cc for one ton of coking tar. The hydrogen required for each ton lignite carbonization tar is 450 $m^3$ and for each ton topped petroleum 200 $m^3$. The temperature influence during hydrogenation is approximately as follows: Already at a temperature of 200°C, a hydrogenation of olefinic double bonds takes place. At 300°C, hydrogenating refining but no splitting of the C-C bonds occurs. As soon as the temperature increases to 400°C, active cracking and active hydrogenation of the cracking components takes place, while at a temperature of 500°C the cracking predominates more than desired for satisfactory results.

## b. The Fischer-Tropsch Synthesis

The synthesis of liquid hydrocarbons according to the Fischer and Tropsch process uses water gas as the starting product, a mixture of carbon oxide and hydrogen (ratio 1 : 2) and applies relatively low pressures, temperatures near 200°C and cobalt or nickel contacts for reacting these two components. The water gas is obtained in generators by dissociation of water vapor over coke and requires a special purification. One of the most important points is removal of hydrogen sulfide by gas-purifying agents or lux mass. The preheated mixture of carbon oxide and hydrogen is then kept rather constant at 190°C in the contact chambers. In principle, the following transformation takes place: $CO + 2H_2 = —CH_2— + H_2O$. The $CH_2$ groups, depending on the duration of reaction and other operating conditions, form an addition product of liquid hydrocarbons. The resultant high heat of reaction must continually be removed from the contact apparatus and is used for steam production in the process. The mixture of liquid hydrocarbons is known as "Kogasin" from which the entire process derives the name of Kogasin synthesis. On the average, 0.12 - 0.5 kg Kogasin are obtained in large-scale manufacture per cc water gas along with approximately 10% gaseous hydrocarbons which are compressed to a bottled gas known as "Ruhrgasol".

The Kogasin obtained in this process is a water-white liquid of extreme purity and is separated from the above components by condensation. Activated charcoal is used for absorbing benzine and gas oil from the remainder. The residual gas is used for heating purposes or returned into the process. The resultant oily components as well as benzine and gas oils are then treated further to obtain the end products of the

Fisher-Tropsch synthesis, i.e., paraffin, Diesel oil, benzine, and Ruhr gas oil. The Kogasin benzine is practically free of sulfur and aromatic compounds and contains mainly chain hydrocarbons. The ratio of the olefins to the paraffins is determined by selection of the contacts. This Fischer-Tropsch synthesis has been used on a large scale in the Ruhrchemie Company.

### c. Characteristics of Synthetic Benzines

While in the IG high-pressure procedure ready engine benzines for automobiles and aircraft engines are obtained, the Kogasin products are mainly used for blending purposes.

Pier who may be considered the pioneer of the IG synthesis of benzines furnishes the following data on the characteristics of this synthesis (bibl. 6):

a) Strongly hydrogenating and cracking catalysts furnish hydrogenation benzine with an octane rating of 67;

b) weakly hydrogenating and strongly cracking catalysts furnish hydrogenation benzines rich in isoparaffins, naphthenes, i.e., basic benzines for aircraft engines with the following test results: d 20 0.714 - 0.721; 57 - 72% distill over up to 100°C; end point of distillation 135 - 145°C; vapor pressure according to Reid 0.48 kg/cm$^2$; octane number (engine method) 72 - 77; lead sensitivity 0.2 cc tetraethyl lead/ℓ = octane number + 7; 0.4 cc tetraethyl lead/ℓ = octane number + 10; 0.6 cc tetraethyl lead/ℓ = octane number + 12; 0.9 cc tetraethyl lead/ℓ = octane number + 15; 2.7 cc tetraethyl lead/ℓ = octane number + 23;

c) Catalysts used for aromatization at strongly-cracking temperatures (500°C), furnish benzines of the following data: d = 0.805; initial distillation 41°C; 90% coming over to 100°C; 47.5% to 140°C; 35.5% to 180°C; end point at 214°C; octane number 94.

The composition of the large-scale production of Kogasin from water-gas synthesis is as follows (according to Martin): 8% liquid gas "Ruhrgasol"; olefin content 50 - 55%; 60% light oil with boiling point of 200°C, i.e., benzines with an olefin content of 30 - 35%; 22% gas oil with olefin content of 5 - 6%; 10% solid paraffin without olefins. In water gas rich in CO, more olefins will be formed while more paraffins are formed in a gas low in CO, so that the characteristics of the desired finished product can be regulated. Boiling range of the above-described Kogasin is between 35 and 360°C.

The benzines coming over to 140°C are unbranched parraffins and olefins and therefore have a tendency to knock. These products are mainly furnished by the activated-charcoal adsorption of the hydrogenation gas. The higher fractions must be cracked for obtaining suitable benzines. The benzines obtained as "Kogasin I" have an average octane rating of 58. The product "Kogasin II" (discussed later in the text) is a valuable component of Diesel fuels.

## 8. ENGINE BENZINE

### a. Coking of Anthracite

Dry distillation of coal at high temperatures is known as coking. Obviously, in this process the high-molecular hydrocarbons and other oxygen, sulfur, and nitrogen-containing organic compounds contained in the coal are completely cracked, but so that short-chain frequently unsaturated fraction components low in hydrogen form addition products of aromatic compounds. In coking, anthracite is used since this is the only material resulting in a packed coke.

In carbonization of anthracite, known under the name of "low-temperature coking", an average of 10% gas, 10% tar, and 80% coke are formed. The carbonization temperatures, as mentioned above, are between 500 and 600°C. In high-temperature coking of anthracite, i.e., at temperatures between 900 and 1300°C the yield is 25% gas with 5% tar and 70% coke. In this case, the composition of the gas and that of the tar in this coking process differs widely from the corresponding products of carbonization. On increase of temperature in the dry distillation of anthracite, the hydrogen content in the formed gas increases while the methane content remains practically constant. The content in higher hydrocarbons decreases due to the splitting. The total yield, i.e., the formation of lowest hydrocarbons increases considerably with the coking temperature and has the following values:

At 500°C between 30 and 100 cc/ton of anthracite
At 600°C between 50 and 140 cc/ton of anthracite
At 700°C between 140 and 330 cc/ton of anthracite
At 800°C between 200 and 270 cc/ton of anthracite
and at 1000°C between 270 and 330 cc/ton of anthracite

The lower values apply for geologically old and the upper values for geologically young anthracite. The aromatization of the cracking components in the tar shows clearly in the fact that the specific gravity of the tar increases with the coking temperature and that the pitch content increases with respect to the oil content of the tar:

| Coking Temperature | Specific Gravity of the Tar | Oil Content | Pitch Content |
|---|---|---|---|
| 500°C | 1.000 | 70% | 30% |
| 600°C | 1.060 | 60% | 40% |
| 700°C | 1.090 | 55% | 45% |
| 800°C | 1.130 | 45% | 55% |
| 900°C | 1.170 | 35% | 65% |

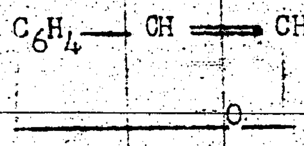
In practical use, coking of anthracite is used for producing the illuminating gas used in towns. The coke is a byproduct, while the large coking plants require the anthracite coke for foundry purposes and consider gas and tar as byproducts.

The light hydrocarbons of anthracite coking are benzene and its homologues. Related to coal, 0.1% of benzene hydrocarbons are obtained over tar and 0.9% over illuminating gas. Benzene is extracted from the gas by washing with light tar oils and from the tar by distillation.

## b. Characteristics of Benzene Hydrocarbons

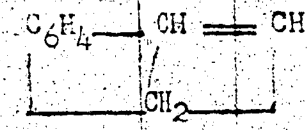
The most important characteristics of pure benzene hydrocarbons are given in Table 6. Pure benzene or technical benzene, even in a blend, are unsuitable for use in a vehicle engine because of poor resistance to low temperatures (fusion point 4 - 6°C) and because of sooty combustion. Engine benzene is a naturally-obtained mixture of benzene and toluene with a specific gravity d/20 of 0.879, boiling range 51 - 134°C, and boiling point of 89. The BV benzene is a much better mixture of benzene, toluene, and zylene with the following data: 75% benzene, 17% toluene, and 8% zylene at a specific gravity of 0.875 - 0.879, refractive index 1.4940, initial distillation between 80 and 87°C, 75% coming over to 100°C, and 95% to 145°C. A blend of 60% benzene with 40% zylene and tolueme has a better resistance to low temperatures. This mixture is used in the products. The data on this composition are as follows: d/20 = 0.874, distillation range 51 - 154°C, boiling point 108. Avidtion benzenes are similar mixtures but not products as obtained in an ordinary distillation, since in this case benzene, toluene, and xylene are refined separately and mixed according to specific instructions. Engine benzenes of the prescribed type are never used by themselves in either automobile or aircraft engines but always blended with suitable not necessarily antiknock benzenes. In such mixtures, additions of 25 - 40% engine benzene are added to the automobile benzines, while aircraft fuels of foreign countries have an addition of as much as 50% of the mentioned special benzenes. (Naturally, in wartime the fuel conditions of the own Army are not discussed.)

Table 7 shows data of heavy benzenes and solvents naphtha along with the distillation processes of various technical benzenes and mixtures of benzine and benzene. The high boiling curve found in the solvent naphtha and heavy benzenes is due to large amounts of coumaron



$$\underset{\lfloor\underline{\qquad\qquad\qquad O\qquad}\rfloor}{C_6H_4-CH=CH}$$

(d 1.107; BP 174°C) and indene



$$\underset{\lfloor\underline{\qquad\qquad CH_2\qquad}\rfloor}{C_6H_4-CH=CH}$$

(d 1.006; BP 181°C).

Benzene additions to benzine have the purpose to increase the antiknock characteristics of the mixture. Engine benzene has been known to have an octane number of 97 or, as recently stated, an octane number of 110. This rather large difference is explained by the fact that slight benzine additions do not have the effect which would correspond to their octane number. Conversely, polymeric benzines are an example for the fact that slight additions will increase the compression resistance of knocking benzines much more than expected from their octane rating. An arithematic relation exists only in isoparaffins. The mentioned conditions are expressed in the diagram shown in Fig.1.

This diagram is based on a knocking straight-run benzine with an octane number of 40. The addition of i-paraffin (iso-octane) produces a rectilinear increase of the octane number in the mixtures. Addition of benzene produces a retarded increase in octane rating which would result in an apparent octane number of 80 for the benzene in the first 25% of benzene addition. The true octane number of the benzene is 110. Conversely, addition of polymeric benzine will result in too rapid an increase in octane number which, at wrong interpolation, would indicate that the octane number of polymeric benzine is near 115. However, the octane number of polymeric benzine actually is 83.

## 9. METHANOL

### a. Production of Methyl Alcohol

In the beginning of chemical developments, methyl alcohol or methanol $CH_3OH$ was obtained by dry distillation of wood and was isolated as the main component of wood alcohol. In modern methods, water gas is subjected to high-pressure hydrogenation at 200 atm pressure and 350°C temperature in presence of a catalyst. Reaction takes place according to the following formula: $CO + 2H_2 = CH_3OH$.

b. Characteristics of Methyl Alcohol

Methyl alcohol, in the purified state, is a colorless liquid which is water-miscible in any proportion. The specific gravity d/20 is 0.791 with a refractive index nD/20 of 1.331. The dispersion nF-nC is 0.0054, the boiling point 66°C, the vapor-pressure 0.36 kg/cm², the specific heat 0.62, and the heat conductivity related to water 27%. The lower calorific value Hu - 4650 cal/kg is much lower than that of benzines (Hu - 10,350 cal/kg). However, since the air required for proper combustion is much lower in methanol than in benzines, i.e., 6.5 kg air per 1 kg methanol or 14.5 kg air per 1 kg benzine or 13.3 kg air per 1 kg benzene, the calorific value of the mixture of benzine, benzene, and alcohols (calorific value of 1 cc fuel-air mixture) generally is 750 - 800 cal. This shows that, at equal power, methanol operation or alcohol operation of automobile engines is much more expensive than operation with benzine hydrocarbons. The heat of evaporation of methanol with a value of 260 cal/kg is extremely high compared to benzine with a heat of 80 cal/kg and benzene with a heat of evaporation of 100 cal/kg. Ethyl alcohol shows a heat of evaporation of 220 cal/kg. Due to the high heat of evaporation, a considerable cooling of the supplied air occurs in the Otto-cycle engine. In the theoretical fuel-air mixture (bibl. 7) this cooling is 20°C for benzine, 30°C for benzene, 75°C for ethyl alcohol, and as high as 125°C for methyl alcohol. As known, the superiority of alcohol fuels in racing cars is due to the "cold engine". However, in practical application these strong temperature drops are not always obtained since the vapor tension of liquids and other moments have an influence. Mixing of alcohol fuels is rather difficult at low temperatures, at least much more difficult than that of benzines. Table 8a shows the fuel quantities in kg absorbed by 1 kg air at various temperatures. In Table 8b, saturation pressure in mm Hg are given. The values indicated in Table 8a do not necessarily furnish a conclusion as to the combustion, since the quantities absorbed at saturation must be compared with the quantities required by the same air volume (for example, air ratio $\lambda = 1$). However, these fuel quantities are independent of the temperature and have the following values for the various substances: 0.068 kg benzine, 0.075 kg benzene, 0.111 kg ethanol, and 0.155 kg methanol. In addition, the temperatures at which a theoretical fuel-air mixture is no longer possible, are -20°C for benzine, -6°C for benzene, + 20°C for ethanol, and + 17°C for methanol. Consequently, dry fuel-air mixtures are possible only above these temperatures.

One of the most important factors in starting is the rate of evaporation. This rate is much lower in methanol than in benzine. Despite a lower boiling point of the methanol, evaporation and mixture formation are much lower than in benzines which produces starting difficulties at low temperatures. Wilke (bibl. 7) measured temperatures at the end of the intake stroke of 77°C for benzine as compared to 46°C for methanol (because of cooling due to evaporation). In the ratio of absolute temperatures the following values are obtained: (273 + 77) : (273 + 46) = 1.1 which means that an engine operated with methanol will absorb 1.1 times the mixture absorbed by benzine, resulting in a higher power. The secret in this process merely is a supercharging from 1 to 1.1, i.e., by approximately 10%. The antiknock characteristics of methyl alcohol are not given uniformly, since they cannot be measured directly. However, they are extremely high. Wilke, based on mixing-coefficient tests in the CFR engine, gives this value as 135 - 140 octane units, of ethanol as 130, and of benzene as 102. In their antiknock behavior, the alcohols similarly as benzene are more dependent on the temperature. The compression ratio of methanol is as high as 1 : 2 and is limited only by the suitability of the spark plugs used.

## 10. ETHANOL

a. Production of Ethyl Alcohol

Ethyl alcohol or ethanol $C_2H_5OH$ is produced by decomposition of dextrose $C_6H_{12}O_6$ whose dilute solutions yeast can be grown. This process of alcoholic fermentation is shown by the following equation:

$$C_6H_{12}O_6 = 2\ C_2H_5OH + 2\ CO_2$$

To obtain sugar, potato starch is frequently used in agriculture, while modern industry produces sugar from wood cellulose by a reaction with dilute hydrochloric acid under pressure. In both cases, i.e., in fermenting potato or grain starch as well as in wood fermentation, the transformation of starch or cellulose into sugar can be expressed as follows:

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$$

The alcohol produced in the fermenting vats of the mash is distilled and purified by rectification. However, removal of the water from the alcohol is possible only up to 95.6% of the alcohol content.

In ethyl alcohol to be used in fuels, complete dehydration is of basic importance. Several methods are used in general technique, such as:

1) Azeotropic method: Alcohol, as mentioned above, can be concentrated by distillation only to 95.6%. The residual water will form a so-called azeotropic mixture with the alcohol. Azetropy is the phenomenon of a constant boiling point occurring in liquid mixtures of a definite composition. This boiling point is either lower or higher than that of the components. The binary mixture alcohol and water of the above composition, i.e., 95.57% alcohol with 4.43% water has a constant boiling point near 78.15°C, while the boiling point of absolute alcohol is 78.3°C. If a slight amount of benzene is added to this product, the resultant ternary mixture of 18.5% alcohol, 7.4% water, and 74.1% benzene will furnish a new azeotropic mixture with a constant boiling point of 64.85°C. Consequently, this mixture can be split off by distillation at this temperature. Then an azeotropic residue will remain. This residue consists of alcohol and benzene with a constant boiling point of 68.25°C, which can be split off resulting in anhydrous alcohol of 78.3°C BP. Since tri-chloro-ethylene has a similar tendency for forming azeotropic mixtures it can be used for dehydration of alcohol;

2) The Hiag Method: In this method, a column filled with Raschig rings is charged with melted alcoholic potassium-sodium acetate, reacting with alcohol vapors and removing all traces of water. The resultant aqueous salt solution is heated in the regenerator to 300°C and dehydrated;

3) Calcium-pressure method (Merck, Darmstadt): In this method, dehydration is made with quicklime under pressure;

4) Modern gypsum method (IGF): In this method, gypsum is completely dehydrated at 160°C. Then, this gypsum is used for immetiately removing the water from alcohol under formation of a nonhardening semihydrate which can be readily regenerated.

## b. Characteristics of Ethyl Alcohol

Anhydrous ethyl alcohol has the following characteristics:

| | |
|---|---|
| Specific gravity d/15 | 0.794 |
| Boiling point | 78.3°C |
| Refractive index nD/20 | 1.3619 |
| Dispersion nF-nC | 0.00611 |

| | |
|---|---|
| Vapor pressure | 0.18 kg/cm$^2$ (40°C) |
| Specific heat | 0.61 |
| Surface tension at 20°C | 22 dyne/cm |
| Heat conductivity | 30.1% of that of water |

The lower calorific value is 6300 cal/kg or 5100 cal/liter. The same data as given under methanol apply for the lower heat content with respect to benzines. The solidifying point of absolute ethanol is -120°C. At increasing water content, the specific gravity of alcohol increases but not linearly, since considerable volume contractions occur in mixing with water under heat which are due to formation of hydrates. In a mixing ratio of 1 mol alcohol to 3 moles water, the contraction is evan 3.7%. Additional data are given in Table 9.

Dietrich (bibl. 8) denotes as "water coefficient" the number of cc of water to be added to 100 cc of a benzine-alcohol mixture for producing a slight turbidity, resulting in segregation. Table 10 shows the existing critical values of alcohol-benzine mixtures and water compatability:

Table 10

| % Benzine | 100 | 95 | 90 | 85 | 80 | 70 |
|---|---|---|---|---|---|---|
| % Alcohol abs | 0 | 5 | 10 | 15 | 20 | 30 |
| % Water | 0 | 0.15 | 0.28 | 0.71 | 2.54 | 5.22 |

This table shows clearly that alcohol-rich benzine mixtures are not as sensitive to water as alcohol-poor mixtures. As soon as benzene is added to this three-component mixture it will act as a "solvent" which means that the alcohol may have even a higher water content without producing any turbidity in the mixture. Benzine-alcohol mixtures with a turbidity due to water content can be clarified by adding benzene. However, the danger of segregation exists as soon as the temperature drops. For example, 80% benzene will absorb 20% of 87% alcohol and 70% benzene will absorb 30% of 83% alcohol.

The resistance to low temperature of benzine-alcohol mixtures which is of decisive importance for practical engine operation, increases with concentration of the alcohol but depends also on the constitution of the benzene. According to Hubendick (Stockholm), the low-temperature resistance of 97.5% ethyl alcohol in benzine-alcohol mixtures (always with a 20% alcohol content) fluctuates between +10 and -15°C while the fluctuation in a 98% alcohol is between +5 and -28°C. The values in a 98.5% alcohol are between -5 and -38°C, in a 99% alcohol between -20 and -50°C, and in a 99.5% alcohol between - 28 and -50°C.

The antiknock characteristics of ethyl alcohol is extremely high and generally can be expressed by an octane rating of 130. In many cases, the effect of alcohol in mixed fuels is even so high that an octane rating of 200 can be expected for ethyl alcohol. With respect to the temperature dependence of the compression resistance of alcohol-containing fuels opinions differ widely. Kamm (bibl. 9) mentioned the fact that alcohol has $2 - 2\frac{1}{2}$ times the antiknock characteristic of benzene and states that "even at high temperatures in which the antiknock characteristic of benzene decreases, alcohol will still be resistant to knocking". However Philippovich (bibl. 10) is of the opinion that at such high temperatures as used in aircraft engines with air or glycol evaporation cooling, the effect of alcohol as an antiknock agent decreases considerably. This author plotted a diagram for an aircraft benzine with an octane number of 100 at 100°C whose antiknock characteristics at 150°C dropped to 91.5. For comparison, he showed an alcohol-containing aircraft benzine with an octane rating of 101 at 100°C and a rating decreased to 92.5 at 150°C. This shows that the antiknock characteristics of all fuels decreases noticeably with increasing operating temperatures.

The following mixtures are known as alcohol-containing fuels and have proved satisfactory in the engine:

50% benzene with 25% tetralin and 25% alcohol;

20% benzene (slight amount of tetralin) and 80% alcohol;

57% benzene, 9% tetralin, and 34% alcohol;

30% benzene, 5% ether, and 65% alcohol (Monopolin in its oldest form);

33.5% benzine, 3% ether, and 63.5% alcohol (Monopolin in old form);

30% benzine, 20% benzene, and 50% alcohol (Monopolin extra);

50% benzine with 50% alcohol (French "Carburant national");

75% benzine with 25% abs alcohol (Swedish "Laettbentyl", according to Hubendick)

An interesting phenomenon is the fact that an alcohol addition to benzines will always disturb the steady boiling process by a double discontinuity in the boiling curve, as shown in Fig.2 in which an average automobile benzine (broken curve) is shown without addition of spirits and after an addition of 20% alcohol (solid curve).

Explanation of this phenomenon is obviously the fact that the alcohol content will produce a boiling delay in the lower branch of the boiling curve up to a range of 80°C. After removing the last alcohol residues by distillation, the temperature increases suddenly and shows the expected course of an alcohol-free benzine in the last part of the boiling curve. It is definite that in the lower branch of the boiling curve, the removal of azeotropic benzine-alcohol mixtures by distillation is clearly indicated. In the so-called "three-component mixture" of benzine, benzene, and alcohol this influence on the boiling curve becomes more complicated since several azeotropic mixtures become effective.

### c. Azeotropic Mixtures

In Table 11a, the constant boiling points of well-known two-component mixtures (binary systems) and in Table 11b the constant boiling points of well-known three-component mixtures (ternary systems) are shown as obtained from data from Gmelin (bibl. 11). The parenthesized values shown next to the substances represent their boiling points in the pure state. The volume ratio in the mixtures is given in weight % resulting in the boiling point of the azeotropic mixture.

## 11. ETHYLFLUID

### a. Tetraethyl Lead

Tetraethyl lead $Pb(C_2H_5)_4$ is obtained by reacting a lead-sodium alloy with ethyl chloride (or ethyl bromide) and subsequent steam distillation

$$Pb + 4Na + 4\ C_2H_5Cl = 4NaCl + Pb(C_2H_5)_4$$

This results in an oily colorless liquid of sweetish but disagreeable odor with a specific gravity d/20 of 1.655 and a boiling point of 200°C. The product cannot be distilled without dissociation. The solidifying point is near -156°C. Since tetraethyl lead without any addition carbonizes to lead oxide (fusion point 900°C) and since this has a very disturbing effect in engine operation, this product is not by itself as antiknock agent but only in a mixture with other substances which make the combustion products less harmful. Such a combination is the Ethylfluid.

### b. Ethylfluid

According to data given by the Ethyl Company in Berlin, Ethylfluid is produced in two types in Germany: "1-T Fluid" for aircraft fuels and "Q-Fluid" for automobile benzines. The composition is as follows:

| | 1-T Fluid (for aircraft benzines) | Q-Fluid (for automobile benzines) |
|---|---|---|
| Weight % tetraethyl lead (tetraethyl lead pure = TEL) | 61.42 | 63.30 |
| Weight % ethylene dibromide | 35.68 | 25.75 |
| Weight % ethylene dichloride | - | 8.72 |
| Weight % pigment, petroleum, and other additives | 2.90 | 2.23 |
| Specific gravity d/20 | 1.755 | 1.671 |
| Solidifying point | -10.5°C | -23°C |
| Flame point | Above 110°C | |

Addition of ethylene dibromide or ethylene dichloride has the purpose of producing lead bromide (fusion point 380°C) or lead chloride as a combustion product, which are less harmful for the exhaust manifolds than lead oxide.

Tetraethyl lead and Ethylfluid similarly as other organic lead compounds, are highly toxic and must be handled with extreme care. Persons employed in "ethylating" of Otto fuels must be protected by special gas masks and rubber clothing and gloves. Even in the strong dilutions used for tetraethyl lead in Otto fuels (if such fuels are "leaded"), hands should be carefully washed especially before meals.

### c. Tetraethyl-Lead Effect and Leading

The effect of tetraethyl lead (TEL) as an antiknock agent in Otto fuels is extremely intensive. In Germany, the maximum limit for leaded automobile benzines is 0.4 cc addition of TEL per liter of benzine. This quantity corresponds to an addition of 0.632 cc Ethylfluid (Q-fluid) or of 1.056 g Q-fluid per liter of Otto fuel. Consequently, only 105.6 g are needed for maximum leading of 100 ℓ benzine and approximately 1 kg Ethylfluid (Q-fluid) for leading of 100 $m^3$ benzine. In many cases, it is completely sufficient to use the diagram in Fig.3 for production of antiknock automobile benzines, since the maximum octane number permitted in Germany is 74. This diagram shows clearly the amount of Q-fluid to be added to benzines of insufficient antiknock characteristic (OR 54 - 70) for producing an Otto fuel with an octane rating of 74. However, the diagram does not consider the differing lead sensitivity of benzines which will be discussed later in the text.

Ethylfluid is furnished in strong iron drums with safety locks. For "leading" of benzines only stationary or mobile systems can be used in which the fittings are specially designed for the intended purpose and where all joints are properly sealed. The iron drums with the Ethylfluid are tapped by a suction pump with a tight coupling flange which empties the barrels and supplies the tank with the Ethylfluid for the benzine to be leaded. As soon as the proper amount has been added, the entire quantity of the leaded benzine must be circulated several times by pumping for uniform distribution and solution of the Ethylfluid in the benzine.

Ethylfluid has a reddish-brown color in its original state. However, to identify leaded benzines the Ethylfluid frequently is colored blue or green so that this color immediately mixes with the leaded benzine. In aircraft benzines a leading up to 1.2 cc tetraethyl lead per liter is usual, depending on the antiknock characteristic to be reached. An excessive leading has a damaging effect on the exhaust manifolds of the engines, resulting in corrosions on the valve and valve seat. A deposit of lead hydroxybromide may produce a short on the spark plugs and corrosion on the electrodes.

Even in normal operation with leaded benzine, a grayish-yellow deposit is found on the cold parts of the engine cylinder after a longer period of time, especially on the inlet end. This color changes to brownish or reddish shades in the hotter zones. In automobile engines temperatures as high as 800°C occur in the outlet valves at full power, while an overheating produced by insufficient valve clearance and inadequate heat dissipation will result in damage to the valve. Nickel steel used as material for valves shows scaling already at 600°C. The only material with sufficient corrosion resistance for leaded-benzine operation is silicon-chromium steel. Recently, sodium-filled outlet valves are suggested. Widmaier and Nenninger (bibl. 12) found yellowish small crystals of lead bromide on the piston crown and in the cylinder head but also observed that these precipitations do not produce corrosion without addition of water. As soon as water vapor was present, zinc, aluminum, and aluminum alloys were noticeably eroded. Table 12 shows an abstract of this report where the corrosion is given as a decrease in weight percent of the metal test specimens after a 24-hr reaction of lead bromide with benzine with and without influence of dampness.

The lead sensitivity of benzines shows noticeable differences; the lead sensitivity of paraffins and naphthenes is considerable and that of olefins and aromatic compounds is much less. Sulfur compounds show a disturbing effect. The lead sensitivity, related to the octane-number increase, can be given as follows:

Octane-Number Increase after Addition of

| | | 0.2 | 0.4 | 0.6 ccm TEL/liter |
|---|---|---|---|---|
| To: | Straight-run benzines | 10 | 15 | 18 |
| | Cracked benzines | 5 | 8 | 9 |
| | Reformed benzines | 5 | 10 | 13 |

To show the effect of sulfur content and volume of unsaturated compounds in the various benzines on the lead sensitivity ($\Delta$or) the following data can be given for a 0.05 vol% TEL addition:

Distillate benzines with iodine numbers below 20, $\Delta$ OR 12 - 20;
Cracked benzines with iodine numbers of approximately 120, $\Delta$OR 10; of 150, $\Delta$OR 7;
Fischer-Tropsch benzines with iodine numbers between 50 and 60, $\Delta$OR 20 - 23;
Fischer-Tropsch benzines with iodine numbers of 120, only $\Delta$ OR 14.

In the distillate benzines the sulfur content normally is less than 0.02% (assuming suitable purification). In this case, the above-given data on lead sensitivity OR 12 - 20 applies. In distillate benzines with a sulfur content between 0.02 - 0.1%, the lead sensitivity OR is only 10 - 13. Also in the cracked benzines, a differentiation of benzines with a sulfur content below 0.1% and a lead sensitivity of OR 7 - 14 and such with 0.1 - 1% sulfur and OR 5 - 10 is made.

Recently, the lead sensitivity as a product of the octane rating of the basic benzine ($OR_0$) and the octane increase ($OR_{Pb}-OR_0$) is expressed by dividing it by a correction factor (k). This factor k depends on the amount of leading:

$$\text{Lead sensitivity} = \frac{OR_0\,(OR_{Pb} - OR_0)}{k}$$

In this equation, k has the following values depending on the lead addition:

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Values for k | 25 | 43 | 56 | 67 | 75 | 82 | 93 | 100 | [illegible] | [illegible] | 116 | 120 | 124 |
| cc TEL/liter | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 | 2.0 |

The lead-sensitivity coefficients of ordinary fuels are then between 8 (olefins, aromatic compounds) and 13 (paraffins), according to this nomenclature.

To have a rectilinear course of the curves for leaded benzines (bibl. 13), an alignment chart (Fig. 4a) was developed in Oppau. In this chart, the octane number is shown in a linear scale on the ordinate while the cc tetraethyl lead per liter are given on the abscissa in a tapered scale. This representation is more logical than the "ethyl-blending chart" used in the USA and based on investigations by Hebl and Rendel (bibl. 14 and 15). The Americans denote the slope of the antiknock curves as lead sensitivity (PbS) and express this sensitivity as the quotient of increase in critical compression ratio ($\Delta\varepsilon$) by 0.75 times number (n) of the cc tetraethyl lead per US gallons, i.e.,

$$(PbS) = \Delta\varepsilon / 0.75\, n$$

The values of this quotient are approximately 1 : 1.6 for lead-sensitive distillate benzines and light benzines, while the ratio is 0.75 to 1 for benzines of lower lead sensitivity. To change these lead-sensitivity curves into a straight line for obtaining better comparison data, the scale of the octane number in the mentioned " ethyl-blending chart" is tapered with decreasing octane number, while the lines for the lead addition (cc TEL per gallon) are drawn diagonally through the field. In addition, this leading chart contains a numerical column for the lead sensitivity.

Of considerable interest are recent reports by Hammerich (bibl. 16) who indicates that the behavior of fuels to tetraethyl lead follows simple mathematical relations. The percentual increase in basic octane rating ($\Delta$ or %) and the lead content (c) are in a logarithmic ratio to each other. This makes it possible to derive mathematically the lead sensitivity (Em) and to develop a logarithmic diagram. In this diagram, the lead content c is laid off in logarithmic scale on the ordinate in vol% while the octane-number increase ($\Delta$ or %) is laid off in metric scale on the abscissa. In addition, two zero points for the octane rating according to the research and engine method as well as two numerical columns for Em are used for linear determination of the lead sensitivity. By means of this Hammerich diagram (Fig. 4b), the antiknock characteristic of fuels with octane ratings above 100 can be readily interpolated. For the CFR research method, it follows that

$$Em = \frac{\Delta\ or}{50 \log 100\, C + 2}$$

For the CFR-engine method, it follows that

$$Em = \frac{\Delta\ or}{50 \log 100\, C + 15}$$

where $\Delta$ or is the percentual increase of the original octane rating and c the percentual lead content (vol% TEL).

In this relation, measurements of the lead sensitivity on pure hydrocarbons made by Campbell and collaborators (bibl. 17) are of interest. The criterion of lead sensitivity is the increase in critical compression ratio ($\Delta\varepsilon$) in a single-cylinder testing engine produced by an addition of 1 cc tetraethyl lead per US gallon. The values for lead sensitivity ($\Delta\varepsilon$) determined by these researchers in individual hydrocarbons fluctuates strongly and cannot always be clearly defined. However, in the individual hydrocarbon groups noticeable differences occur. For example, $\Delta\varepsilon$ shows mean values between 0.2 and 0.3 for n-paraffins, while $\Delta\varepsilon$ has a noticeably higher value of 0.3 - 0.9 for i-paraffins. The $\Delta\varepsilon$ value for olefins is between 0.25 and 0.8 and in naphthenes the cyclopentane with a value of 2.7 predominates. The side-chain substituted cyclohexanes are rather insensitive to lead with values of $\Delta\varepsilon$ between

0.10 and 0.15. In aromatic compounds, the simple ring bodies (benzene, cyclopentadiene, indene) are known to be insensitive to lead and show negative values for $\Delta\varepsilon$. However, the side-branch substituted benzine rings (ethyl benzine, methyl isopropyl benzene, amyl benzene) are highly sensitive to lead at values of $\Delta\varepsilon$ between 1 and 2.

### d. Other Antiknock Agents

Other antiknock agents according to Church, Mack, and Boord (bibl. 18) expressed in percent of tetraethyl lead efficiency, are as follows:

| | |
|---|---|
| Tetraphenyl lead | 59% |
| Diphenyl dimethyl lead | 97% |
| Diethyl dichloride lead | 67% |
| Diphenyl diethylene lead | 93.5% |
| Trixylene lead | 64.7% |
| Bismuth triphenyl | 18.2% |
| Bismuth trimethyl and triethyl | 20.2% |

In a more recent report, Midgley and Boyd (bibl. 19) give the following compilation on the relative efficiency of various antiknock agents:

| | |
|---|---|
| Benzene | 1 |
| Toluene | 1.1 |
| Xylene | 1.2 |
| Ethanol | 1.9 |
| Aniline | 11.5 |
| Toluidine | 11.9 |
| Xylidine | 12 |
| Tetraethyl tin | 20.4 |
| Diethyl selenide | 62.5 |
| Diethyl telluride | 250 |
| Iron carbonyl (Motyl of IGF) | 250 |
| Nickel carbonyl | 277 |
| Tetraethyl lead | 528 |

Most additions of the above type have never reached any practical importance. An addition of 3.5% aniline will increase the antiknock characteristic of benzines by approximately 10 units.

## 12. AVIATION BENZINES

The special requirements made on aircraft fuels with respect to various characteristics such as compression resistance, stability, and low-temperature behavior require a special grouping of this type of fuel. Consequently, aircraft benzines are discussed in a separate chapter to give their various characteristics. Naturally, during wartime all information which may indicate the composition and characteristics of German aircraft fuels are avoided. However, foreign data on foreign aircraft fuels, as far as known to the author, will be discussed in this section.

### a. Basic Benzine

Already the "basic benzine" requires special selection when used as basis for Otto fuels in aviation. Knocking straight-run benzines and unstable cracked benzines are eliminated from the beginning. Usually, distillate benzines of a special refining degree and special original characteristics with an octane rating of 65 - 76 or 70 - 76 are used as basis for the benzines. Obviously, isoparaffins and naphthenes predominate in such distillate benzines if special stability is to be expected. Several coefficients for such basic benzines are given in Table 13.

The vapor pressure of these benzines must not exceed 7 - 7.5 lb/sq in, i.e., 0.5 kg/cm$^2$. These benzines, as shown by the boiling curve, must be free of natural gasoline which has a high knocking resistance but would possibly result in carburetor icing or in a vapor lock. The content in total sulfur must be below 0.1% or even below 0.05%. The amount of aromatic and unsaturated compounds may fluctuate between 3 and 12% and that of naphthenes between 30 and 50%. The content in paraffins (preferably i-paraffins) must be between 40 and 55%.

### b. Aviation Benzines

Aviation benzines are subdivided by a US nomenclature into four stages:

1) Aviation benzines with an octane rating of 100 (usually colored green);
2) Aviation benzines with an octane rating between 93 and 95 (usually colored green);
3) Aviation benzines with an octane rating of 87 (usually colored blue);
4) Aviation benzines with an octane rating of 80 (usually colored blue or red).

To produce such a high compression resistance, the basic benzine in the first two stages must be supplied with additions of tetraethyl lead and of hydrocarbons with a high antiknock rating such as iso-octane. In stages 3 and 4 it usually is sufficient to ethylate the basic benzine with tetraethyl lead.

An aviation benzine with an octane rating of 100 can be produced from 50 parts of basic benzine and 50 parts of technical iso-octane (OR 96) to which 1 : 1.2 cc TEL/liter are added. An aviation benzine with an octane rating of 93 is obtained from 85 parts of basic benzine with 15 parts of technical iso-octane and 1.2 cc tetraethyl lead/liter. An aviation benzine with an octane number of 87 is obtained by leading of basic benzine (OR 73 - 75) with 1 cc TEL/liter, which means that an addition of the expensive iso-octane is no longer needed. An aviation benzine with an octane rating of 80 can be produced from a basic benzine with an octane rating of 73 and 0.6 cc tetraethyl lead/liter or from light benzines (OR 63 - 67) with 1 cc TEL/liter.

As a matter of fact, a number of other additions are made and it seems of importance to describe the characteristics of these components.

### c. Components of Aviation Benzines

An excellent report by Marder (bibl. 20) exists on the components of aircraft benzines, i.e., on the additives used in rather large amounts for such fuels. These components are mainly the technical iso-octane and other polymeric benzines. To increase the "starting volitility" of these materials, iso-pentane in the form of neopentane (= 2,2 dimethyl propane), neohexane (= 2,2 dimethy butane), certain ketones, and finally additives such as higher alcohols and higher ethers as far as they have a suitable lead sensitivity.

### d. Iso-Octane

The iso-octane mentioned frequently as a reference fuel and having an octane number of 100, has a specific gravity d/20 of 0.691, nD/20 of 1.392, B.P. 99.5°C, and a vapor pressure according to Reid of 0.155 kg/cm$^2$. Pure iso-octane is obtained from technical iso-octane by refining with 65% sulfuric acid at a temperature of 80°C. As additive for aircraft benzines generally the technical iso-octane of an octane rating of 96 with the following characteristics is used: d/20 0.697, nD/20 1.393, initial distillation 36°C, 5% coming over up to 56°C, 15% up to 73°C, 25% up to 87°C, 37% up to 100°C, 45% up to 106°C, 55% up to 108°C, 65% up to 109°C, 75% up to 110°C, 85% up to 111°C, 95% up to 113°C, boiling number 101°C.

Large-scale production of iso-octane uses the "stabilizer gas" of cracking plants as basis. "Stabilization" of cracked benzines is the removal of gaseous components which would result in too high a vapor pressure in the benzine. The butane-butene fraction of the stabilizer gas is used in polymerization to a mixture of di-isobutylene (iso-octene) and tri-isobutylene (dodecene). In the method according to Ipatieff used in the Universal Oil Products, phosphoric acid is used as catalyst at a temperature of 177°C and a pressure of 42 atm, while in the Shell method (bibl. 21) polymerization is obtained in presence of sulfuric acid. In both cases, a mixture of approximately 80% iso-octene and 20% dodecene is obtained. The iso-octene fraction boiling between 90 and 130°C is then submitted to a weak catalytic hydrogenation to form iso-octane of an octane number of 90-97.

Pure iso-octane is the 2, 2, 4 trimethyl pentane $CH_3—C(CH_3)_2—CH_2—CH(CH_3)—CH_3$.

## e. Polymeric Benzine

Other polymeric benzines produced according to the UOP method (phosphoric acid as catalyst) at low temperatures (130 - 300°C) and low pressures (8 - 21 atm) without subsequent hydrogenation furnish polymeric benzines of approximately the following characteristics: d/20 0.737, initial distillation 28°C, 5% coming over up to 67°C, 50% up to 98°C, 25% up to 116°C, 35% up to 123°C, 45% up to 128°C, 55% up to 136°C, 65% up to 158°C, 75% up to 180°C, 85% up to 190°C, and 95% up to 195°C, boiling number 139, aniline point 41°C, and octane rating 82.

In the Alco polymerization of olefinic gases at 480 - 540°C under a pressure between 42 and 56 atm, a polymeric benzine with the following characteristics is obtained: d/20 0.755, initial distillation 32°C, 10% coming over up to 41°C, 30% up to 63°C, 50% up to 83°C, 90% up to 162°C, end of distillation 203°C, and octane rating of 76. In the Alco pyrolysis method at a temperature between 420 and 700°C and a pressure of 3 - 17 atm, aromatization to a product of the following data is obtained: d/20 0.892, initial distillation 49°C, 10% coming over up to 78°C, 30% up to 88°C, 50% up to 96°C, 70% up to 107°C, 90% up to 131°C, end of distillation 178°C, and octane rating 86.

Obviously, in these polymeric benzines the content in unsaturated hydrocarbons is so high that only a subsequent hydrogenation will produce stable fuel components suitable for aviation. The antiknock characteristic may be slightly decreased but the lead sensitivity will be improved. In addition, it is known that polymeric benzines in a mixture with distillate benzines furnish excellent mixed octane values (see Section 8).

Marder (bibl. 20) indicateds that approximately 2.4 million cc polymeric benzine and 0.7 million cc technical iso-octane are produced yearly in 25 polymerization plants. World production of 100-octane aviation benzine is 1.5 million cc per year.

## f. Iso-Pentane

Iso-pentane or neopentane 2,2 dimethyl butane $(CH_3)_2CH-CH_2-CH_3$ is obteined from natural gases and has a specific gravity d/20 of 0.621, boiling point of 28, and vapor pressure according to Reid of 1.43 kg/cm$^2$. In the US, the yearly production is approximately 450,000 cc iso-pentane which in itself is rather knockproof, increases the lead sensitivity of all benzines, and finally is required for increasing the starting volitility of iso-octane. However, an excess of iso-pentane in aircraft benzines would increase the danger of vapor lock considerably. A mixture of 50%

iso-pentane and 50% iso-octane shows a vapor pressure of 0.366 kg/cm$^2$, while a mixture of 70% iso-pentane with 30% iso-octane has a vapor pressure of 0.58 kg/cm$^2$ and a mixture of 85% iso-pentane with 50% iso-octane a vapor pressure as high as 0.855 kg/cm$^2$. A 100-octane aircraft fuel made of basic benzine with an octane rating of 74 generally will not be able to absorb more than 25% iso-pentane if a Reid vapor pressure of 0.6 kg/cm$^2$ is not to be exceeded. Only for winter operation, to increase the starting quality of fuels, up to 40% iso-pentane are permitted in aircraft fuel in the US. The Reid vapor pressure of such a winter aviation benzine will then be approximately 0.8 kg/cm$^2$. It should be mentioned that high-class aviation benzines with octane ratings between 110 and 125 can be produced with polymeric benzine, iso-pentane, and tetraethyl lead.

## g. Alcohols, Ethers, and Ketones

Methyl alcohol and ethyl alcohol are not useful for aviation as fuel additives because of the danger of water segregation and the only relative resistance to low temperatures. More advantageous are tertiary monovalent alcohols, i.e., alcohols with the OH group bounded to a tertiary C atom, especially tertiary butyl alcohol $(CH_3)_3C-CH$ and tertiary amyl alcohol $CH_3-CH_2-C(CH_3)_2OH$ (dimethyl ethyl carbinol). However, these isomeric alcohols are technically not available in large quantities. The iso-amyl alcohol produced as byproduct in alcoholic fermentation, is a primary alcohol $(CH_8)_2-CH-CH_2-CH_2-OH$.

Of the ethers, the di-isopropyl ether $(CH_3)_2-CH-O-CH-(CH_3)_2$ is used in many cases as additive for aviation benzine in the US. As stated, it is obtained cheaply and simply from the propylene of the cracked gases. Isopropyl ether with an octane rating of 101 has a high compression resistance and furnishes favorable mixed octane values. However, the lead sensitivity is poor and the calorific value (8750 cal/kg) is unfavorable. The miscibility with water and the tendency to form explosive peroxides is of considerable disadvantage. Egloff (bibl. 22) investigated the behavior of various isomeric ethers with respect to their antiknock characteristic and lead sensitivity. Table 14 shows some of these values. The lead sensitivity in this table is expressed in octane units after addition of 1 cc tetraethyl lead per US gallon (= 0.265 cc TEL/liter).

Of the ketones the following types are used for increasing the starting volitility of iso-octanes: acetone $CH_3-CO-CH_3$ and methyl ethyl ketone $CH_3-CO-C_2H_5$. The main characteristics of these two ketones are as follows:

| | 3/20 | nD/20 | BP | LS | Vapor Pressure | OR |
|---|---|---|---|---|---|---|
| Acetone, CP | 0.790 | 1.36 | 56 | 94 | 0.24 kg/cm$^2$ | 100 |
| Acetone, techn. | 0.802 | | 56-75 | | 0.21 kg/cm$^2$ | |
| Methyl ethyl ketone | 0.805 | 1.38 | 79 | 86 | | 99 |

## h. Significance of Octane Rating in Aviation

The antiknock characteristic of aviation benzines is highly important, which is not always considered. Insufficient antiknock characteristics strongly decrease the power of an aircraft engine. For example, Philippovich (bibl. 10) reports on tests made in a Pratt & Whittney engine, running on aviation benzine of an octane rating 80 at a power of 550 hp. The power in this engine was decreased to 460 hp when using 75-octane benzine, due to the decreased compression and precompression possibility. In another case, a test made on a Wright-Cyclon aircraft engine gave the following picture:

| Aircraft benzines | Compression Ratio | Power |
|---|---|---|
| OR 87 | 6.4 : 1 | 715 hp |
| OR 80 | 5.75 : 1 | 675 hp |
| OR 73 | 5.3 : 1 | 645 hp |

i.e., approx. 4 - 5 hp power loss per octane unit

In another report by Philipovich (bibl. 23), these data are plotted in a diagram in a more general form which is shown in Fig. 5 in this report.

### i. Specifications

Under these conditions it is obvious that aviation benzines are ruled by certain specifications in the various countries in which aviation has been sufficiently developed. Table 15 shows a short compilation of specifications for foreign aviation benzines which are taken from the National Petroleum News 1937 of 28 July.

In most cases, the requirement is made that the resin content must not exceed 10 mg/100 cc (glass-dish evaporation) and the sulfur content must be below 0.1%. The vapor pressure according to Reid is limited to 7 lb/sq in, i.e., 0.5 kg/cm$^2$. In the British Standard Specification complete absence of unsaturated hydrocarbons is required.

### j. Additives and Octane Rating

Hubner, Egloff, and Murphy (bibl. 24) developed uniform families of curves in the octane scale by representing the lead sensitivity of conventional aircraft basic benzines together with the effect of various additives such as iso-octane, iso-pentane, isopropyl ether, benzine, toluene, zylene, and ethyl benzene. These diagrams are so evaluated in Tables 16a - g that only the octane-number increase produced by the additives in a straight-run 70-octane basic benzine are given rather than the absolute value of antiknock characteristic.

For evaluating the properties of Otto fuels, a number of investigation methods are used. A brief summary of such methods will be given below. It is of considerable importance to give a critic of these methods, to represent their main importance, and to prevent any overvaluation or underestimate. Naturally, it is impossible to evaluate an Otto fuel from a single characteristic. A certain number of such characteristics will be needed for drawing a useful and valid conclusion.

### k. Color and Appearance

Refined or satisfactorily rectified distillate benzines have a completely colorless appearance not only in a test tube but also in a thicker layer. Refined cracked benzines are slightly yellowish, while crude crack benzines or crude benzines in general are yellow or brown in their original state. Formation of rust-brown flocculates in cracked benzines indicates precipitation of insoluble resins, a case which is relatively rare. Turbidity would indicate mechanical impurities due to dirt or water. Separation of water is possible in benzine-alcohol mixtures, i.e., in many cases any addition of moisture may even result in a layer segregation of benzine and alcohol. Benzine-benzene mixtures may show in incipient crystallization at low temperatures of -35°C and will then become heterogeneous. To characterize benzines for definite application purposes or to give certain data on the components, these fuels are colored artifically. Generally, a benzine-alcohol mixture was colored green in Germany, while green Otto fuels are used for aviation in the US and other countries which contain, along with a high lead content, substances such as iso-octane, iso-pentane, etc. In Germany, the BV-Aral representing a three-component mixture of benzine, benzene, and alcohol was colored blue. In other countries, aviation benzines with an octane rating up to 90 are characterized by this color. Benzine-benzene mixtures were colored red in Germany while 90-octane fuels were colored red in other countries, so that the color does not give any definite information on the type and suitability of an Otto fuel if its origin is not clearly indicated.

## 13. SPECIFIC GRAVITY

The specific gravity (formerly density) of a substance is its absolute mass at a definite temperature d(t), i.e., the mass of 1 cc of this substance per gram, which ~~is not~~ exactly a very accurate definition. The specific weight generally is the ratio of weight to volume expressed in g/cc. In practical application, the concepts of specific gravity and specific weight are used without any differentiation.

### a. Hydrometer

The specific gravity of fuels is determined by means of hydrometers if the quantity is sufficient. Hydrometers or specific-gravity spindles are glass immersion bodies filled with buckshot which submerge into the liquid to a certain depth corresponding to the specific gravity. The specific gravity for the given measuring temperature can then be read directly on the scale. Since the specific gravity must be standardized to temperatures of 15 or 20°C for comparison purposes, a correction of approximately 0.0008 must be made for benzines per each degree Celsius temperature difference of the measurement from the reference temperature. Obviously, in measurements below 20°C the correction must be deducted from the test value while in measurements above 20°C it must be added, since liquids (as also other bodies) contract in cold and expand in heat.

### b. Pycnometers

At an insufficient quantity of material to be tested in which hydrometers cannot be used, a pycnometer or weighing bottle calibrated to 10 or 20 cc content is used. Application of these pycnometers is generally known. In a pycnometer without indication of capacity, the empty weight is determined first by weighing, deducting the air in the pycnometer (1.2 mg/cc) and then the weight with boiled distilled water of 20°C is determined (water value). As far as the temperature correction in weighing of fuels is concerned, the above statements apply.

### c. Specific Gravity of Otto Fuels

The specific gravity of automobile benzines fluctuates between d/20 of 0.715 - 0.755 and in benzines blends up to 0.790. Especially light benzines (starting benzines) with a low boiling point show a specific gravity d/20 of less than 0.700. For chemically defined hydrocarbons, the specific gravity is a definite characteristic but in benzines forming an extremely complicated and continually varying mixture of hydrocarbons as to origin and treatment, the conclusions drawn from specific gravity are not too accurate. However, Marder defined a linear relation between the specific gravity and the hydrogen content of petroleum benzines free of additives, shown in the following numerical block:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| d/20 | 0.640 | 0.660 | 0.680 | 0.700 | 0.720 | 0.740 | 0.760 |
| %H$_2$ | 15.7 | 15.4 | 15.1 | 14.75 | 14.45 | 14.15 | 13.35 |

In benzines of the Kogasin synthesis, the following relations exist:

| | | | | | |
|---|---|---|---|---|---|
| d/20 | 0.640 | 0.660 | 0.680 | 0.700 | 0.720 |
| %H$_2$ | 15.7 | 15.33 | 14.36 | 14.56 | 14.31 |

### d. Specific Gravity and API

Between the specific gravity d/15.6°C (60°F) and the graduation according to API

(American Petroleum Institute) generally used in the US, the following relations exist:

$$d/15.6 = \frac{141.5}{131.5 + API^{o}} \qquad API^{o} = \frac{141.5}{d} - 131.5$$

## 14. DISTILLATION

Chemically-defined substances of corresponding purity, such as hydrocarbons, alcohols, ethers, ketones, etc. have a very definite boiling point giving a clear characterization. However, benzines representing a complicated mixture of various hydrocarbons of different groups (paraffins, naphthenes, aromatic compounds, and olefins) are characterized by number of subsequent boiling points or by a "boiling curve". Since the reciprocal solution takes place between the individual hydrocarbons and since formation of azeotropic mixtures with a definite boiling point is involved, it is extremely difficult to separate hydrocarbons by distillation. For a qualitative evaluation of fuels or fuel mixtures it is not necessary to isolate the individual components of hydrocarbons. In these cases, it is sufficient to make a distillation according to definite rules, to determine the general boiling range of an Otto fuel, and probably to investigate the various boiling sectors (fractions).

Table 18a - d contains the most important characteristics of well-defined hydrocarbons of the paraffin, olefin, naphthene, and aromatic series as far as these hydrocarbons exist in petroleum products of the boiling range of benzines or are formed by cracking or hydrogenation, or can be used as additive. The extremely high number of hydrocarbons occurring in benzines are clearly defined only by considering (in view of the isomerism of hydrocarbons) that mathematically 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, 35 nonanes, 75 decanes, and 159 undecanes are possible. The phenomenon of isomerism, i.e., hydrocarbons with branched chains, is shown also in the olefin series. In combination with naphthenes and aromatic compounds, a large number of individual components constitute the hydrocarbon mixture of benzines.

### a. Characteristics of Pure Hydrocarbons

The characteristics and coefficients of pure hydrocarbons are given in Table 18. Francis (bibl. 25) made extensive investigations on the relations between physical characteristics of paraffin hydrocarbons, and the numerical values in Table 18a are mainly based on this report. Francis establishes mathematical relations between the coefficients of pure hydrocarbons. In this respect, the statement made by Kronecker, a well-known mathematician, should be mentioned who stated that the integrals were created by the Lord and that anything else is human handiwork. This formula established by Francis furnishes the following values:

$$t = 76.4 + 36.4\ n - 1.047\ n^2 + 0.016\ n^3 - \frac{270}{n} + \frac{216}{n^2}$$

where t denotes the boiling point in °C and n the number of carbon atoms. This formula merely permits calculation of the boiling points of n-paraffins up to hexadecane. For calculating the boiling points of isomeric paraffins, the boiling point of those n-paraffins whose chain lengths coincide with the longest chains of the corresponding branched paraffins is used as basis. Then, the following increments $\Delta t$ must be added:

2-methyl $\Delta t = 20.7 - 0.75\ n +$ 28[illegible]/$n^2$
3-methyl $\Delta t = 17.55 - 0.5\ n + 450/n^2$
4-methyl $\Delta t = 8.45 + 680/n^2$
3 ethyl $\Delta t = 32.45 - 0.6\ n + 1428/n^2$

2,2-dimethyl $\Delta t = 51.52 - 2.88\, n + 576\, n^2$

2,3-dimethyl $\Delta t = 24.6 + 1428/n^2$

2,5-dimethyl $\Delta t = 58.0 - 2.75\, n + 288/n^2$

3,3-dimethyl $\Delta t = 19.52 + 0.18\, n + 1428/n^2$

The mathematical relations given by Francis for pure paraffin hydrocarbons between density or refraction and number of carbon atoms, as well as the relations between density or refraction, aniline point, and number of carbon atoms and the relations given for approximate determination of the octane number will be discussed later in the text.

### b. Engler Distillation

For distillation according to Engler (DIN No. 2, German Industrial Standards DVM 3672) a thick-walled 100-cc glass flask with a ball diam of 65 mm and a diam of the neck of 16 mm is used. The length of the neck is 150 mm, the adapter of the delivery tube is 90 mm above the liquid level, and the delivery tube is inclined at an angle of 75°. The distillation flask, for shielding it from room temperature, is covered with a metal casing. Similarly, the heat source is shielded to distribute the heat as uniformly as possible over the flask. The cooler is either a glass Liebig condenser of 60cm length and 12 mm inside diam or a seamless brass tube led through a metal box filled with water or ice. As absorption bulb, either a graduated cylinder or a rotating frame with graduated test tubes are used for separating the individual fractions. The thermometer has a length of 38 cm, a measuring range between 0 and 300 (or 400°C) with a thickness of 6 - 7 mm. The distance of the 0° graduation from the mercury bulb must be 10 - 11 cm for distillation of Otto fuels, while the distance should be 3 cm for distillation of higher-boiling fuels (Diesel oils). The thermometer is so introduced into the flask through the cork that the upper end of the mercury bulb cuts off with the lower bend of the delivery tube. The delivery tube of the distilling flask must extend 3 cm into the cooler. Strictly speaking, the temperature data of a thermometer apply only under the condition that the mercury thread is immersed completely into the fluid to be measured. In all other cases, corrections must be made. However, in commercial analyses these determinations generally are not made. The corrections must be added to the temperature reading and are as follows:

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature reading | °C: | 60 | 80 | 100 | 120 | 140 | 160 | 180 | 200 | 220 | 240 | 260 |
| Correction | +°C: | 0.8 | 1.6 | 2.3 | 3.1 | 3.9 | 4.9 | 5.9 | 7.2 | 8.7 | 10.3 | 12.2 |

Even at a low barometer reading, corresponding corrections must be made for exact measurements and have to be added to the read temperature. These corrections are as follows with respect to normal pressure of 760 mm Hg per millimeter of mercury-column atmospheric-pressure drop:

| | |
|---|---|
| In the boiling range of 30 - 50°C | 0.038°C |
| In the boiling range of 50 - 70°C | 0.040°C |
| In the boiling range of 70 - 90°C | 0.042°C |
| In the boiling range of 90 - 110°C | 0.045°C |
| In the boiling range of 110 - 130°C | 0.047°C |
| In the boiling range of 130 - 150°C | 0.050°C |
| In the boiling range of 150 - 170°C | 0.052°C |
| In the boiling range of 170 - 190°C | 0.054°C |
| In the boiling range of 190 - 210°C | 0.057°C |
| In the boiling range of 210 - 230°C | 0.059°C |

It is of importance to note the mentioned corrections in any distillation analyses, since the correction for the protruding mercury thread may reach considerable values.

The rate of distillation is to take place within the following limits: initial distillation approximately 5 - 10 min after starting the heat, in which case the temperature degree is denoted as the incipient distillation at which the first condensed drop falls from the cooler tip into the absorption bulb. Then, the distillation is to proceed at approximately 2 drops per sec, i.e., 4 - 5 cc per min must be distilled at suitable regulation of the burner flame. The end of the distillation is reached when the temperature at which the flask is either empty or at which a whitish decomposition vapor shows above a small residue of liquid. The liquid collected in the condensers is known as "distillate" while the remainder in the flask is known as distillation residue. The component lost per 100 cc of initial material is denoted as the distillation loss. This distillation loss, in highly-volatile benzines, especially gas benzines, may be as high as 4%. In this case, the amount should be added to the lower boiling fraction (below 100°C). Normally, approx 97 - 98% should come over up to the end of distillation.

If distillation is made in such a manner that the temperatures at which 5, 15, 25 up to 85.95% of the initial quantity has come over and if the arithmetic mean of these temperature values is taken, the distillation range will be characterized (according to Ostwald) by the so-called boiling characteristic or boiling coefficient.

### c. Boiling Coefficient

This value is very near the 50% boiling point used in foreign countries but defines the character of the lower and upper fraction much better. However, even this definition is not sufficiently accurate for drawing any conclusions as to vapor-lock formation or lubricant dilution. Aviation basic benzines are characterized by boiling coefficients of 95 - 100, light benzines by coefficients between 100 and 110, benzine-benzene mixtures by coefficients between 110 and 120, and medium automobile benzines by coefficients up to 125. At a boiling coefficient of 125 or 130, higher operating temperatures or higher preheating is required. Benzines with a coefficient above 130 are considered heavy benzines and, especially in cold weather, will thin the oil in the crankcase of motorized vehicles.

### d. Boiling Curves

If distillate volume and temperatures obtained in a distillation are brought into a graphical ratio, uniform boiling curves are obtained for benzines. Addition of benzene and alcohol in larger amounts influences the course of these curves by forming of discontinuities. In Fig. 6 showing boiling curves of various Otto fuels, the boiling course of an aviation basic benzine is plotted along with an automobile benzine free of additives, a benzine-benzene mixture, a benzine-alcohol mixture, a heavy benzine, and a petroleum.

In the case of automobile benzines it generally is required that not more than 35% should come over up to 75°C in the distillation (to avoid vapor lock due to the highest-boiling fractions). In addition, the amount of components boiling up to 100°C should not be less than 25%. Taken more strictly, it is desirable that not more than 25% should come over up to 75°C and 30 - 45% up to 100°C, but not less than 95% up to 200°C. Accurately defined, the requirements made on basic benzine for aircraft fuels are as follows: 10% up to 75°C, 50 - 60% up to 100°C, 90% up to 135°C, and end of distillation not above 150°C. Special benzines for low-temperature starting must have the boiling range between 400 and 100°C. Obviously, such "petroleum ethers" must have a high vapor pressure (approx 1.3 kg/cm$^2$) and a low specific gravity (d less than 0.650).

Frequently, a moderate initial distillation (not below 40°C) is desired for Otto fuels. However, in this case determination of initial distillation fluctuates strongly with the room temperature and the rate of distillation. Therefore, it may be more suitable to make the requirement that the components boiling below 50°C should not be more than 2.5% in summer operation. The conventional evaluation of benzines according to the so-called "10% boiling point" (10% BP) has a certain justification. This 10% BP, for easy starting in cold weather, should be between 60 and 75°C since the starting characteristic depends on the temperature in the cold engine at which a sufficient amount of the coarsely atomized benzine must evaporate for producing a sufficiently combustible fuel-air mixture. According to a rule of thumb it may be stated that at +5°C no starting difficulties may occur even if only 10% distill over up to 100°C for a given benzine. At a temperature of 0°C, the 10% BP must be below 85°C and at -10°C this boiling point must be in the range of 65 - 70°C. At a temperature of -20°C, the 10% BP must be between 60 and 65°C. At lower temperatures it will be necessary to inject temporarily a special benzine (petroleum ether). According to Edgar, Hill, and Boyd, the following relation exists between the 10% BP of benzines and their starting ability in low temperature for the usual fuel-air ratio (air-excess coefficient 1.1):

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10% BP 20 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 |
| Starting Temperature °C: | -45 | -40 | -36 | -33 | -30 | -26 | -23 | -20 | -17 | -13 | -10 | -7 | -3 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 10% BP | 85 | 90 | 95 | 100 | 105 | 110 | 115 | 120 |
| Starting Temperature °C: | 0 | +3 | +6 | +9 | +13 | +16 | +19 | +22 |

In enriched fuel-air mixtures the starting temperatures are several degrees more favorable. However, starting at low temperatures depends also on the engine and lubrication state and especially on the battery and dry spark plugs. Wherever possible, the cold iron parts of the intake line will have to be heated to prevent any separation of gasoline droplets which then would be missing for a correct benzine-air mixture inside of the engine. The value of the 90% BP gives a criterion on the lubricant thinning by the "petroleum distillation tail" of the benzine. This thinning generally should not be more than 10% in wintertime, but becomes much more pronounced at larger additions of higher-boiling components in a given benzine. Bridgeman (bibl. 26) defines the dew point (Dt) in °F as that temperature at which benzine evaporates in the air excess (generally 12%) corresponding to practical engine conditions. This dew point is to furnish a satisfactory criterion for lubricant thinning and is calculated as follows: Dt (°F) = (90% BP (°F) : 1.4) - 131. Between the dew point and the 90% BP, the general relation exists:

| | | | | | | |
|---|---|---|---|---|---|---|
| 90% boiling point | °C: | 150 | 160 | 180 | 200 | 220 |
| Dew point (USA) | °C: | 17 | 31 | 45 | 59 | 73 |

In this case, (according to the US nomenclature), the dew point is that temperature at which a theoretically composite fuel-air mixture has completely evaporated under atmospheric pressure or just starts condensating.

### e. Evaporation Test

Dieterich (bibl. 27) was the first to make the suggestion that Otto fuels should be tested as to their evaporation behavior. His method was as follows: An amount of 10 cc is pipetted on a watchglass and the resultant loss in weight is determined by weighing at intervals of 10 min, resulting in evaporation curves. However, the suggestions were not put into practical application.

Wawrziniok (bibl. 28) resumed this general concept and constructed an evaporation balance for measuring the evaporation period (min) for various fuels at a temperature of 45°C and a subpressure of 80 mm Hg. This evaporation balance consists in principle of a glass vessel filled with the benzine to be tested and suspended from a balance beam. The opposite lever arm is equipped with a stylus sliding over a clockwork-controlled paper tape and recording the progressive evaporation. This apparatus can be put under vacuum and can be heated. In well-defined hydrocarbons, the evaporation period necessarily will be a linear function of the volume available for evaporation, resulting in a clear relation to the constant boiling point. However, in benzines the lines show a considerable curvature since the volatile components are evaporated more rapidly than the components with higher boiling points. The evaporation periods are shorter at higher vacuum. Figure 7 (according to Wawrzinick) shows the evaporation curves, i.e., the ratio of evaporation volume to evaporation periods for several fuels or fuel components. Obviously, pure substances such as pure benzine and absolute alcohol furnish rectilinear functions, while hydrocarbon mixtures (technical example: Leuna benzine and normal benzine) as well as benzine-alcohol mixtures will result in curved lines. The evaporation coefficient according to Wawrzinick is analogous to the Ostwald boiling coefficient which means that it represents the arithmetic mean of the evaporation periods of 5, 15, 25, etc. up to 95% of the corresponding quantities of benzine to be tested.

## 15. VAPOR PRESSURE

A liquid will boil as soon as its vapor pressure exceed a value of 1 kg/cm$^2$ (1 atm) and thus overcomes the atmospheric pressure exerted on it. Any chemically-defined body of such liquids, i.e., water, alcohol, benzine, acetone, etc. has a vapor pressure of 1 kg/cm$^2$ at its boiling point. However, in liquid mixtures such as benzines, the vapor pressure of 1 atm is reached only by the fraction distilling over at a given moment, so that the vapor-pressure measurements on benzines only have the significance of an average value.

### a. Measuring Units of Vapor Pressure

Measuring units of vapor pressure are the kg/cm$^2$, the atmosphere, and the lb/sq in. in foreign countries, and finally the barometric reading of the mm-Hg column. The various relations existing between these units are given in Tables 20a - b.

### b. Vapor-Pressure Determination According to Reid

The vapor-pressure apparatus according to Reid consists of a steel benzine container of 52 mm inside diam and 64 mm height, including an air cylinder of the same diameter and 254 mm height connected to this container by a tight threaded adapter. A manometer is screwed to the head of this cylinder. The manometer is a tubular-spring instrument with graduations up to 1 kg/cm$^2$ or a second instrument with a graduation up to 4 kg/cm$^2$. Since the vapor pressure depends strongly on the temperature, the temperature must be given for each measurement. To keep this temperature constant, a water-jacketed vessel into which the bomb is immersed up to the manometer tip is used.

Taking the sample must be done carefully if water-vapor losses are to be avoided. In open fuel containers, the benzine container of the bomb is simply immersed and filled, while tanks under pressure or pipe lines require a separate benzine container with two valves in which case filling takes place through the lower valve. Simple pouring of the samples into the benzine container is impermissible in comparison analyses. In other cases it is permissible with certain limitations, requiring suitable cooling of the sample and the benzine container. For fuels with a vapor pressure of 0.6 kg/cm$^2$, cooling must go to temperatures of +10°C and for fuels with vapor pressure up to 0.8 kg/cm$^2$ to + 4°C. Fuels with pressures of 1.1 kg/cm$^2$ require a cooling to -1°C, fuels with 1.4 kg/cm$^2$ pressure to -4°C, and the most volitile starting fuels with a vapor pressure of 1.8 kg/cm$^2$ must be cooled to -7°C.

For this experiment, the air cylinder must be rinsed several times with lukewarm water for removing all benzine-vapor residues of previous tests. The threaded connections must be coated with a shellac solution after assemblying. The vapor-pressure apparatus must then be inverted and shaken several times in this position. Then, the apparatus is inserted into the water bath so that the manometer tip cuts off with the water level. After 5 min, the bomb is removed shortly and shaken vigorously. This process is repeated at 2-min intervals until finally the vapor-pressure indication remains constant. Any inertia in the manometer must be removed by tapping it lightly.

The vapor-pressure of fuels is generally measured at 100°F = 37.8°C. In special cases, plotting of the vapor-pressure curve as a function of the temperature is of considerable interest. Figure 8 shows that no rectilinear functions are involved in this case. If the vapor-pressure is measured at 37.8°C, a correction must be made for exact experiments, since the difference between initial air temperature and bath temperature causes a pressure variation in the air cylinder. The following numerical series contains these corrections in kg/cm², compared to the initial air temperature. Since this temperature generally is below the bath temperature, the corrections must be deducted from the reading.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Air temperature °C: | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Correction kg/cm²: | -0.20 | -0.18 | -0.155 | -0.13 | -0.105 | -0.075 | -0.047 |

c. Vapor-Pressure Curves and Vapor-Pressure Values

Table 21 contains the vapor-pressure values in kg/cm² according to Gnamm (bibl. 29) for several known substances at different temperatures. This table can be used for supplementing the graph in Fig. 8.

The vapor pressure of commercial automobile benzines, measured at 37.8°C (100°F), must not be below 0.25 kg/cm² and not above 0.6 kg/cm². In cold weather, the vapor pressure can be slightly higher and especially the lower limit can be raised since a high vapor pressure facilitates starting at low temperatures. For aircraft benzines of foreign countries, a fixed value of maximum of 7 lb/sq in, i.e., 0.49 kg/cm² is given.

d. Vapor Lock

The vapor-pressure measurement according to Reid is frequently used as a criterion for danger of vapor lock which interferes with regular fuel supply. However, no clear relation between vapor pressure and vapor lock exists. For example, Heinze, Marder, and Trubetzky (bibl. 30) reported that formation of vapor bubbles at a 5 - 10% alcohol addition to benzines increases strongly which could not be expected from the vapor pressure of the alcohol. Aromatic compounds decrease the vapor pressure at increasing amount of additives and the effect of di-isopropyl ether is much more favorable, while acetone increases the vapor pressure as expected. In this connection, it should be mentioned that American benzines (straight-run) frequently have an original addition of 5% butane and propane which naturally furnishes one third of the vapor pressure of benzine.

The temperature (t) at which danger of vapor lock exists, can be calculated according to an American formula: 10% BP (°F) - 9 (°F) - t (°F) = 0.07 (10% BP - 9) + 33. However, this formula does not seem very suitable for practical application. The US Bureau of Standards recommends the formula t = 259 - 140 log p where t denotes the temperature (°F) at which vapor lock may be expected, while p is the Reid vapor pressure (lb/sq in at 100°F).

Schmidt and Scholz (bibl. 31) do not use the Reid vapor-pressure measurement as a suitable criterion for the expected formation of vapor bubbles, since the Reid method measures the fuels in presence of air. Benzines have a good dissolving power for air and low-temperature distillation of benzines generally furnishes 15 cc of air per each 100 g of benzine. Consequently, it is possible that in the vapor-pressure apparatus by Reid the air above the benzine enters into solution with the benzine itself, resulting in a vapor-pressure drop. To approach the natural conditions of vapor lock, Schmidt uses an apparatus in which a 1 m long copper tube as used for fuel feeding in motorized vehicles, ascends diagonally into a water-jacketed vessel. In this manner, a volume of 120 cc is conducted through per min (corresponding to approx 15 ℓ of benzine per 100 km). The gas developed from the benzine is collected in a graduated measuring tube of a pulsating device, closed at the upper end and connected to the upper tip of the fuel line. Then, the time required for forming 10 cc of gas in each benzine sample is measured. The benzine in which the time for forming this gas is shorter will have a higher tendency for vapor-bubble formation. Various values of this experiment are given in Table 22a.

The vapor pressure in Table 22a was determined according to the Bridgeman and Aldrich method. Since no suitable relations between vapor pressure, density, initial distillation, and vapor-bubble formation could be found, a vapor-pressure difference (pa - pb) was produced by subjecting the fresh samples with a vapor-pressure pa to a 2-hr evaporation to a vapor pressure pb. In this experiment, it was expected that the vapor-pressure difference will probably be proportional to the vapor-bubble formation. In the vapor-pressure determination according to Bridgeman, degased benzine is used, cooling the benzine sample with liquid air and removing the gases above this benzine by suction, to determine the so-called "true" vapor pressure of the benzine.

A new device for evaluating formation of vapor bubbles is mentioned by Hammerich. This author attempts to find a correlation to the trouble occurring in practical engine operation and suggests use of the so-called "relative stalling temperature" as criterion. This stalling temperature is the temperature at which the delivery of a membrane pump, due to vapor-bubble formation, decreases from an original value of 10 ℓ/hr to 2 1/2 ℓ/hr. Koch (bibl. 32) investigated the various influences of operating conditions on the test results of the Hammerich testing equipment and finally produced the following suggestion: The relative stalling temperatures determined in the Hammerich apparatus are equal to those temperatures at which the individual fuels, due to their vapor tension, overcome an atmospheric-air pressure of 1 kg/cm². In Fig. 9, the vapor-pressure curves of several fuels investigated by Koch are plotted with an emphasis on the critical temperatures for vapor-bubble formation on reaching the vapor pressure of 1 atm. Table 22b contains the most important coefficients for these fuels. A calibration benzine is denoted by E, aviation benzines by F, benzine-benzene mixtures by BB, and benzine-alcohol mixtures by BSp.

In the mentioned report, Koch comes to the conclusion that an Otto fuel in summer definitely will produce trouble in the fuel supply if its vapor-pressure overcomes the atmospheric air pressure at 60°C or earlier. However, in winter any fuel with a critical temperature of more than 50°C at 1 kg/cm² can be used for operation free from any possible vapor lock.

### e. Saturation Pressure

The saturation pressure of the vapor tension of a liquid is the pressure of the liquid vapor above the liquid to be tested and located in the Toricelli vacuum.

Ostwald-Luther (physico-chemical measurements) described a method of determining the vapor pressure in the Toricelli vacuum as follows:

A glass tube of 1 m length, 10 mm width and closed at one end is filled with dry mercury (free of bubbles). Then, this glass tube closed off by the finger, is inverted into a cup under mercury. The mercury level in the measuring tube will then drop to the level (H) of the Toricelli vacuum. The tube is then sufficiently tilted (always under mercury seal) until the mercury touches the upper tip. At this moment, the air-free benzine sample is introduced into the vacuum by means of a bent pipette. The liquid evaporating in vacuo then reduces the mercury level further (H'). However, this measurement must be corrected by adding the value h·d/13.6 to H'. In this ratio, h denotes the level of the benzine not evaporating in vacuo and d its specific gravity. The difference H - (H' + hd/13.6) will then be the vapor tensions of the investigated liquid, expressed in mm Hg. In the Ostwald-Luther apparatus, merely a jacket is placed around the Toricelli tube through which vapor or liquid for temperature control can be conducted.

Wawrziniok has improved this test setup (see Fig. 10) in many points: a 108 cm long, 17 mm wide measuring tube (1) filled with mercury is immersed with its lower tip (2) into the mercury trough (3). At point (4), this tube is tapered and closed by a ground-glass stopper (5). A glass-tube adapter (6) is used for charging the tube with mercury or liquid to be tested. A rubber gasket (7) can be screwed to the tube end (2). A jacket tube (8) remains continually filled with air, and an additional jacket tube (10) is filled with heat-insulating liquid (glycerine) through which a thermometer (9) is conducted. The heating coils are shown as (11); the mm-graduation (12) is equipped with a reading slide. For using the apparatus, (2) is closed tightly by means of (7), and the measuring tube (1) is filled across (6) with air-free mercury above the level of (5). Then, this tube is closed by (5), inserted into (3), and then (7) is separated from (2). The mercury in (1) will then drop and adjust itself to the prevailing barometer reading. Above the mercury in tube (1) a Toricelli vacuum will then exist. As soon as (6) is charged with the benzine to be tested and as soon as (5) is carefully opened, the residual mercury and a small amount of test liquid will flow into (1). Naturally, the stopper (5) is closed long before (6) is completely evacuated and the mercury seal is immediately established again in (6). Then, a part of the liquid will evaporate in vacuo, decreasing the mercury level at the same time. This makes it possible to calculate the saturation pressure from the difference of the corrected mercury column, as described above.

Another interesting item in the report by Wawrziniok is the fact that fuel mixtures generally show higher or even much higher saturation pressures than expected from their components. This is demonstrated in Table 23. The abnormalities shown in this table indicate a possible increased vapor-bubble formation of certain mixtures, especially of alcohol mixtures.

## 16. EVAPORATION RESIDUE

A suitable Otto fuel should evaporate practically without residues, i.e., an evaporation residue of less than 20 mg/100 cc benzines is of no importance especially if it is soluble in the fuel. The distillation residue in the Engler distillation may have increased the pigment or changed the color, but this pigment should not be turpid or dirty and should not contain any mechanical impurities. Benzine and benzine mixtures must evaporate on filter paper without leaving any spots. Such spots would indicate that they either contain too much of the upper distilling tail or have been adulterated with "top oil" for additional lubrication.

### a. Gum Test

For determining the evaporation residue, a popular method is the "gum test" (resinous residue) according to Hunn, Fisher, and Blackwood (bibl. 32) or according to Littlejohn, Thomas, and Thompson (bibl. 33), although its value is only of limited use. Basically, it is correct that cracked benzines can be detected in this test on their content of formed resin. In this test, 100 cc benzine are evaporated over a boiling water bath in a 4 - 4.5 cm high and 9 - 10 cm wide glass dish of hard glass (weight not more than 50 g). For more rapid evaporation, an air stream of sufficient force is led over the benzine surface so that the test is finished after 10 - 20 min. The blower tube must have a distance of 5 - 10 cm from the benzine level and have an inside diam of 13 mm at the point of contact. The tube is closed off by a wire netting and a tampon of loose cotton. The then empty glass dish with a possible residue is dried in an air bath for 1 hr at 110°C (according to other data, 150°C), then cooled in the desiccator over calcium chloride, and finally weighed. If the permissible "resin amount" is exceeded in lead-containing fuels, the residue in the dish must be absorbed by benzene and alcohol in the ratio of 2 : 1 and filtered. Then the benzene and alcohol are evaporated in the same manner, determining finally the lead-free resin residue. The American copper-cup method furnishes much too high a value in this gum test, using the sulfur attack on copper and the catalytic resin saturation by copper. To eliminate any doubtful cases, the working method generally is given in determinations of the evaporation residue, i.e., either glass-dish or copper-cup method.

The "Benzene Association" (Benzolverband) took over the method described by Brunschwig and Jacque (bibl. 34) but added a moderate aging test to the determination of the evaporation residue. In this test, 100 cc benzine are kept at moderate boiling for 3 hrs on the reflux condenser while conducting 35 cc of oxygen per min through the condenser. Then, 80% of the treated benzines are distilled over and the remainder in a weighed glass dish is evaporated on a boiling water bath. The residue is then dried in the drying oven at 105°C until the weight is constant.

### b. Resin Afterformation

At least as important as determination of already formed resin in Otto fuels is the investigation of the resin afterformation. Completely formed resin in quantities of more than 25 mg/100 cc may create trouble in a vehicle engine but subsequent formation of resin produces considerable aging and reduces the storage properties. Benzines of such type probably will afterform considerable amounts of resin within a few months. It had been mentioned above that cracked benzines with insufficient pretreatment are one of the main causes for this phenomenon.

Weller and Conrad (bibl. 35 and 36) reported in this connection on bomb tests in which benzine samples were exposed to a pressure of 7 atm oxygen in 500 cc steel bottles and then were placed into boiling-water baths for a longer period of time. Manometers or pressure recorders were used for determining the pressure increase due to heating. After a certain time, the pressure drop produced by the fact that the oxidizable benzine components absorb oxygen more or less eagerly and create resinification was measured. The time used for this pressure drop is a characteristic factor for resin afterformation in benzines and is even known as "induction period". The amounts of resin in benzine after such bomb experiments has a varying value (50 - 800 mg), depending on the individual test conditions. Generally, a 4-hr duration is used. This has the disadvantage that a distorted picture of the aging is obtained since no noticeable resin afterformation takes place during the induction period. However, as soon as the pressure drops, oxidation becomes more vivid and the final value will then depend entirely on the oxidation period, i.e., on the duration of the active reaction. Otherwise, the found aging values of resin afterformation scatter considerably which was expected in accelerated tests of this type.

In various bomb experiments with cracked benzines, Weller determines that additives of straight-run benzines and benzenes act as thinning agents and prolong the induction periods. Slight additions of alcohol will rather shorten this period and only alcohol additions above 12% will inhibit aging.

It is unfortunate that no usual correlations have been detected between the accelerated aging test (length of induction period) and the natural aging (length of storage period). Consequently, an overvaluation of this test is dangerous and in certain cases, the investigation of natural aging of Otto fuels especially cracked benzines will be the only possible means. In the described bomb tests, stable benzines produced induction periods between 100 and 300 min and unstable cracked benzines periods of less than 40 min.

In the section on cracked benzines, the natural aging, observation of storage property, and influence of incorrect refining (sulfuric acid as catalyst for resin afterformation) were discussed. Consequently, the natural aging of fuels will be investigated before and after a given storage period of several months as to a large number of characteristics: specific gravity, refraction, distillation curve, gum test, antiknock characteristics, etc.

## 17. VISCOSITY

The viscosity of Otto fuels has only a scientific interest and becomes of practical importance only at extremely low temperatures. However, the viscosity values and the viscosity temperature gradient of several hydrocarbons are given in Table 24. These values generally are considerably below the viscosity of water (1 cp/20°C).

It is of importance that the paraffins have a much more shallow viscosity/temperature curve than the aromatic and hydroaromatic compounds, a fact which is well known in lubricants.

## 18. LOW-TEMPERATURE RESISTANCE

The stability at low temperatures of all benzines is completely sufficient at all practically-occurring temperatures (even Arctic temperatures), since the paraffinic, olefinic, and naphthenic hydrocarbons have extremely low solidification points (see Table 18a - d). Consequently, a low-temperature resistance of benzines as mixtures of these hydrocarbons of -50 to -60°C can always be expected. An exception in the hydrocarbons is the benzene (pure benzene: solidification point +6°C), while the homologues of benzene frequently show a very low solidification point. However, benzine-benzene mixtures may show incipient crystallization already as -35°C and, in presence of even traces of water, separations at -15°C. Philippovich mentioned that in the latter case (which may become troublesome in lines, benzine pump, and carburetor), an addition of only 2% methyl alcohol will prevent "snow" formation.

Benzine-alcohol mixtures, especially if only slight amounts of water from alcohol have remained in the system, may segregate in cold which will create considerable trouble. Absolute ethyl alcohol and methyl alcohol have a very low solidification point (-116°C and 98°C respectively). Other possible benzine additives are given at this point, together with their solidifying point: isopropyl alcohol: -188°C, isobutyl alcohol: -108°C, ethyl aniline: -64°C, ethyl amine: -81°C, acetone: -94°C, and methyl ethyl ketone: -86°C.

### a. Test for Low-Temperature Resistance

For testing the low-temperature stability of Otto fuels, the most suitable method is the ether evaporation developed by Stelling (Fig. 11). The test tube (1) with the benzine sample and the thermometer (2) is inserted into the Dewar vessel (3) by means of a cork with several holes. The temperature of the Dewar vessel is controlled by the thermometer (4). To produce cold, the suction pump (7) is used for drawing air through the apparatus. This air is dried in a small calcium-chloride tube (6) while dripping ether from the container (5). This ether evaporation in the Dewar vessel makes it possible to obtain temperatures as low as -35°C. If still lower temperatures are required, a similar apparatus is used in which the test tube is inserted into a Dewar vessel with alcohol (or benzine) and carbon-dioxide snow, resulting in a temperature of -[illegible]. Then, the mean is taken between the temperature of first crystallization and disappearance of these crystals on heating.

## 19. CALORIFIC VALUE

As "upper calorific value" or as "true heat of combustion", is the amount of heat developed by a fuel when the water having existed in the fuel before combustion in liquid form and the water formed during combustion will be in the liquid state after combustion. The technically usable "lower calorific value" known at present as simply "calorific value" or heat value is that amount of heat developed when the liquid and gaseous water existing in the fuel before combustion and the water formed during combustion are in the gaseous state (at 20°C) after combustion.

Calorimetric heat-value determination is made according to the German Industrial Standards DIN DVM 3716 and need not be described in this paper.

The calorific value is measured in cal/kg or cal/g or in cal/ℓ. The kilogram calorie (large calorie) is that amount of heat by which 1 kg water is raised by 1° celsius (from 14.5 - 15.5°C). The British Thermal Unit (BTU) occurring frequently in literature, naturally, is that amount of heat required for heating a British pound water (= 453.6 g) by 1°F. Consequently, 1 BTU = 0.252 cal and 1 cal = 3.968 BTU and 1 BTU/lb = 0.55 cal/kg.

The technically-useful "lower calorific value" (Hu) naturally is smaller than the calorimetrically-defined "upper calorific value" (Ho) since, as mentioned above, this upper calorific value includes the heat of condensation of water vapor and the heat liberated on cooling the combustion products to the initial temperature, while in all technical combustion processes the water goes off in gaseous form and the combustion gases escape at temperatures above 100°C.

The general formula reads as follows: $Hu = Ho - 5.85\% \times H_2O$ in which case the water of combustion determined by elementary analysis must be used in weight % in the calculation.

If a fuel contains W% of water and H% of hydrogen, the total heat of evaporation of the water of combustion will be $5.85 (W + 9H)$ and, for water-free liquid fuels, practically $52.65\ H$ (cal/g), i.e., $Hu = Ho - 52.65\ H$.

a. Calculation of the Calorific Value

For calculating the calorific value from the elementary analysis of the fuel, a number of formulas is in common use as follows:

According to Dulong: $Ho = 80,\ C + 344.6\ (H - O/8) + 25\ S$

According to Grumell and Davis: $Ho = (3625\ H + 235.9)\ [1/3\ C + H - 1/8\ (O - S)]$

Formula of the Association: $Hu = 8100\ C + 29{,}000\ (h - O/8)$ cal/kg

According to Wawrziniok: $Hu = 7855\ C + 28{,}800\ (h - O/8)$ cal/kg

These calculation formulas for the heat value cannot be used in the fuel analysis since, even in the formula corrected by Wawrziniok, the values compared to calorimetric values are too high and the heat of formation of approx 600 - 800 cal/kg must be deducted from the calculated lower calorific value. However, these corrections are higher than the heat-value differences existing between benzines.

b. Calorific-Value and Density Relation

Between the upper and lower heat value and the specific gravity, Marder (bibl. 37) established rather unflexible numerical relations; the relations in benzines presumably will scatter more strongly. However, temporary correlations are given in Table 25 which are definitely suitable for technical purposes. Other heat values are as follows: benzene: 9630 cal/kg = 8400 cal/ℓ; ethyl alcohol: 6420 cal/kg = 5140 cal/ℓ; methyl alcohol: 5080 cal/kg = 3570 cal/ℓ.

c. Mixed Calorific Value

For power in an engine the heat value of the fuel itself is not as important as the heat value of the fuel-air mixture. However, since the theoretical air requirement of benzines is higher than that of benzene or even alcohol, all fuels show practically a uniform mixed calorific value between 930 and 960 cal/ℓ. The condition that energy-rich benzines require more air for a theoretically-accurate fuel mixture than the energy-poor alcohols shows that possible engine operation with alcohol-rich fuels (racing-car fuels) is relatively expensive.

d. Combustion Process and Energy Balance

The calorific value is the expression of a complete combustion of hydrocarbon to carbon dioxide and water vapor. However, in an engine only a partial combustion takes place and, along with the above-mentioned products of a complete combustion, $CO_2$ and $H_2O$, also CO, $H_2$, and fuel residues are obtained as the remainders of an incomplete combustion. As a matter of fact, the thermal efficiency of motorized-vehicle engines is only 15 - 45%.

The complete combustion is characterized by the equation: $C + O_2 = CO_2$ and by $2H_2 + O_2 = 2\ H_2O$. The liberated heat can be given since each kg hydrocarbon contained in the fuel will furnish approx 8000 cal and each kilogram hydrogen approx 29,000 cal.

The theoretically possible maximum amount on $CO_2$ in percent and combustion water in ~~kg~~ per kg fuel are as follows:

| At | % $CO_2$ | kg Water |
|---|---|---|
| Hydrocarbon | 21 | 0 |
| Anthracite tar oil | 18 | 0.65 |
| Lignite tar oil | 16.7 | 0.90 |
| Gas oil | 15.7 | 1.15 |
| Benzine | 14.8 | 1.35 |
| Engine benzene | 17.7 | 0.70 |
| Alcohol | 15 | 1.20 |
| Liquid gas | 13.9 | 1.60 |
| Methane | 11.8 | 2.25 |
| Hydrogen | 0 | 9.00 |

The air required for a theoretically-complete combustion is as follows:

| | kg Air/kg Fuel | kg Air/ℓ Fuel |
|---|---|---|
| Hydrocarbon | 11.4 | - |
| Anthracite tar oil | 13.0 | 10,500 |
| Lignite tar oil | 14 | 9,700 |
| Gas oil | 14.5 | 9,700 |
| Benzine | 15 | 8,600 |
| Engine benzene | 13 | 9,000 |
| Ethyl alcohol | 9 | 5,500 |
| Methyl alcohol | 6.4 | 4,000 |
| Liquid gas | 17 | |

The ratio of oxygen to nitrogen in air is 21 : 79, which means that the air requirement is 79 : 21, i.e., 3.76× of the oxygen requirement needed for complete combustion. For this reason, fuel components which, as alcohols, contain oxygen already in their molecule require less air for combustion than hydrocarbons. It is known that 100 cc hydrogen weighs 0.09 kg, 100 cc oxygen 1.43 kg, 100 cc nitrogen 1.25 kg, and 100 cc air 1.287 kg.

The theoretical air requirement (L) in $m^3$ air/kg fuel can be calculated from the following equation:

$$L = \frac{1.865}{0.209} \left[ c + 3 \left( h + \frac{s - o}{8} \right) \right] N\ m^3/kg$$

or, related to $10^\circ C$ and 735 mm Hg:

$$L = \frac{2}{0.209} \left[ c + 3 \left( h + \frac{s - o}{8} \right) \right] N\ m^3/kg$$

Consequently, the hydrocarbons of the paraffin series in the benzine range (pentane to octane) required 12.7 to 12.5 $m^3$ air/kg hydrocarbon and the conventional automobile benzines will require 12.1 to 12.2 $m^3$ air/kg benzine. The air requirement of pure benzene is 11 $m^3$ air/kg benzene and that of BV benzene 10 $m^3$ air/kg benzene. Ethyl alcohol requires 7 $m^3$ air/kg alcohol and methyl alcohol 5 $m^3$ air/kg methanol.

Practical combustion in the Otto-cycle engine requires a slight air excess, which means that the ratio of actual to theoretical air amount is designated as "air-excess number". If an engine operates at an air excess below 1, the mixture is known as "rich" while operation at an air excess above 1 is known as "lean" mixture. Normally, 10% air excess is most economical while 10% air deficit produces the highest power. At a higher air deficit, the power will decrease considerably. As known, in aircraft engines at high altitudes automatic enriching of the mixture takes place due to lack of air, resulting in a drop in power. The temperature of the combustion flame is highest at correct carburetor adjustment and decreases at "rich" adjustment since such an enrichment has a cooling effect. This fact is used in operating racing cars. Even at "lean" adjustment, the flame temperatures will decrease but the excess oxygen carbonizes the valves by burning the carbon in the steel. Consequently, normal carburetor setting results in economical fuel consumption and in an approach to peak power. The characteristics of rich carburetor setting are as follows: black exhaust, sooty spark plugs or, in hot spark plugs, a bluish-gray glaze when leaded benzines are used. The characteristics of lean mixtures are as follows: carburetor backfire on starting, dry spark plugs and, in using leaded benzines, grayish-yellow powdery deposits. To calculate the air-excess coefficient from the exhaust analysis, Waworziniok (bibl. 38) gives the following formula:

$$\lambda = 0.209 \left[ \frac{1 - 0.5\,CO - 1.5\,H_2 - 2\,CH_4}{CO_2 + CO + CH_4} + (\sigma - 1) \right]$$

$$\sigma = 1 + 3 \left( \frac{h - O/8}{C} \right)$$

In these formulas, c, h, and o must be inserted according to the elementary analysis while $CO_2$, $O_2$, $CO$, $H_2$, and $CH_4$ must be used according to the components of the exhaust gases related to 1.

## 20. HEAT OF EVAPORATION

Heat of evaporation is that amount of heat in calorie required for transforming 1 kg of liquid of the boiling-point temperature into 1 kg of vapor of the same temperature. However, the "total" heat of evaporation is that amount of heat required for transforming a liquid of unit weight and room temperature into vapor of the boiling point of the liquid. This heat is increased by the "liquid-heat" (q) required for heating the liquid up to the evaporation temperature (t). This heat is a function of the specific heat (c) and is obtained from: $q = c \cdot t$.

For water, $c = 1$ and $t = 100$ is required and, consequently, also $q = 100$ cal. In fuels, c is located between 0.4 and 0.6 and t varies with increasing boiling curve. Generally, the boiling coefficient is used as mean.

Values for the total heat of evaporation are as follows: automobile benzines 150 - 160 cal/kg; pure benzine 138 cal/kg; engine benzine 141 cal/kg; toluene 159 cal/kg; zylene 184 cal/kg; ethyl alcohol abs. 276 cal/kg; methyl alcohol 304 cal/kg; water 600 cal/kg; gas oil 310 cal/kg; Diesel oil 360 cal/kg.

The total heat of evaporation of alcohols is high and that of benzines low. In mixtures of these two substances no linear relations are obtained. The curves usually show a sag which means that the measured values are below the arithmetic mean (bibl. 39). In correct engine operation, the "total" heat of evaporation must be supplied to the fuel-air mixture by a preheating of the mixture. If this is not done, the evaporating fuel taps this heat from the supplied combustion air, resulting in a more or less strong cooling of the mixture. As a further result the mixture forms larger droplets, the fuel will separate prematurely, the mixture will become lean, and finally will no longer be sufficiently ignitable, a phenomenon which is rather troublesome in winter. Benzine-alcohol mixtures frequently have this fuel separation due to the high heat of evaporation of alcohol. Increased compression in the engine can be used for counteracting this phenomenon. Benzines with low boiling points do not require any preheating of the mixture in normal weather. However, at extremely low temperatures the intake tube should be heated in a car for preheating the air. A makeshift means frequently are heated bricks or bags of heated sand. In benzine-alcohol operation, this fact should be considered in designing the engine since starting at low temperatures is extremely difficult. Heating of the mixture is definitely required in any farming tractors equipped with heavy-oil carburetors and using heavy benzine or petroleum. These machines are equipped with twin carburetors, are started with benzine, and then run until the exhaust gases surrounding the intake manifold heat the air sufficiently that heavy benzine or petroleum can be properly converted.

### a. Measurement of Heat of Evaporation

Wawrziniok and Schildwaechter (bibl. 40) described an apparatus for determining the total heat of evaporation which, in principle, consists in evaporating a certain fuel amount in a Dewar vessel by electric heating. This Dewar vessel is closed at the top and is connected with a Liebig condenser, an absorption bulb, and several adsorption U-tubes. A pump with a 20-mm water column removes the resultant vapors. The absorption bulb and the U-tube are then weighed for determining the weight (G) of the evaporated liquid. The total heat of evaporation (Q) used for evaporation is calculated from the resistance R of the heating coil, the mean value of the read current intensity (J), and from the measured time (t) in sec, resulting in $Q = 0.2387\ J^2\ Rt/G$.

## 21. WATER AND ALCOHOL CONTENT

### a. Water Determination

The water determination, especially in benzine-alcohol mixtures, is made according to the German Industrial Standards DIN DVM 3656 by using a short-neck round-bottom flask into which 20 - 100 g fuel are weighed and mixed with 100 cc of water-saturated xylene. A bent glass tube with ground tip is attached to the flask, connecting it with a reflux condenser with a graduated water trap at its lower end. The benzine-xylene mixture dripping from the reflux condenser separates from the water, fills first the water trap, and then deposits the water at the lowest point of this trap. As soon as the droplets coming from the reflux condenser are no longer turbid (at the earliest after 15 min), the distillation on the reflux condenser is interrupted and the water, sharply stratified by the xylene, is read on the graduated trap. This water determination with xylene does not furnish sufficiently useful values. For exact determinations, calcium carbide, under development of acetylene, or magnesium nitride must be used.

### b. Water-Miscible Benzine Additives

Water-miscible benzine additives are alcohols and acetones. Qualitatively, the alcohol content of a benzine can be rapidly determined by touching a line made with indelible pencil on filter paper with alcohol-containing benzine, which will blur the mark if alcohol is present while no change occurs in the opposite case.

Quantitatively, the sample to be investigated is shaken in a corked cylinder with twice the amount of water or, better, with 30% calcium-chloride solution. Then the volume decrease of the benzine layer is determined. Then, the calcium-chloride solution is fractionated in a suitable column. The parts distilling over up to 60°C are used for determining possible acetone content, the fraction boiling at 60 - 75°C will contain the methyl alcohol, and the fraction boiling at 75 or 80°C the ethyl alcohol. For the acetone test, the corresponding fraction is mixed with the same amount of dilute caustic-soda solution and five drops of a 25% sodium nitroprusside solution. The red coloration which, on acidulation with acetic acid, will change to a raspberry color indicates the presence of acetone. Then, 0.2 cc of the methyl-alcohol fraction are oxidized with 5 cc of potassium permanganate solution (3 g $KMnO_4$ + 15 cc 85% $H_3PO_4$ + 100 g water) for 10 min at room temperature. For decolorization, 2 cc of a solution of 5 g oxalic acid in 50 cc sulfuric acid (1.84) are added, shaking the mixture until discoloration takes place. If a red or violet color is produced by addition of 5 cc Shiff's reagent, presence of methanol is indicated. To prepare the Schiff reagent, 0.2 g fuchsin are dissolved in 120 cc hot water and mixed, after cooling, with 2 g anhydrous sodium sulfite in 20 cc water, adding 2 cc of hydrochloric acid (1.19) and filling the tube to 200 cc with water. The ethyl-alcohol fraction is shaken with 5 - 10 mg aniline blue 2B and filtered after standing for 1/4 hr. An alcohol content of 3% will produce a light-blue color while a higher alcohol content shows a deep blue due to the solution of the dye.

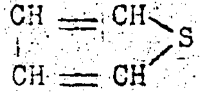
## 22. SULFUR CONTENT AND CORROSION

### a. Active and Inactive Sulfur

The active forms of sulfur in fuels are as follows: free sulfur, hydrogen sulfide, mercaptane, and alkyl disulfide. The inert forms are thioether and thiophene. A high corroding effect on metals is shown by hydrogen sulfide and free sulfur especially in benzines containing mercaptane, while the mercaptanes alone have a lower corrosive effect. Thiophenes and thioethers do not have any harmful effect in storage of benzines but will have a corrosive effect after combustion due to formation of sulfur dioxide.

Active sulfur corrodes the copper fuel line and other copper parts, while the total sulfur, after combustion with the benzine as sulfur dioxide, in combination with water vapor will corrode the exhaust end and probably also the crankcase.

The mercaptanes act slightly acid, similarly as hydrogen sulfide and are substituted in the SH group by the metal: SMeI. The alkyl disulfides RS-SR are produced in the benzines from the mercaptanes by aging. As soon as these products contain any unsaturated double bonds, their reactivity will increase.

Of the mercaptanes the following types may occur in benzine: ethyl mercaptane $C_2H_5SH$ (d = 0.839, BP = 37°C), propyl mercaptane $C_3H_7SH$ (BP 67°C), isopropyl mercaptane (BP 58°C), butyl mercaptane $C\ H_5SH$ (BP 98°C), amyl mercaptane $C_5H_{11}SH$ (BP 127°C), hexyl mercaptane $C_6H_{13}SH$ (BP 152°C), heptyl mercaptane $_7H_{15}SH$ (BP 176°C), and octyl mercaptane $C_8H_{17}SH$ (BP 199°C). Presence of ethyl disulfide $C_2H_5-S-C_2H_5$ had a specific gravity $d$ of 0.993 and a BP 154°C. Of the thioethers, $C_2H_5-S-C_2H_5$ boils at 92°C and $C_3H_7SC_3H_7$ at 142°C. The thiophenes  boils at 84°C (d = 1.062), the thiotolenes (methyl thiophenes) boil at 112°C, and the thioxenes (dimethyl thiophenes) boil at 135°C.

The total sulfur content in purified distillate benzines is rather low and has a value of 0.025%. Only in straight-run benzines of especially sulfur-rich crude oils (for example, California) the sulfur content may be as high as 0.1% and more. The benzines of the Fischer-Tropsch synthesis are practically free of sulfur, similarly as the purified lignite hydrogenation benzines. In cracked benzines and impure polymeric benzines the sulfur content generally is high, normally between 0.02 and 0.1% but frequently as high as 0.1 or 0.4% and more. The sulfur content is usually, in blends with engine benzine, (0.1 - 0.3% S).

It is of importance that a higher sulfur content in light fuels is undesirable not only from the viewpoint of possible corrosion but also because the desired increase in octane rating is prevented on addition of lead tetraethyl for improving the compression resistance. The extent of this interference is discussed in the chapter on lead sensitivity on light fuels. At present, it is rather difficult to make a differentiation in the facts that also unsaturated hydrocarbons, combined with sulfur compounds will decrease the lead sensitivity of benzines. Widmaier (bibl. 41) reported on the influence of sulfur compounds on the antiknock characteristics with artificial addition of thiophene, carbon disulfide, and ethyl mercaptane to benzines of different types. This author concluded that these artifical sulfur additions to leaded fuels will have a definite and unfavorable influence which is more noticeable the higher the lead sensitivity of the benzines. In this case, the ethyl mercaptane with a content of 51.6% sulfur is more effective in a negative sense than carbon disulfide with a sulfur content of 42.1% and thiophene with a sulfur content of 38.1%. Lead-containing fuels are sensitive to light and produce lead-salt flocculates which naturally decrease the antiknock characteristics. The light sensitivity is considerably increased by artificial addition of slight amounts of carbon disulfide. The decrease in octane rating in the experiments made by Witmaier are given in the following table:

|  | Paraffinic Benzine | Leuna Hydrogenation Benzine | Naphthenic Benzine | Aviation Fuel (4) |
|---|---|---|---|---|
| I — (unleaded) | 43.5 | 74.5 | 64.0 | – |
| II — (leaded) | 73.2 | 91.5 | 74.2 | 90.0 |
| II + 0.05% thiophene | 70.0 | 88.0 | – | 88.6 |
| II + 0.10% thiophene | – | – | 73.[illegible] | 87.3 |
| II + 2.00% thiophene | 56.0 | 80.0 | [illegible] | 82.0 |
| II + 0.10% [illegible] | 63.4 | 85.3 | [illegible] | 85.6 |
| II + 0.10% $C_2H_5SH$ | 63.8 | 84.0 | 72.0 | 84.5 |
| II + 2.00% $C_2H_5SH$ | 43.8 | 73.8 | 64.0 | 72.[illegible] |

b. Doctor Test

A qualitative experiment for presence of active sulfur in form of $H_2S$ and mercaptanes in benzines is the so-called doctor test (bibl. 42). The reagent in this case is a sodium plumbite solution prepared as follows: 125 g sodium hydroxide are dissolved in 1 ℓ water. Then, 50 g lead oxide PbO are stirred into this caustic-soda solution, mixing it for 6 hrs with compressed air at temperatures between 65 and 80°C. Then, water is added to make 1 ℓ, the solution is decanted from the undissolved lead oxide, or filtered over asbestos. This $Na_2PbO_2$ solution must be stored under exclusion of air. For making the experiment, 10 cc test benzine are shaken for 15 sec with 5 cc of plumbite solution and then mixed with 25 mg of finely-ground flowers of sulfur, and again shaken for 15 sec. The sulfur flowers then show as a skin at the interface between the two liquids. If the benzine and this interface show a distinct discoloration, the benzine was "sour", i.e., contains sulfur while if the benzine remained unchanged and the sulfur skin has a shiny and yellow appearance (or possibly gray), the benzine sample is "sweet", i.e., free of corroding sulfur.

c. Quantitative Determination of Active Sulfur

Quantitative determination of corroding sulfur has been made by Kattwinkel and Garner and Evans (bibl. 43 and 44). The experiment takes place as follows: 100 cc benzine are mixed with 0.5 g copper-bronze powder (Kahlbaum) in a 250 cc round-bottom flask with reflux condenser and are boiled for 1-1/2 hrs. After cooling, the fuel is decanted through a quantitative filter and washed with petroleum ether. Then, the flask and filter with the now sulfidic bronze powder are dried in the drying oven at 105°C. After this, flask and filter are treated with 40 - 50 cc water and liquid bromine in excess, until bronze and sulfide have become dissolved. Then the mixture is combined with 2 - 3 cc hydrochloric acid and filtered into a beaker. As soon as this liquid is mixed with a slight amount of hydrogen peroxide and if the sulfur is precipitated by boiling with barium chloride as barium sulfate, a division of the weight of barium sulfate by 7.28 will furnish the weight per volume of the corroding sulfur in the investigated benzine sample. Fuels with less than 0.5 mg sulfur per 100 cc benzine do not have a corroding effect, while fuels with 1 mg sulfur are still satisfactory. However, fuels with values higher than this are probably harmful.

d. Quantitative Determination of Total Sulfur

For quantitative determination of the total sulfur, the method described by Grote and Krekeler (bibl. 45) is preferrably used. The apparatus built by Schott & Gen. in Jena (Fig. 12) is very suitable for this purpose. The setup is as follows: A 50 cm long, 17-mm wide combustion tube of quartz (1) have three fused inserts, namely a perforated clear quartz plate (2) and two quartz-filter plates (3 and 4). The glass vial (6) filled with the benzine is placed into the porcelain dish (5). Proper filling of this vial will be described later. Two bottles (7) filled with caustic-potash solution and with dry glass wool respectively, are placed in front of this apparatus for drying the air flowing through the setup. An adsorption bulb (8) is filled below and above the finely-perforated glass filter plate (9) with glass balls. In addition, this bulb is filled with 50 cc of a 3% hydrogen peroxide solution. The bulb is connected with the quartz tube by a ground glass stopper (10). The vial (6) used is a thin glass tube drawn into a glass tip which can be closed with a small cork and is weighed before and after filling with the benzine. On inserting this glass vial into the porcelain dish, the glass tip is broken off so that the opening points in direction of the air stream and the escaping vapors are burned between (3) and (4). Careful evaporation of the benzine sample (6) in the porcelain dish (5) is started only after the space between (3) and (4) have been sufficiently preheated. The quartz plate (2) is used for mixing the benzine vapors with the passing air, the filter plate (3) prevents a flashback of the flame to the porcelain dish, and the filter plate (4) collects the soot which naturally must be burned completely. The entire combustion is to take between 5 and 10 min. The weighed portions of benzine, if sulfur content of less than 0.1% is expected, should weigh approximately 3 or 5 g and at a sulfur content up to 1%, approx 1 - 2 g.

The sulfur in the benzine burns to sulfur dioxide and oxidizes in the adsorption bulb filled with hydrogen peroxide to sulfur trioxide which can be determined in the water in the form of sulfuric acid. The hydrogen peroxide containing the sulfuric acid is titrated with caustic-potash solution or sodium carbonate under afterwashing. It is recommended to remove the dissolved carbonic acid by a short oiling. After cooling either titration with 0.05 n KOH in presence of phenolphthalein is made until pink coloration or with n/16 $Na_2CO_3$ in presence of methyl orange. If k denotes the consumption in caustic-potash solution, expressed in cc and if g denotes the weighed portion in gram, the sulfur content in percent will be as follows:

At titration with 0.05 n KOH: $\%S = 0.08\ k/g$
At titration with n/16 $Na_2CO_3$: $\%S = 0.001\ k/g$

Sulfur can be determined similarly according to a method described by Sielisch and Sündke (bibl. 46) or in the apparatus suggested by Wernicke and manufactured by Dittmar & Vierth in Hamburg.

In addition, the Mahler calorimeter bomb is frequently used for sulfur determinations. However, the dependability of the weighed portions and the adsorption of the burnt gases is doubtful. For this experiment, 0.8 - 1 g substance are weighed in a cellophane capsule or in a miniature weighing tube and then inserted into the small quartz disk of the bomb. The ignition wire is wound around the capsule or inserted into the benzine sample in the weighing tube and then attached to the two electrodes. After tightly closing the bomb, it is filled with oxygen from the steel bottle under a pressure of 10 atm, read on the manometer. As current for igniting and melting the ignition wire, the ordinary electric house current is used, choked across a lamp resistance. Shortly before ignition, the lamps will light and will extinguish as soon as the wire is burned through. The combustion products of the benzine, $CO_2$, $H_2O$, and (if sulfur is present) $SO_3$, are then adsorbed in a solution of 2 g sodium carbonate C.P. in 25 cc of water. Under afterwashing of the bomb with distilled water, the caustic-sodium solution which may contain some sulfate is filtered hot through a pleated filter in which case flocculates of iron hydroxide (from the combustion of the ignition wire) will be precipitated. The filtrate is mixed with hydrochloric acid, the carbon dioxide is then boiled out, and any existing sulfuric acid is precipitated with barium chloride solution in form of barium sulfate. The precipitate of barium sulfate is filtered in an ash-free paper filter after standing overnight, retained, and determined as to weight. The obtained weight of $BaSO_4$ multiplied by 0.1373 will furnish the weight of the sulfur in the sample.

For automobile benzines, a maximum sulfur content of 0.2% and for aviation benzines a content between 0.05 and 0.1% are permissible.

e. Corrosion Test

The behavior of light fuels with respect to copper is tested in the corrosion bomb developed by Heinze and Marder. This corrosion bomb consists of a cylindrical chromium-plated iron tube closed at the lower end. The bomb is inserted into a 60 cc glass vessel filled with the fuel to be investigated up to the 50 cc mark. Then, a copper strip (100 × 10 × 1 mm) cleaned with "Abrazzo" cleanser and roughened with emery cloth 00, is immersed into the fuel, the glass stopper is inserted, and the iron cover of the bomb is screwed on. Then, the entire setup is heated in the drying oven to 50±1°C. After this treatment and short cooling of the bomb in running water, it finally is opened. The copper strip is investigated as to any possible corrosion. Dark coloration or iridescent coloration indicates presence of corroding sulfur. This method is highly sensitive, since already a content of 0.005% of sulfur (active) will show a dark coating. Peroxides in cracked benzines have a similar effect on copper and frequently simulate presence of corroding sulfur. The copper-cup method is rather old-fashioned. In this method, 100 cc benzine are evaporated in a copper dish in the water bath, and the dark coloration of the cup by formation of CuS is determined.

In addition to sulfur, the lower naphthenic acids may produce corrosion when added to benzines. Sulfuric acid ester produced by incorrect refining of cracked benzines may become very troublesome. The boiling point of this sulfuric acid ester is near 205°C, so that its presence in benzines with an earlier distillation end is rather improbable. Alcoholic fuels create corrosion only in presence of traces of water, if the water content exceeds 0.5%. At a high hygroscopicity (under addition of benzine and three-component mixtures) a higher water content has no harmful effect. However, amounts of water sufficient for bringing such mixtures to the limit of segregation will definitely produce corrosion. Finally, traces of acetic acid produced by alcohol, water, and atmospheric oxygen will create considerable corrosion in amounts as low as 0.005 g/100 cc alcohol.

## 23. FLAME POINT AND IGNITION POINT, EXPLOSION RANGE

a. Flame Point

The flame point of benzines is not measured in practical application, since it merely has a theoretical interest and generally is considerably below -20°C in fractions boiling below 120°C. Heavy-benzine fractions will have a flame point above 0°C, benzine will have a flame point of -30°C and abs ethyl alcohol will have a flame point of 12°C, while 96% alcohol has a flame point of +16°C. An addition of noninflammable carbon tetrachloride will increase the flash points of light hydrocarbons considerably.

b. Ignition Point

The ignition point or, more accurately expressed, the "self-ignition point" is that temperature at which a liquid spontaneously ignites on mixing with air or oxygen. This self-ignition point is dependant on various test conditions, on the apparatus, pressure, and amount and concentration of air or oxygen. The ignition can also be represented as the chemical decomposability of a substance, in this case of the hydrocarbons. Since the thermal decomposition of hydrocarbons mainly takes place in long-chain structures, the paraffins are characterized by much lower decomposition temperatures and self-ignition points than the stable ring hydrocarbons, a fact which had been brought in relation to engine behavior of fuels in Otto-cycle and Diesel engines by Jentzsch.

c. Ignition-Value Tester

The ignition-value tester developed by Jentzsch and produced by Julius Peters Company consists mainly of an electrically-heatable block containing a crucible with three ignition chambers and one thermometer base. Oxygen is supplied from the steel bottle across a pressure-reducing valve which is so controlled that a given amount is supplied per minute (bubble counter) to the ignition chambers. At corresponding time intervals, the fuel is dripped slowly through a pipette into the ignition chamber, determining the temperature at which self-ignition takes place for the first time.

The amount of oxygen has such a determining effect on the self-ignition point that the data for an individual ignition point are of no practical significance. Jentzsch constructed so-called "self-ignition curves", consisting of a series of ignition points plotted against the oxygen volume. Naturally, the ignition points of a hydrocarbon at oxygen deficiency will be much higher than at oxygen excess. However, the correlations are not simple.

The self-ignition point (Szp) in a more limited sense of the word was designated by Jentzsch as the lowest temperature at which self-ignition takes place in a full oxygen stream (300 - 400 bubbles per min). The upper ignition value (oZ) is that temperature at which self-ignition just takes place without any oxygen, while the lower ignition value (uZ) is the quotient of self-ignition point divided by bubble number per min plus 1, i.e., $uZ = Szp/(b + 1)$. The characteristic ignition value (Zk) finally is formed by the quotient $Zk = (oZ - uZ)/(b + 1)$, which represents a rather arbitrary value. Despite this fact, Zerbe and Eckert (bibl. 47) have come to surprising conclusions in a rather valuable report. They found that splitting of hydrocarbon molecules is more difficult at lower characteristic initial values. Rather difficult to split are the conjugated double bonds of aromatic and unsaturated compounds of the type of isoprene. In addition, the high isomeric hydrocarbons such as 2, 2, 4-trimethyl pentane (= iso-octane) are difficult to split, while the unbranched chain hydrocarbons are more readily split at increasing chain lengths. These data are based on the following numerical values: characteristic ignition values (Zk) benzene 0.19; toluene 0.24; xylene 0.38; hexamethyl benzene 0.68; isoprene 0.39; iso-octane 0.45; cyclohexadien 0.35; cyclohexene 1.6; cyclohexane 3.4; diallyl 1.17; hexylene 3.1; pentane 3.14; hexane 5.35; heptene 23, and n-octane 56.

Beyond this, Jentzsch states to have found a correlation between characteristic ignition value and octane rating in the following ratio:

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Characteristic ignition value: | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 |
| Octane number: | 102 | 98 | 94 | 89 | 84 | 80 | 73 | 68 | 63 | 58 | 53 | 48 | 43 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Characteristic ignition value: | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 | 9.5 | 10 |
| Upper ignition value: | 39 | 36 | 33 | 31 | 28 | 26 | 24 |

Alcohol-containing fuels and cracked benzines do not follow this relation which also in many other respects is rather unstable. While normally the differences between "Jentzsch octane number" and octane number in the CFR engine (according to Zerbe and Eckert) fluctuate by +6 to -10 octane units, differences of -10 to -25 octane units occur in cracked benzines which means that the Jentzsch values are much too low, probably due to the fact that premature partial self-ignitions occur in the cracked benzines investigated in the ignition-value tester. A later section on the antiknock characteristics of Otto Fuels shows that an interpretation of the compression resistance of benzines in the engine by self-ignition characteristics of this type is impossible.

## d. Explosion Range

The explosion range of various fuel-air mixtures according to Berl and Fischer is as follows: hydrogen 9 - 58%; carbon oxide 15 - 72%; water gas 6 - 72%; illuminating gas 8 - 19%; methane 6 - 14%; ethylene 3 - 34%; acetylene 3 - 81%; pentane 2 - 8%; hexane 2 - 7%; ethyl alcohol 3 - 13%; ethyl ether 3 - 7%; acetone 4 - 9%; carbon disulfide

2 - 31%; and ammonia 16 - 27%.

## 24. CONSTITUTION

An explanation of the composition, i.e., the exact analysis of benzine hydrocarbons has been attempted over many years with a rather unsatisfactory result. Up to now, no working methods are known for separating benzines, qualitatively and quantitatively into their individual components. It was not even possible to separate the benzines into the various hydrocarbon groups in such a manner that suitable correlations would be obtained between the structural pattern and the antiknock characteristic which represents the most important property in engines. A large number of determination methods for unsaturated and aromatic hydrocarbons are known but it is definite that these values fluctuate strongly. Generally, the selective solubility of the aniline is used for determining the content of "naphthenes", without having any clear concept on the nature of the naphthenes existing in benzines. As a matter of fact, it is completely impossible to separate the knocking n-paraffins from the antiknock i-paraffins. This basic viewpoint is used in the following discussions.

### a. Unsaturated Hydrocarbons

To determine the amount on unsaturated hydrocarbons alone, 10 cc of benzine with 30 cc of a solution of 5 g boric acid in a 100 cc sulfuric acid 1.84 are shaken in an Eggertz tube (45 - 50 cm long, 12 - 13 mm internal diam, 50 cc capacity, lower part blown into a ball) under cooling by ice (bibl. 48). The decrease in benzine layer after standing for 2 hrs, related to 100, is to indicate the amount of unsaturated hydrocarbons. However, it must be stated that these values are unsatisfactory at a high content of unsaturated hydrocarbons and aromatic compounds. It is much more suitable to use only 93% sulfuric acid (d = 1.833) without any boric acid in straight-run benzines, while only an 85% sulfuric acid (d = 1.785) without boric acid should be used in cracked benzines. In this case, the ratio of benzine to acid should be 15 to 30 cc, with cooling for 1 hr in ice. Then, the mixture is shaken for 10 min under elimination of any increase in temperature. It is logical that in such differences in test setup the values must vary widely, are presumably rather arbitrary, and make a comparison of data of straight-run and cracked benzines impossible if different acid concentration is used.

In addition, the iodine number is frequently suggested as a symbasic or proportional scale for the amount of unsaturated hydrocarbons in benzines. The iodine number and the various methods for determination are discussed in a separate section. However, it should be stated at this point that not only an iodine addition to the double bonds takes place in hydrocarbons but that also a definite substitution occurs, so that a characterization of unsaturated hydrocarbons by the iodine number is completely impossible. Various intensive or mild methods of influence of halogens possible, so that substitution is less important than the addition to double bonds. However, the problem, where the definite limit is located and whether such methods can be used as criterion, has never been defined.

Other methods for determining unsaturated hydrocarbons use mercury acetate (bibl. 49) for addition under subsequent splitting of the resultant double bonds. Faragher, Morell, and Levine (bibl. 50) suggest sulfur monochloride for determining unsaturated compounds. However, since sulfur and chlorine form addition products and since aromatic compounds react with $S_2Cl_2$, this suggestion is more than questionable. Hugel and collaborators (bibl. 51) use thiocyanide in acetic solution for olefin determination. An efficient and justified critical discussion on the various analyses methods for determining unsaturated and aromatic compounds and naphthenes is given by Winkler (bibl. 52).

### b. Aromatic Hydrocarbons

For determining aromatic hydrocarbons in benzines the dimethyl sulfate number is generally used. The method is as follows: 15 cc of fresh dimethyl sulfate $(CH_3)_2SO_4$ (Note: dangerous poison for skin and respiratory tracts are filled into a cylinder graduated in 0.1 cc. Then, 10 cc of the benzine to be investigated is added as a supernatant layer, and the entire mixture is shaken vigorously. The determined decrease in volume of the benzine, multiplied by 10, will furnish the dimethyl sulfate number, i.e., the amount in % of dimethyl-sulfate soluble benzine components. Presumably, all olefins present are dissolved at the same time. Straight-run benzines usually have a mean dimethyl sulfate number (DiZ) of 12 while cracked benzines have a DiZ of 16. Then, the approximate content on aromatic compounds in straight-run benzines is calculated as follows:

$$\% \text{ Aromatic compounds} = \frac{100\ (\text{DiZ} - 12)}{100 - 12} = 1.136\ (\text{DiZ} - 12)$$

and in cracked benzines:

$$\% \text{ Aromatic compounds} = \frac{100\ (\text{DiZ} - 16)}{100 - 16} = 1.19\ (\text{DiZ} - 16)$$

A dimethyl sulfate number below 20 indicates presence of distillate benzine without any cracked benzine. At a higher aromatic content, normal benzine (with a Diz of 10) must be used for dilution in proper proportion so that the DiZ of the mixture does not exceed 40%. The less poisonous diethyl sulfate cannot be used instead of the dangerous dimethyl sulfate because of the fact that the aliphatic compounds are soluble up to 40% in diethyl sulfate $(C_2H_5)_2SO_4$. According to this method, the aromatic content normally is too low by as much as half in extreme cases. Only in fuels rich in aromatic compounds the error finally reverses. However, even in dimethyl-sulfate 5 - 10% of paraffin hydrocarbons (especially the lower members of this series) are dissolved, so that this determination method is more than problematic.

Normally, aromatic compounds and unsaturated hydrocarbons are determined together according to the Kattwinkel method. The so-called "Kattwinkel acid" is a mixture of 1000 cc sulfuric acid 1.84 with 300 g phosphor pentoxide, i.e., a sulfuric acid intensified by water removal, which attacks not only the unsaturated hydrocarbons but also the aromatic hydrocarbons. Presumably, the attack is hightly quantitative. In the test, 30 cc of Kattwinkel acid are stratified with 10 cc benzine and shaken for 5 min. In a different type of this type, it is suggested to stratify 30 cc of the 100% sulfuric acid with 15 cc of benzine, to shake the mixture, and to immerse the tube (in the case of straight-run benzines) for several minutes in a water bath of 40 - 50°C. However, in cracked benzines this heating should not take place. Then the mixture is shaken for 5 or 10 min and the decrease in volume is determined after standing for 2 hrs. Instead of using any heating, three parts of sulfuric acid to one part of benzine may be used (bibl. 53). In this method, the aromatic compounds are transformed into acid-soluble sulfonic acids. To determine their quantity itself, the unsaturated hydrocarbons must be determined in a separate experiment and then deducted.

Determination of aromatic compounds by nitration is possible only in straight-run benzines but not in cracked benzines. A Hess nitration flask (bibl. 54) is filled with 60 cc of benzine and 200 cc of sulfuric acid 1.84, under cooling with ice water, shaken for 5 - 10 min, and then mixed with 50 g of nitrating acid (one part of nitric acid 1.42 [70%] and two parts sulfuric acid 1.84) from a drip funnel under vigorous shaking for 15 min, without having the temperature exceed +10°C. After reaction is completed, the flask is filled with sulfuric acid to the top mark and left standing for several hours. The aromatic compounds are transformed into acid-soluble mononitroderivates which clearly shows the volume decrease of the benzine. However, 1 cc must be added mathematically to the resultant value of benzine since it is assumed that such an amount of nonnitratable components have been kept in solution by the sulfuric acid. Naturally, the olefins have become dissolved in the sulfuric acid.

A new method for determining the aromatic compounds was described by Jostes (bibl. 55). This method consists in ultraviolet absorption by means of a Zeiss quartz-crystal spectrograph.

For heavier benzines with a boiling number above 125, for benzine-benzene mixtures, and especially for carbonization and cracked benzines, Towne (bibl. 56) developed a method described by Bandte (bibl. 57) in an abbreviated form: 150 cc of ice-cooled 93% sulfuric acid (d = 1.833) are stratified with 50 cc benzine and shaken for 1 min. After standing overnight, the volume decrease is determined as $U_1$% sulfuric-acid soluble unsaturated aromatic compounds. In a second experiment, 300 cc of ice-cooled 98% sulfuric acid (d = 1.841) are shaken with 100 cc of the same benzine for 30 min. After standing overnight, the volume decrease is measured as $(A + U_1)$% of aromatic and unsaturated compounds. Then, the original benzine is subjected to an Engler distillation, determining the temperature degree at which 95% will be distilled over as well as the distillation residue in the flask (a vol %). The benzine remaining after removal of the aromatic and unsaturated compounds is then subjected to an Engler distillation up to the same degree of temperature at which 95% of the original benzine had come over. The residue in the flask will be b vol % in this case. Since (b-a)-does represent the amount of polymerized unsaturated hydrocarbons, $(U_1 + U_2)$% will be the total amount of unsaturated compounds to be deducted from $(A + U_1)$% for determining the corrected amount of aromatic compounds $(A_o)$%.

c. Aniline Point

The aniline point of fuels is that temperature at which a hot mixture of equal parts of fuel and aniline just becomes turbid starting from a clear solution, i.e., at which aniline-insoluble hydrocarbons are precipitated from the fuel in small droplets. For determining the aniline point, 10 cc benzine and 10 cc freshly distilled aniline in a 3 - 4 cm wide test tube with glass stirrer and thermometer (graduation 0.1°) are heated in the water bath until the solution is clear. Then, the solution is stirred and cooled until definite turbidity occurs. This turbidity is then measured and used as the aniline point. The turbidity must be so pronounced that the thermometer bulb is no longer visible.

In Fig.13a, the aniline points of individual hydrocarbon groups is given. In the "islands" the aniline points and resultant scatterings of conventional automobile benzines and benzine-benzene mixtures as well as several carbonization benzines are shown. The diagram indicates the aniline solubility (aniline point) as a function of the boiling point of the hydrocarbons or, in benzines forming hydrocarbon mixtures, as a function of the mean boiling coefficient. The diagram shows that the paraffins within a boiling range of 0-200°C have aniline points between 70 and 80°C, while the olefins in the boiling range between 40 and 100°C have an aniline point between 20 and 30°C. Naphthenes as homologues of cyclopentane and cyclohexane in a boiling range between 50 and 120°C have an aniline point of 20 - 50°C and the cyclo-olefins are more similar to aromatic compounds and are completely insoluble in aniline even at temperatures below 0°C. Alcohol-free and benzene-free automobile benzines (if cracked benzines do not predominate in the mixture) with a boiling coefficient between 100 and 150 have a relatively narrow range of 45 - 53°C aniline point. These substances, as expected, have a middle position between paraffins and olefins and naphthenes which, of course, may form some of their components. Noticeable artificial additions of engine benzene in the so-called benzine-benzene mixtures will produce a considerable decrease in aniline point to 10 or 12°C. The carbonization benzines richer in olefins and aromatic compounds also show a quite different aniline point from the conventional automobile benzines on a petroleum basis.

The numerical values given by Evans (bibl. 58) shown in Table 26 and the values given by Francis (bibl. 25) shown in Table 18a given for aniline points of well-defined n-paraffins and i-paraffins, do not show any characteristic in the range of molecular sizes $C_5$ - $C_{10}$ but rather show a scattering of the aniline point between 7 and 12°C in pentanes, hexanes, heptanes, and up to decanes.

### d. Naphthenes

For determining the naphthenes in benzine hydrocarbons, the residual benzine produced in the shaking test for unsaturated and aromatic compounds according to Kattwinkel or Riesenfeld-Bandte is used, i.e., a benzine which is practically free of olefins and aromatic compounds. In this residual benzine, the aniline point naturally is higher than that of the initial material with a more or less high content of aniline-soluble components. Under the assumption that the mean aniline point of naphthenes (characteristic boiling point 100 - 120) is 40°C and that of paraffins 70°C, a temperature decrease of (70 - 30)/100 = 0.3°C will correspond to each percent of naphthenes at the aniline point. The naphthene content of the benzine to be tested will then be

$$\% \text{ Naphthene} = \frac{70 - \text{AP (measured)}}{0.3}$$

In addition to this, Garner developed a diagram (Fig. 13b) in which the fact that the height of the boiling point will have an influence on paraffins and naphthenes with respect to the aniline point is considered. The agreement of the values for the corresponding benzines and percent of naphthenes, calculated from the formula and determined from the diagram by Garner, is completely unsatisfactory. In any case, the results of the naphthene determination varies so much that this method by Garner cannot be definitely preferred.

### e. Paraffins

The amount in paraffins is calculated as a residue related to 100, after determining the unsaturated and aromatic compounds and the naphthenes. Since no qualitative and quantitative separation method for knock-producing n-paraffins and antiknock i-paraffins is in existence and since the accuracy of determining unsaturated and aromatic compounds as well as naphthenes is rather undependable, this method is rarely used for analyzing Otto fuels.

### f. Iodine Numbers

It had been mentioned previously that the iodine numbers do not permit a quantitative evaluation of the unsaturated hydrocarbons in benzines, since not only addition to the double bond but also substitution at adjacent points takes place. It should be added that, according to an opinion of Kaufmann and Grose-Oetringhaus (bibl. 59), not only the amount but also the type of unsaturated compounds will show differently in the iodine number and in the storage property. That means, the double bonds in hydrocarbon chains are much more active than those in hydrocarbon rings.

In the iodine number according to Hanusch, the weighed portion of the sample must not exceed 1 g in benzines. The reagent known under the name of "Hanus solution" is a solution of 10 g iodo-monobromide (JBr) in 500 cc acetic acid. The weighed portion of benzine to be tested is diluted in the "iodine flask" with 10 cc chloroform. Then, 25 cc of Hanus solution are added and the mixture is shaken for 1/4 hr. Then, 15 cc of an aqueous iodine potassium solution (1 : 9) and 50 cc water are added, titrating with n/10 sodium thiosulfate under continuous shaking until yellow coloration occurs. After addition of 1 cc starch solution, titration from grayish-blue to colorless is made. Along this experiment, a so-called "blank experiment" without benzine is carried on.

If g denotes the weighed portion in gram, a the consumption in thiosulfate in cc of the blank experiment, b the same consumption in the experiment with benzine, and f the factor of the thiosulfate solution, the following relation is obtained:

$$JN = 1.2692\ (a - b)\ f/g$$

Alcohol-containing fuels must be freed of alcohol by shaking with water before determining the iodine number. The Hanus method is used as the first German Standard method of the "Wizoeff", an abbreviation for the Wissenschaftl. Zentralstelle fuer Oel- und Fettforschung, Berlin (Scientific Central Station for Oil and Fat Research, Berlin).

The iodine number according to Kaufmann is used as the second German Standard method of the "Wizoeff". The halogen reagent consists in this case of chemically pure methyl alcohol which was saturated with desiccated (at 130°C) sodium bromide at room temperature. Approximately 12 - 15% of this will go into solution. Then, the liquid is decanted from the undissolved portion and 5.2 cc bromide (pro analysis) is added for each liter of the clear solution. Presumably, the bromide will be combined to an addition product NaBr, $Br_2$ since the solution does not have the odor of bromide and is resistant to titration. For using this method in the determination, approximately 1 g benzine are weighed and diluted with 10 cc chloroform in the iodine flask. Then, 25 cc of the above-described $NaBr_3$ solution in methanol will be added and left to react for 1/2 hr. Then, 15 cc of 10% KJ solution are added and titration and calculation takes place as above. According to Galle (bibl. 60) a modification of rapid method by Margosches for determining the iodine number will furnish favorable results in fuel tests. In this method, 0.1 g benzine in 10 cc ether acetone (1 : 2) are dissolved in an iodine flask under addition of 8 cc abs alcohol. Then, 25 cc of 0.2 n alcoholic iodine solution at 200 cc water are added. After a reaction period of 5 min, the remaining iodine is titrated back with n/10 thiosulfate. For calculating the iodine number, the above formula is used.

Rosenmund and Kuhnhenn used pyridine sulfate bromide $C_6H_5NH_2SO_4Br_2$ in acetic acid as a mildly reacting bromination agent. It actually seems true that in this method the substitution reactions are much less noticeable than the desired addition. For producing the reagent, 8 g pyridine and 10 g conc sulfuric acid are dissolved separately and under cooling in 20 cc acetic acid each. Then, these solutions are carefully mixed. To this mixture, 8 g bromine in 20 cc acetic acid are added, and the volume is filled up to 1 l with acetic acid. The solution then will be almost 0.1 n. For making the determination, the weighed amount of benzine is dissolved in 10 cc chloroform, adding 25 cc of the n/10 pyridine sulfate dibromide solution, letting the mixture react for 3 - 5 min. Then, 7 cc of 10% KJ solution are added and the freed iodine is titrated with thiosulfate solution, as described above. The iodine number is calculated similarly as in the Hanus method.

In the method described by Ilhiney, 0.5 - 1 g benzine are dissolved in 10 cc carbon tetrachloride under addition of 20 cc of a n/3 bromine solution in $CCl_4$. Reaction takes place in the dark for 18 hrs. A blank experiment is conducted at the same time. After cooling the flask in a refrigerant, 25 cc of distilled water are rapidly added. After this, 25 cc of 10% (iodate-free) KJ solution and another 75 cc water are added. Titration takes place as usual with thiosulfate. The apparent iodine number is then obtained by regular calculation. For making the necessary correction and for eliminating the halogen amount consumed by substitution, the titrated solution as well as the blank sample are mixed with 5 cc of a 2% potassium iodate solution ($KJO_3$). This solution reacts with the dissolved HBr and KJ as follows:

$$KJO_3 + 5\ KJ + 6\ HBr = 3\ J_2 + 6\ KBr + 3\ H_2O$$

The freed iodine will then be titrated with n/10 $Na_2S_2O_3$. Since each mole of HBr corresponds to a mole of $Br_2$ consumed for substitution but frees only 1 iodine atom, the number of cc of thiosulfate consumed in the second titration must be doubled to correctly interpret the bromine consumption required for the substitution. If the thiosulfate consumption for the blank or main experiment before iodate addition is either a or b cc and, after iodate addition, c or d cc, the true iodine number based merely on addition will be $JN = 1.2692 [ (a - b) - 2 (d - c) ] / g$.

For evaluating the unsaturated hydrocarbons in fuels, the iodine-number methods according to Wijs and Huebl are rather unsuitable. It has not been accurately defined whether the thiocyanogen number by Kaufmann (bibl. 61) or the recently developed iodine thiocyanogen number (bibl. 62) are useful for investigating unsaturated hydrocarbon components. In any case, the latter report and a contribution by Grosse-Oetringhaus (bibl. 63) show that the iodine numbers in various benzine samples may differ as far as numerical values are concerned but still are in a certain correlation.

### g. Differentiation of Distillate and Cracked Benzines

For rapid and incidental differentiation of straight-run and cracked benzines the method developed by Burstin (bibl. 64) is used. This method is based on the heat effect occurring in the polymerization of unsaturated hydrocarbons with conc sulfuric acid. In this experiment, a Shukoff apparatus, representing a glass-jacketed vacuum vessel with ground stopper and thermometer insert is used. In this apparatus, 50 cc of benzine are shaken separately while reading the temperature. Then, 5 cc sulfuric acid 1.84 are added and shaking is continued until the temperature remains stable. In this sulfuric-acid treatment, refined distillate benzines will show a temperature increase of only 1 - 3°C, unrefined distillate benzines an increase of 2 - 5°C, while cracked benzines (as well as lignite and shale tar benzines) will show an increase of 30 - 50°C. Even mixtures of cracked benzines and straight-run benzines can be defined in this manner. On addition of liquid bromine or a solution of bromine and $CCl_4$, cracked benzines or cracked-benzine blends will show by forming addition products with bromine under simultaneous discoloration. The exothermic heat in this case will be so high that the samples in the test tube start boiling and bubbling.

### h. Peroxides

Peroxides form in large amounts in unsaturated benzines under the influence of light and air. Such peroxides are the reason for poor storage quality and for a progressive decrease in antiknock characteristics. Qualitative analysis of peroxides is rather simple and well-defined. For this analysis, 10 - 15 cc of the benzine to be tested are shaken with 2 cc of a freshly-prepared 5% iodine potassium solution for 5 min. Peroxides will cause free iodine to precipitate which shows by a yellow coloration of the solution or even more clearly by the blue coloration as soon as a small amount of starch is added. A quantitative determination was made by Youle and Wilson (bibl. 65) in which the "peroxide number" is given as the cc of a n/100 titanium chloride solution ($TiCl_3$) which is consumed by the ferric salt formed from ferrous salt by oxidation of the peroxides present in the benzine. Unfortunately, the determination method is influenced strongly by the titration instability of the reference liquids, ferrous sulfate and titanium chloride, which must be kept in air-tight containers. In addition, application of corrections in benzines with a peroxide number above 3 interferes considerably with the method.

### i. Refraction

Refraction or refractive power is the property of liquid and solid bodies to diffract the light ray coming from outer space. White light is resolved into its basic colors (diffraction spectrum) by the refraction. In measuring the refraction, this color dispersion must be eliminated.

For measuring the refraction of liquids, the Abbe refractometer is used. The fuel sample is injected between the two flint prisms of this apparatus. Daylight (or more accurately, the light of a sodium flame, Fraunhofer D-line, 0.588 microns) is reflected by a rotatable mirror into the illumination prism, then passes the 0.15-mm thick layer of the matter to be tested, and finally reaches the observation telescope through the test prism. By means of the micrometer screw attached to the telescope, the color dispersion is eliminated (or else measured on the drum graduation, for the compensator) until a sharp boundary line of the total reflection is shown in the field of view of the eyepiece. By means of the micrometer screw on the side sector, the line of total reflection is made to coincide with the cross hairs. Then, the refractive index nDt at the measured temperature t can be read on the micrograduation of the sector. For comparison purposes, nD/20°C is given and the temperature correction for n will be 0.0004 per each °C.

As mentioned above, the refraction is dependent on temperature, while the specific refraction (r) is independent of temperature. The molecular refraction (Mr) is the product of molecular weight (m) and specific refraction (r):

$$r = \frac{n^2 - 1}{n^2 - 2} \cdot \frac{1}{d} \qquad Mr = Mr$$

In well-defined chemical compounds, the molecular refraction can be calculated also by addition of the refraction equivalents of the individual atoms under consideration of the "increments" of their type of bonds (see Table 28).

In Fig. 14, boiling points of the individual hydrocarbon groups (according to Bielenberg) are plotted as a function of refraction nD/20. Between these curves, the band, shown by the fractions of a large number of automobile benzines with respect to refraction, is located. Since the origin of automobile benzines and their composition differed widely, the regularity of the relation between boiling curve and refraction is rather surprising. A definite deviation is represented only by a mixture of 60 parts benzine and 40 parts benzene whose curve shows a definite bulging in the boiling range of benzene and toluene. In Table 29 (taken from Fig. 14), the dependence of the individual fractions on the refraction for conventional alcohol and benzene-free automobile benzines is shown.

Obviously, the lower refraction values in each distillation fraction show the prevalence of paraffinic components, while the upper values indicate presence of olefins, naphthenes, and aromatic compounds. In the expressions (n - 1): d of the original formula for "specific refraction" and the so-called refraction intercept (n - d):2, the values of practically all automobile benzines show satisfactory agreement. The value (n - 1)/d is rather constant for all benzines and petroleum types with 0.555-0.565. Only alcohol blends with values of 0.538 make an exception, while benzene blends all are in the vicinity of 0.565. The refraction intercept (n - d)/2 fluctuates between 0.31 and 0.34 for benzines and petroleum in which case also the alcoholic fuels make no exception.

In pure n-paraffins and i-paraffins, a unique linear dependence exists between the density and refraction which is expressed by the numerical series below:

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| d/20 : | 0.560 | 0.570 | 0.580 | 0.590 | 0.600 | 0.610 | 0.620 | 0.630 | 0.640 | 0.650 |
| nD/20: | 1.325 | 1.330 | 1.335 | 1.340 | 1.345 | 1.350 | 1.355 | 1.360 | 1.365 | 1.370 |
| d/20 : | 0.660 | 0.670 | 0.680 | 0.690 | 0.700 | 0.710 | 0.720 | 0.730 | 0.740 | 0.750 |
| nD/20: | 1.375 | 1.380 | 1.385 | 1.390 | 1.395 | 1.400 | 1.405 | 1.410 | 1.415 | 1.420 |
| d/20 : | 0.760 | 0.770 | 0.780 | 0.790 | 0.800 | | | | | |
| nD/20: | 1.425 | 1.430 | 1.435 | 1.440 | 1.445 | | | | | |

If the molecular size of pure paraffins or, which amounts to the same, the number of carbon atoms is used in this relation, two formulas can be developed according to Francis (bibl. 20) for calculating the density and refraction of pure paraffin hydrocarbons. In these formulas, n denotes the number of carbon atoms and a, b, A and B four constants:

$$d/20 = a - \frac{b}{n} + 0.00062\,n + \frac{0.48}{n^2}$$

$$nd/20 = A - \frac{B}{n} + 0.00027\,n + \frac{0.27}{n^2}$$

For these constants, the following values are given: a = 0.835; b = 1.22; A = 1.468; and B = 0.651. These relations naturally apply only (which should be emphasized specifically) for n-paraffins and i-paraffins. The olefins and naphthenes (see numerical series above) as well as the aromatic compounds show a different behavior and fluctuate with the ratio of density to refraction about a rectilinear relation:

Olefins

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| d/20 : | 0.700 | 0.710 | 0.720 | 0.730 | 0.740 | 0.750 | 0.760 | 0.770 | 0.780 | 0.790 | 0.800 |
| nD/20 : | 1.402 | 1.407 | 1.412 | 1.417 | 1.422 | 1.427 | 1.432 | 1.437 | 1.442 | 1.447 | 1.452 |

Naphthenes

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| d/20 : | 0.740 | 0.750 | 0.760 | 0.770 | 0.780 | 0.790 | 0.800 | 0.810 | 0.820 | 0.830 |
| nD/20 : | 1.403 | 1.409 | 1.415 | 1.421 | 1.427 | 1.433 | 1.439 | 1.445 | 1.451 | 1.457 |

Benzene homologues:

| | | | | | |
|---|---|---|---|---|---|
| d/20 : | 0.855 | 0.860 | 0.865 | 0.870 | 0.875 |
| nD/20 : | 1.483 | 1.490 | 1.496 | 1.501 | 1.506 |

According to these definitions, it is logical that the ratio of density to refraction of conventional automobile benzines will fluctuate within certain limits, as actually shown in Table 30.

For comparison, the refraction values of several other liquid substances are given: Methyl alcohol 1.331; water 1.333; ethyl ether 1.357; acetone 1.359; ethyl alcohol 1.362; n-propylalcohol 1.381; i-propylalcohol 1.386; n-butyl alcohol and i-butyl alcohol 1.396; amyl alcohol 1.408; dioxane (diethylene dioxide) 1.423; glycol (diethylene glycol) 1.427; piperidine 1.445; chloroform 1.447; carbon tetrachloride 1.461; methyl hexalin 1.464; hexalin (cyclohexanol) 1.468 glycerine 1.473; turpentine 1.471 - 1.475; picoline 1.503; perchloro-ethylene 1.506; decaline 1.507; pyridine 1.509; furfurol 1.526; m-cresol 1.536; o-cresol 1.542; tetraline 1.548; phenol 1.550, nitrobenzene 1.553; styrene 1.563; naphthalene (at 98°C) 1.582; aniline 1.586; $\alpha$ -methyl naphthalene 1.618; carbon disulfide 1.620; chinoline 1.624; methyl- $\alpha$ -naphthol 1.623; $\alpha$-naphthol (at 99°C) 1.620.

### j. Molecular Weight

In usual investigations on Otto fuels, determination of the mean molecular weight is hardly in question as a characteristic. This method has a certain interest for scientific research on problems of fuel, which naturally cannot be discussed in this brief monograph. However, reports by Marder have shown that within the individual hydrocarbon classes an almost linear dependence of specific gravity and refraction on molecular weight exists. Table 31 shows these correlations.

### k. Parachor

The parachor is a characteristic established by Sudgen and Mac Leod (bibl. 66 and 67):

$$P = \sqrt[4]{\sigma}\ \frac{M}{D}$$

In this equation, P denotes the mole parachor, M the molecular weight, D the specific gravity (in liquid phase at the temperature t), and $\sigma$ the surface tension at t. The parachor P is independent of temperature.

The parachor resembles greatly the above-mentioned molecular refraction. Exactly as in that refraction a definite increment occurs in the parachor for each atom. The increments for the parachor are as follows: or C 4.8; for H 17.1; for O (in esters) 18.4; for O (in OH) 13.3; for N 12.5; for S 48.2; for double bonds 23.2; for triple bonds 46.6; for the five-membered rings 8.5; for the six-membered ring 6.1. The following formula for the parachor is slightly more accurate:

$$P = \sigma^{1/4}\ \frac{M}{D - d}$$

where d denotes the density of the gaseous substance = M/24055.

The mole parachor of a given hydrocarbon class shows a strong dependence on the molecular weight. For comparison purposes the specific parachor (p): p = P/M is more suitable:

$$P = \frac{\sqrt[4]{\sigma}}{D - \frac{M}{24055}}$$

Heinze and Marder (bibl. 68) have used the specific parachor and boiling coefficient for determining the engine behavior of Otto fuels, especially the octane rating. However, these are mere development works which are not terminated. The report mentions that the octane number of Otto fuels can be determined from density and boiling coefficient. The density of alcohol-free and benzene-free benzines has only a very loose and fluctuating correlation with the boiling coefficient, since the relations are approximately as follows:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| d/20 : | 0.715 | 0.720 | 0.725 | 0.730 | 0.735 | 0.740 | 0.745 | 0.750 |
| Boiling Coefficient: | 90-97 | 99-107 | 95-117 | 110-124 | 110-129 | 120-134 | 126-138 | 130-142 |

Benzene blends show clearly with specific gravities d of 0.760 - 0.790 and boiling coefficients between 109 and 121. A frequently assumed correlation between density and initial distillation or density and 10% boiling point, does not exist.

## 25. ENGINE BEHAVIOR

The thermal efficiency of an Otto-cycle engine depends mainly on the possible compression of the fuel-air mixture. At an increase in compression ratio from 1 : 4 to 1 : 6, the power of an Otto-cycle engine will increase by approximately 20% under otherwise equal test conditions. A further increase in compression from 1 : 6 to 1 : 7 will increase the engine output by 5.5% and an increase in compression from 1 : 7 to 1 : 8 will show a power increase by 4.5%. In the German automobile engines, the compression ratio is on the average 1 : 5.5 to 1 : 6.5. Sports models and racing cars, especially, however, aircraft engines, have a still higher compression ratio.

Fuels for Otto-cycle engines have the characteristic that they do not correspond to these methanical conditions, especially to the extreme requirements. Certain benzines and especially certain distillate benzines have a very low compression resistance which means that they will knock strongly at excessive compression, which is harmful to the engine, especially at full power and low rotational speed or whenever the ignition cannot be [illegible]. This knocking starts with a bright tinkling (pinking) and finally changes into a loud hammering sound (knocking). Consequently, the antiknock characteristic of a fuel for Otto-cycle engines is the maximum compression ratio at which this fuel still burns without producing any knock. The fact that various influences are produced by the engine itself and its design, will be discussed in a separate section. This ratio between antiknock characteristic of the fuel, expressed as octane rating, and the maximum permissible compression ratio (HUC, high useful compression ratio) is strictly valid only for the Ricardo test engine and reads approximately as follows:

| OR | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
|---|---|---|---|---|---|---|---|
| ε | 1 : 4.65 | 4.78 | 5.00 | 5.28 | 5.67 | 6.23 | 6.80 |

### a. Compression Resistance and Nature of Hydrocarbons

Saturated and unsaturated aliphatic compounds with unbranched chains, i.e., n-paraffins and n-olefins lose compression resistance with increasing molecular size. This is not the same in hydrogenation benzines. In saturated and unsaturated isomeric chain hydrocarbons, i.e., in i-paraffins and i-olefins, the antiknock characteristic increases with the number of methyl groups branched in the molecule. In addition, the antiknock quality increases at a more central arrangement of the $CH_3$ groups in the molecule and finally reaches an octane number of 100 in iso-octane, in 2, 2, 4-trimethyl pentane. This octane number is used for reference purposes. The aromatic compounds have a very high antiknock rating in themselves but will have a poorer result in the so-called "mixed octane rating" in small additions than in high additions. Consequently, the antiknock quality of benzine-benzene mixtures [illegible] with homologues of the benzene does not furnish a linear function of the amount of additive (as mentioned before). The naphthenes are not quite as resistant to knocking as the aromatic compounds and the isomeric chain hydrocarbons but exceed the characteristics of n-paraffins by far. No noticeable influence of the side branches for increase in compression resistance has been observed in naphthenes. The olefins are clearly superior in antiknock characteristics to the paraffins. However, they have the disadvantage of a tendency for resinification. The hydrogenated benzines generally have a good antiknock behavior but cannot be compared directly with natural products, i.e., with the chain hydrocarbons of petroleum conversion, since they are synthetic products.

### b. Octane Number

One of the hydrocarbons producing the highest knocking is the n-heptane. For this reason, an antiknock rating and an octane number of 0 have been given to this n-heptane for reference purposes. In contrast to this, iso-octane or 2,2, 4-trimethyl pentane is one of the hydrocarbons with the highest antiknock quality. Therefore, iso-octane received the antiknock rating and octane number of 100:

| | | d/20 | BP°C | nD/20 | Octane Number |
|---|---|---|---|---|---|
| n-Heptane | $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ | 0.684 | 98.4 | 1.3878 | 0 |
| i-Octane | $CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$ | 0.691 | 99.3 | 1.3921 | 100 |

The n-heptane is obtained in a high degree of purity from the balsams of the Jeffrey pine. The iso-octane is obtained either by treating tertiary butyl alcohol with sulfuric acid and by hydrogenation of the resultant octene, or by the large-scale method described previously (Section 12d). Since these reference fuels, i.e., n-heptane and i-octane, are too expensive and are not available at a given location, subreference fuels or so-called "substandards" are used. Such substandards are represented by the IG calibration benzine with an octane rating of 43 or the standard benzines with an octane rating of 50 or 67.6.

Muecklich and Conrad (bibl. 69) created the concept of a so-called "quality factor" equals 100; paraffins/boiling coefficient. Philippovich found satisfactory agreement of fuels characterized in this manner with their engine behavior. However, the concept of quality factor has not been used extensively. The relative scale is still the octane scale.

The antiknock quality of Otto fuels is opposite to the ignition quality of Diesel fuels. In other words, an antiknock benzine will always be a Diesel fuel with a poor ignition quality while a knocking benzine will have a better ignition quality in a Diesel engine. Similarly, a Diesel fuel of low boiling range (at preheating of the mixture) with a poor ignition quality can be used in the Otto-cycle engine while a Diesel fuel with a high ignition quality is completely unsuitable for use in an Otto-cycle engine. It is rather doubtful whether opposite requirements in fuels should be brought into any relation since the scale can never be exact in such cases. According to the IG-Leuna fuel manual by Jantsch (Third Edition 1941), the relations are approximately as given in Table 34.

### c. Characteristic of Knocking

In knock-free combustion, the flame propagating from these spark plugs passes the combustion chamber rather regularly and burns the compressed fuel-air mixture under a downward motion of the piston. The normal rate of combustion is 20 - 25 m/sec. At knocking combustion, the flame propagating from the spark plug propels a part of the unburnt mixture in front of itself and compresses it furthermore. Pressure and temperature in the mixture remainder then increase suddenly up to a critical point at which spontaneous combustion of this remainder takes place. The rate of knocking combustion in this state had been found by Schnauffer to be 250 m/sec or, according to more recent measurements, even 300 m/sec. That means, the rate is approximately 10 - 12 times that of knock-free combustion. The knocking sound itself is produced by vibrations developed in the burnt gas. This knocking will show only in loaded engine but not in an idling engine. According to modern concepts of physical chemistry, these combustion processes in the engine are chain reactions which do not have to be initiated by the ignition spark. Special wall reactions are created by the hot exhause valve and, at knocking combustion, these chain reactions will produce a sudden interruption by explosion-like disintegration of the molecules, known as chain or heat explosions. At this instant, actual explosions take place in the Otto-cycle engine while the former designation of "explosion engine" was completely wrong for an Otto-cycle engine with a normal combustion.

Basic investigations on the nature of knocking which have eliminated a large number of erroneous concepts, were made mainly by Schnauffer (bibl. 70). This author describes an electric measuring setup for recording rapidly-progressing pressure phenomena, which make it possible to observe the flame motion and flame propagation in engine cylinders during actual run. The method is based on the phenomenon that a gas gap is ionized by the flame, so that a current circuit connected to the electrodes of the gas gap will carry electric current at the instant of flame passage. This current controls an oscillograph loop across a high-frequency connection, which shows a deflection on arrival of the flame, due to the ionization. The instant of the flame arrival can be determined accurately in the oscillogram. Schnauffer used a long combustion path in his test setup, extending from a spark plug (a) attached at the side, over two test points (b, c) in the cylinder head to the test point (d) at the opposite cylinder wall. The arrival of the flame front at the test points (b, c, d) is characterized in the oscillogram by a sharp deflection of the luminous line. The instant of ignition (a) is marked by a different connection setup in the same manner which furnishes the times required for the flame to pass the individual gaps for the total distance. These times are approximately 0.005 - 0.01 sec and are recorded on the moving oscillograph tape (see Fig. 15a). Simultaneously-recorded tuning-fork oscillations make a time measurement possible. Since the spacings of the amplitudes of 0.02 sec are known and since the path of the combustion can be measured, the rate of combustion can be determined. In operation free of knocking (Fig. 15a) a uniform progress of the flame front (slightly accelerated toward the end of the combustion) is observed. In knocking, a sudden combustion of the entire gas-mixture residue takes place with an almost simultaneous occurrence at the flame at points c [illegible] In Fig.15b, the resultant strong pressure peak is plotted against the regular "soft" and knock-free combustion. In knock-free operation, a sharply-limited flame front can be assumed which burns the mixture components directly in front of it, while in knocking operation the mixture residue (frequently half of the charge) detonates suddenly after an initial regular almost inhibited combustion of the charge. Withrow and Boyd (bibl. 71) were able to photograph the flame front in a high-speed combustion engine. In this case, the cylinder head was equipped with a quartz-glass window extending over the longest flame path. In front of this quartz window a film drum turned at constant rotational speed.

The violence of the knock itself apparently depends on the quantity of the mixture residue which burns suddenly. Naturally, the actually-reached height of the pressure peaks is an indication of the knock intensity. The damage of engine knock is mainly a damage of the power-plant parts and a noticeable decrease in power. Chemically, the detonation of a mixture residue during the knocking process frequently has been explained by formation of peroxides, i.e., by spontaneous disintegration of these extremely unstable intermediary products during the above-mentioned chain reactions. This "peroxide theory" (bibl. 72 - 74) is disputed by Serruys (bibl. 75) and also by Boerlage and Jost (bibl. 76 and 77) who believe the reason for knocking to be a certain type of activation of molecules. Jentzsch who frequently has been mentioned in this report as to his research on self-ignition characteristics of hydrocarbons, believes that a parallel exists between knocking tendency and splitting ability of hydrocarbons.

### d. Knocking and Engine Design

The knock phenomena in Otto-cycle engines are not only produced by the fuels themselves. Rather, certain structural designs and actual engine conditions favor knocking or inhibit knocking. Consequently, the fuel chemist must be clear on the fact that the influences by engine design and engine handling on knocking of the engine are rather considerable.

Already Maxwell and Wheeler, Ricardo and Glyde (bibl. 77 - 79) found this decisive influence of engine type and combustion-chamber design on knocking in Otto-cycle engines. Representation of the frequently-voiced opinions which have either been retained or else rejected, would confuse the over-all picture in a brief description, so that only a short survey on the present state of the research will be given.

A separate section had been used for discussing the type and chemical structure of fuels and their influence on engine knocking. In addition, the entire problem was the main subject of the first part of this book. Therefore, the mechanical influences on engine knocking must be treated in a separate section. These influences are subdivided into effects produced by the design of the combustion chamber and into effects due to operational conditions of the engine. These effects will be discussed later in the text.

Knocking in an engine is favored by unfavorable position of the spark plugs. For example, if the spark plugs are placed in the vicinity of the cool inlet valves, so that a long flame path is created, the mechanical prerequisites for knocking are given, especially if the stagnated mixture residue is additionally heated by the hot outlet valve.

Consequently, it is an advantage to install the spark plugs as far as possible from the outlet valve. Side chambers in the combustion chamber itself are of disadvantage because of the length of the resultant flame path. A semispherical or conical combustion chamber with the valves installed diagonally in the head has been found to be the most favorable design.

e. Knocking and Operating Conditions of the Engine

Of the operating conditions of an engine, the ignition setting has the main influence on engine knocking. Advancing the ignition (preignition) will increase knocking since a premature ignition will result in an additional compression by the rising piston. Accurate ignition setting must be so matched to the combustion process that the maximum permissible combustion pressure is obtained without resulting in knocking. Consequently, a retarded ignition will eliminate the knocking since the combustion then lags behind the downward-moving piston. However, handling of engines with retarded ignition is uneconomical and results in a decrease in power and increase in fuel consumption. Lower rotational speeds favor knocking since the piston at incipient combustion is near the top center which means that the combustion space is very small, resulting in an additional compression which, in turn, creates engine knocking. Since any additional pressure increase will increase the knocking, use of supercharging will increase the knocking tendency. In a theoretically-accurate fuel-air mixture, maximum knocking tendency exists. Rich or lean carburetor setting will decrease the knocking but is uneconomical and has other drawbacks. An increase in engine temperatures (hot summer air, preheating in aviation, individual overheated points, or carbon deposits at the piston crown, insufficiently heat-resistant spark plugs, hot exhaust valves, etc.) will always increase engine knocking. Hubendick shows an example (see diagram in Fig. 16) of the influence of mixture preheating and mixture formation on the engine power. A mixture preheating is rather unfavorable for the obtainable at air deficiency, while an air excess is favorable. According to tests, Otto-cycle engines will have their maximum power at air deficiency (air-excess coefficients 0.75 - 0.90). At actually-increasing air excess, the power will decrease while the fuel utilization becomes more economical. Only at air-excess coefficients between 1.1 and 1.25, the engines will fail since no ignition nor detonation can occur. Obviously, the antiknock characteristics depend mainly on the mixture composition and mixture temperatures, independent of special characteristics of the fuel itself. Finally, it should be remembered that a tendency for knocking increases with the engine load and does not exist in idling.

Singer (bibl. 80) has demonstrated the scope of these influences on the IG testing engine, reproduced in a diagram in Fig. 17. The values in this graph cannot be generalized and applied similarly to each engine type but furnish a satisfactory general view and permit corresponding extrapolations to other types of engines.

f. Testing Engines

The most important method for engine testing of Otto fuels was developed by Ricardo with his E-35 engine (cylinder bore 114 mm diam, stroke 203 mm, variation in compression ratio from 1 : 3.7 to 1 : 8 by raising and lowering the cylinder by means of screw threads). At the same time, Ricardo found the Highest permissible compression ratio (HUCR = highest usable compression ratio) to be a criterion for the compression resistance of Otto fuels.

International significance has been obtained in the meantime by the CFR engine of the Cooperative Fuel Research Committee, the Horning engine, (bibl. 81) which will be discussed in detail in its present state. Finally, the IGF developed a testing engine which was rather similar to the CFR engine and naturally is of special use for reference purposes at present. Since the CFR engine (manufactured by the Waukesha Motor Company in Waukesha, Wisconsin, USA) and the IG testing engine for light fuels (manufactured by the Daimler-Benz Company in Mannheim) differ only slightly in structure, mode of operation, and handling, it will be sufficient to describe the engine test of Otto fuels in the single-cylinder testing engine of the IG. The differences of the IG testing engine and the CFR engine will be given in technical data:

| | CFR Engine | IG Engine |
|---|---|---|
| Bore mm | 82.5 | 65 |
| Stroke mm | 114.3 | 100 |
| Swept volume cc | 610 | 332 |
| Compression ratio | 1 : 4 to 1 : 12 | 1 : 4 to 1 : 15 |
| Variation in compression | Infinite | Infinite |
| Ignition | Battery or magneto | Battery |
| Ignition setting | Automatic | Generally fixed |
| Spark plugs | DM 145/1 | Bosch DM 145 T 1<br>or Siemens AG 30 |

| Valve Periods: | CFR Engine | IG Engine |
|---|---|---|
| Inlet opens | 0° dead center | 11° A. T. C. |
| Inlet closes | 44° A. T. C. | 173° A. T. C. |
| Outlet opens | 64° B. B. C. | 173° A. T. C. |
| Outlet closes | 21° A. T. C. | 3° A. T. C. |

### g. IG Testing Engine for Light Fuels

The main parts of the system are the carburetor, generator, and the instrument panel. The carburetor engine is a stationary single-cylinder engine with variation in swept volume created by moving the cylinder by means of flat threads, worm wheel, and worm in vertical direction so that the lowest compression is obtained at the highest position of the cylinder and the highest compression at the lowest position of the cylinder. The variation in compression ratio can take place during operation by turning the worm with a hand crank for moving the cylinder. The resulting variation in compression ratio can then be read on a drum graduation. A second graduation will furnish the approximate octane number if the scale had been adjusted corresponding to the applied testing method. A bouncing-pin indicator is attached to the cylinder head. The character and mode of operation of this indicator, used for measuring the knock intensity, will be discussed later in the text. For ordinary investigations in the IG engine, constant preignition is used which can be marked by flashing of a small neon tube. However, the ignition point can be varied and measured on a dial. The cylinder is cooled by evaporation cooling with water (100°C) according to the research method or with a mixture of water and glycol (150°C) according to the engine method. The carburetor is equipped with three floating boxes which can be connected to a common nozzle if desired. To each of these boxes, a fuel tank is mounted which increases the level when turned up and thus raises the benzine gradient, so that the fuel-air mixture can be enriched. The adjustment is shown by marks on the gauge glasses. For working with the so-called "engine method" in testing aircraft fuels, the fuel-air mixture in the supply line can be preheated by an electric heater up to 150°C and the mixture temperature can then be read on a thermometer. Driving and loading the testing engine takes place by means of a polyphase-current squirrel-cage induction motor across a V-belt. The polyphase motor can be displaced on tracks for installing belt pulleys of various diameters and for adjusting various rotational speeds in the testing engine. The knock meter, output meter, and ammeter are attached, together with the main switch and a rheostat for preheating of the mixture.

In Germany, automobile benzines are evaluated according to the research method and aircraft fuels mainly according to the engine method. The latter method generally gives slightly lower octane values due to the stricter test conditions. The test conditions for both methods are as follows:

| | Research Method | Engine Method |
|---|---|---|
| Rotational speed rpm | 600 | 900 |
| Corresponding belt pulleys mm diam | 145 | 220 |
| Coolant | Water | 93% glycol + 8% water |
| Cooling temperature | 100°C | 150°C |

In both methods, the outlet temperature of the condenser cooling water should be 30°C; the ignition should be 22° before top center, the carburetor must be adjusted to maximum knocking, and all fuel samples must be investigated at equal knock intensity. This knock intensity in the research method is $\varepsilon = 1 : 5.5$ (research octane rating 65) and in the engine method $\varepsilon = 1 : 5.8$ (engine octane rating 87). In the three-float carburetor, the Otto fuel to be investigated is compared to two reference mixtures. Determination of the antiknock rating starts by adjusting the compression ratio to medium knocking (pointer deflection on the knock meter set to 40) by turning the hand crank. Then, the float in the carburetor is set to maximum knocking, the compression is adjusted to 50 on the knock meter, and the value is read on the octane disk on which the research octane ratings (ROR) and engine octane ratings (EOR) are given for combustion ratios within 1 : 4.3 to 1 : 6.5. For accurate determination of the octane number of a given benzine, reference mixtures of substandards are so selected that they will define the antiknock characteristic of the benzine to be tested within the rather narrow range of 2 - 4 octane units. As substandards for the IG Otto-cycle engine, a IG calibration benzine and pure benzene are used. Table 35a shows the ratio of research octane rating (ROR) and engine octane rating (EOR) to the mixtures of calibration benzine or benzene or calibration benzine and tetraethyl lead with respect to the IG engine. For testing fuels with a high antiknock value (aircraft fuels), either iso-octane with different degrees of leading or mixtures of calibration benzine with constant lead ratio (lead addition 1 cc/ℓ) with leaded iso-octane.

For starting the calibration mixtures and for leading of benzine in the laboratory, special burettes are used.

Accurate handling of the IG testing engine, procedure for the investigations, adjustment of carburetor and indicator, and all corresponding manipulations are given in an excellent manual for the IG testing engine compiled by Singer.

### h. Measuring the Knock Intensity

For measuring the knock intensity, the bounding-pin indicator is used in both CFR and IG testing engines as developed by Midgley (bibl. 82). This device mainly is based on the principle that the cylinder head is drilled and equipped with a threaded steel membrane (1), as shown in Fig.18. This membrane shows a flexure under combustion pressure which is stronger in knocking combustion than in normal combustion. This membrane acts on the freely-movable bouncing pin (2) which will vibrate together with this membrane at knock-free combustion. As soon as knocking starts, this pin is moved unward rapidly and closes a contact (4/5), while a spring (3) is used for returning the pin. The contact (4/5) closes a circuit which, in the first types of this indicator, was used for electrolytical decomposition of water. The amount of oxy-hydrogen gas developed per unit time was then used as criterion for the knock intensity. Recently, a filament and a thermal transformer are inserted into the knock circuit for indicating the knock intensity on the knock meter. Exact adjustment of the instrument and any possible adjustment error are given in the above-mentioned manual of the IG testing engine. However, reporting of knocking sounds is extremely difficult since combustion periods as short as 1/200 sec are produced, resulting in extremely short intervals during which the pressure wave created by the knocking is to be observed. Originally, it was attempted to determine knocking sounds by ear but the hearing ability of human beings differs widely. The ear is sensitive only to frequencies between 800 and 3000 cps and is unable to separate any partial sounds, not mentioning the possible sensory illusions. Naturally, automatic recording of the pressure course is independent of such illusions. The incipient knocking (of main importance for the test) would show in sudden pressure surges. However, all possible indicators, even the modern high-speed indicators, fail completely at the rapid processes in an Otto-cycle engine since they are too sluggish. The same is true of the Juhasz indicator in which the pressure diagram is recorded in points by means of a controlled slot, as well as for the British Farnborough indicator in which the pressure curve is recorded by spark perforations.

A considerable progress in recording high-speed processes is the fact that a recording device consisting of connecting rods and joints was finally replaced by an electronic indicator. Such an optical indicator was first used by the author for observing the combustion process in an Otto-cycle engine during tests made in the Benzol-Verband. Other inertia-free instruments operate on the electrical principle. For example, the DVL has developed a pressure indicator in which a thin metal membrane is exposed to the combustion pressures. The vibrations of this membrane operate a condenser plate in an electrical field which, in turn, produces oscillations in an electric circuit which then are photographed by means of a reflector on a film strip. In this connection, the electric indicator developed by Schauffer in the DVL should be mentioned. By this indicator, the ionization produced in burning of combustion gases is used for determining the character and time of a combustion process.

A recently developed method for recording pressure peaks in Otto-cycle engines is the piezoelectric method based on the characteristic of quartz to change its electrical systems on any change in pressure. In this case, a small quartz plate is exposed to the combustion pressures, and the variations in resistance are recorded photoelectrically.

In developing the measurements in this particular field, the recent work by Kawrziniok(bibl. 83) are of importance and valuable as to technical information. Figure 19a shows a schematic sketch of the basic test setup used by Wawrzinick. A condenser microphone freely suspended (1) is connected to the motor (2) by a short 7-cm wide hose section (3) which is to keep any secondary noises away from the instrument. A cathode-ray oscillograph (4) equipped with a volume amplifier (5) is used for recording the noise pattern. For marking the time, the vibration pattern of a tuning fork is recorded as a sine line on the film strip of the oscillograph. The ignition point is marked by an additional brief interference of the amplifier by the ignition current from the motor and (Fig. 19b) is recorded as a steep curve slope. The dead center is marked at the upper film edge by a string electrometer (6) shown in Fig.19a. This electrometer is operated across a short-circuit contact (7) by the flywheel. It may be assumed that the noise frequency can be used as a characteristic of engine knocking (knock frequency 3200 - 3400 cps). A choke installed in the amplifier output was used by Wawrziniok for creating a short circuit for the lower unimportant frequencies, in order to obtain purer sound patterns. Wawrziniok was able to determine that the noise amplitude, equal to the noise intensity, increased with the degree of preignition and that probably the degree of obtainable preignition could be used as a criterion for the tendency to knock or for the antiknock characteristic. In addition, he determined that n = 1000, the instant of knocking lags with respect to the ignition point by approximately 1/130 sec, while Auer (bibl. 84) found a time difference of 1/50 sec.

Schmidt and Generlich (bibl. 85) further developed the photoelectric measuring method of pressure processes in an Otto-cycle engine and finally refined the method so much that the amplitudes could be measured in mm. These amplitudes were recorded by the oscillograph on the moving film strip since obviously the oscillograph makes it possible to detect optically the acoustics of engine knocking. Figure 20a shows that the knock-free iso-octane will retain this quality even on increasing the combustion in the testing engine with variable compression. However, the knock-producing n-heptane resulted in loud knocking noises at any compression. Dollberg benzine and standard benzine were resistant to knocking up to ε 6 : 1, while a cracked benzine showed considerable knocking at this compression ratio. In Fig.20b, the increase in antiknock characteristic of a benzine by a gradual addition of benzene is shown. Figure 21 represents work done by Schmidt and collaborators and, related to the test setup used by these authors, shows the families of curves of antiknock characteristic, expressed in octane rating and located between the compression ratio and the knock intensity (mm mean knock deflection). This diagram shows that a fuel with an octane rating of 60 will show considerable knocking while a 74-octane fuel hardly shows any knocking. However, an Otto fuel with an octane rating of 74 shows high knocking while an 80-octane Otto fuel hardly shows incipient knocking. Finally, in the range of aircraft fuels this evaluation is especially valuable since benzines with octane ratings of 87 cannot be used beyond a compression ratio of ε = 1 : 6.5, while a 93-octane fuel has this limit only at a compression ratio of 1 : 7.1. A benzine with an octane rating of 60 will already be useless at a compression ratio of 1 : 5.3.

### i. Antiknock Test in Multicylinder Engines

Testing of antiknock characteristics of fuels in a single-cylinder testing engine was frequently believed unsuitable since the conditions in multicylinder automobile engines were not closely approached. As a matter of fact, determination of antiknock characteristics in the single-cylinder engine frequently shows no agreement with the apparent fuel behavior in the multicylinder engine. Kneule (bibl. 86) and other researchers indicate three main reasons for this observation. All three of these reasons refer only to the corresponding vehicle or its state or operating conditions but not to the fuel itself. These reasons are as follows: differences in ignition points, differences in heat condition of the cylinders, and an irregularity in distribution of the fuel-air mixture over the cylinders. With respect to this last reason, a gas removal from the cylinders by means of electrically-controlled gas-tapping valves (bibl. 87), it was determined that the front cylinders with the longer intake line generally are supplied with lean fuel-air mixture, while the rear cylinders have a richer mixture due to the fact that the air carries the wall condensates in direction of the flow toward the rear. The fuel-air ration in the individual cylinders may fluctuate between 10 and 18 and changes frequently without any apparent regularity within the same range on increase in rotational speed. In road tests, the following influences act on the knock behavior:

(a) Structure and engine state, i.e., compression ratio, combustion-chamber form; volumetric efficiency, carburetor design, oil-carbon formation, cooling conditions, etc.;

(b) Operating conditions such as opening of the throttle valve, mixing ratio, preignition, engine speed, road condition and grade, temperature, and humidity of the air, and barometer reading.

This makes it logical that the antiknock characteristic of a fuel in a road test does not seem to be represented by the antiknock characteristic of the fuel but rather is the result of a large number of components which have none or only a minor relation to the nature of the fuel. Backwood and collaborators (bibl. 88) created the concept of "car knock coefficient" and determined that the octane number in 10 cars of the same type may fluctuate by 10 or 15 units in road tests, while a fuel can have only one antiknock characteristic expressed by a definite octane rating. Consequently, for testing a given fuel as to its antiknock characteristics, test conditions adapted to its characteristic must be used and any influence of the engine must be kept to a minimum if not completely eliminated. These requirements cannot be met in a road test. The difficulties, for the same reason, will always be larger in a multicylinder engine than in a single-cylinder engine. Schmidt (bibl. 89) made tests on the Vario-Opel multicylinder test-stand engine developed by the BV and determined that a knocking of all cylinders hardly ever occurs at the same time. Rather, one or two cylinders will show a definite knock while the others are completely normal. Finally, the sound intensity of knocking differs in the various cylinders. For determining the knock behavior of a fuel, a single-cylinder engine will re preferable since all engine influences can be kept relatively constant. In multicylinder engines and in stationary engines, it was impossible to have the multitude of effects on knocking act exactly alike on each individual cylinder. Similarly, Berg (bibl. 90) mentioned that the octane number does not have sufficient value for a criterion of knocking in multicylinder engines. This author determined that a calculation of "knock-limit values" or critical knock curves as a function of the air-excess coefficient was definitely required for obtaining better comparison. He also believed that the characteristics or the knock behavior of engines cannot be characterized by one single value. For example, Seeber (bibl. 91) showed the considerable influence of the air-excess coefficient and mixture temperature on the combustion ratio obtained without knocking, in various antiknock tests made in the CFR engine. The critical knock values are shown in three curves for two aircraft benzines with octane ratings of 86.5 and 87.5. Obviously, rich mixtures were insensitive to knocking in all investigated cases and the maximum knock sensitivity (see Fig. 22) was obtained at an air-excess coefficient of $\lambda \approx 1.15$. An increase in temperature also will increase the knocking.

### j. Road Antiknock Tests

As demonstrated above, it is difficult to measure the antiknock characteristic of a given fuel in the multicylinder engine on the test stand. Naturally, it is much more difficult to obtain suitable results with a multicylinder engine in a road test as far as the knock behavior of a given fuel is concerned.

If the antiknock characteristic is not expressed in octane units and if fuels of unknown knock rating are merely compared to those of known octane rating (as showing or not showing knocking tendency), the following method should be used: At a given preignition and a given cooling-water temperature, the car on a level highway should be accelerated from high gear at 20 km/hr by simply giving gas. A fuel of a known antiknock characteristic (for example, octane rating 74 reference fuel) will then lose an incipient knock at a definite speed reached during this acceleration. A knocking fuel will still show knock phenomena even at higher speed, while a fuel with less knock tendency will produce no knock or only a short-time knock in this type of test. If the fuel is found to have too low a antiknock value, such road tests make it possible to add tetraethyl lead, benzene, or alcohol to the benzine under test until the desired antiknock characteristic is reached.

In hilly terrain, the grade is taken at open throttle and a definite high speed. By decreasing the speed, the point at which incipient knocking starts will be fixed. The above statement will then apply with respect to a reference mixture, i.e., the antiknock characteristic of the investigated fuel will be lower at higher speed at which knocking first occurs.

Finally, the antiknock characteristic of benzines can be evaluated by changing the ignition setting. In this case, an adjustable lever is attached to the steering wheel, sliding over a graduated dial. A fuel has a higher antiknock characteristic, the more preignition can be given without producing any audible knock. It is recommended to mark several calibration fuels with a known-octane rating on this graduated scale and to interpolate between these fuels and the fuel to be tested.

### k. Comparison of Antiknock Characteristics

The subcomitee for fuel testing collected a large number of test results on orders of the Reich Communication Ministry, reported by Kessler (bibl. 92) in a rather complete compilation. This report shows that the octane fluctuations do not exceed 1 - 4 octane units in the CFR and IG engines (research method) and that the octane ratings in the IG engine generally are one unit lower in the CFR engine, so that a rather satisfactory coincidence is obtained. Testing the antiknock characteristic of Otto fuels by means of the Jentzsch ignition tester, creates differences up to 20 octane units. In calculations made according to the Heinze-Marder density method, the results generally are 7 - 12 octa units lower than in practical engine testing. In road tests, the scattering range of the octane-rating measurement depends considerably on the skill of the driver and observer, but an approximate value to within 4 - 7 octane units can be found in most of these tests.

## 1. Experiments for Calculating the Octane Number

Experiments to replace engine testing of antiknock characteristics in Otto fuels by calculating the octane number, have been made at various times. Unfortunately, the results obtained in this respect are rather unsatisfactory.

In the frequently report by Francis, it had been mentioned that the relation shown in Table 36a existed between a standard (X) and the octane rating (OR) of pure n-paraffins and i-paraffins.

However, this type of representation becomes less important when considering that Francis relates the X-value to the expression 1000d - 2(BP) + P, where d denotes the density at 20°C, BP the boiling point, and P a parameter of the following values:

butane 142, pentane 157, hexane 178, octane 232, nonane 261, decane 290, and higher paraffins P = 29 n, where n denotes the number of carbon atoms.

The Americans definitely will have to construct a criterion in which the boiling point of the respective hydrocarbon is deducted twice from the density which had been multiplied by 1000. A slightly more logical relation was established by this same author Francis between octane number and the summation value: boiling point plus aniline point, since this value at least furnishes a uniform temperature data. Table 36b shows that the antiknock characteristic of pure n-paraffins and i-paraffins increases with chain branching and decreases with the number of C-atoms.

Cox (bibl. 93) recently attempted to define the correlations between density and distillation behavior of benzines and the antiknock characteristics. These are in principle the same calcucaltions made by Heinze and Marder (bibl. 94) for a physical determination of octane ratings. Hammerich and Pier (bibl. 95 and 96) showed a clear correlation existing in pure hydrocarbons between octane value, boiling point, and density. Certain analogies in the ratios of density to boiling point and octane number to boiling point, caused Cox to assume the distillation behavior of benzines (free of benzene and alcohol) to be rectilinear between 10% BP and 90% BP. He stated that the octane rating was inversely proportional to this boiling value and to the API density, according to the following formula:

$$OR = \frac{K}{a \cdot \log(API) + b \cdot \log(10\%\ BP) + c \cdot \log(90\%\ BP)}$$

In this equation, K, a, b, and c are numerical values to be empirically determined. Cox had originally given the following data for these values:

|  | Highly Knock-Resistant Benzines | Knocking Benzines |
|---|---|---|
| Values for a | 4.0 | 3.5 |
| Values for b | 2.0 | 1.25 |
| Values for c | 1.3 | 1.6 |

This results in the following values for benzines with and without knock resistance:

| Range | | Benzines No Knocking | Benzines Knocking |
|---|---|---|---|
| $d_{15}$ 0.700 - 0.770 | $f_1 = a \cdot \log (API)$ | 7.40 - 6.87 | 6.43 - 6.01 |
| 10% BP 50 - 100°C | $f_2 = b \cdot \log (10\% BP)$ | 4.17 - 4.65 | 2.61 - 2.91 |
| 90% BP 100 - 200°C | $f_3 = c \cdot \log (90\% BP)$ | 3.02 - 3.37 | 3.72 - 4.15 |

Using $F = f_1 + f_2 + f_3$, a value of F = 14.3 to 14.7 for knock-resistant benzines and a value of 13.12 to 12.87 for knocking benzines is obtained with a corresponding octane rating of 90 to 70 for knock-resistant and 45 to 76 for knocking benzines. In the formula abbreviated from the above equation (OR = K/F), K is no constant value but a variable quantity. Cox stated that F as a rectilinear function of OR resulted in the following numerical values:

| Highly Knock-Resistant Benzines | Knocking Benzines |
|---|---|
| F with OR<br>of 14.35 with 90<br>to 14.66 with 70 | F with OR<br>of 12.96 with 65<br>to 13.28 with 25 |

This seems a rather arbitrary compilation, which has been proved by the fact that actually measured octane ratings furnished no agreement with the values calculated by Cox. Assuming that the equation and the factors in this equation established by Cox would have been selected with any logic, Tannenberger and Seifert (bibl. 97) suggest a coupling of the linear dependence of F on OR for knock-resistant benzines as follows:

F 14.31 with OR 90 and F 14.87 with OR 70

These authors indicated that satisfactory agreement of the calculated values with the actually measured octane ratings were obtained for knock-free lignite hydrogenation benzines and Fischer benzines. The author himself found that the Cox octane ratings for knocking benzines of petroleum products, generally were by 5 - 10 units too low. If it is desired to retain the arbitrarily selected numerical values for a, b, and c the numerical values F-OR should be changed as follows:

F 12.92 with OR 76 and F 13.15 with OR 50 in a rectilinear connection. Naturally, the practical value of such calculation methods is more than problematic. If empirical data must be used, at least the data collected over a long period of time should be used without formulating elaborate equations merely to impress others with mathematics. Illustrative representation is much better for approaching natural conditions than simplified formulas. For example, the author suggests in this connection to fractionate the benzines to be investigated as usually according to the Engler or ASTM method. Then, these 10 fractions should be used for determining the refraction nD/20 and the distillation cross section. Finally, the octane rating in the individual fractions should be determined according to definite empirical rules. The octane values obtained from the fractions are added and a mean value is established by dividing by 10 since it can be assumed that the OR has an additive behavior. In this manner, the octane number would be calculated similarly to the boiling coefficient.

## 26. DETERMINATION OF ADDITIVES

### a. Determination of Tetraethyl Lead

Qualitative determination of leaded benzines is rather easy by dripping 1 cc fuel into a test tube and mixing it with a solution of liquid bromine in carbon tetrachloride (1 : 2) until the brown color in the fuel persists. A voluminous precipitation generally indicates a separation of lead bromide. If no precipitation shows, the sample is free of lead. It should be mentioned that benzines mixed with aniline will react similarly when mixed with bromine and show precipitation. Kiemstedt (bibl. 98) observed that metallic organic compounds (lead tetraethyl, iron carbonyl) in benzines will precipitate on irradiating the mixture with a mercury-vapor lamp. Steiger (bibl. 99) suggested a spot reaction with green dithizone solution which must be freshly prepared by dissolving 3 mg diphenyl thiocarbazone in 3 cc carbon tetrachloride. A drop of lead-containing benzine on filter paper is irradiated for 30 sec with the mercury-vapor lamp and then touched with green dithizone solution until the color reverses to red. Schulze (bibl. 100) described the following rapid method: 10 - 20 mg potassium chlorate are stratified with 5 cc fuel and mixed with 3 - 5 drops hydrochloric acid (1.19) without shaking. In presence of $Pb(C_2H_5)_4$, a definite turbidity will occur with a flocculent formation of $PbCl_2$. The reaction is accurate to within a lead content of 1 : 5000.

For quantitative determination of tetraethyl lead, the method is as follows: 100 cc water and 100 cc normal benzine are cooled in a half-liter Erlenmeyer flask and kept to a low temperature by outside ice-water cooling. Then, 10 cc of liquid bromine are added and 100 cc of the fuel to be investigated under continuous shaking. If the unsaturated hydrocarbons in the benzine should have absorbed the bromine in the meantime, i.e., if the mixture has become discolored, 10 cc of additional bromine should be added until definite reddish-brown color persists. The flask content is transferred to a separating funnel under afterrinsing with twice 75 cc water. Then, the aqueous lead-bromide containing layer is separated from the benzine layer. This aqueous solution is then freed from the excess in bromine by boiling. A small amount of ammonia is used for neutralization. Then, the mixture is assidulated and finally precipitated with sodium bichromate by adding 3 cc of a 10% $K_2Cr_2O_7$ solution at boiling temperature and by continuing the boiling until the precipitate of lead chromate forms a ball. After 1-hr standing in a warm room, the mixture is filtered through a weighed crucible, washed with hot water, dried at 150°C, and finally weighed. The weight of lead chromate multiplied by 6.019 will furnish the number of cc of tetraethyl lead per liter.

Edgar and Calingaert (bibl. 101) suggested the following method: 100 cc of benzine are mixed with a solution of 1 : 3 bromine in carbon tetrachloride until persistant brown color is obtained. The cracked benzines will show by progressive discoloration and considerable exothermic heat. The downy precipitate of $PbBr_2$ in the leaded benzines is filtered through a porcelain-filter crucible (Gooch crucible), washed with petroleum ether, and then boiled with nitric acid. The nitrous lead-nitrate solution is then evaporated to 3 cc, neutralized with ammonia, and mixed with 5 cc 50% acetic acid and 40 cc of 5% potassium bichromate solution. The mixture is heated to boiling and kept there for about 5 min under stirring in a warm room. After a short standing, the precipitate of lead chromate is filtered, washed, dried at 105°C, and weighed. The weight unit of lead chromate (molecular weight 323) accidentally corresponds to that of tetraethyl lead (molecular weight 323).

In the rapid method for lead determination according Uberich, 100 cc of the fuel to be investigated are mixed with 10 cc of a solution of 10% bromine in carbon tetrachloride and shaken for 1/2 min. Then, 5 cc 65% nitric acid are added for dissolving the precipitated lead bromide. The mixture is shaken until all flakes have gone in solution. This process is repeated twice with 5 cc 10% nitric acid each time. Finally, the lead-nitrate containing nitric acid filtrates are combined in a high, annealed and weighed porcelain crucible, adding 1 cc 10% sulfuric acid at the same time. Evaporation must be done cautiously to avoid any shock or spilling. Then, the crucible is waved over an open flame for removing the last acid vapors, then annealed for removing organic substances, moistened with nitric acid after cooling, and with two drops of sulfuric acid after the nitric acid has stopped fuming. Finally, also the sulfuric acid is evaporated.

The crucible content is determined as lead sulfate, and the amount of sulfate is calculated in gram. Multiplied by 0.6427, the vol % of Pb $(C_2H_5)_4$ per 100 cc of test benzine are obtained.

b. Determination of Iron Carbonyl

Iron pentacarbonyl (known formerly as "Motyl" of the IGF) as an additive to Otto fuels is determined by irradiation with a mercury-vapor lamp. In this experiment, a powdery precipitate of iron nonacarbonyl. In a different method, the test benzine is extracted with nitric acid, and the iron is determined by rhodane ammonium salt or rhodane potassium. Presence of Fe ions shows by a bluish-black color on addition of alcoholic tannic acid or gallic-acid solution (with or without irradiation).

c. Benzene and Other Additives

A larger amount of benzene or benzene homologues in benzines can be immediately detected by an increase in density and refractive index. A very accurate determination can be made by refractometric treatment of the fractions obtained by an Engler distillation. While benzene-free benzines show a rather regular correlation in their refraction to the distillation (as mentioned previously), benzene-containing Otto fuels show distinct deviations. It must be considered whether a quantitative method more suitable than the conventional determination of aromatic compounds by sulfuric acid or nitration, could be developed. Figure 23 shows this gradual increase of the nD at gradual blending of a benzine with pure benzene. The qualitative determination with dracorubin paper (manufactured by Helfenberg) is undependable since in addition to benzene and its homologues, also alcohol, acetone, ether, turpentine, and tetraline (but not decaline) will show the same reaction. If a small grain of isatine and a drop of concentrated sulfuric acid are added to a benzene-containing benzine, blue rings will form around the crystal due to a reaction of the thiophene of the benzene with the isatine (indophenine reaction).

d. Determination of alcohol and other water-soluble additives had been described above.

Determination of ethyl ether (used formerly in priming benzines as additive and found at times as a component of priming fuels in tubes) is done as follows: 5 cc of a 1% potassium bichromate solution are assidulated with three drops of dilute sulfuric acid and shaken with 5 cc of the lowest-boiling benzine fraction and 2 cc of a 3% hydrogen peroxide solution. A persistent blue color indicates presence of ether due to formation of perchromic acid, while in the case of alcohols the blue coloration changes to green or yellow. Additives of tetraline, decaline, topped oil and the so-called "benzine extender" which fortunately has been banned from sale by Government control, can be detected in the end of the Engler distillation and identified in the last fraction.

## DIESEL FUEL
## PART II:

### 1. PETROLEUM DIESEL FUEL

a. Distillate Diesel Fuel

The largest fuel for Diesel engines has been covered by petroleum fractions between 150 and 360°C until shortly before outbreak of the war. The composition of such distillate Diesel oils naturally varies with their origin but fluctuate in more narrow limits than that of benzines if the structure of Diesel oils is considered mainly with respect to their ignition quality. The ignition quality of a Diesel fuel is higher, the lower the energy required for splitting the hydrocarbon molecules. For this reason, the n-paraffins are the components in Diesel oils with the highest ignition quality but also substances which will interfere considerably with the low-temperature resistance. The aromatic compounds do not ignite readily, naphthenes and olefins as well as the isomeric paraffins occupy a middle position, and it is of special interest with respect to the latter compounds that they produce considerable ignition delay. As a matter of fact, all hydrocarbons which have high antiknock qualitites in an Otto-cycle engine are not suitable for a Diesel engine and vice versa. In the petroleum Diesel fuels, the amount in aromatic compounds and unsaturated hydrocarbons is relatively low and does not exceed 15 or 30%. The ignition qualitites are finally determined by the ratio between n-paraffins and i-paraffins as well as naphthenes. Gas oils of petroleum industry rich in n-paraffins show considerable paraffin precipitation in low temperatures and an insufficient pour point. The ignition quality of petroleum Diesel fuels generally has a cetane rating between 45 and 65 or a cetene rating between 62 and 82.

### b. Kerosene

Kerosene is the fraction of petroleum boiling between 150 and 300°C, either unrefined or refined depending on the purpose. For kerosene No. I quality, 90% nuclear fraction, and for kerosene of No. II quality 75% nuclear fraction are specified, denoted by "nuclear fraction" the boiling range between 150 and 300°C. The density of paraffinic kerosenes is between 0.795 and 0.810 with a turbidity point at -10°C. The density of naphthenic and aromatic kerosenes is between 0.810 and 0.830 with a turbidity point between -20 and -70°C. In farm tractors, kerosene is used as fuel for the rather obsolete heavy-oil carburetors. For operation of medium-pressure engines (mixed-cycle Hesselman engines), kerosene is used as injection fuel. In Diesel engines, kerosene alone is not used since the fuel pump would have insufficient lubrication and may even leak. In addition, the atomization may be too pronounced on injection and cause knocking. However, kerosene should be added to Diesel fuel in considerable amounts for improving the low-temperature characteristics for winter operation.

### c. Cracked Diesel Oil

In cracking processes in petroleum industry, distillates in the boiling range of Diesel oil occur, but cracked Diesel oils with cetane ratings between 30 and 40 have a rather poor ignition quality since the ignitable chain hydrocarbons are eliminated by the cracking process and the poorly-igniting ring hydrocarbons are increased in amount. The usual sulfuric-acid refining has less effect in cracked Diesel oils for improving the ignition qualities than the "refined eanuzation", i.e., the treatment with liquid sulfur dioxide as selective solvent. However, a corresponding loss in yield of as high as 50% must be expected which seems to indicate that refining by this method is uneconomical.

### d. Characteristics of Petroleum and Petroleum Diesel Fuels

The various characteristics for these fuels are given in Table 37.

## 2. LIGNITE DIESEL OIL

### a. Carbonization Tar Oil

Carbonization of lignite furnishes approximately 8% low-temperature tar (crude tar) or approximately 3% tar oil. The crude lignite tar oil, along with a complicate mixture of hydrocarbons, in which the ring hydrocarbons and the unsaturated compounds have a value of 55 - 75%, contains a fluctuating amount of acid components known as creosotes (up to 20%) and slight amounts of basic substances and neutral oxygen compounds. In chemical composition, the lignite Diesel oil differs fundamentally from Diesel fuels of petroleum production and just as much in ignition quality. The crude creosote-containing lignite tar oils with a specific gravity d/20 of 0.92[illegible] - 0.945 and boiling coefficient of 280 - 340 show cetane numbers between 30 and 4[illegible], while the refined lignite tar Diesel oils with specific gravity d/20 of 0.880 - 0.925 and boiling coefficient of 260 - 320 has an ignition quality with cetane number of 38 - 44. The lignite Diesel fuels refined with selective solvents and having a specific gravity d/20 of 0.880 - 0.910 and boiling coefficients between 270 and 310, show cetane ratings between 44 and 48.

Very few data are known on the nature of hydrocarbons contained in lignite carbonization tar oil within the boiling range of Diesel fuel. Separation methods for determining the hydrocarbons in lignite carbonization benzines show considerable difficulty, which becomes much more complicated in the higher fractions. That means, estimates are the only means for furnishing any data. The amount of unsaturated, aromatic and hydroaromatic hydrocarbons probably predominate over the amount of chain hydrocarbons in carbonization tar oils. Obviously, no single olefins are present, but unsaturated cyclic hydrocarbons with one or more double bonds are definitely components of this product. The single ring structures of the type of naphthalene, indene, cumaron, etc. which are obtained as typical decomposition products by middle and high-temperature carbonization in anthracite tar, are completely absent in lignite carbonization tar. However, homologues of these ring bodies presumably exist in large quantities.

The creosote in lignite tar oil consists less of phenol than phenol homologues, i.e., creosole, xylenols, mesitol, pseudocumenol, thymol, and carvacrol. In unrefined lignite tar oils, these substances interfere considerably with the ignition quality. The amount in basic substances in lignite carbonization tears is rather low and hardly ever exceeds 0.5%. However, also in this case (in contrast to the high-temperature coking of anthracite) the homologues of pyridine and chinoline, i.e., picoline, lutidine, collidine, etc. are involved rather than the pyridine and chinoline itself. The amount of sulfur compounds generally exceeds 0.5% in the heavy lignite fuels with thiophene and disulfide sulfur as main components. Of the neutral oxygen compounds present in a rather noticeable amount, the ketones and furanes derivates prevail.

Since refining of lignite tar oils is rather difficult and does not have the desired effect due to high yield losses, carbonization products for domestic fuel economy presumably will be done according to the high-pressure hydrogenation method developed by the IG.

### b. Hydrogenated Tar Oil

The characteristic of the IG high-pressure hydrogenation has been mentioned briefly in the section on synthetic benzines. The middle oil of the sludge phase and the distillate residues of the vapor phase are used for producing hydrogenated lignite Diesel fuel which has rather satisfactory characteristics since the olefins and aromatic compounds were hydrogenated into more ignitable materials. The creosotes as such disappear by water separation and increase the amount of hydrocyclic compounds, so that high-pressure hydrogenation includes a refining process. Consequently, the typical odor of hydrogenated aromatics is found in Diesel fuels produced by IG high-pressure hydrogenation.

### c. Characteristics of Lignite Diesel Fuels

The main characteristics of lignite Diesel fuels are given in Table 38.

## 3. ANTHRACITE CARBONIZATION TAR OIL

The composition and structure of anthracite tars is mainly the expression of the production process. At high-temperature coking, only aromatic compounds are formed while in anthracite carbonization, a large number of aliphatic and naphthenic compounds are created and make the crude tar differ considerably from coking tar. One of the main characteristics in anthracite carbonization tars is the extremely high content on phenols and the absence of naphthalene in any noticeable amount. Despite this fact, the ignition quality of anthracite carbonication tar oils is so low (cetane number below 20) that they cannot be used by themselves in automobile engines but only as a fuel for low-speed stationary Diesel engines. The specific gravity of anthracite tar Diesel fuels is always above 1 and the ignition quality generally between cetane ratings of 11- 18, i.e., products of this type frequently do not ignite at all in high-speed vehicle Diesel engines. When blended with products of the Fischer-Tropsch synthesis, these products may be used along with other substances.

## 4. SHALE TAR OIL

In carbonization of bituminous shale, fractions are obtained in manufacture of the tar oils, which can be refined into Diesel fuels under correspondingly high yield losses. Quality and ignition characteristics of these oils depend entirely on the penetration effect of the refining process. In this type and in anthracite carbonization, only the refining high-pressure hydrogenation should be used for improving such products. All other methods seem uneconomical.

## 5. KOGASIN II

Kogasin II is the Diesel fuel obtained in the Fischer-Tropsch synthesis. This fuel is a mixture practically free of aromatic compounds of mainly unbranched chain hydrocarbons with extremely favorable ignition quality. The ignition delay of Kogasin II is so low that this fuel cannot even be fully utilized in the conventional vehicle Diesel engines, so that it was attempted to use the Kogasin only for improving other Diesel fuels of a lower ignition quality. Successful blending of lignite oil with Kogasin was reported by Marder and Schneider (bibl. 102), showing an almost linear increase in ignition quality of the lignite oil on addition of Kogasin. Also anthracite tar oils can be refined by an addition of Kogasin but special characteristics are involved since the Kogasin has the property of precipitating the asphalt from oils rich in asphalt. The Rheinpreussen Company was able to utilize the selective solving power of Kogasin with respect to tar oils. This process will be described later in the text. Table 39a contains the characteristics of several Kogasin Diesel oils (according to Rothe) and Table 39b the characteristics of mixtures of Kogasin with lignite oil according to Marder and Schneider.

## 6. COLOR, ODOR, APPEARANCE

Diesel fuels are dark and discolored only in the unrefined state. Depending on the fraction, Diesel oils of petroleum base are colorless or light yellow or brownish or possibly may show a bluish-violet fluorescence. The odor is rather characteristic but not disagreeable. Carbonization tar oils generally have a deep red to blackish-red color with a penetrating and disagreeable odor. Diesel fuels of the high-pressure hydrogenation, generally blended with other types of Diesel oil, have a yellowish color and the characteristic odor of hydrogenated naphthenes. The Kogasins are colorless or fainty yellow with a dull and undefined odor.

## 7. SPECIFIC GRAVITY

Determination of the specific gravity was described in the section on Otto fuels.

The specific gravity of paraffinic petroleum types is between 0.795 and 0.810, as mentioned above, and that of the petroleum types richer in aromatic compounds between 0.810 and 0.830. The gas oils of petroleum industry have a specific gravity between 0.825 and 0.865 while the lignite carbonization tar oils have a specific gravity d/20 in the unrefined state of 0.920 - 0.950 and 0.880 - 0.910 in the refined state. The Diesel fuels obtained in the IG high-pressure hydrogenation have a specific gravity between 0.840 and 0.880. The Kogasins II of the Fischer-Tropsch synthesis have a specific gravity of 0.760 - 0.780 in the unmixed state.

### a. Specific Gravity and API

The relations shown in Table 40 exist between the density data according to American API degrees and d/15 within the boiling range of the Diesel fuels.

### b. Specific Gravity and Hydrogen Content

The specific gravity and hydrogen content of Diesel fuels was characterized by Marder in the following numerical table:

| d/20 | 0.800 | 0.820 | 0.840 | 0.860 | 0.880 | 0.900 | 0.920 | 0.940 | 0.960 | 0.980 |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | 13.70 | 13.40 | 13.10 | 12.75 | 12.45 | 12.15 | 11.85 | 11.50 | 11.15 | 10.85 |

The following expression is used as the value for the "disposable hydrogen":

$$H - \frac{O + N}{8}$$

Marder indicates the following values for the disposable hydrogen in relation to the specific gravity:

| d/20 | Petroleum | Diesel Fuel of Lignite Tar | Anthracite Tar |
|---|---|---|---|
| 0.800 | 13.5% | 13.5% | - |
| 0.820 | 13.3% | 12.8% | - |
| 0.840 | 13.1% | 12.3% | - |
| 0.860 | 12.7% | 11.6% | - |
| 0.880 | 12.4% | 11.2% | - |
| 0.900 | 12.1% | 10.7% | - |
| 0.920 | 11.7% | 10.4% | - |
| [illegible] | 11.4% | 10.0% | - |
| 0.960 | - | 9.6% | - |
| 0.980 | - | 9.2% | 7.5% |
| 1.000 | - | - | 7.0% |
| 1.020 | - | - | 6.7% |
| 1.040 | - | - | 6.4% |
| 1.060 | - | - | 6.2% |
| 1.080 | - | - | 6.0% |

Consequently, the density of heavy fuels increases with the molecular size and with the content in aromatics in the following sequence: i-paraffins, n-paraffins, olefins, naphthenes, aromatic compounds. However, the ignition quality decreases in a different sequence: n-paraffins, olefins, i-paraffins, naphthenes, aromatic compounds. Any attempt to evaluate or derive the ignition quality of Diesel fuels from the specific gravity will be made more difficult by the above facts. Similarly, as in an Otto fuel, no useful qualitative or quantitative means are available for differentiating the n-paraffins with a high ignition quality from the i-paraffins with a lower ignition quality even if it would be possible to separate analytically the chain hydrocarbons from the ring hydrocarbons.

### c. Specific Gravity and Calorific Value

Harder established the relations shown in Table 41 between calorific value and specific value.

## 8. DISTILLATION

In the main section on Otto fuel it had been mentioned that a large number of hydrocarbons is created alone by the isomerism in the paraffinic series within the boiling range of benzines. The number of these hydrocarbons will increase to an almost unbelievable amount in the higher fractions. For example, in hydrocarbons with seven carbon atoms, 9 paraffins, 27 olefins, and 29 cycloparaffins are possible, while in the hydrocarbons with 8 carbon atoms already 18 paraffins, 66 olefins, and 73 cycloparaffins occur. The paraffins of the formula $C_{14}H_{30}$ in the boiling range between 235 and 265°C show already 1858 isomers and the paraffins $C_{20}H_{42}$ show more than 360,000 isomeric forms. The same large number of aromatic compounds had been defined previously by Karrer (bibl. 103). The number of isomeric cyclic hydrocarbons is given in Table 41a.

The compilation of these derivates of aromatic compounds should be supplemented by the homologues of indene, diphenyl, acenaphthene, and fluorene which actually occur in tar oils. These concepts are mentioned at all not only to demonstrate the multiplicity of hydrocarbons occurring in heavy fuels on petroleum and tar base but also for limiting the importance of the boiling curve as the connection of the boiling points of numerous hydrocarbons in Diesel oils.

### a. Boiling Curves of Petroleum and Gas Oil, Boiling Points of Hydrocarbons

In Fig.24, P 215 indicates the boiling curve of an American petroleum (d = 0.790, boiling coefficient 215), P 225 that of a Rumanian petroleum (d = 0.806, boiling coefficient 225), and G 279 the boiling curve of a light Rumanian gas oil (d = 0.837, boiling coefficient 279). In addition, a heavy American gas oil H 310 (d = 0.868, boiling coefficient 310) is shown. On both sides of the diagram, the boiling points or boiling ranges of well-defined hydrocarbons are given. These hydrocarbons are found either in petroleum or in tar oils. The marks denoted by n $C_7$ - n $C_{22}$ indicate the boiling points of the n-paraffin hydrocarbons between which the boiling points of the numerous isoparaffins are located. The arrows or asterisks indicate the boiling points of the naphthenes found in petroleum, and the zones marked by rings characterize the boiling ranges of the aromatic compounds, i.e., of the homologues of benzene, naphthalene, anthracene, etc. The numerals 7 - 24 entered next to these marks designate the number of C-atoms in the respective hydrocarbons or hydrocarbon groups. This representation is to show the interrelation of hydrocarbons in natural products (in this case the Diesel fuels of petroleum and tar production), so that the boiling curves of such oils furnish a cross section but no characteristic for these complicated hydrocarbon mixtures. This is more so the case in the boiling coefficient which is again a cross section for the level of the distillation point rather than a general characteristic.

Tables 42a - d contain characteristics of several hydrocarbons of the paraffin, olefin, naphthene, and aromatic series such as may occur in kerosene and gas oil of petroleum industry or in Diesel oil from carbonization tar or high-pressure hydrogenation. The predominant part of compounds occurring in the boiling range of Diesel fuels have not been isolated so far. Table 42d finally contains a general view on the most important acid and basic components in curde tar oils and data on neutral oxygen or sulfur compounds in these oils.

The characteristics of the one-olefins, alkyl-cyclopentanes, alkyl-cyclopentenes, alkyl-cyclohexanes, alkyl-benzenes, and alkyl-toluenes, and of the diphenyl compounds, especially all viscosity data, were taken from recent reports by Schmidt, Schoeller, Eberlein, Germassmer, Grosser, Hopp, and Hartmann (bibl. 104).

### b. Temperature Correction and Vacuum Distillation

For testing, the Diesel fuels are subjected to the above-described Engler distillation. If any temperature corrections for the protruding mercury thread of the thermometer are to be made, the following values have to be added to the indicated temperature:

| Reading °C: | 160 | 180 | 200 | 220 | 240 | 260 | 280 | 300 | 320 | 340 | 360 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Correction °C: | 4.9 | 5.9 | 7.2 | 8.7 | 10.3 | 12.2 | 14.1 | 16.3 | 18.8 | 21.8 | 26 |

For correcting the barometer reading, the following values must be added to the indicated temperature at an air pressure below 760 mm Hg per mm mercury column:

| | |
|---|---|
| In the boiling range of 200 - 250°C | 0.060°C |
| In the boiling range of 250 - 300°C | 0.065°C |
| In the boiling range of 300 - 350°C | 0.070°C |

If vacuum distillation is used for more accurate results, the nomogram developed by Geale and Docksey shown in Fig. 25 should be used for converting the boiling temperature of the vacuum read on the mercury manometer to the boiling temperature at normal atmospheric pressure. The numerical scale on the left-hand side of the diagram is graduated in °C and °F for the temperatures actually read in a vacuum distillation. The right-hand curve is equipped with the scale of mm Hg vacuum. By connecting the values for temperature and vacuum obtained in a vacuum distillation, the temperature degree which would be obtained at atmospheric pressure, i.e., 760 mm Hg, are laid off on the center scale.

### c. Boiling Point/Density, Constant

Jackson used the density and the cross section of the distillation course for developing the characteristic of the "boiling point/density constant" for which he established the following formula:

$$(API) = (BDC) - [68 - 0.703\,(BDC)\,\log\,(50\%\,BP)]$$

In this formula, the following symbols are used:

(API) = density in API degrees
(BDC) = boiling point/density constant
(50% BP) = 50% boiling point, i.e., the distillation mean in °F

Between the boiling point/density constant and the ignition quality, correlations presumably exist. However, this is true only conditionally and with considerable restrictions, so that the value of this characteristic should not be overestimated.

Petroelum Diesel fuels generally are characterized by boiling point/density constants between 162 and 169. Their ignition quality is between 55 and 72 cetane rating. Lignite Diesel fuels of the carbonization tar production, according to Rothe (bibl. 105), show boiling point/density constants between 168 and 194 and the ignition quality is indicated to be between cetane ratings of 34 and 48. The boiling point/density constant of Kogasin II is near 146 and the ignition quality above that of cetane. For the synthetic heavy fuels of the IG high-pressure synthesis, no suitable relation between point/density constant and cetane rating can be established.

It is of importance that in various publications the boiling point/density constant is calculated from the 50% boiling point in °C which naturally will shift the data for the constant upward.

## 9. VISCOSITY

The viscosity of Diesel fuels is of a certain importance and, corresponding to a general requirement, the limits of 1.1 - 2 E/20 should not be exceeded upward or downward in fuels for high-speed Diesel engines in motorized vehicles. A Diesel fuel with too high a viscosity, according to statements made by Boerlage and Broeze, will disperse too much during the injection and will not reach the flame temperature rapidly enough, resulting in a knocking of the engine. In high-speed Diesel engines, it must be expected that a viscosity above 3 E/20 will create difficulties. In this connection, the special case of using fatty oils as Diesel fuel in tropical zones should be mentioned. At the abnormally high temperatures during daytime, the fatty oils are satisfactorily atomized but the low temperatures at night frequently liquefy the fuel during injection and prevent the oil-vapor formation which is required for correct combustion. To be able to use fatty oils or any oils of higher viscosity in a motorized-vehicle Diesel engine the fuel slot must be adjustable which would then result in an easier maneuverability of the vehicle on using Diesel fuels of a higher viscosity. However, thin fuels will produce leakage losses in the pump and atomizer nozzle. This loss may be approximately 20 g/hr at a viscosity of 20 cst/38°C, and approximately 40 g/hr at a viscosity of 10 cst/38°C. Use of such fuels in trucks may result in increased consumption of as much as 10%. Finally, a lower limit for the viscosity of Diesel fuels is required for insuring proper lubrication of the moving injection parts.

### a. Viscosimeter

For a turbulence-free measurement of the viscosity of thin oils, capillary instruments developed on the principle of the Ostwald viscosimeter (bibl. 106) are mainly used. The Vogel-Ossag viscosimeter consists of a small metal container with a capacity 15 cc. A capillary is screwed to this container, enlarged into two ball-shaped bulbs at the top. The inner space of the metal container is filled with the oil or fuel sample. A special thermometer inserted into the container permits determination of the temperature at which the measurement is made. Then, the fuel or oil sample is aspired to the upper mark between the two bulbs, and the time required for the liquid sample to flow quietly and undisturbed between the two marks is recorded. This time is a function of the capillary and, for fuel samples of the Diesel type, capillaries with a factor between 0.01 and 0.1 must be used. Since the viscosity depends largely on temperature, the viscosimeter is inserted into a water bath and the viscosity measurements are made only when the temperature of oil and bath liquid is equal. The time required for the sample to flow between the marks, multiplied by the capillary factor, will directly furnish the kinematic viscosity in centistokes (cst). The dynamic viscosity in centipoises (cp) is calculated by means of the specific gravity as cp = cst · d. The viscosimeter developed by Ubbelohde is very similar in mode of operation and manipulation to the Vogel-Ossag viscosimeter. The older Engler instrument for determining the viscosity of oils is unsuitable for fuel samples because of the width of the nozzle.

Table 42 contains the correlations between absolute viscosity in centistokes and viscosity in Engler degree for low viscosity degrees.

### b. Viscosity/Density Constant

The viscosity-temperature gradient of oils is characterized by a number of coefficients such as viscosity height, viscosity direction constant, viscosity index, and viscosity/density constant according to Hill and Coats. Obviously, also the paraffinic Diesel fuels will differ from fuels of aromatic nature by the slope of the viscosity-temperature function but the characteristics used for the oils cannot be applied for evaluating Diesel fuels. However, Moore and Kaye (bibl. 107) suggested a second viscosity/density constant for the constitutional quality evaluation of heavy fuels, calculating as follows:

$$d/15.6 = 1.082\ (VDC) + 0.0887 - [\,0.776 - 0.72\ (VDC)\,]\ \log \log\ (mst - 4)$$

This formula, d/15.6 denotes the specific gravity at 15.6°C = 60°F, the viscosity/density constant VDC is the constant calculated according to Moore and Kaye (not to be confused with the VDC according to Hill and Coats). The number of millistokes at 37.8°C = 100°F is denoted by mst.

Also in the VDC according to Moore and Kaye, a correlation for the Diesel fuels with the ignition quality is assumed by Moore and Kaye, based on the concept that n-paraffins in Diesel oils reduce the viscosity-temperature gradient and show lower values for the density. At the same time, they have a higher ignition quality while the aromatic compounds in Diesel oils at high density show a more unfavorable viscosity-temperature behavior and are lower in ignition quality. The fact that n-paraffins and i-paraffins do not differ in specific gravity but show high differences in ignition quality, has been disregarded in this characteristic so that the value of the characteristic is considerably impaired.

The VDC of petroleum Diesel fuels moves within narrow limits at a value of 0.700 – 0.805, while the VDC of Diesel fuels made of lignite carbonization tars fluctuates between 0.820 and 0.890. The VDC of Kogasin is extremely low (0.690 – 0.700) and that of hydrogenated heavy fuels obviously drops with the hydrogen content or the hydrogen addition.

## 10. LOW-TEMPERATURE RESISTANCE

Diesel fuels, especially such of paraffinic nature, show a separation of acicular crystals, resulting in trouble in the injection fuel and nozzle and probably shifting the fine screen in front of the pump sufficiently to prevent controlled fuel supply. Considering that the compression temperature is too low due to the cold intake air in a Diesel engine, so that only incomplete ignition of the fuel results, a combination of the two factors may produce a complete stoppage of the engine.

### a. Pour Point

The pour point or solidifying point of oils and heavy fuels (known also as setting point) denotes the degree of temperature at which a sufficient amount of solid (usually paraffinic) substances separates from the liquid that the entire mass changes into a paste-like or paraffinic substance. According to the German Industrial Standards DIN DVM 3662, the pour point is determined in a test tube of 18 cm length and 4 cm internal diam, filled with the sample to be investigated up to the mark (approximately 4 cm above the bottom of the tube). The calibrated thermometer is so inserted that its bulb has a distance of 1.7 cm from the bottom of the tube. A heat-insulated Dewar vessel is used for the test tube and a refrigerant. The fuel or oil sample must be preheated to 50°C and then cooled to room temperature. On cooling the sample, the temperature at which the first precipitations occur should be recorded, using this temperature degree as the cloud point. On further cooling, the stock point will be denoted by that temperature at which the oil has solidified sufficiently that it no longer flows within 10 sec and forms a ridge on the shaft of the thermometer. Similarly, the pour point is determined according to the ASTM method represented as the point 3°C above the actual solidifying point.

Refrigerant mixtures for producing low temperatures can be prepared in various manners. Several examples are given below:

| | |
|---|---|
| 30 parts ammonium chloride with 100 parts water | from 13.3°C to -5°C |
| 110 parts sodium thiosulfate with 100 parts water | from 10.7°C to -8°C |
| 250 parts calcium chloride, cryst. with 100 parts water | from 10.8°C to -12.4°C |
| 60 parts ammonium nitrate with 100 parts water | from 13.6°C to -13.6°C |
| 150 parts potassium thiocyanate with 100 parts water | from 10.8°C to -23.7°C |

In addition, 100 parts snow of a temperature of -1°C will result in the following values when mixed with:

| | |
|---|---|
| 30 parts potassium chloride | -11 °C |
| 25 parts ammonium chloride | -16 °C |
| 45 parts ammonium nitrate | -17.5°C |
| 33 parts sodium chloride | -21 °C |
| 143 parts calcium chloride, cryst. | -55 °C |

Solid carbon dioxide mixed with ether or alcohol or acetone into a paste furnishes temperatures of -78°C. By ether evaporation according to the method by Stelling, temperatures as low as -35°C can be reached.

### b. Filterability at Low Temperatures

The stock point in the above-described form gives a wrong picture on the suitability of Diesel fuels at low temperature. Rather, the cloud point should be used which, in paraffinic Diesel oils, characterizes the first precipitation of paraffin crystals. In Diesel oils on a tar base, naphthalene may precipitate. Consequently, the degree of temperature at which the crystal separation becomes so active that the filter screens are clogged should be used as a criterion for the low-temperature resistance of Diesel fuels. Based on this consideration, Hagemann and Hammerich (bibl. 108) had developed a method for filterability, supplemented by Heinze and Marder (bibl. 109).

The testing apparatus in its older design (see Fig. 26a) consists of a ball-shaped storage vessel (a) connected with a second spherical vessel (b) used as the testing vessel, across a double-bend glass tube and a filter section with screen inserts (d). Into the vessel (a) a low-temperature thermometer is inserted. A glass tube closed with cocks (g) and (h) branches off from this vessel and makes the connection to the water jet pump with one leg (f) for producing a low vacuum, while compressed air is supplied by (e). The filter section (d) contains a metal disk with a center bore of 3.2 mm diam and a number of screen plates made of 10 copper screens with a 0.1 mm mesh width. Above the vessel (b) a reserve container (d) is attached. Above and below (b), glass-tube sections slightly staggered with respect to each other, are equipped with marks (m') and (m) indicating a volume of 20 ±0.5 cc (at 20°C). Test for filterability of Diesel fuels is made as follows: The glass ball (a) is filled with 100 cc Diesel oil and cooled with carbon-dioxide snow and alcohol. To make the low-temperature influence more uniform, a weak current of predried air is sucked through the apparatus from Point f until the measuring temperature is reached. At this instant, the cocks (g) and (h) are closed. Compressed air is then supplied from (c) at 0.5 ±0.05 atm gage and the cock (c) is quickly opened. This forces the Diesel fuel in the tube (a) to rise through the filter section (d), and the time required by the rising fluid to pass between the marks (m) and (m') is multiplied by 2. The time required for 100 cc fuel to flow through this section at a given temperature is used as the filterability criterion for the fuel. The correlation of various Diesel fuels in the filtering period with the temperature was discussed by Heinze and Marder (bibl. 109) who found that in many heavy fuels the stock point and filterability limit are at the same temperature, while considerable differences occur in other heavy fuels, so that the limit of applicability of Diesel fuels at low temperature by a measurement of the stock point cannot be determined accurately.

Hammerich in cooperation with the HWA attempted to improve the described apparatus for determining the filterability fo Diesel fuels and developed an apparatus shown in Fig. 26b. In this test, 250 cc of the heavy fuel to be investigated are filled into the Dewar bottle (a) and kept in motion by predried air, reducing the temperature with dry ice in the outer container (A). In this manner, premature separation of paraffin or naphthalene due to subcooling is avoided. As soon as the cloud point of the fuel is reached, the temperature is permitted to increase by 3 or 5° until the Diesel oil is clear. Then, the cock (c) is closed and air is removed with the water jet pump (W) until the vacuum meter (V) indicates 400 mm subpressure. Then, cock (h) is closed and the connection to the water jet pump is opened. As soon as cock (h) is opened suddenly (starting a stop watch), the outside air will force the Diesel oil from (a) through the filter section (d), consisting of 10 copper-wire screens with a 0.1 mesh width and 5 mm dia., into the test vessel (b). The liquid will have to reach a level of 200 cc at mark (t). The characteristic for the filterability is represented by the filtering period of these 200 cc Diesel fuel. Depending on the viscosity of the fuel, the time will be approximately 2 - 20 sec at +20°C. As limit of filterability the temperature at which the passage period is not more than 60 sec is used. After completing the measurement, the Diesel oil is returned to the original vessel (a) by suction and the experiment is repeated after readjusting the temperature. It may happen that the filtering period is changed by an additional precipitation of solid particles.

Generally, a stock point (DVM) of not more than -20°C is required for Diesel fuels and a cloud point of not more than -15°C. As limit of filterability, the filtering period of not more than 60 sec and -15°C for 200 cc of fuel is used. In zones of extremely low temperature or in the case of aviation Diesel fuels, the requirements as to low-temperature resistance must be increased. For improving the low-temperature characteristics a limited addition of lighter fuels such as petroleum or knocking heavy benzine (which then will have a certain ignition quality) is recommended. In this case, it is of importance that the addition of light fuels may considerably decrease the ignition quality of the mixture and that such mixtures of light fuel with up to 5% engine oil or spindle oil are auxiliary means for counteracting extremely low temperatures at which use of normal heavy fuels is no longer possible.

## 11. ASPHALT AND COKING TEST

Combustion of a fuel in a Diesel engine never is complete. The disagreeable phenomenon of incomplete fuel combustion is a coking which may interfere with the injection mechanism. This residue formation is not always a consequence of the fuel, since overheated or insufficiently cooled injection parts, throttled air supply, incomplete fuel atomization, supercharging, overlubrication, and other operation errors may result in residue formation in an otherwise suitable fuel, similarly as the Diesel oil itself which has a natural tendency for coking. However, it is of interest to investigate fuels as to their tendency for residue formation and to define the existing differences in residue-formation tendency which, frequently, are rather pronounced.

### a. Asphalt Test

Determination of the content of hard asphalt in Diesel fuels is made according to DIN DVM 3660. In this experiment, 5 - 10 g of Diesel oil are dissolved in 40 times the volume of normal benzine (Kahlbaum) and will precipitate the benzine-insoluble hard asphalt in dark flakes after standing for 12 hrs. During this period, the sample must be kept in the dark. Then, filtering takes place through a double Schleicher & Schuell filter, Weissband (white ribbon) 589, or through a Jena-glass filter crucible with a cryolite power insert. The precipitate is washed quantitatively and dried. On using a paper filter, this filter is extracted in an extraction apparatus with reflux condenser with boiling normal benzine. Then the asphalt is dissolved with boiling benzene, the benzene is removed, the concentrated residue is dried at 150°C, and weighed. On using a filter crucible, the mixture is washed several times with preheated normal benzine and the asphalt is then dissolved with hot benzine under removal of the filtrate. The concentrated benzine extraction is analyzed for asphalt residue in the above-mentioned manner. This asphalt test is of importance only for heavy fuels on a tar basis since the values obtained with petroleum Diesel fuels are insignificant especially since in residue formation from Diesel fuels not only the amount of already formed and dissolved asphalt is of importance but also the unsaturated oxygen and sulfur-containing compounds which result in carbon-rich residues during the combustion process and turn into coke-like substances or pitch-like products. That means, these substances are not actually asphalt but rather asphalt-producing agents. Consequently, aging tests of any type are preferable to the asphalt test for evaluating the residue formation. This item will be discussed later in the text.

### b. Coking Test

Since it was impossible to correlate the hard-asphalt test for practical residue formation of Diesel fuels in engine operation, the coking test according to Conradson (scheduled as a DIN specification DIN 3796) will be used for evaluating the coming tendency of Diesel fuels and fuel oils.

Figure 27 shows the apparatus for testing the coking tendency of Diesel fuels. A porcelain crucible (a) is used for carbonizing the oil sample. The following other parts are used: A so-called Skidmore crucible (b) made of steel with cover, inserted into a wider steel-sheet crucible in a sand bath (c); a metal hood (e) with bracket (h), an asbestos block (f), or a hollow metal can, and a Meker burner (g). The oil sample in (a) of 10 g + 2.5 mg must be so heated with a high strong flame of the Meker burner that the time until ignition of the vapors is approximately 10 min. As soon as smoke forms above the metal hood, the burner must be so moved that the gas flame covers the sides of the outer crucible and ignites the vapors escaping under the loose cover of the crucible (c). Then, the burner is removed for a short time and so adjusted that the flame does not reach above the wire bridge above the hood. Combustion of the vapors should not take more than [illegible] - 14 min. If the flame is extinguished, the burner must be turned high until the bottom of the steel crucible turns cherry red. This state must be maintained for 7 min. Then the entire setup is left to cool for 15 min. The porcelain crucible with the coking residues is weighed after complete cooling in a desiccator. Determination must be made twice or repeated until the percentage in coke residues does not deviate more than 10% from the permissible mean value.

The coking test of Conradson and also that of Ramsbottom has the disadvantage to require normal pressure under exclusion of air. This coking test is a carbonization test. However, in a Diesel engine the fuel is burned under pressure and in presence of a large amount of oxygen. On revising the Conradson test by a supply of oxygen, the coking residues can no longer be measured.

Hagemann and Hammerich (bibl. 110) adapted their test conditions to the Diesel engine and coked the Diesel-oil samples on a metal bath at 150°C with a pressure of 20 atm gage compressed air. After a 2-hr test duration, the amount precipitable by normal benzine is used as a criterion for the coking tendency. Hammerich (bibl. 111) found that the Conradson test furnishes satisfactory results as to nozzle coking but that the reproducibility is rather poor since the temperature is not accurately defined. According to this author, cracked benzines are evaluated too favorably by the Conradson test, i.e., wrongly.

The Conradson test of Diesel fuels must not show higher values than 0.05%. The coke and asphalt content according to Hagemann-Hammerich must be below 2%.

## 12. ASH AND WATER CONTENT

The ash content of Diesel fuels should not exceed 0.5% and the water content also should remain below 0.5%. As "ash content" the mineral residue of an oil after combustion is used. Determination of ash, according to DIN 3657, takes place in the following manner: The oil sample is weighed in a porcelain crucible, evaporated over a small free flame, and so combusted that the flame does not reach above the crucible height. In heavy fuels the porcelain crucible should be so inserted into cut-out of an asbestos plate that the Bunsen flame cannot ignite the escaping vapors. As soon as the largest part of the oil sample has evaporated, the crucible is heated for a long period of time and weighed after cooling.

Water determination is similar as that in Otto fuels.

## 13. CALORIFIC VALUE

The heat values for heavy fuels of different origin are given as follows:

| Diesel Fuel of | Upper Calorific Value<br>cal/kg | <br>cal/ℓ | Lower Calorific Value<br>cal/kg | <br>cal/ℓ |
|---|---|---|---|---|
| Petroleum | 10,300 to<br>11,000 | 9,000 to<br>10,000 | 9,700 to<br>10,300 | 9,500 to<br>9,700 |
| Lignite tar, oil shale, and cracked gas oil | 10,000 to<br>10,600 | 9,100 to<br>9,600 | 9,400 to<br>10,000 | 9,600 to<br>9,300 |
| Anthracite carbonization tar | 9,700 | 9,500 | 9,300 | 9,200 |
| Anthracite coking tar | 9,000 to<br>9,500 | 9,500 to<br>10,000 | 8,700 to<br>9,200 | 9,200 to<br>9,700 |
| Fischer-Tropsch synthesis | 11,200 to<br>11,400 | 8,600 to<br>8,800 | 10,500 to<br>10,700 | 8,100 to<br>8,300 |

The correlations between specific gravity and heat value (cal/kg) of Diesel fuel were mentioned in Table 41 (bibl. 112). In Fig.28 (bibl. 113), the graphical relation of liter and kg heat value (lower calorific value) to the density of heavy fuels is given. For technical determination of the heat value, a hydrometer was developed by Marder, manufactured by Bardewyck in Berlin. In petroleum products, 70 cal/kg or 70 cal/ℓ must be deducted from the value read on the hydrometer for each 1% of sulfur content. In lignite Diesel oils, 20 cal/kg or 20 cal/ℓ must be deducted from the hydrometer value per each 1% creosote (differential method).

## 14. SULFUR CONTENT

The sulfur content in heavy fuels must not be above 1%. The forms of active and inert sulfur as well as the determination methods were described in the section on Otto fuels. Hammerich (bibl. 111) recently mentioned that a test for corrosive sulfur by means of the copper-strip method may not be necessary since no trouble in operation had occurred which would require such an experiment. In addition, it does not seem true that combustion of sulfur products in heavy fuels would increase the disagreeable odor of exhaust gases.

## 15. CORROSION

Corrosion of heavy fuels especially of fuels obtained from carbonization tar, mainly is due to oxygen compounds with an acid character, i.e., creosotes. Creosotes will attack galvanized shipping containers. Consequently, the test for corrosive effect on zinc is of main importance.

According to the test method suggested for standardization by Hammerich (bibl. 114), a zinc strip (refined zinc with more than 99% zinc, 0.5 - 1% lead, and less than 0.2% other metals) with 100 : 10 : (0.5 - 1) mm dimensions is rubbed with emery cloth 00 and then cleaned thoroughly with cotton saturated in benzene and alcohol mixture 1 : 1. After drying for 15 min, the specimen is weighed at 105°C. Then the Diesel-fuel sample together with the zinc strip is inserted into the Heinze-Marder corrosion bomb (described previously). A temperature of 100 + 1°C is maintained for 24 hrs, any incrustations of zinc salts and zinc naphthenates formed by attack of the acid are removed after cooling by rubbing with benzene-saturated cotton. Then, the arrangement is weighed after drying at 105°C. The experiment should be repeated and the arithmetic mean of the obtained weight loss should be used. The average corrosion will be between 0 and 40 mg. However, a heavy fuel is already considered corrosive if the weight decrease is more than 4 mg. Such corrosions occur not only in creosote-containing tar-oils but also in acid Diesel oils on petroleum basis, especially in cracked Diesel oils.

a. Neutralization Number

Determination of the neutralization number (formerly "acid number"), as shown by experience, does not have parallel values to the corrosion test for zinc. The neutralization number indicates the milligram of potassium hydroxide required at room temperature for neutralizing the free acids contained in 1 g oil or fuel. For this purpose, according to specification DIN DVM 3653, an amount of 2 - 10 g Diesel oil are weighed in Baader flask and mixed with 5 - 10 times the amount of a 2 : 1 benzene-alcohol mixture. Then, 2 cc of a 2% alkali blue 6B solution are added. Under shaking of the flask content, the mixture is rapidly titrated from blue to red with n/10 alcoholic caustic-potash solution. A so-called blank experiment is made at the same time, consisting of the same mixture without weighed portions of oil. The neutralization number is then calculated from the following formula:

$$\text{Neutralization number} = (a - b)\ 5.611/G$$

In this formula, a denotes the cc caustic-potash solution of the main experiment, b the cc caustic-potash solution in the blank experiment, G the weighed portions in gram, and 5.611 the titer of the n/10 caustic-potash solution.

In Diesel fuels a neutralization number up to 1 is permissible but such fuels especially when produced from tar no longer have sufficient storage characteristics, so that normally a neutralization number of 0.4 should not be exceeded.

## 16. STORAGE PROPERTY AND MISCIBILITY

Petroleum Diesel fuels change their general characteristics within one year so little that they may be considered resistant to storage. The case is different in lignite Diesel oils (bibl. 115) in the specific-gravity range of 0.880 - 0.930 which show an increase in specific gravity from 0.003 to 0.006 and a decrease in cetane rating of 2 - 3 units within one year. This results in a stationary state as soon as the unsaturated hydrocarbons in the Diesel oils have become stabilized.

Petroleum Diesel fuel and Kogasin II are practically free of asphalt and only petroleum heavy fuels on a naphthene or asphalt basis show a 0.1 - 0.03% asphalt content and 0.03 - 0.05% asphalt after one year storage. Lignite-tar Diesel oils in the refined state show an asphalt content of 0.02 - 0.03% and then will age within a year to 0.04 or 0.10% asphalt. Unrefined tar oils have an asphalt content between 0.1 and 0.5%. In mixtures of heavy fuels, especially of different characteristics such as lignite oil or anthracite oil and Kogasin, increased formation of hard asphalt insoluble in normal benzine occurs. The strongest precipitations are created by the Diesel oils showing an asphalt-precipitation tendency when mixed with strongly paraffinic fuels. A simple method for determining the storage ability and miscibility of Diesel fuels was developed by Marder (bibl. 116) and consists in mixing the fuel with a large excess of Kogasin and using the precipitate obtained after 24 hrs known as the "maximum precipitation value" in weight % as a criterion for these characteristics. According to the suggestion by Marder, 5 g oil in 200 cc Kogasin II should not deposit more than 0.3% after 24 hrs at room temperature.

In this connection, the work done by Koelbel (bibl. 117) should be mentioned who made experiments with mixed Diesel fuels of anthracite tar oil and Kogasin. Anthracite tar oils whose ignition quality is unsatisfactory and which are unsuitable as fuel for high-speed vehicle Diesel engines, can be improved considerably in blends with Kogasin, resulting in the following values:

Anthracite oil cetane rating 20 with 10% Kogasin II furnishes a fuel with cetane rating 30;

Anthracite oil cetane rating 20 with 20% Kogasin II furnishes a fuel with cetane rating 40;

Anthracite oil cetane rating 20 with 30% Kogasin II furnishes a fuel with cetane rating 52;

Anthracite oil cetane rating 20 with 40% Kogasin II furnishes a fuel with cetane rating 63;

Anthracite oil cetane rating 20 with 50% Kogasin II furnishes a fuel with cetane rating 74

Koelbel developed a method in the Rheinpreussen Company, which is rather suitable for applying the selective solving power or the characteristics of Kogasins to precipitate asphalt from asphalt-rich oils. While an unrefined mixture of equal parts of anthracite tar oil and Kogasin has a coking tendency of 0.743% of benzine-unsoluble substances (according to Hagemann and Hammerich) in one case of which 0.376% were coke and 0.365% asphalt, a suitably refined tar oil and Kogasin mixture has a coking tendency of only 0.42% with the following characteristics: d = 0.860; boiling coefficient 260, cetane rating 82; flame point 94°C, viscosity 1.2 E/20, and stock point -20°C. That means, it seems a rather suitable Diesel fuel of satisfactory storage property.

## 17. FLAME POINT

The previously-used specification according to which the lower limit of the flame point was given as 66°C for heavy fuels, merely has a statistical but not a technical importance. The combustion and ignition qualities of Diesel oils have no relation whatever with the flame point or fire point. The flame point of Diesel fuels (especially in blends for increasing the low-temperature) may be near 30°C or lower.

The flame-point determination of heavy fuels takes place mainly in the closed tester developed by Pensky-Martens in which the crucible with the test oil is covered and in which the ignition tests are made across an automatically-controlled slot. In addition, heating of the crucible is not done directly. Two bell-shaped shields cover the heat source toward the bottom and maintain an air jacket between each other for a heat transmitter. In the open-cup test according to Marcusson, an open cup is heated in a sand bath. Consequently, the flame points of heavy fuels in the open cup are 12 - 20°C higher than in the closed Pensky-Martens apparatus. The fire point, i.e., the temperature at which an artificially-ignited heavy fuel will continue burning by itself, is generally 30 - 40°C higher than the flash temperature.

## 18. CONSTITUTION

It had been mentioned that investigation of the constitution of benzine hydrocarbons is extremely difficult and that a clear definition and definite correlations between structure and engine behavior have not been established. These statements apply also to the irregular mixture of higher-molecular hydrocarbons and components of these Diesel fuels. Fractionated distillation and solvent methods are unsuitable to produce clear definitions. The phenomena of reciprocal solubility of these substances, of azeotropy, of combination of molecules (association) and other phenomena are well known, but no means for clear separation are available. For example, the characteristics for these products are cross sections of the nature of the products which frequently furnish a general picture but never a thorough information.

a. Hydrocarbon Groups

It is absolutely definite that analyses of benzines and separation into groups of paraffins, unsaturated hydrocarbon, naphthenes, and aromatic compounds by means of sulfuric acid and aniline-point determination is of a rather problematic value. In the higher-molecular hydrocarbons within the boiling range of Diesel oils, the scattering of the results is considerably larger. In these higher-viscosity hydrocarbons, sulfuric acid will not only fix those components with which they react, so that it may be assumed that group determination of aromatic compounds and unsaturated hydrocarbons according to this method will result in too high a value. For this reason, the previously-described sulfuric-acid method cannot be used for quantitative determination of aromatic compounds and unsaturated hydrocarbons in Diesel oils. Consequently, the further analysis for determining naphthenes and paraffins also cannot be used.

b. Aniline Point

However, it seems that the aniline point, i.e., the solution temperature of Diesel oils in aniline will furnish a better criterion. The pure aromatic compounds and their homologues are soluble in aniline even at room temperature, while the paraffins show relatively high aniline point which increases with their boiling point and molecular weight. Naphthenes and especially olefins and cyclo-olefins occupy a middle position which shows clearly when the aniline points of pure hydrocarbons shown in Table 26 are plotted against the molecular size in a graph. However, it would be impossible to make a quantitative extrapolation from the aniline-point coefficient of Diesel fuels to the components in naphthenes or aromatic compounds. Sachanen and Virabianz (bibl. 118) defined the aniline-point coefficient as the percentage on naphthenes or aromatic compounds which result in an aniline-point decrease of 1°C with respect to the paraffins. These coefficients (for the boiling range of Diesel oils) indicate that a decrease in aniline point of 1°C would correspond approximately to an amount of 5% naphthenes or 1.5 - 1.8% aromatic compounds. Griffith and Hollings (bibl. 119) are of the opinion that 1°C difference in aniline point indicates only a content of 2.5% naphthenes, so that calculation is useless at present, especially since the olefins are not considered and since no criterion for synthetic products is available. In Table 44, the aniline points of pure hydrocarbons are given for a molecular range from $C_9$ to $C_{20}$, compared to the complementary aniline points obtained from fractions of a Diesel oil of medium quality.

This table merely is to indicate that in the mixture of hydrocarbons in Diesel oils accurate knowledge of the entire subject is required rather than differences in aniline solubility from which the composition frequently is determined. It is definite that at lower aniline points of Diesel fuels and especially carbonization tar oils, the aromatic hydrocarbons are more clearly defined while the nature and structure of higher "naphthenes" is insufficiently known for use in calculations. In Table 45, as a result of numerous practical measurements, the attempt was made to coorelate the aniline point of Diesel fuels to the content of aromatic compounds and unsaturated hydrocarbons. The parenthesized symbols have the following significance: B = lignite carbonization tar oils, H = hydrogenated oils, E = petroleum Diesel fuels, and K = Kogasin. Figure 29 shows the attempt of the author to establish a temporary relation between the aniline point, refractive index or density, distillate cross section, and cetane rating (calculated according to Marder) for commercial Diesel fuels. Application of this diagram requires conventional Engler or ASTM fractionation of the Diesel oil, as well as determination of the distillation cross section (DC) and the refractive index (nD/20) in the various fractions. It is insufficient to use the boiling characteristic, refraction, or aniline point of the Diesel oil as a wide cross section since the diagram had been developed by determining distillation cross section, refractive index, and aniline point by measurement during fractionation of different Diesel fuels.

The families of curves of the cetane ratings calculated according to Marder is plotted into the resultant grid. For the total amount of Diesel fuel, the desired characteristics cetane rating or aniline point are then calculated as an arithmetic mean of the fractions.

c. Elementary Analysis

For a thorough analysis of Diesel oils the elementary analysis is frequently used. Hydrocarbons are converted into carbon dioxide and water vapor by complete combustion. This combustion analysis can be a quantitative analysis if the water vapor is absorbed in anhydrous calcium chloride and the carbon dioxide in caustic-potash solution. For this purpose, the oil amount weighed in a platinum or procelain dish is filled into a quartz tube charged with manganese dioxide. The mixture is heated (under passing a oxygen stream regulated to four bubbles per minute) until all oil has evaporated from the dish and appears to be completely combusted over manganous oxide powder. The amount of water of combustion and cargon dioxide is then used as weight increase of the absorption vessels used in this test (calcium-chloride tubes and potash apparatus). The result will be as follows:

$$\% \text{ C} = \text{found } CO_2 \times 300/\text{substance} \times 11$$
$$\% \text{ H} = \text{found } H_2O \times 201.52/\text{substance} + 18.0152$$

In the analysis of sulfur-containing hydrocarbon oils, it is of importance that $SO_2$ is completely retained in a zone of colder $MnO_2$ for preventing a wrong increase of the C and H values. Any oxygen present in creosote-containing Diesel oils must be determined by hydrogenation from the formed water of combustion.

For establishing average formulas, the found values are divided by the atomic weight, i.e., %C : 12 and %H : 1. If the C : H ratio is to be determined, H should be related to C = 1 which makes it possible to find the general gross formula $C_nH_{2n-xn}$.

The following is an example: A Diesel fuel was found to contain 86.61% C and 13.08% H in a combustion analysis. Dividing by the atomic weights will furnish the following values:

$C = 86.61 \div 12 = 7.22$; $H = 13.08 \div 1 = 13.08$. Relating these values to C = 1, the ratio

$C : H = 7.22 \div 13.08 = 1 : 1.814$ is obtained and the gross formula $CnH_{2n-xn}$ will have a value of $2 - x = 1.814$, i.e. 0.186 for x. The gross formula in its true magnitude requires knowledge of the mean molecular weight M, and a simple calculation for the hydrocarbon oils CnHy will furnish the following formulas:

$$M = 12\,n + y \qquad y = hn \qquad y = 2\,n - xn = n\,(2 - x) \qquad h = 2 - x$$

For example, if the selected Diesel oil on a petroleum basis has a molecular weight M of 202, the formula will read:

$$M = 12\,n + y = 12\,n + 1.814\,n = 13.814\,n; \quad 202 = 13.814\,n; \quad n = 12.95;$$
$$y = 1.814 \times 12.95 = 23.5$$

Consequently, the Diesel fuel has a gross formula $C_{21.95}H_{23.5}$ or $C_nH_{2n-2.4}$.

d. Molecular Weight

In determining the molecular weight of Diesel fuels, it is of importance to consider that a general cross section on the mixture of numerous hydrocarbons is involved rather than a determination of molecular weight for one component in a hydrocarbon. Similarly, all characteristics of such products are average characteristics but not definite characteristics as used in general practice. For determining this mean molecular weight, the ebullioscopic method (according to Beckmann) which consists of an increase in boiling point of a solvent (benzene) by the dissolved substance (Diesel oil). This method has been described by Ostwald-Luther (bibl. 120). The mean molecular weight of Diesel fuels remains in the neighborhood of M = 200, i.e., it represents a cross section of a molecular-weight range between 125 and 275. It is absolutely questionable whether the cross section of such a large range can be used in calculations which are to furnish a certain degree of accuracy. It is much more suitable to investigate the individual fractions, i.e., the usual fractions of heavy fuels and to use them for comparison purposes.

### e. Surface Tension

As criterion for the surface tension of liquids with respect to air, i.e., as a criterion for the force which tends to decrease the free surface of the liquid, the weight of the volume (mg) rising in a capillary against the center of gravity is used. The maesurement of surface tension of oil against air is done with sufficient accuracy in an ascending tube with a suspended level, developed by Ubbelohde. The surface $\lambda$ in mg/mm is calculated according to the following formula:

$$\lambda = rd\ h/2\ (\text{mg/mm})$$

where r denotes the radius of the capillary tube in mm, d the specific gravity of the investigated liquid in the air saturated by its vapor, measured in g/cm$^3$ (at the corresponding test temperature p), and h the corrected height of ascent. If the surface tension is to be expressed in dyne/cm, the value of the above formula must be multiplied by 9.81. The surface tension is highly dependent on the temperature; the values for $\lambda$ in the density range of petroleum Diesel fuels are 24 - 29 dyne/cm and the specifically heavier lignite Diesel oils generally have a value between 28 and 31 dyne/cm. The temperature dependence of the surface tension is approximately parallel to the following values: 28 dyne/cm at 20°C = 25.3 dyne/cm at 50°C = 21.3 dyne/cm at 100 C, so that a temperature correction of 0.084 dyne/cm per °C must be expected.

### f. Parachor

The concept and significance of the "parachor" had been previously discussed. Between the specific density and the specific parachor within the boiling range of Diesel fuels, the relation shown in Table 46 can be established.

Heinze and Marder (bibl. 121) attempted to establish correlations between specific parachor and ignition quality of Diesel fuels but made this ratio dependent on a third quantity, i.e., on the molecular size. In this case, the average was either the mean molecular weight or else naturally the boiling coefficient. As a matter of fact, a correlation exists between mean molecular weight and boiling coefficient of commercial Diesel fuels, which almost coincides with the relation of molecular weight to boiling points of well-defined chain hydrocarbons. The relation shown in Table 47 applies for Diesel oils as hydrocarbon mixtures.

In using these two average characteristics it is of disadvantage that the mean value has been formed of values whose starting and end points are too far apart. This obviously applies to the characteristics of mean molecular weight and boiling characteristic.

### g. Refraction

In Table 29, the relation between boiling range and refraction of benzines is given. Actually, in benzines the observed refractive indices for the individual fractions are near the mean of the indicated limiting values. The relation between boiling range and refraction naturally continues in the Diesel fuels but it should be remembered that the obtained values scatter in the given range and no longer concentrate near the mean, especially if the products of Leuna and Fischer-Tropsch syntheses are included. Table 48 shows the existing conditions in Diesel fuels. Naturally, the relation between density and refraction of Diesel fuels continues in a linear direction.

The refraction values of pure hydrocarbons are shown in Table 42 as far as they are located in the boiling range of Diesel fuels. In this connection, it is of interest to compare the ratio of specific gravity and refraction for pure hydrocarbons (chain and ring hydrocarbons) as done in Fig.49b.

### h. Ring Analysis

Vlugter, Waterman, and van Westen (bibl. 122) attempted with their "ring analysis" to obtain a quantitative information on the structure of mineral-oil mixtures. Kreulen (bibl. 123) used the ring analysis for research on the constitution of Diesel fuels, but had to admit that only approximate relations as to the ignition quality of these fuels can be established. For calculating the correlation of oils in the ring analysis, the specific gravity, the refraction, the aniline point, and the mean molecular weight are required. A diagram is used for reading the aniline-point corrections for the oil from which all aromatic compounds are assumed to be removed by hydrogenation. Several simple calculations are then used for indicating the percentage of naphthenes, aromatic rings, and paraffinic side chains.

### i. Diesel Index

The Diesel index (according to Becker and Fischer) DI is the product of the aniline point ($^\circ F$) multiplied by the API density and divided by 100, i.e.:

$$DI = AP\ (API)/100$$

This arbitrary characteristic has been related to the ignition quality of Diesel fuels at various times with the result that certain correlations have become obvious, similarly as the aniline point in itself can be correlated with the ignition quality of Diesel fuels, since it expresses the internal nature of such oils. Rothe (bibl. 124) suggested use of the aniline-point density constant, i.e., the quotient of the aniline point ($^\circ C$): specific gravity (g/cc) instead of the Diesel index. This would furnish an expression which is free of the too systematic scale of the American API density. Petroleum Diesel fuels have a Diesel index of 48 - 60 or an aniline point of AP/d 68 - 88. Heavy tar oils have a Diesel index of 20 - 40 or an aniline point AP/d of 30 - 40, hydrogenated tar oils have an index of 30 - 50, and Kogasins a Diesel index between 100 and 110.

It will hardly be possible to establish a suitable relation to the ignition quality of Diesel fuels by a single numerical value or characteristic unless this coefficient would combine several characteristics of the fuel in a logical and correct ratio. In the parachor, surface tension, density, and molecular size are expressed while the Diesel index indicates the aniline solubility and density. However, it seems that these coefficients must be corrected by other values for obtaining suitable relations with the ignition quality. Conversely, exactly in the chemistry of hydrocarbons calculations cannot be supplied for every single item and wherever such calculations do not furnish accurate results, it is much better not to use any.

## 19. ENGINE BEHAVIOR

### a. Ignition Lag

Combustion in the Diesel engine is a constant-pressure process and consequently requires that the fuel should be burned at the moment of injection. Actually, this is not the case. A certain time elapses until the fuel ignites after injection, and this time characteristic for suitability of a given fuel in a Diesel engine is known as ignition lag. At higher ignition lag, the Diesel fuel is poorer. This rule of thumb is valid with the restriction that design and operating conditions of the engine may be of influence on the ignition lag.

In Fig.30, the pressure curve in a Diesel engine is shown. The instant of fuel injection is denoted by A, the first ignition by B, the main combustion and thus the pressure increase at knock-free operation beyond compression of the air [35 - 38 atm (gage)], and D the resultant pressure maximum. The piston travel from A to C, or the angle of the crank rotation corresponding to this piston travel is known as ignition lag of knock-free Diesel-oil combustion. The hatched area CDG represents the work done at knock-free combustion. However, if the ignition is delayed from A to $K_0$, a spontaneous knocking combustion will occur under simultaneous steep pressure increase and formation of a pressure peak. The sketch (exaggerated) shows that the work done during a knocking combustion $K_0K_1H$ is less than that of a knock-free combustion CDG. Similarly, the ignition lag $C' = A - K_0$ in a knocking combustion has become higher than in a knock-free combustion: $Z = A - C$. It may also be stated that the angle $\alpha$ or $\alpha'$ formed with the horizontal will be higher at a steeper pressure increase $C - D$ or $K_0 - K_1$. Finally, the run of the Diesel engine will become harder, rougher, and increase in knock. The limiting line $EACK_0GF$ indicates the compression of the air taken into the Diesel engine. At a compression ratio of 1 : 18, absolute values of 35 - 38 atm (gage) and temperatures up to 350°C are reached. A further pressure increase is produced only by the fuel combustion and, at knocking combustion in a vehicle Diesel engine, pressure peaks up to 100 atm have been found to exist. Figure 31 shows a schematic representation for the fact that the ignition lag AC decreases with increasing compression and that thus the Diesel principle is diametrically opposite to the Otto-cycle principle since in the Otto-cycle engine the fuel knocking is increased with increasing compression. If the compression in a Diesel engine is decreased on purpose by throttling the air supply, the ignition lag ($A_2C_2$ or $A_3C_3$) is increased. According to Boerlage and Broeze (bibl. 125), the points $C_1$, $C_2$, $C_3$, i.e., the times at which the main combustion starts, are located on one line. In practical use, the decrease in ignition delay occurs in aircraft Diesel engines whenever air rarification takes place at high altitudes. In cases of extremely high ignition lag, the fuel will evaporate without igniting by cooling the air charge and preventing any ignition. In Fig.31, the case in which the Diesel engine is operated with extreme throttling of the air supply is denoted by $A_4 - C_4$. If the engine can be kept running at all, the run will be rather soft since ignition will take place so late that the piston already starts the expansion stroke.

In a normal smooth combustion of the fuel in a Diesel engine, a uniform burning of the injected fuel vapor takes place. This burning propagates uniformly toward the core of the injection, starting from the sleeve and finally extending over the parts furnished by the nozzle. In this case, the pressure increase is uniform. However, Diesel knocking is based on the fact that a large amount of fuel is ejected from the nozzle during the long ignition lag. This fuel is changed into a vapor which burns spontaneously under detonation at a corresponding spontaneous pressure increase.

If a Diesel engine is operated with a fuel of too high an ignition quality, the preinjection (Point A) must be reduced to prevent a noticeable loss in power and an irregular run by premature ignition and pressure development. An increased preinjection probably will reduce knocking of heavy ignitable Diesel oils but the limit is rather narrow also in this case (similar to the Otto-cycle engine with delayed ignition), since complete stoppage of the ignition may take place.

An addition to a pure ignition-lag measurement Wilke (bibl. 126) suggested observation of the pressure increase in atmosphere per degree of crank angle and to use this as a criterion of the combustion violence. As long as ignition delay and pressure increase coincide, an ignition-lag measurement will be sufficient. However, the parallelism of the values does not always apply, so that the ignition delay itself is not sufficient for evaluation. Consequently, at given cetene or cetane ratings the fuels with a lower pressure increase $dp/d\varphi$ in atm/°KW can be better evaluated.

b. Ignition Quality and Nature of Hydrocarbons

For evaluating the ignition quality of Diesel fuels, the requirements are practically opposite to those made on Otto fuels. In an Otto fuel, the chain hydrocarbons generally lose compression resistance at increasing molecular size. In Diesel fuels, the ignition tendency is higher the less energy is required for splitting the hydrocarbons. This splitting is least resisted by long-chain aliphatic compounds, while the isomeric paraffins and olefins have a much higher thermal stability. The aromatic compounds have the highest thermal stability. Consequently, the n-paraffins which knock in an Otto-cycle engine have a satisfactory ignition quality in a Diesel engine, while the absolutely compression-resistant aromatic compounds in the Otto-cycle engine have a poor ignition quality in the Diesel engine. The olefins and naphthenes occupy a middle position in both cases. The highly valued isoparaffins in the Otto-cycle engine have a poor ignition quality in the Diesel engine which obviously is a consequence of the branched chain structure which resists thermal splitting.

c. Cetane and Cetene Rating

One of the hydrocarbons with the lowest ignition quality in a Diesel engine is the α-methyl naphthene. Consequently, for relative evaluation in engine behavior, this substance was designated by the value zero. A hydrocarbon with an extremely good ignition quality is cetene $C_{16}H_{32}$ which had been used as a reference fuel for a long period of time and had been designated with a cetene number 100 for ignition quality. However, since cetene is an unstable mono-unsaturated chain hydrocarbon, the cetane (hexadecane) $C_{16}H_{34}$ with a cetane rating of 100 is used as a reference fuel, since it is a higher ignition quality. A substandard fuel is the so-called "Abadan", i.e., the refined product of a Persian gas oil with a cetene rating of 75 and the product "S 300" which is an extract of the same gas oil with a cetene rating of 28.5.

The characteristics of these reference fuels (standards and substandards) are as follows:

|  | d/20 | Boiling Limits in °C | Viscosity | Incipient Crystallization | Flame Point | Cetane Rating |
|---|---|---|---|---|---|---|
| Cetane | 0.774 | 282 - 287 | 4.52 cst/20 = 2.45/50 | +16°C | 129°C | 100 |
| α-methyl naphthalene | 1.019 | 241 - 246 | 3.18 cst/20 = 1.76/50 | -39°C | 103°C | 0 |

The characteristics of cetene are as follows: d/20 0.783, boiling characteristic 279, cetene rating 100 = cetane rating 85;

The characteristics of "Abadan" are as follows: d/20 0.841, boiling characteristic 296, cetene rating 75 = cetane rating 63.8;

The characteristics of "S 300" are as follows: d/20 0.871, boiling characteristic 219, cetene rating 28.5 = cetane rating 24.2

Between cetane rating (CaR) and cetene rating (CeR) the following relations exist:

CaR = 0.85 CeR; CeR = 1.176 CaR.

The fact that the cetane scale frequently is opposite to the octane scale has been mentioned before (see Table 34). Jantsch (bibl. 127) establishes the arbitrary relations:

OR = 120 - 2 CaR at known cetane rating and
CaR = 60 - 0.5 OR at known octane rating

In the conversion tables of the IGF for the technical pamphlet on knocking (bibl. 128) the interrelation shown in Fig.32 between engine octane rating (MOR) and CaR exists.

## d. Ignition Quality, Engine Type, and Operating Conditions

Naturally, similarly as in an Otto-cycle engine also the Diesel engine is of influence as far as design and operating conditions are concerned on the following rhythm: ignition lag-ignition process-main combustion-aftercombustion. Consequently, the ignition behavior is not only a consequence of the fuel itself. Of the Diesel engines of various designs, that with direct injection has the highest sensitivity to ignition lag. If structural measures make it possible to start a precombustion as done in the prechamber and turbulence-chamber engines, Diesel engines will become much less sensitive to a given fuel. It is not necessary that these engines operate at maximum compression. In addition, the requirements on the atomization of the fuel are not as high as those made in a Diesel engine with direct injection. This difference is rather considerable in vehicle engines during cold weather. The operating conditions of influence on ignition lag will be investigated point by point:

1) Summer temperatures favor the degree of fuel atomization and decrease the ignition lag. The air cushion assumes relatively high temperatures in a Diesel engine which favor the ignition of the injected fuel. A high compression ratio has a similar effect. Conversely, in cold weather the same high temperature of the air cannot be reached by compression in a Diesel engine, resulting in an ignition delay. As mentioned above, a decrease in air density at higher altitudes has a similar effect in the aircraft Diesel engine;

2) Engine damage will favor ignition lag. Any worn cylinders, dragging piston rings, and spoiled valves decrease the compression, lower the possibility of reaching the necessary temperature of the compressed air, and interfere considerably with the ignition process;

3) While an increase in load in the Otto-cycle engine will raise the knocking tendency, it is exactly the opposite in the case of a Diesel engine. In idling and at low load, a Diesel engine shows the roughest run and the ignition lag will decrease with the load. Any overload in an Otto-cycle engine will produce knocking, and throttling of the intake air in a Diesel engine will raise the ignition lag for the above-described reasons;

4) In cold-starting, the Otto-cycle engine except for other obstacles does not show any difficulties as to knocking. However, the Diesel engine shows an ignition lag since the temperatures are insufficient for ignition. In this case, the driver must preheat the engine, i.e., initiate the combustion by means of the glowplug installed in the prechamber. The Lanova engine (air-storage Diesel) makes it possible to increase the compression for a short time and creating sufficiently high air temperatures for the start;

5) On any increase in rotational speed, the crank angle to the ignition lag naturally increases in the Diesel engine. However, since the engine temperatures rise with the rotational speed, the first-mentioned moment is practically compensated;

6) Finally, an increase in injection pressure will effect a certain decrease in ignition lag. The nozzle form has a considerable influence on the ignition due

to the dispersion of the fuel droplets.

### e. Testing Engines and Testing Method

For engine testing of Diesel fuels, three different methods are used: The starting method, the misfire method, and the ignition-lag method.

a) In the starting method, the instant of the first ignition is determined in an engine with a secondary drive. In this case, the lowest combustion is used as basis and increased until incipient ignition occurs under certain test conditions. The increase in compression can take place by adjusting the cylinder head or by decreasing the throttling of the air supply. With respect to injection, the fuel to be tested is injected at a lower compression. If no ignition takes place, the compression is increased gradually and the injection process is repeated until the compression ratio at which incipient ignition takes place is accurately defined. A prerequisite for this test setup is a constant heat state of the engine;

b) Misfire method: In the misfire method the compression (cylinder-head adjustment or throttling) is reduced until ignitions stop entirely. To make these values reproduceable, the measurements must be repeated frequently and a mean value must be taken. In the HWA testing engine, the intake air is throttled to the critical ignition at constant intake-air temperature of 80°C, in which case the resultant subpressure in the intake manifold is used as a criterion for the ignition tendency of Diesel fuels. The instant at which ten times three injections ignite without misfire is considered a perfect ignition. Between the three ignitions an interval of 1 sec is kept with spaces of 20 sec. Figure 33 shows the relation of intake subpressure to cetene rating in the HWA engine, according to Ernst (bibl. 129);

c) Ignition-lag method: In the ignition-lag method, two possibilities exist: Either the time of the ignition lag is measured in crank-radians and the compression ratio is kept constant (bibl. 130) or the compression ratio is varied at constant ignition lag (IGF testing engine). The ignition-lag method can be considered suitable for practical engine operation and will require an accurate definition of the possibility whether or how the fuel ignites, considering the reaction period required for ignition. In the meantime, application of electric-measuring methods has made it possible to measure the injection point and the instant of incipient ignition as ignition lag. The ignition lag and pressure curve are recorded by a piezoelectric quartz indicator in combination with a cathode-ray tube. Special devices and deflecting instruments permit recording of the individual times (injection, top center) as well as the expansion of the pressure diagram near the dead center appearing on the fluorescent screen of the cathode-ray tube.

In a small book of this type, it is impossible to include a critical evaluation of the advantages and disadvantages of an engine-testing method, especially since these methods continue to develop. However, it should be mentioned that the values obtained by various methods for the ignition quality of Diesel fuels do not necessarily agree as desired and show differences of considerable magnitude at first. In all methods, the investigated fuels are compared to complimentary mixtures of methyl naphthalene and cetane (or substandards), expressing the ignition quality in either cetene or cetane numbers. Generally, it may be stated that the HWA throttle method furnishes the highest cetane ratings and that the values obtained by the starting method in various Diesel-testing engines scatter considerably. For example, Neumann (bibl. 131) described 25 experiments on HWA Diesel engines in which the ignition qualities were determined according to the starting and ignition-lag method. In Table 50 the cetene numbers of both methods measured on the HWA Diesel engine, are compared.

A large number of experiments have been made for correlating the determination of ignition quality in Diesel oils of the various testing methods with their results. Kessler (bibl. 132) reported on ring experiments made on orders of the RVM by the Committee for Fuel and Lubricants of the Automobile Association. Since this report has a rather historical importance, Table 51a gives an excerpt of these valuable reports which all were based on the possibility of eliminating the testing methods of foreign countries and to use own procedures for producing clear relations.

This compilation shows that the cetene values obtained by the starting method show a considerable scattering, frequently by more than 8 - 16 cetene units. In addition, the values are by 3 - 10 cetene units higher than the results obtained by the ignition-lag method. However, such deviations are impermissible from a measuring-technique viewpoint. The HWA method has the highest values when used in the starting procedure while the method by Schmidt has better values when using the ignition-lag procedure. Wilke (bibl. 133) reported on ring experiments by the IG, whose results are shown in Table 51b.

Note: The cetane numbers marked by asterisks in Table 51b deviate considerably from the uniform series. It is of importance that the cetane numbers measured in the IG test Diesel engine by using the method with "fixed ignition lag" agree satisfactorily and scatter by not more than 1 - 2 cetane units. Schmidt (bibl. 134) made an extensive report on the fact that he obtained no suitable agreement in the ignition-lag method of Diesel-fuel tests for the obtained values. The same author compared the method of fixed ignition lag (IG method) with the method of variable ignition lag suggested by him. Table 51c contains a compilation of the report by Schmidt.

## f. The IG Testing Engine for Heavy Fuels

As example of the test-stand engines used for evaluating Diesel fuels, the IG testing Diesel engine will be described briefly. The entire unit consists of a MM Diesel engine, a brake dynamo, and a measuring unit. The Diesel engine itself is a stationary 1-l single-cylinder engine. By turning a hand wheel at the side, the cylinder can be adjusted together with the cylinder head, which makes it possible to vary the compression ratio between 1 : 7 and 1 : 25. A dial on the hand-wheel shaft indicates the corresponding state of compression. The compression chamber is a semispherical indentation in the piston crown which has a considerable advantage from a combustion viewpoint and facilitates the exact measurement of the ignition delay. The Diesel engine is loaded either by a polyphase squirrel-cage induction motor or by a direct-current dynamometer. The measuring equipment consists mainly of an inertia-free piezoelectric indicator and the injection-nozzle contact pickup. The pressure diagram for this piezoelectric quartz indicator is installed in the cylinder head directly next to the combustion chamber. To expand the part of the pressure diagram in the range of the ignition lag, which is of main interest, a deflecting unit consisting mainly of a water ring used as an electric resistance and rotating with the engine, is installed. If the electrodes are staggered by 180°, normal staggered diagrams will be obtained on the fluorescent screen. However, if the electrodes are arranged at an angle of 45°, a graph which expands the combustion process is obtained. This diagram appears on the fluorescent screen of the cathode-ray tube as a stationary image, giving an indication of the ignition lag and pressure rise. The ignition lag in the IG Diesel-testing method is adjusted constantly to 18 crank radians, shown by two marks in the diagram. The ignition-nozzle contact pickup makes the instant of incipient ignition visible in the pressure diagram. A device developed by Bosch permits adjustment of incipient injection.

Three test vessels are in existence for investigating the fuels. These vessels can be connected with the injection pump. The apparatus is started with a good-quality Diesel fuel and then the Diesel oil to be investigated is used. This oil and the reference mixtures of cetane and methyl naphthalene or substandards are used in this test at the same ignition lag of 18° KW. Consequently, the compression will vary (by moving the cylinder head) until the ignition lag has reached this fixed value.

The compression adjustment can then be read directly and extrapolated to cetane ratings by means of a diagram. Individually, the process is as follows: The mark in the diagram corresponding to incipient injection is made to coincide with the beginning of the first pip 20° KW before top center by changing the pump setting.

Then, the compression itself is changed until the pressure rise (incipient ignition) produced by the ignition appears at the second pip, i.e., 2° KW before top center. That means, the device is adjusted accurately to ignition lag of 18° KW. In investigating individual fuel samples, the samples are placed between two reference fuels and the cetane numbers of the Diesel fuels to be checked will be calculated from the known cetane ratings of the mixture. In serial investigations, a calibration curve should be established for compression setting and cetane rating. This curve will be practically a straight line. Consequently, it is sufficient to determine the compression setting for two different mixtures (approximately 20% cetane + 80% metyl naphthalene and 60% cetane + 40% methyl naphthalene). A straight line representing the relation between compression setting and cetane rating is then drawn through these two points. This calibration line shown as an example in Fig.34, can be shifted up to three cetane ratings but will keep its direction. It is suggested to check the curve at the beginning and end of the measurement with reference fuels since it may be possible that the Diesel engine will foul by impurities in the fuel or by coking fuels, resulting in a change of the test conditions. At considerable fouling, the testing engine must be cleaned before continuing the tests.

Since the cetane rating can be calculated from the mixture components, fuels with a poor ignition quality should be mixed with a Diesel oil of high ignition quality to prevent any unnecessary fouling of the engine. Then, the cetane value can be calculated by percentage as the arithmetic mean.

### g. Laboratory Methods for Determining Ignition Quality

In this respect, it should be mentioned that all attempts for establishing relations between certain characteristics as an expression of the internal structure of Diesel fuels and their ignition quality will fail as long as the engine test had not produced definite values for the ignition quality and as long as corrections had to be made for balancing the values obtained by the starting or ignition-lag methods. This same viewpoint must be used for considering all other relations made up to now by laboratory experiments. Corresponding corrections will be required until definite cetane ratings are established.

It frequently had been attempted to establish relations between the hydrogen content or the C:H ratio of Diesel fuels and the ignition quality. However, satisfactory agreement was found since aromatic compounds, naphthenes, olefins, and paraffins are not in a simple numerical ratio to the hydrogen content when mixed with heavy hydrocarbons in Diesel oils (bibl. 135). It had been determined previously that numerical ratios can be established between hydrogen content and specific gravity of Diesel oils (mentioned previously in the relations established by Marder). Heinze and Marder finally made determination of the parachor clear and brought the specific gravity in relation to the ignition quality. In this case, it became necessary to correct this relation by the distillation cross section or the mean molecular weight. Figure 35 shows the diagram established by Heinze and Marder (bibl. 136). The specific gravity ($d_2 20$) is plotted in that diagram as a function of the cetene rating (CFR Diesel engine), related to a boiling cross section with a boiling coefficient of 300°C. Table 53 containes the values of this diagram, expressed in cetene and cetane ratings.

Heinze and Marder made the suggestion to calculate the cetene rating according to the following formula for correct grouping of Diesel fuels of lower and higher distillation range:

$$CeR = CeR_0 - (300 - BC)\ f$$

In this formula, CeR denotes the desired cetene rating, $CeR_0$ the cetene number found from the specific gravity of the diagram, BC the boiling coefficient of the Diesel fuel to be investigated and f a correction factor parallel to the boiling coefficient having the following values:

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| f | 0.40 | 0.39 | 0.38 | 0.37 | 0.36 | 0.35 | 0.34 | 0.33 | 0.32 | 0.31 | 0.30 | 0.29 | 0.28 |
| BC | 200 | 210 | 220 | 230 | 240 | 250 | 260 | 270 | 280 | 290 | 300 | 310 | 320 |

Heinze and Marder have created a specific-gravity spindle (hydrometer according to Marder for determining the cetene number, manufactured by Bardowyck, in Berlin) which permits direct reading of the cetene rating $CeR_0$ and will have to be corrected according to the above formula. Tannenberger evaluated the Marder specific gravity/cetene number (CFR) in a nomogram (bibl. 137) shown in Fig.36. However, in Fig.37 the author shows a family of curves for the boiling coefficient in the range between 200 and 300 between specific gravity and cetene number, used by Heinze and Marder for establishing the above-mentioned formula and developed by both authors in numerous practical measurements. This diagram is used for deriving Table 54. However, the ignition quality of the Diesel fuels as a function of specific gravity and boiling cross section (BC) is given in cetane units.

A similar derivation had been established by Ward, Kurtz, and Fulweiler who combined viscosity and specific gravity of Diesel fuels, relating these factors to the ignition quality. These relations are shown in Table 55.

Also in the Diesel index/cetene rating relation, considered rather suitable by Kreulen (bibl. 139), has been considerably improved by Heinze and Marder (bibl. 140) by using the boiling cross section as a correction. The proportions shown in Table 56 apply for a boiling coefficient of 300 between the Diesel index and the cetene rating.

For other boiling coefficients of the Diesel oils, the following formula applies: $CeR = CeR_0 - (300 - BC)\ f$. In this case, the factor f has approximately the value of 0.2. The cetene rating $CeR_0$ can be taken from Table 56 with respect to the established value of the Diesel index. For the relation of the specific parachor to the cetene rating, Heinze and Marder have recently established a ratio (bibl. 141) given in Table 57 and related to a boiling coefficient of 300. In a previous work (bibl. 142), the authors gave values deviating from the above data.

For correcting to other boiling coefficients of the Diesel oils, the formula $Cer = CeR_0 - (300 - BC)\ f$ where the factor f will have an average value of 0.3.

Best (bibl. 143) compiled six numerical scales in a nomogram for fuel evaluation (with truly American "generosity"), shown in Fig.38. In this diagram, the two scales at both sides of the nomogram with the designation "cetane delay" indicate the cetane scale (presumably CFR ignition-lag method; CFR delay-angle method). The scale "cetane CCR" indicates (bibl. 144) the cetane number calculated from the critical compression ratio (CCR: critical compression ratio) which had been determined in a modified CFR engine. This critical compression ratio indicates the lowest compression ratio at which a Diesel fuel will just ignite. Between cetane rating and critical compression ratio, the following relation exists in the Waukesha CFR engine according to Marder and Schneider (bibl. 145):

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Critical Compression Ratio 1 to | 6.8 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 | 10 | 11 | 12 | 14 | 16 | 18 |
| Cetane Rating (CFR) | 102 | 79 | 57 | 51 | 45 | 50 | 34 | 30 | 25 | 17 | 9 | 0 |

Note: This relation shows immediately that fuels with cetane ratings below 45 are too poorly evaluated compared to fuels with higher values. As a consequence, only a very slight variation of the CCR is obtained at high values per cetane unit, which interferes with the measuring accuracy. The third numerical column of the nomogram in Fig.38 shows the Diesel index, the fourth column shows the UOP factor which represents a characteristic of the Universal Oil Products, while the opposite scale of the octane rating (blending octane No.) is laid off on the fifth scale. The next scale is that for boiling point/density constant (boiling point gravity, calculated from the 50% BP in °C), and the last scale is that of the viscosity/density constant (viscosity gravity).

Application of the results of investigations in the Jentzsch ignition tester for a laboratory evaluation of the ignition quality of Diesel fuels has been frequently attempted, since correlations definitely exist between the self-ignition point of oils and the dissociation tendency in practical engine operation. Unfortunately, the numerical relations are unsatisfactory.

Table 58 contains the cetane ratings of Diesel fuels (Nos. 1 - 30) from the above-mentioned report by Kessler on ring experiments on orders of the RVM (bibl. 146) as a supplement to Table 51a. These data were determined as mean values of engine tests and by laboratory methods, consisting mainly of the Heinze-Marder density method and the Jentzsch ignition tester.

Obviously, the cetene numbers obtained from the starting method scatter considerably, while the scattering limits in the ignition-lag method are much more narrow. Of course, the reproduceability of the Heinze-Marder method is rather satisfactory but the values are slightly too high compared to the ignition-lag method. Consequently, this method will not respond to Diesel fuels with addition of "chemical boosters", i.e., ignition accelerators (Diesel oils marked with an asterisk). The values obtained in the Jentzsch ignition-value method generally are much too low and scatter too strongly to justify this laboratory method in its present form for evaluating Diesel fuels.

## 20. IGNITION ACCELERATORS

Ignition accelerators or "dopes" are substances which will increase the ignition behavior when added in small amounts to Diesel fuels with poor ignition quality. A prerequisite for such substances is an unstable nature and a ready dissociation.

Schmidt and Mohry (bibl. 147) reported on successful experiments made with certain oil-soluble peroxides for increasing the ignition quality of heavy fuels. Table 59 gives an abstract of these experiments and, in the cases of positive effect of such additives, shows a decrease in ignition lag expressed in crank radians. The fact that an increase in ignition lag will take place at decreasing compression ratio, is shown clearly in this table. In the cases shown in this table, 2% peroxide was added.

In all peroxide additives, it was found that the fuel samples remained unchanged after a year as far as aging and storage stability is concerned. In addition, the efficiency of the additives for shortening the ignition lag was retained.

In a rather voluminous report, Heinze, Marder, and Veidt (bibl. 148) produced valuable data on this subject. The numerous patents are evaluated as to advantage and disadvantage in this report and not only the effect of certain ignition accelerators is established but the rather undesirable influence of these additives as to coking and corrosion is investigated. The authors found that the storage stability of dope fuels in most cases was influenced. Another item of importance is the confirmation of the finding made by Schmidt and Mohry that the efficiency of dope additions is fully retained even after longer storage of the refined Diesel fuels. Table 60 contains a part of the results obtained by Heinze, Marder and Veidt. The cetane numbers were measured in the HWA Diesel engine.

It was found that the following substances are effective as ignition accelerators: alkyl nitrates, alkyl nitrites, peroxides, nitroso compounds, and polysulfides, in contrast to many patent claims, certain nitrosamines, oximes, and ketones. Naturally, the type of fuel is of considerable influence on the possible increase in ignition quality. The activating effect of butyl bromide, benzyl bromide, and copper stearate in slight admixtures for ignition acceleration, mentioned frequently in literature, could not be verified. All ignition accelerators (with the exception of tetraline peroxide) even as a 1/2% addition will increase the coking tendency of fuels beyond the permissible limit. In actually effective additions of 2% and more, this tendency is increased to Conradson values of as much as 0.7% and even 1%. The corrosion tendency of doped Diesel fuels is slightly higher than that of untreated oils. Only tetraline peroxide has a clearly corrosive effect and exceeds the permissible limit of zinc corrosion of 4 mg/16 cm when added in a concentration of 2%.

## 21. APPENDIX: ENERGY DISTRIBUTION IN ENGINE AND MOTORIZED VEHICLES

| | Otto Cycle Engine | Diesel Engine |
|---|---|---|
| + Energy content of the fuels | 100% | 100% |
| - Energy losses by | | |
| -Exhaust gases (pressure and heat) | 36% | 29% |
| -Cooling water (heat) | 33% | 32% |
| + Work transmitted to the piston | 32% | 40% |
| Energy loss by engine friction | 7% | 7% |
| + Effective work on the crankshaft | 24% | 32% |
| Energy losses by | | |
| -Propeller and generator | 2.5% | 2.5% |
| -Switch gear | 1.5% | 1.5% |
| -Compensation gear | 1.0% | 1.0% |
| -Axles and shafts | 1.0% | 1.0% |
| -Rolling resistance on highway | 4.0% | 4.0% |
| -Air resistance (relative wind) | 10.0% | 10.0% |
| + Reserve power for acceleration, slope, tractive power | 4.0% | 12.0% |

The thermodynamic efficiency ($\eta_{th}$) is as follows:

| At $\varepsilon$ 1: | 6.0 | 6.5 | 7.0 | 7.5 | 12 | 15 | 22 |
|---|---|---|---|---|---|---|---|
| In the Otto-cycle engine: | 46% | 48% | 49% | 50% | - | - | - |
| In the Diesel engine: | - | - | - | - | 58% | 62% | 66% |

If the following symbols are used:

Ne brake horsepower (hp), $V_h$ swept volume (liter), $p_0$ mean effective pressure (kg/cm$^2$), n rotational speed (rpm), s stroke (mm), vk piston speed (m/sec), d cylinder bore (mm), Md torque (mkg), $\varepsilon$ compression ratio, $V_c$ compressed volume (liter) at a piston position in the top center, $p_1$ initial pressure, $p_2$ end pressure (kg/cm$^2$), $\eta_{th}$ thermodynamic efficiency, and $\varphi$ crank angle (°C), it follows that:

Piston-displacement power (in hp/ℓ) = $Ne/V_h$

Mean working pressure (in kg/cm$^2$) in a four-cycle engine $pe = 900\ Ne/V_h\ n$

in the two-cycle engine $pe = 450\ Ne/V_h\ n$

Mean piston speed (in m/sec) $Vk = sn/33{,}000$

Maximum piston speed (in m/sec) $V_k = 1.6\ \ sn/33{,}000$

Swept volume $V_h = 0.785 \times 10^{-6}\ d^2\ s$ (liter per cylinder)

Brake Horsepower $Ne = Md\ n/716.2$ (hp)

Torque $Md = 716.2\ Ne/n$ (mkg)

Compression ratio: $\varepsilon = V_h : V_c$

End pressure $p_2 = p_1\ \varepsilon^v$ (kg/cm$^2$)

$$\eta_{th} = 1 - \left(\frac{1}{\varepsilon}\right)^{v-1}$$

$$\varphi = 6\ nt$$

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| 56. | Towne | - IPT (1931), 134 |
| 57. | Bandte | - Erdoel u. Teer (1931), 576 |
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| 59. | Kaufmann and Grosse-Cetringhaus | - Oel u. Kohle (1938), 199 |
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73. Egerton and Gates - IPT. (1927), 244, 281
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76. Boerlage - IPT (1935), 40
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Boyd, Refiner (1931) No. 11
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83. Nawrzinioks - ATZ (1931), 544
84. Auer - VDI-Forsch. Heft No. 340
85. Schmidt, A.W. and Generlich - Braunkohle (1936), 535
86. Kneule - VDI (1940), 869
87. Bartholomew and Mitarb - SAE (1938), 141
Kuehner - VDI (1939), 293
88. Blackwood and Mitarb - SAE (1938), 427
89. Schmidt, A. - Oel u. Kohle (1940), 350
90. Berg - ATZ (1939), 41
91. Seeber - RDT No. 29, (1938)
92. Kessler - Oel u. Kohle (1938), 341
93. Cox, R. - Refiner (1940), No. 2
94. Heinze and Marder - Ang. Chem. (1935), 335, 776 and Oel u. Kohle (1935), 923
95. Hammerich - Oel u. Kohle (1941), 149
96. Pier - Vorber. d. D. Akad. Luftfahrforschung, V (1939)
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Heinze and Marder - Ang. Chem. (1937), 747

110. Hagemann and Hammerich - Oel u. Kohle (1936), 371, 499

111. Hammerich - Oel u. Kohle (1938), 855

112. Marder - Oel u. Kohle (1936), 1061

113. Marder - Oel u. Kohle (1938), 836

114. Hammerich - Oel u. Kohle (1938), 539

115. Heinze and Marder - Brennstoff-Chemie (1937), 117

116. Marder - Oel u. Kohle (1937), 1162

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123. Kreulen - IPT (1937), 253

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130. Slowak, Schmidt, A. - DVL

131. Neumann - ATZ (1939), 263

132. Kessler - Oel u. Kohle (1938), 341

133. Wilke - ATZ (1940), 377

134. Schmidt, A. - Oel and Kohle (1941), 705

135. Vorberg - Oel u. Kohle (1939), 497

136. Heinze and Marder - Brennstoff-Chemie (1935), 286 and Oel u. Kohle (1935), 734

137. Beziehung - Kraftstoff (1941), 218

138. Ward, Kurtz and Fulweiler - Science of Petrol. II, 1185

139. Kreulen - IPT (1937), 253

140. Heinze and Marder - Deutsche Kraftfahrtforschung (1938), No. 7

141. Heinze and Marder - Deutsche Kraftfahrtforschung (1938), No. 7, 17

142. Arbeit – Oel u. Kohle (1935), 724
143. Best – Nat. Petrol. News (1937)
144. Pope and Murdock – SAE (1932), 136
145. Marder and Schneider – ATZ (1937), 195
146. Kessler – Oel u. Kohle (1938), 341
147. Schmidt and Mohry – Braunkohle (1936), 535
148. Heinze, Marder and Veidt – Oel u. Kohle (1941), 422

Kraftstoff-Fibel Bewertungsgrundlagen
fuer Otto- und Dieselkraftstoff.
Union Deutsche Verlagsgesellschaft Ber
1942
221 pp, 66 Tables, 38 illus.

Translated and Edited by
the C.W.Leibiger Research Laboratories, Inc.
Petersburg, N. Y.
31 May 1948

## AUTHOR INDEX

Reports by the following authors are used:

Aldrich
Auer

Bandte
Bartholomew
Beale
Becker
Beckmann
Berg
Bergius
Berl
Best
Bielenbert
Blackwood
Boerlage
Boord
Boyd
Bridgeman
Broeze
Brunschwig
Buchan
Burstin

Calingaert
Callendar
Campbell
Charch
Coats
Conrad
Conradson
Cox

Danaila
Davis
Dieterich
Docksey
Dulong

Eberlein
Eckert
Edgar
Egerton
Egloff
Engler
Ernst

Faragher
Fischer (Frz)
Fischer
Fisher
Francis
Fulweiler

Galle
Garner
Gates
Gemassmer
Generlich
Glyde
Gnamm
Goldschmidt AG., Essen
Griffith
Grosse-Oetringhaus
Grosser
Grote
Grumell
Gruse

Hagemann
Hammerich
Hanusch
Hartmann
Hebl
Heinze
Henkels
Hess
Hill
Hollings
Hopp
Hubendick
Hubner
Huebl
Hugel
Hunn

I. G. Farbenindustrie A. -G.
McIlhiney
Ipatieff

Jackson
Jacque
Jantsch
Jentzsch
Jonescu
Jost
Jostes

Kadmer
Kamm
Karrer
Kattwinkel
Kaufmann
Kaye
Kessler
Kiemstedt
Kneule
Koch
Koelbel
Krauch
Krekeler
Kreulen
Kronecker

Kuehner
Kuhnhenn
Kurtz

McLeod
Levine
Littlejohn

Mack
Marder
Margosches
Maxwell
Midgley
Mohry
Moore
Morell
Moudain
Muecklich
Murphy

Nenninger
Neumann

Ostwald
Ostwald-Luther

v. Philippovich
Pier
Podbielniak

Ramsbottom
Reid
Rendel
Ricardo
Riesenfeld
Rosenmund
Rothe

Sachanen
Sandke
Seeber
Seifert
Serruys
Sielisch
Singer
Slowak
Sudgen

Schildwaechter
Schmidt (AW)
Schnauffer
Schneider
Schoeller
Scholz
Schulze

Stansfield
Steiger
Stelling
Tannenberger
Thomas
Thompson
Torricelli
Towne
Tropsch
Trubetzky

Ubbelohde
Ubrich

Veidt
Vlugter
Vorberg

Walther
Ward
Waterman
Wawrziniok
Wellard
Weller
Wernicke
van Westen
Wheeler
Widmaier
Wijss
Wilke
Wilson
Winkler
Wirabianz
Withrow

Youle

Zerbe

## INDEX

Abadan
Abbe Refractometer
Stalling Temperature
Acenaphthene
Acetone
Acetophenone
Acetylene
Acetyl benzoyl peroxide
Acridine
Actual gums
Ethane
Ethanol
Ether
Ether oxygen
Ether evaporation (for refrigeration)

Ethyl alcohol, see Ethanol
Ethylamine
Ethylamylether
Ethyl aniline
Ethyl benzene
Ethyl bromide
Ethyl butyl ether
Ethyl chloride
Ethyl cyclobutane
Ethyl cyclohexane
Ethyl cyclopentane
Ethyl cyclopentene
Ethyl disulfide
Ethylene
Ethylene dibromide
Ethylene dichloride
Ethylene heptane
Ethylene hexane
Ethyl isopropyl ether
Ethyl mercaptan
Ethyl nitrate
Ethyl pentane
Ethyl toluene
Energy of activation
Activated Charcoal
Alco polymerization
Alco phrolysis
Alkali blue
Alcohol content of fuels
Alcohol-mixture fuels
Alcohol-oxygen
Alkyl benzenes
Alkyl cyclohexanes
Alkyl cyclopentanes and -pentenes
Alkyl disulfides
Alkyl nitrates
Alkyl nitrites
Alkyl toluenes
Aging of benzines
Aminophenol

Ammonia
Ammonium chloride
Ammonium nitrate
Amyl alcohol, tertiary
Amyl benzene
Amyl cyclohexane
Amylene
Amyl mercaptane
Amyl nitrate
Amyl nitrite
Amyl toluene
Aniline
Aniline point
Aniline point/density constant
Aniline point coefficient
Starting method
Anthracene
Antiknock agent
Antioxidants
API
Hydrometer
Working pressure
Aromatic compounds
Aromatization
Asphalt
Asphalt-basic oils
Asphalt producers
Association
ASTM (American Society for Testing Materials)
Atomic weights
Misfire (ignition)
Misfire methods
Automobile benzine
Azeotropy
Azeotropic mixtures
Barium chloride
Barium sulfate
Auxiliary Diesel fuel
Loading
Benzine "stretchers"
Benzene
Benzene homologues
Benzene blends (benzine-benzene mixtures)
Benzonitrile
Benzoyl acetone
Benzoyl bromide
Bergin method
Grade testing
Fuel consumption
Diffraction spectrum
Bib-Eibat benzine
Binary systems
Lead bromide
Lead chloride
Lead chromate

Diethyl tetrasulfide
Density
Dicyclohexyl
Dicyclopentyl
Diesel index
Diesel engines (data)
Di-isobutylene
Di-isopropyl
Di-isopropyl ether
Di-sec butyl ether
Dimethyl ethyl carbinol
Dimethyl butane
Dimethyl butene
Dimethyl quinoline
Dimethyl cyclohexane
~~Dimethyl heptane~~
Dimethylhexane
Dimethyl naphthalene
Dimethyl octane
Dimethyl pentane
Dimethyl peroxide
Dimethyl propane
Dimethyl sulfate number
Dimethyl thiophene
diolefins (dienes)
Dioxane (Diethylene dioxide)
Diphenyl
Diphenyl methane, propane, butane,
etc. to hexadecane
Diphenylene sulfide
Dispersion
Disposible hydrogen
Disulfides
Dithizone (diphenyl Thiocrarazon)
~~Doctor solution~~
Dodecane
Dodecene
Dodecyl benzene
Dodecyl cyclohexane
Dodecyl cyclopentane, and pentene
Dodecyl toluene
Dollberg benzine
Dopes
Twin carburetor
Drakorubin paper
Torque
Rotational speeds
Trimix
Three-component mixtures
Pressure distillation
Pressure peaks
Pressure curve in Diesel engine
Dubbs cracking method
Nozzle coking (Diesel)
Durene
DVL, Deutsche Versuchanstalt
fuer Luftfahrt
Dynamic viscosity
E-35 engine

Ebullioscopic method
Edeleanu extract
Edeleanu refined product
Edeleanuzation
Eggertz tube
Calibration benzine
Elicosane
Injection
Iron carbonyl
Iron hydroxide
Acetic acid
Elementary analysis
Energy distribution in the engine
Engler distillation
Engler viscosimeter
Segregation
Dehydration of alcohol
Activated earths
Natural-gas benzine
Solidifying point
Primary benzine
Glacial acetic acid
Ethyl blending chart
Ethylfluid
Ethylation
Euco benzine
Explosion range
Explosion engine
Extractor
Extraction benzine
Precipitation value
Color
Color dispersion
Farnborough indicator
Barrel capacity (calculation)
Ferrous sulfate
Rich mixtures
Fatty oils
Filter crucible
Filter period
Filterability
Fischer-Tropsch benzine
Fischer-Tropsch synthesis
Flame front
Flame path
Flame point
Pour point
Liquid gas
Heat of liquifaction
Aviation benzines
Aviation benzene
Aviation Diesel fuel
Aviation Diesel engine
Flight performance and octane rating
aircraft engines (data)
Fluorene
Fractions
~~Fraunhofer D-line~~
Preignition

Volumetric efficiency
Furane derivatives
Furfural
Gallon
Gallic acid
Gas benzine, gasoline
Gasol
Gas oil
Gas phase
Gas purifier
Mixture formation
Mixture head value
Mixture octane rating
Mixture preheating
Tannic acid
Total sulfur
Gypsum method (alcohol
dehydration)
Glass-filter crucible
Glass-dish method (resin
determination)
Mixed-cycle engines
Glycol
Glycol evaporation cooling
Glycerin
Alumina earth
Gray process
Grosmij cracked benzine
Basic benzine
Basic octane number
Quality factor
Gum test
Semicracking
Hahus solution
Hard asphalt
Resinification
Resins, benzine-insoluble
Resins, potential
Resins, preformed
Resin content
Resin afterformation
Heat value
Heat value/density relation
Heneicosane
Heneicosene
Heptadecene
Heptadecane
Heptane
Heptene
Heptyl benzene
Heptyl cyclohexane
Heptyl toluene
Hesselman engine
Hexadecane (cetane)
Hexadecyl benzene
Hexadecyl cyclohexane
Hexadecyl cyclopentane
Hexadecyl cyclopentene
Hexadien
Hexalin

Hexamethyl benzene
Hexane
Hexene (hexylene)
Hexyl cyclohexane
Hexyl mercaptan
Hexyl toluene
Hiag method
High-pressure hydrogenation
Wood alcohol
Wood saccharification
Horning engine
Swept-volume efficiency
Swept-volume variation
Swept volume
HUC, Highest useful compression ratio
HWA, Heereswaffenamt
Hydrate formation
Hydrogenation benzine
hydrogenated napthalenes
Hydrogenated Diesel oil
Hydrindene
Hydroaromatic compounds
IG Diesel testing engine
IG calibration benzine
IG high-pressure hydrogenation
IG Leuna fuel handbook
IG Otto-cycle testing engine
Indene
Indole
Indophenin reaction
Induction period (resin afterformation)
Inhibitors
Increments
Isatine
Iso-amyl alcohol
Iso-amylene
Isobutane
Isobutyl alcohol
Isobutylene
Isoquinoline
Isodurene
Isomerism
Iso-octane
Iso-octene
Isoparaffins
Isopentane
Isopentene
Isoprene
Isopropyl ether
Isopropyl alcohol
Isopropyl mercaptan
IT-Fluid
Jeffrey pine
Jentzsch octane number
Iodine addition
Potassium iodide
Iodine flask
Iodomonobromide
Iodocyanogen number
Iodine numbers

Juhasz indicater
Low-temperature resistance
Refrigerants
Potassium bichromate
Potassium chlorate
Potassium iodate
Potassium iodide
Lead diethyl dichloride
Lead diphenyl diethyl
Lead diphenyl dimethyl
Lead susceptibility
Lead sensitivity
Lead content
Lead-sodium alloy
Lead oxide
Lead sulfate
Tetraethyl lead
Lead tetraphenyl
Lead trixylene
Blending octane number
Blank experiment
Potassium ferrocyanide
50% Boiling point
Boiling-point-gravity constant
Bomb test (resin afterformation)
Boric acid
Bosch
Bouncing-pin indicator
Brabag
Lignite benzine
Lignite Diesel oil
Lignite carbonization
Lignite tar oil
Cathode-ray tube
Pyrolusite
Diffracting power, see refraction
Fire point
Combustion-chamber shape
British Standard specification
Bromine
BTU ( = British thermal unit)
Butane
Butyl alcohol
Butyl benzene
Butyl bromide
Butyl cyclohexane
Butyl cyclopentane
Butyl cyclopentene
Butylene (butene)
BV = Benzolverband
BV-Aral
BV-benzene
Cal (calorie)
Calcium chloride
Calcium carbide
Carbazole
Carbon, hydrogen
Carburant national
Carvacrol

Number of C-atoms
CCR, critical compression ratio
Cetane (hexadecane)
Cetane delay
Cetane rating
Cetene
Cetene rating
CFR method, Diesel
CFR method, Otto
Chemical boosters
Quinoline
Chloroform
Sulfur chloride
C:H ratio
Cloud Point
Collidine
Conradson test
$C_p$, centipoises
Cracked benzine
Cst, centistokes
Coumarone
Cycloheptane
Cyclohexane
Cyclohexanol (hexaline)
Cyclohexanonoxime
Cyclohexadien
Cyclohexene
Cyclohexyl cyclopentane
Cyclo-olefins
Cycloparaffins
Cyclopentadiene
Cyclopentane
Cyclopentene
Cymenes
Daimler-Benz
Vapor-bubble formation
Vapor-bubble measurement
(Schmidt and Scholz)
Vapor-pressure difference
Vapor-pressure curves
Vapor-pressure measuring units
Vapor-pressure values
Vapor tension
DAPG
Dapolin benzine
Decane
Decene
Decyl cyclopentane
Decyl cyclopentene
Decyl toluene
Decaline
Distillate benzine
Distillate Diesel oil
Deurag
German Standard method
Dewar vessel
Dew Point
Diacetone diperoxide
Diallyl

Diethylene glycol
Diethyl hexane
Diethyl pentane
Diethyl peroxide
Diethyl selenide
Diethyl sulfate
Diethyl telluride
Potassium permanganate
Potassium thiocyanate
Calcium pressure method (alcohol
dehydration)
Calorimetric heat-value determination
Cold-starting possibility
Capillary viscosimeter
Catalysts, nontoxic
Cathode-ray oscillograph
Kattwindel acid
Characteristic ignition value
Core fraction
Ketones
Chain explosion
Chain reactions
Kinematic viscosity
Antiknock agents
Knocking, knock intensity
Antiknock characteristic
Knock limiting curves
Knock limiting values
Knock meter
Cobalt contacts
Kogasin
Kogasin II
Carbon dioxide
Carbon monoxide
Carbon-dioxide snow
Carbon
Carbon atom number
Liquifaction of coal
Piston speed
Compression
Compression resistance
Conjugated double bonds
Constitution
Contraction
Indelible-pencil test (alcohol)
Correction of boiling temperature
Corrosive sulfur
Corrosions
Corrosion bomb
Corrosion test
Motorcycles
Creosote
Cresol
Critical pressure
Critical temperature
Copper-bronze powder
Copper test
Copper-dish method (resin)
Crank angle

F & VM naphtha
Laettbentyl
Storage property
Kerosene
Lanova engine
Trucks (data)
Light benzine
Power drop
Power, effective
Power-weight ratio
Illuminating gas
Leuna automobile benzine
Photoelectric indication
Light sensitivity of leaded fuels
Ligroin
Solvent, selective
Solvent naphtha
Solubilizer
Logarithmic table
Air requirement
Air humidity
Air storage Diesel
Air-excess coefficient
Air ratio
Air preheating
Lurgi method
Lutidine
Lux paste
Lean mixtures
Magnesium nitride
Mahler calorimeter
MAN
Manganese dioxide
Marcusson flame-point crucible
Maximum precipitation value
Supercharging
Multicylinder testing engine
Mercaptans
Mesitol
Mesitylene
Methane
Methanol
Methyl alcohol, see methanol.
Methyl ethyl cyclohexane
Methyl ethyl pentane
Methyl ethyl ketone
Methyl butane
Methyl quinoline
Methyl coumarone
Methyl cyclohexane
Methyl cyclohexene
Methyl cyclopentane
Methyl cyclopentene
Methyl heptane
Methyl hexaline
Methyl hexane
Methyl isopropyle ether
Methyl isopropylbenzene
Methyl naphthalene

Methyl naphthol
Methyl nonane
Methyl octane
Methyl orange
Methyl pentane
Methyl pentene
Methyl tertiary butyl ether
Methylthiophene
Mineral-seal-oil
Miscibility of Diesel oils
Mixed octane rating
Middle benzine
Middle oil
Molecular weight
Molecular refraction
Mole parachor
Mole refraction
Monoperparaldehyde
Monopolin
Engine design
Engine data
Engine benzene
Engine Works Mannheim, MM
Engine handling
Engine behavior
Engine method
Motyl (IGF)
Engine octane rating
Millistoke
Naphthalene
Naphthalene homologues
Naphthene
Naphthenic acid
Naphthol
Sodium bromide
Sodium plumbit
Sodium thiosulfate
Natural gasoline
Neohexane
Neopentane
Neutralization number
Nickel carbonyl
Nickel contacts
Nitrating acid
Nitration
Nitro benzene
Sodium nitroprusside
Nitrosamines
Nitrosodimethyl aniline
Nitrosodimethyl urethane
Nonadecane
Nonane
Nonene
Top oil
Surface tension
Octadecane
Octane
Octene
Octylbenzene

Octyl cyclopentane
Octyl cyclopentene
Octyl mercaptan
Octyl toluene
Octane values
Octane number
Olefins
Oppau
Oppau alignment chart
Ostwald viscosimeter
Oscillograms
Oxalic acid
Oximes
OZ calculation
Parachor
Paraffins
Pensky-Martens flame-point cu
Pentadecane
Pentadecene
Pentadien
Pentane
Pentene
Perchloroethylene
Peroxides
Peroxide number
Automobile (data)
Petroleum ether
Petroleum
Phenanthren
Phenol
Phenolphthalein
Phenylhydrazine
Phosphorous pentoxide
Phosphoric acid
Picolin
Piezoelectric method
Pinking
Piperidin
Polymeric benzine
Polymerization
Polysulfides
Pour point
Pratt & Whittney engine
Primary benzine
Propane
n-propyl alcohol
Propyl benzene
Propylbutyl ether
Propyl cyclohexane
Propyl cyclopentane
Propyl cyclopentene
Propylene
Propyl mercaptan
Propyl toluene
Pseudocumene
Pycnometer
Pytidine
Pyridine sulfate bromide
Pyrocatechin

Pyrolysis
Q-Fluid
Mercury acetate
Mercury-vapor lamp
Mean values
Refining hydrogenation
Test-tube experiment
Redwood seconds
Reformed benzine
Refraction
Refraction equivalents
Refraction intercept
Refractometer
Research method
Rheinpreussen Company
Potassium thiocyanate
Thiocyanate number
Ricardo engine
Ring analysis
Rolle oven
Research octane number
Reflux oil
Ruhrchemie Company
Ruhrgasol
RVM, Reich Ministry of Communication
Saturation pressure
Acid tar
Acid number
Oxygen compounds (in tar oil)
Intake subpressure
Acid benzine
Saybolt seconds
Reflecting unit
Self-ignition curves
Self-ignition point
Selective solvency
Specific-gravity spindle
(density)
Setting point
Shell benzine
Shell method for iso-octane
Shukoff apparatus
Boiling fractions
Initial distillation
End of disstillation
Boiling characteristic
Boiling curves
Boiling points
10% boiling point (10% BP)
90% boiling point (90% BP)
Boiling-point/density constant (BPC)
Boiling cross section
Distillation residue
Distillation tail
Distillation procedure
Distillation lag
Silica gel
S-300
Slowak Diesel Engine
Solvent naphtha

Stock point
Straight-run benzine
Road tests
Styrene
Tank capacity, calculation
Dew point
Temperature scales
Ternary systems
Terpentine
Test benzine
Tetraethyl tin
Carbon tetrachloride
Tetradecane
Tetradecyl benzene
Tetradecyl cyclohexane
Tetradecyl cyclopentene
Tetradecyl toluene
Tetraethyl lead (TEL)
Tetralin
Tetralin peroxide
Tetramethyl butane
Tetramethyl hexane
Tetramethyl pentane
Tetramethyl pyridine
Thermal efficiency of motorized vehicles
Thermal stability
Thioether
Thiophenes
Thiosulfate, see sodium thiosulfate
Thiotolene
Thioxene
Thomassen-Gardner engine
Thymol
Low-temperature distillation
Low-temperature tar
Low-temperature coking
Titanium chloride
Toluidine
Toluene
Topped benzine
Topping
Torricelli vacuum
Dead center
Tractors
Trichlorethylene
Tridecane
Tridecene
Railroad-engine Diesels
Tri-isobutylene
Trimethyl ethylene
Trimethyl benzenes
Trimethylbutane
Trimethylbutene
Trimethylheptane
Trimethylhexane
Trimethylpentane
Trimethylpentene
Trinitrotoluene
Triptane
Dry Distillation

Turbidity
Cloud point
Ubbelohde viscosimeter
Perchromic acid
Enriching, automatic
Supercharging
Ultraviolet absorption
Undecane
Undecene
Unsaturated hydrocarbons
Substandards -
UOP = Universal Oil Products
Crude tar
US gallons
vacuum distillation
Verband formula (calorific value)
Leading
Rate of combustion
Combustion process
Evaporation residue
Heat of evaporation
Compression
Compression temperature
Compression ratio
Rate of evaporation
Heat of Evaporation
Evaporation characteristic
Evaporation curves
Carburetor icing
Coking
Coking tendency
Coking test
Viscosity-gravity
Viscosimeter
Viscosity
Viscosity/density constant
Viscosity index
Viscosity height
Viscosity directional constant
Viscosity/temperature gradient
Vogel-Ossag viscosimeter
Preinjection
Preheating
Prechamber Diesel
Precombustion

Precompression
Preignition
Weighing bottle
Thermal explosion
Heat conductivity
Heat of reaction
Car knocking
True combustion heat
Wall reactions
Water
Water determination
Water gas
Water content
Hydrogen
Hydrogen content
Hydrogen blisters (steel)
Hydrogen peroxide
Water value of alcoholic fuels
Waukesha engine
White spirits
Specific gravity
Turbulence chamber, Diesel
Efficiency
Bismuth triethyl, trimethyl, and triphenyl
Wizoeff, Wissenschaftl. Zentralstelle f.
Oel - und Fettforschung
Surgical benzine
E-Values (viscosity)
Xylenol
Xylidine
Xylenes
Ignition accelerator
Ignition point
Ignition setting
Ignition lag
Ignition-lag method
Ignition value
Ignition-value tester
Ignition quality
Two-component mixtures

Table 11 - Distribution of Hydrocarbon Groups over the Individual Fractions in Russian Cracked and Distillate Benzines (bibl. 2)

Siedeabschnitte = Fractions

Grosnij-Spaltbenzin = Grosnij cracked benzine

Surachany-Spaltbenzin = Surachany cracked benzine

Bibi-Eibat straight-run = Bibi-Eibat straight-run

bis = to

Table 12 - Characteristics of Polymeric Benzines

Characteristics of several typical polymeric benzines: 1 denotes a crude polymeric benzine obtained by catalysis; 2 a polymeric benzine obtained from the cracking gas of the vapor-phase cracking of gas oil; 3 a polymeric benzine obtained from the cracking gas of a gas-oil cracking in liquid phase; 4 a polymeric benzine of a gas mixture of 30% propylene/70% propane; 5 a polymeric benzine of a gas mixture of 40% butylene/60% butane; 6 a polymeric benzine of a gas mixture of propane, butane, propylene, and butylene.

Dichte = $pecific gravity

Oktanzahl = Octane number

Schwefelgehalt = Sulfur content

Dampfdruck nach Reid in kg/cm$^2$ = Vapor pressure according to Reid in kg/cm$^2$

Siedebeginn = Initial distillation

Siedeverlauf = Distillation

bis = to

Siedekennzahl = Boiling characteristics

Table 3 - Effect of 5, 10, 15, 20, and 25% Blend of Polymeric Benzine with Straight-Run Benzines (bibl. 5); Increase in Octane Number

Straight-run-Benzin = Straight-run benzine

Polymerbenzinzusatz von = Polymeric benzine addition of

Table 4 - Characteristics of Several Carbonization Benzines

1 - 3 carefully refined lignite carbonization benzines of German origin; 4 - 6 French shale benzines in the following stages of processing: crude benzine, refined product, and redistillate (automobile benzine), in which case refining with sulfuric acid of 60 Be and caustic-soda solution of 30 Be will result in a 10% yield loss with an additional 10% loss by rectification; 7 and 8 are British anthracite carbonization benzines.

Deutsche Braunkohlenschwelbenzine = German lignite carbonization benzines

Franzoesische Schiefer-Schwelbenzine, Spaltdestillate = French shale carbonization benzines, cracked distillates

Englische Steinkohlenschwelbenzine = British anthracite carbonization benzines

Dichte = Specific gravity

Farbe = Color

% Aromaten + Ungesaettigte = % Aromatic + unsaturated compounds

% Naphthene = % naphthenes

% Paraffine = % paraffins

Siedebeginn = Initial distillation

Siedeverlauf = Distillation

bis = to

Siedekennzahl = Boiling characteristic

Oktanzahl = Octane number

Schwefelgehalt in % = Sulfur content in %

hydrierend raffiniert = Refined by Hydrogenation

gelb = Yellow

braun = Brown

schwarz = Black

farbl. = Colorless

dunkel = Dark

Table 5 - Characteristics of Synthetic Benzines Obtained in High-Pressure Hydrogenation; Leuna Automobile Benzine in Original Form Compared to Three British Aviation Benzines Obtained in High-Pressure Hydrogenation (Presumably Imperial Chemical Industries, Billingham)

Siedeverlauf = Distillation

Leuna-Autobenzin = Leuna automobile benzine

Engl. Flugbenzin = British aviation benzine

SHZ = BC

[illegible] = CR

The vapor pressure of the British hydrogenation benzines is given as 7 lbs/sq in = 0.49 [illegible], the sulfur content less than 0.01%, resin content 1 - 2 mg/100 cc, and lead sensitivity 0.3 cc tetraethyl lead/[illegible] at an octane rating of [illegible] or 0.6 cc TEL/l at an octane rating of [illegible]. [illegible] cc TEL/l the octane rating was [illegible].

Table 6 - Important Characteristics of Pure Benzene Hydrocarbons Existing in Light Oil of Anthracite Tar

Name and Formel = Name and formula

Mol.-Gew. = Molecular weight

Wichte = Specific gravity

Refraktion = Refractive index

Dispersion = Dispersion

Siedepunkt = Boiling point

Schmelzpunkt = Melting point

Benzol = Benzene

Toluol = Toluene

Xylole = Xylene

und zwar: = as follows:

o-Xylol, 1,2-Dimethylbenzol = o-xylene, 1,2-dimethyl benzene

m-Xylol, 1,3-Dimethylbenzol = m-xylene, 1,3-dimethyl benzene

p-Xylol, 1,4-Dimethylbenzol = p-xylene, 1,4-dimethyl benzene

Aethylbenzol = Ethylbenzene

Trimethylbenzole = Trimethyl benzenes

Pseudocumol = [illegible]ine

Mesitylen = Mesitylene

Cymole, Methyl-Isopropyl-benzole = Cymene, methyl isopropyl benzenes

p-Cymol = p-cymene

Table 7 - Characteristics of Technical Benzenes and Benzene Mixtures

Siedeverlauf = Distillation

Benzol, technisch rein = Benzene, technically pure

Benzol, technisch = Benzene, technical

Motorenbenzole = Engine benzenes

mit 10% Toluol = With 10% toluene

mit 25% Toluol, Xylol = With 25% toluene/xylene

Toluol, technisch = Toluene, technical

Xylol, technisch = Xylene, technical

Lösung benzol = Solvent naphtha

Schwerbenzol = Heavy benzene

Solventnaphtha II = Solvent naphtha II

Benzin-Benzolgemische = Benzine-benzene mixtures

25% Benzole = 75% benzenes

Table 8a - Fuel Quantities in kg Absorbed by 1 kg Air (According to Wilke)

Temperaturen = Temperatures

Benzin = Benzine

Benzol = Benzene

Aethanol = Ethanol

Methanol = Methanol

Table 8b - Saturation Pressures in mm Hg (According to Wilke)

Temperaturen = Temperatures

Benzin = Benzine

Benzol = Benzene

Aethanol = Ethanol

Methanol = Methanol

Table 9 - Specific Gravity d/15 and Percentage in Ethyl Alcohol and Water Mixtures Compared to Methyl Alcohol and Water Mixtures

Aethanol = Ethanol

Methanol = Methanol

Table 10 -

% Benzin = % benzine

Alkohol abs. = Alcohol abs.

Wasser = Water

Table 11a - Constant Boiling Points of Known Two-Component Mixtures

n-Hexan (69): Benzol (80) = n-hexane (69): benzene (80)

Chloroform = Chloroform

Aethylalkohol = Ethyl alcohol

Isopropylalkohol = Isopropylalcohol

Methanol = Methanol

Aethanol = Ethanol

Cyklohexan (81) Benzol (80) = Cyclo hexane (81) benzene (80)

Benzol = Benzene

Isopropylalkohol = Isopropyl alcohol

Toluol = Toluene

Tetrachlorkohlenstoff = Carbon tetrachloride

Trichloraethylen = Trichloroethylene

Aceton = Acetone

Wasser = Water

n-Propylalkohol (97) Wasser (100) = n-propyl alcohol (97) water (100)

i-Propylalkohol = Isopropyl alcohol

Aether = Ether

Aethylalkohol = Ethyl alcohol

Dioxan = Dioxane

Table 11b – Constant Boiling Points of Known Three-Component Solutions

Captions same as Table 11a

Table 12 – Lead Corrosion of Zinc and Aluminum Alloys in 24-hr Tests (Widmaier and Renninger)

Benzin, trocken = Benzine, dry

Benzin, feucht = Benzine, wet

Table 13 –

Siedeverlauf = Distillation

OZ = ON

SB = Initial distillation

SKZ = BC

Table 14 - Characteristics of Several Isomeric Ethers (According to Egloff)

Aether = Ether

Formel = Formula

SP = BP

CZ = CR

Bleiempfindlichkeit (CZ) = Lead sensitivity CR

Di-isopropylaether = Di-isopropyl ether

Methyl-isopropylaether = Methyl isopropyl ether

Methyl-tert. Butylaether = Methyl tertiary butyl ether

Methyl-tert. Amylaether = Methyl tertiary amyl ether

Aethyl-isopropylaether = Ethyl isopropyl ether

Aethyl-sek. Butylaether = Ethyl secondary butyl ether

Aethyl-tert. Butylaether = Ethyl tertiary butyl ether

Aethyl-tert. Amylaether = Ethyl tertiary amyl ether

i-Propyl-tert. Butylaether = i-propyl tertiary butyl ether

n-Propyl-tert. Butylaether = n-propyl tertiary butyl ether

Di-sek. Butylaether = Di sec butyl ether

Table 15 - Specifications for Foreign Aviation Benzines

Oktanzahl Stufe = Octane rating stage

Land = Country

Dichte, max. = Specific gravity, max

Siedeverlauf = Distillation

Kaeltepunkt = Freeze point

Verbleiung ccm TEL/Liter = Residue cc TEL/l

Engl. = England

Russl. = Russia

Frankr. = France

Table 14a – [illegible] Number Increase by Various Additives (Basic Benzine with

a) Additives: iso-octane and tetraethyl lead (TEL)
b) Additives: iso-pentane and tetraethyl lead (TEL)
c) Additives: isopropyl ether and tetraethyl lead (TEL)
d) Additives: benzene and tetraethyl lead (TEL)
e) Additives: toluene and tetraethyl lead (TEL)
f) Additives: xylenes and tetraethyl lead (TEL)
g) Additives: [illegible] benzene and tetraethyl lead (TEL)

Zusatz von = Addition of

Zusatz von Isooktan = Addition of iso-octane

Zusatz von Isopentan = Addition of isopentane

Zusatz von Isopropylaether = Addition of isopropyl ether

Zusatz von Benzol = Addition of benzene

Zusatz von Toluol = Addition of toluene

Zusatz von Xylol = Addition of xylene

Zusatz von Butylbenzol = Addition of butyl benzene

Table 17 - Numerical Ratios Between d/15.6 and API° in the Range of Benzines

Table 18 - Characteristics of Pure Hydrocarbons
a) n-paraffins and i-paraffins

S.P. BP

Smp = Melting point

Anilinpunkt = Aniline point

Oktanzahl = Octane number

Methan = Methane

Aethan = Ethane

Propan = Propane

n-Butan = n-butane

i-Butan, 2-Methylpropan = i-butane, 2-methyl propane

n-Pentan = n-pentane

i-Pentan, 2-Methylbutan = i-pentane, 2-methyl butane

Neo-Pentan, 2,2-Dimethylpropan = Neo-pentane, 2,2-dimethyl propane

n-Hexan = n-hexane

2-Methylpentan = 2-methyl pentane

3-Methylpentan = 3-methyl pentane

Neohexan, 2,2-Dimethylbutan = Neohexane, 2,2-dimethyl butane

Diisopropyl, 2,3-Dimethylbutan = Di-isopropyl, 2,3-dimethyl butane

n-Heptan = n-heptane

2-Methylhexan = 2-methyl hexane

3-Methylhexan = 3-methyl hexane

3-Aethylpentan = 3-ethyl pentane

2,2-Dimethylpentan = 2,2-dimethyl pentane

2,2,3-Trimethylbutan (Triptan) = 2,2,3-trimethyl butane (triptane)

n-Oktan = n-octane

2-Methylheptan = 2-methyl heptane

3-Aethylhexan = 3-ethyl hexane

2,2-Dimethylhexan = 2,2-dimethyl hexane

2,3-Dimethylhexan = 2,3-dimethyl hexane

2-Methyl-, 3-Aethylpentan = 2-methyl, 3-ethyl pentane

2,2,3-Trimethylpentan = 2,2,3-trimethyl pentane

Isooktan, 2, 2, 4-Trimethylpentan = Iso-octane, 2, 2, 4-trimethyl pentane

Trimethylpentan = Trimethyl pentane

2, 2, 3, 3-Tetramethylbutan = 2, 2, 3, 3-tetramethyl butane

n-Nonan = n-nonane

2-Methyloktan = 2-methyl octane

3-Aethylheptan = 3-ethyl heptane

2, 2-Dimethylheptan = 2, 2-dimethyl heptane

2, 2, 4-Trimethylhexan = 2, 2, 4-trimethyl hexane

3,3-Diaethylpentan = 3,3-diethyl pentane

2,2,3,3-Tetramethylpentan = 2,2,3,3-tetramethyl pentane

n-Dekan = n-decane

2-Methylnonan = 2-methyl nonane

2,4-Dimethyloktan = 2,4-dimethyl octane

2,2,6-Trimethylheptan = 2,2,6-trimethyl heptane

3,4-Diaethylhexan 3,4-diethyl hexane

n-Undekan = n-undecane

n-Dodekan = n-dodecane

Olefine = Olefins

Aethylen = Ethylene

Propylen = Propylene

n-Butylen = n-butylene

Isobutylen Isobutylene

n-Amylen, n-Penten n-amylene, n-pentene

2-Amylen, 2-Penten = 2-amylene, 2-pentene

n-Hexen = n-hexene

2-Methylpenten = 2-methyl pentene

3-Methylpenten = 3-methyl pentene

2,2-Dimethylbuten = 2,2-dimethyl butene

3,3-Dimethylbuten = 3,3-dimethyl butene

n-Hepten = n-heptene

2,2,3-Trimethylbuten = 2,2,3-trimethyl butene

n-Octen = n-octene

3-Methylhepten = 3-methyl heptene

2,4,4-Trimethylpenten = 2,4,4-trimethyl pentene

n-Nonen = n-nonene

Hexadien = Hexadien

Pentadien = Pentadien

Naphthene = Naphthenes

Cyklopentan = Cyclopentanes

Aethylcyklobutan = Ethyl cyclobutane

Methylcyklopentan = Methyl cyclopentane

Cyklohexan = Cyclohexane.

Cykloheptan = Cycloheptane

Aethylcyklopentan = Ethyl cyclopentane

Methylcyklohexan = Methyl cyclohexane

Propylcyklopentan = Propyl cyclopentane

Dimethylcyklohexan = Dimethyl cyclohexane

Aethylcyklohexan = Ethyl cyclohexane

Methylaethylcyklohexan = Methyl ethyl cyclohexane

Cyklopenten = Cyclopentene

Methylcyklopenten = Methyl cyclopentene

Cyklohexen = Cyclohexene

Methylcyklohexen = Methyl cyclohexene

Aromaten = Aromatic compounds

Benzol = Benzene

Toluol = Toluene

o-Xylol = o-xylene

Aethylbenzol = Ethyl benzene

Propylbenzol = Propyl benzene

Inden = Indene

Pseudocumol = Pseudocumene

Mesitylen = Mesitylene

Iso-Durol = Isodurene

Tetralin = [illegible]

Dekalin = Decaline

Table 30 - Abstract of Reports by Wawrziniok (Bibl. 26): Characteristics of Several Fuels in their Relation to the Evaporation Characteristic

Benzine und Marken-Kraftstoffe = Benzines and brand fuels

Dichte = Specific gravity

unterer Heizwert = Lower calorific value

Siedebeginn = Initial distillation

Siedeende = End of distillation

SKZ = Boiling coefficient

Oberfl.-Spann. dyn/cm = Surface tension dyne/cm

Vd.Z. min. = Evaporation characteristic

Normalbenzin = Ordinary benzine

Euco-Benzin = Euco benzine

Shell-Benzin = Shell benzine

Leuna-Benzin = Leuna benzine

Dapolin-Benzin = Dapolin benzine

Braunkohlenbenzin = Lignite benzine

Reinbenzol = Pure benzene

BV-Benzol = BV benzene

Alkohol = Alcohol

Aether = Ether

Monopolin (m. Sprit) = Monopolin (with alcohol)

Gasoel = Gas oil

Dieseloel = Diesel oil

sehr hoch = Very high

Table 20a - Relation mm Hg - kg/cm$^2$ - atm

Table 20b - Relation lbs/sq in - atm

Table 21 - Vapor Pressure (According to Reid) for Several Substances at Various Temperatures

Dampfdruck in kg/cm$^2$ bei den Temperaturen = Vapor pressure in kg/cm$^2$ at the following temperatures

1 kg/cm$^2$ bei S.P. = 1 kg/cm$^2$ at BP

Propan = Propane

Butan = Butane

Pentan = Pentane

Hexan = Hexane

Heptan = Heptane

Oktan = Octane

Dekan = Decane

Benzol = Benzene

Methanol = Methanol

Aethanol = Ethanol

Propylalkohol = Propyl alcohol

i-Butylalkohol = Isobutyl alcohol

i-Amylalkohol = Iso-amyl alcohol

Wasser = Water

Aceton = Acetone

Aether = Ether

Schwefelkohlenstoff = Carbon disulfide

Tetrachlorkohlenstoff = Carbon tetrachloride

Chloroform = Chloroform

Table 22a - Experimental Values of Vapor-Lock Measurements by Schmidt ~~and Scholz~~

Siedebeginn = Initial distillation

SKZ = Boiling characteristics

Dampfdruck = Vapor pressure

Dampfblasenbildung = Vapor-bubble formation

Sek. fuer 10 ccm Gas = Sec for 10 cc gas

Durchfluss in ccm = Throughput in cc

Benzin = Benzine

Benzol = Benzene

Alkohol = Alcohol

Motorenbenzol = Engine benzene

Table 22b - Vapor Pressure and Critical Temperature for Vapor Lock in Various Fuels (Ref. 32)

Siedebeginn = Initial distillation

10% S.P. = 10% BP

% bis 100 C = % to 100°C

S.P. = BP

Siedekennzahl = Boiling characteristic

Fluechtigkeit nach Hammerich = Volitility according to Hammerich

Dampfdruck = Vapor pressure

bei = at

Krit. Temp. der Dampfblasenbildung = Critical temperature of vapor-bubble formation

Rel. Abreisstemp. n. Hammerich = Relative stalling temperature according to Hammerich

Table 23 - Saturation Pressure of Benzine, Benzene, Ethyl Alcohol, and Mixtures

Saettigungsdruck in mm Hg bei = Saturation pressure in mm Hg at

Benzin = Benzine

BV Benzol = BV benzene

Alkohol (99prozentig) = Alkohol (99%)

60% Benzin + 40% Benzol = 60% benzine + 40% benzene

70% Benzin + 30% Alkohol = 70% benzine + 30% alcohol

60% Benzol + 40% Alkohol = 60% benzene/40% alcohol

Table 24 - Vescosity of Several Hydrocarbons in Centipoises (cp)

Viskositaet in cP bei = Viscosity in cp at

S.P. = BP

Isopren = Isoprene

n-Pentan = n-pentane

Diallyl = Diallyl

n-Hexan = n-hexane

n-Heptan = n-heptane

n-Oktan = n-octane

Toluol = toluene

n-Nonan = n-nonane

Benzol* = Benzene

Aethylbenzol = Ethyl benzene

Methylzyklohexan = Methyl cyclohexane

n-Dekan = n-decane

o-Xylol = o-xylene

Cyklohexan = Cyclohexane

n-Undecan = n-undecane

n-Dodecan = n-dodecane

Styrol = Styrene

n-Tridecan = n-tridecane

Table 25 - Heat Value/Density Relation According to Marder for Benzines

Wichte = Specific gravity

oberer Heizwert = Upper calorific value

unterer Heizwert = Lower calorific value

6

Heizwertdiffer. = Heat-value difference

Table 26 - Aniline Points of Pure Hydrocarbons According to Evans (Bibl. 68)

Paraffine = Paraffins

n-Pentan = n-pentane

n-Hexan = n-hexane

n-Heptan = n-heptane

2-Methylhexan = 2-methyl hexane

3-Methylhexan = 3-methyl hexane

3-Aethylpentan = 3-ethyl pentane

2,2-Dimethylpentan = 2,2-dimethyl pentane

2,3-Dimethylpentan = 2,3-dimethyl pentane

2,2,3-Trimethylbutan = 2,2,3-trimethyl butane

n-Oktan = n-octane

2,2,4-Trimethylpentan = 2,2,4-trimethyl pentane

n-Nonan = n-nonane

n-Decan = n-decane

n-Undecan = n-undecane

n-Dodekan = n-dodecane

Cyklopentanderivate = Cyclopentane derivatives

Cyklopentan = Cyclopentane

Methylcyklopentan = Methyl cyclopentane

Aethylcyklopentan = Ethyl cyclopentane

1,3-Dimethylcyklopentan = 1,3-Dimethyl cyclopentane

n-Propylcyklopentan = n-Propyl cyclopentane

n-Butylcyklopentan = n-Butyl cyclopentane

Cycloolefine = Cyclo-olefins

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Cyklopenten, unten = Cyclopentene below

Methylcyklopenten = Methyl cyclopentene

Aethylcyklopenten = Ethyl cyclopentene

n-Propylcyklopenten = n-Propyl cyclopentene

n-Butylcyklopenten = n-Butyl cyclopentene

Cyklohexen, unten = Cyclohexene, below

Olefine = Olefins

Penten-1 = Pentene-1

Hexen-1 = Hexene-1

Trimethylaethylen = Trimethyl ethylene

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Hepten-1 = Heptene-1

Octen-1 = Octene-1

Di-isobutylen = Di-isobutylene

Nonen-1 = Nonene-1

Cyklohexanderivate = Cyclohexane derivatives

Cyklohexan = Cyclohecane

Methylcyklohexan = Methyl cyclohexane

Aethylcyklohexan = Ethyl cyclohexane

o-Dimethylcyklohexan = o-dimethyl cyclohexane

m-Dimethylcyklohexan = m-dimethyl cyclohexane

n-Propylcyklohexan = n-propyl cyclohexane

Bicyklonaphthene = Bicyclo naphthenes

Dekalin = Decaline

Dicyklopentyl = Dicyclopentyl

Cyklohexylcyklopentan = Cyclohexyl cyclopentane

Dicyklohexyl = Dicyclohexyl

Table 27 - Iodine Numbers of Several Otto Fuels (bibl. 62)

Table 28 - Atom or Type of Bond; Refraction Equivalent (for D-Line)

Carbonyl-Sauerstoff = Carbonyl oxygen

Aether-Sauerstoff = Ether-oxygen

Alkohol-Sauerstoff = Alcohol-oxygen

(C = C Doppelbindung) = (C = C double bond)

Table 29 - Distillation Fractions and Refraction in Automobile Benzines

Siedeabschnitt = Fraction

Refraktion = Refraction

Table 30 - Density and Refraction of Automobile Benzines

Wichte = Specific gravity

Refraktion = Refraction

Table 31 - d, nD and Molecular Weight of Pure Hydrocarbons

Paraffine = Paraffins

Mol.-Gewicht = Molecular weight

Olefine = Olefins

Naphthene = Naphthenes

Aromaten = Aromatic compounds

Table 32 - Correlation of Mole Parachor (P) to Mole Weight (M) for Individual Hydrocarbon Groups

Mol.-Gewicht = Molecular weight

Werte fuer den Molparachor = Values for the mole parachor

Paraffine = Paraffins

Olefine, 1 Doppelbindung = Olefins, one double band

6-Ring-Naphthene = 6-ring naphthenes

Benzolhomologe = Benzene homologues

Naphthalinhomologe = Naphthalene homologues

Table 33 - Correlation of the Specific Parachor (P) to the Molecular Weight (M) for Individual Hydrocarbon Groups; Isoparaffins as Compared to n-Paraffins Will Slightly Decrease the Specific Parachor

Aromaten Benzol-Homologe = Aromatic benzene homologues

Aromaten Naphthalin-Homologe = Aromatic naphthalene homologues

Other captions same as Table 32

Table 34 - Octane Number and Cetane Number in Interrelation

Oktanzahl = Octane number

Cetanzahl = Cetane number

OZ = OR

CaZ = CaR

Table 35a - Research Octane Numbers, Engine Octane Numbers, and Reference Fuels in the IG Testing Engine

ROZ = Research octane number

MOZ = Engine octane number

Eichbenzin = Reference benzine

Reinbenzol = Pure benzene

oder Vol. °/oo Pb = Or vol. °/oo Pb

Table 35b - Calibration Values of Iso-Octane with Tetraethyl Lead (cc/[illegible]

Oktanzahl = Octane rating

ccm Pb = cc Pb

Table 35c - Calibration Values of Mixtures: Iso-Octane Leaded with Calibration Benzine (Lead Addition Constant 1 cc/l)

Oktanzahl = Octane rating

% Isooktan + Pb = % iso-octane + Pb

% Eichbenzin + Pb = % calibration benzine + Pb

Table 36a -

K-Werte = K-values

Oktan-Zahl = Octane number

[illegible] = [illegible]

Table 36b -

Anzahl der C-Atome = Number of C-atoms

Oktanzahlen = Octane numbers

n-Paraffine = n-paraffins

Methyl = Methyl

Dimethyl = Dimethyl

Trimethyl = Trimethyl

Tetramethyl = Tetramethyl

Table 37 - Characteristics of Kerosene and Diesel Fuel (Gas Oil) of Petroleum Products

Flammpunkt = Flame point

Stockpunkt = Stock point

SB = Initial distillation

SE = End of distillation

SKZ = Boiling characteristic

% Arom. + Ung. = % aromatic + unsaturated compounds

Anilinpunkt = Aniline point

Cetanzahl = Cetane rating

Petroleum, rumaen. = Petroleum, Rumanian

Petroleum, amerik. = Petroleum, American

Gasoel, rumaen. = Gas oil, Rumanian

Gasoel, amerik. = Gas oil, American

Gasoel, deutsch = Gas oil, German

Spalt-Diesel = Cracked gas oil

Table [illegible] - Characteristics of Typical Carbonization-Tar Fuels Compared to Refined Products of the IG High-Pressure Hydrogenation

Braunkohlenschwelteer-Diesel Treiboele = Lignite-carbonization tar Diesel fuels

Braunkohlen-Dieseloele durch Hochdruckhydrierung = Lignite Diesel fuels obtained in High-pressure hydrogenation

% Arom. + Ung. = % aromatic + unsaturated compounds

Dieselindex = Diesel index

SKZ = Boiling characteristic

SDK = Boiling/density coefficient

Cetanzahl = Cetane rating

Table 39a - Kogasin Diesel Oils

% Arom. + Ung. = % aromatic + unsaturated compounds

SKZ = Boiling characteristic

Dieselindex = Diesel index

Cetanzahl = Cetane rating

Table 39b - Blend of Lignite Oil with Kogasin (bibl. 102)

Zusatz von Kogasin II = Addition of Kogasin II

SKZ = Boiling characteristic

Cetanzahl = Cetane rating

Table 40 - API and d/15.6

Table 41 -

Erdoeldieseloel = Petroleum Diesel oil

o.H. = Upper calorific value

u.H. = Lower calorific value

Diff. = Difference

Braunkohlendieseloel = Lignite Diesel oil

Steinkohlendieseloel = Anthracite Diesel oil

Table 41a - Number of Isomers of Cyclic Hydrocarbons

C-Atome im Ring = C-atoms in the ring

Zahl der C-Atome in den Seitenketten = Number of C-atoms in the side branches

Benzolhomologe = Benzene homologues

Naphthalinhomologe = Naphthalene homologues

Anthracenhomologe = Anthracine Homologues

Phenanthrenhomologe = Phenantrene homologues

Table 42 - Characteristics of Pure Hydrocarbons in the Boiling Range of Heavy Fuels

Paraffine = Paraffins

n-Oktan = n-octane

n-Nonan = n-nonane

n-Dekan = n-decane

n-Undekan = n-undecane

n-Dodekan = n-dodecane

n-Tridekan = n-tridecane

n-Tetradekan = n-tetradecane

n-Pentadekan = n-pentadecane

n-Hexadekan - Cetan = n-hexadecane = cetane

n-Heptadekan = n-heptadecane

n-Oktadekan = n-octadecane

n-Nonadekan = n-nonadecane

n-Eicosan = n-eisocane

n-Heneicosan = n-heneicosane

n-Nonadekan = n-nonadecane

n-Eicosan = n-eicosane

n-Heneicosan = n-heneicosane

S.P. = BP

Smp. = Melting point

Viskositaet = Viscosity

Olefine = Olefins

1-Okten = 1-octene

1-Nonen = 1-nonene

1-Deken = 1-decene

1-Undeken = 1-undecene

1-Dodeken = 1-dodecene

1-Trideken = 1-tridecene

1-Pentadeken = 1-pentadecene

1-Heptadeken = 1-heptadecene

1-Heneikosen = 1-heneicosene

Naphthene = Naphthenes

Alkyl-Cyclopentane und Cyklopentene = Alkyl cyclopentanes and cyclopentenes

Oktyl-Cyklopentan = Octyl cyclopentane

| | | |
|---|---|---|
| Oktyl-Cyklopenten | = | Octyl cyclopentene |
| Decyl-Cyklopentan | = | Decyl cyclopentane |
| Decyl-Cyklopenten | = | Decyl cyclopentene |
| Dodecyl-Cyklopentan | = | Dodecyl cyclopentane |
| Dodecyl-Cyklopenten | = | Dodecyl cyclopentene |
| Tetradecyl-Cyklopentan | = | Tetradecyl cyclopentane |
| Tetradecyl-Cyklopenten | = | Tetradecyl cyclopentene |
| Hexadecyl-Cyklopentan | = | Hexadecyl cyclopentane |
| Hexadecyl-Cyklopenten | = | Hexadecyl cyclopentene |
| Alkyl-Cyklohexane | = | Alkyl cyclohexane |
| Butyl Cyklohexan | = | Butyl cyclohexane |
| Amyl-Cyklohexan | = | Amyl cyclohexane |
| Hexyl-Cyklohexan | = | Hexyl cyclohexane |
| Heptyl-Cyklohexan | = | Heptyl cyclohexane |
| Dodecyl-Cyklohexan | = | Dodecyl cyclohexane |
| Tetradecyl-Cyklohexan | = | Tetradecyl cyclohexane |
| Hexadecyl-Cyklohexan | = | Hexadecyl cyclohexane |
| Aromaten | = | Aromatic compounds |
| Alkylbenzole | = | Alkyl benzines |
| Aethylbenzol | = | Ethyl benzene |

Styrol = Styrene

Hydrinden = Hydrindene

Inden = Indene

Durol = Durene

Dekalin = Decalin

Tetralin = Tetralin

Naphthalin = Naphthalene

α -Methylnaphthalin = α -methyl naphthalene

β -Methylnaphthalin = β -methyl naphthalene

Dimethylnaphthaline = Dimethyl naphthalene

Acenaphthen = Acenaphthene

Fluoren = Fluorene

Phenanthren = Phenanthrene

Anthracen = Anthracene

Diphenyl = Diphenyl

Diphenylmethan = Diphenyl methane

Diphenylpropan = Diphenyl propane

Diphenylbutan = Diphenyl butane

Diphenylbuten = Diphenyl butene

Diphenyloktan = Diphenyl octane

Propylbenzol = Propyl benzene

Butylbenzol = Butyl benzene

Amylbenzol = Amyl benzene

Hexylbenzol = Hexyl benzene

Heptylbenzol = Heptyl benzene

Oktylbenzol = Octyl benzene

Dodecylbenzol = Dodecyl benzene

Tetradecylbenzol = Tetradecyl benzene

Hexandecylbenzol = Hexadecyl benzene

p-Alkyl-toluole = p-alkyl toluenes

Aethyltoluol = Ethyl toluene

Propyltoluol = Propyl toluene

Butyltoluol = Butyl toluene

Amyltoluol = Amyl toluene

Hexyltoluol = Hexyl toluene

Heptyltoluol = Heptyl toluene

Oktyltoluol = Octyl toluene

Decyltoluol = Decyl toluene

Dodecyltoluol = Dodecyl toluene

Tetradecyltoluol = Tetradecyl toluene

Diphenylokten = Diphenyl octene

Diphenyldodeken = Diphenyl dodecene

diphenylhexadekan = Diphenyl hexadecane

Diphenylhexadeken = Diphenyl hexadecene

Sauerstoff-, Stickstoff- und Schwefelverbindungen in Teeroel = Oxygen, nitrogen, and sulfur compounds in tar oil

Name = Name

Formel = Formula

Siedepunkt = Boiling point

Schmelzpunkt = Melting point

Cumaron = Coumarone

Phenol = Phenol

o-Kresol = o-cresol

m-Kresol = m-cresol

Methylcumaron = methyl coumarone

Acetophenon = Acetophenone

Xylenole = Xylenols

α-Naphthol = α-naphthol

β-Naphthol = β-naphthol

α-Picolin = α-picoline

β-Picolin = β-picoline

Lutidine (Dimethylpyridine) = Lutidine (dimethyl pyridine)

Collidin (Trimethylpyridin) = Collidine (trimethyl pyridine)

Anilin = Aniline

Benzonitril = Benzonitrile

Tetramethylpyridin = Tetramethyl pyridine

Chinolin = Quinoline

Isochinolin = Isoquinoline

Methylchinolin = Methyl quinoline

Indol = Indene

Dimethylchinoline = Dimethyl quinolines

Methylindole = Methyl indenes

Carbazol = Carbazole

Acridin = Acridine

Thionaphthen = Thionaphthene

Diphenylensulfid = Diphenyl sulfide

Table 43 - Viscosity in Centistokes and Engler Degree

von hier ab gelten folgende Beziehungen = From here, the following relations apply:

Table 44 - Aniline Points in the Molecular Range $C_9$ - $C_{20}$

Molekulargroesse, Anzahl der C-Atome = Molecular size, number of C-atoms

Reine Kohlenwasserstoffe = Pure hydrocarbons

Paraffine = Paraffins

Naphthene = Naphthenes

Olefine = Olefins

α-Methylnaphthalin = α-methyl naphthalene

Cyklo-Olefine = Cyclo-olefins

Dieseloel = Diesel oil

Table 45 – Aniline Point (AP) and Aromatic Compounds with Unsaturated Compounds (% A + U) in Diesel Fuels (B, H, E, K)

Olefine = Olefins

Table 46 – Specific Parachor and Specific Gravity of Diesel Oils

Wichte = Specific gravity

Spez. Parachor = Specific parachor

Table 48 – Boiling Range and Refraction of Diesel Fuels

Siedeschnitt = Fraction

Refraktion = Refraction

Table 49a – Specific Gravity and Refraction of Diesel Fuels

Table 50 – Starting and Ignition-Lag Cetene Ratings in the HWA Diesel Engine

Anlass-CeZ = Starting cetene rating

Zuendverzug CeZ = Ignition-lag cetene rating

Table 51a – Ring Experiments for Comparative Suitability Tests of Diesel Fuels, as Ordered by the RVM. The Table Contains the Cetene Numbers of Diesel Fuels Nos. 1 – 30; the Following Symbols are Used:

$A_1$ = Starting method in original form

$A_2$ = Misfire method

$A_3$ = Starting method RWA

$Z_1$ = Ignition-lag method (IGF), fixed ignition lag

$Z_2$ = Ignition-lag method DVL

$Z_3$ = Ignition-lag method (AW Schmidt), stationary compression

Verfahren = Method

Motor = Engine

Dieselkraftstoff Nr. = Diesel fuel No.

Table 51b – Ring Experiments of the IG, Cetane Ratings of 7 Diesel Fuels in 14 Test Engines, in which 10 Ignition-Lag Methods and 4 Starting Methods were Used

Verfahren = Method

Motor = Engine

Versuchsstelle = Testing station

Kraftstoff = Fuel

Zuendverzugverfahren = Ignition-lag method

Anlassverfahren = Starting method

Table 51c – Cetane Ratings According to the Ignition-Lag Method (Schmidt)

Nr. = No.

Kennzahlen der Dieselkraftstoffe = Characteristics of Diesel fuels

Visk. = Viscosity

Fmp. = Flame point

Stp. = Stock point

Fester Zuendverzug = Fixed ignition lag

IG Motor = IG engine

Kamm Motor = Kamm engine

Variabler Zuendverzug = Variable ignition lag

Slow.-Motor = Slowak engine

Table 52 - Important Engine Characteristics for the Test-Stand Engines Used for Diesel-Oil Experiments

IG-Diesel = IG Diesel

Schmidt-Slowak-Diesel = Schmidt-Slowak Diesel

Motorenwerke Mannheim = Engine Works in Mannheim

Waukesha-Wisconsin = Waukesha, Wisconsin

Humboldt-Deutz = Humboldt in Deutz

Slowak = Slowak

Drehzahl, U/min = Rotational speed, rpm

Bohrung = Bore

Hub, mm = Stroke

Hubraum, Liter = Swept volume, liter

Verdichtung = Compression

Einspritzdruck, atue = Injection pressure, atm (gage)

Temperatur Ansaugluft = Temperature intake air

Temperatur Kuehlwasser = Temperature cooling water

fest = Fixed

Table 53 - Cetane and Cetene Ratings of Diesel Fuels of Arbitrary Origin with Boiling Coefficient 300, Calculated from the Specific Gravity According to Heinze and Marder

Table 54 - Cetane Ratings of Diesel Oils from Specific Gravity d/20 and Boiling Coefficient (According to Heinze and Marder)

Wichte = Specific gravity

Cetanzahlen = Cetane ratings

Table 55 - Cetane Ratings of Diesel Oils from Viscosity and Specific Gravity (bibl. 138)

Viskositaet = Viscosity

Wichte = Specific gravity

Table 56 - Cetene Ratings and Diesel Index of Diesel Oils with Boiling Coefficient 300

Table 57 - Cetene Ratings and Specific Parachor of Diesel Oils, Boiling Coefficient 300

Table 58 - Comparison of Cetene Ratings from Engine and Laboratory Testing Methods (According to Kessler)

Verfahren = Method

Dieselkraftstoff Nr. = Diesel fuel No.

Anlassverfahr. = Starting method

Zuendverzug = Ignition lag

Marder Verf. = Marder method

Jentzsch = Jentzsch

## Table 59 - Ignition Acceleration by 2% Peroxide Additions to Heavy Diesel Fuels (According to Schmidt and Mohry), Ignition lag °KW

Verdichtungsverhaeltnis = Compression ratio

Braunkohlenschweloel allein = Lignite carbonization oil, alone

Dimethylperoxyd = Dimethyl peroxide

Diaethylperoxyd = Diethyl peroxide

Diacetondiperoxyd = Diacetone diperoxide

Monoperparaldehyd = Monoperparaldehyde

Acetylbenzoylperoxyd = Acetyl benzoyl peroxide

Tetralinperoxyd = Tetralin peroxide

Steinkohlenschweloel = Anthracite carbonization tar

Erdoel Dieselkraftstoff = Petroleum Diesel fuels

also unwirksam = i.e., ineffective

hier unwirksam = Ineffective in this case

## Table 60 - Ignition Acceleration by Various Dopes in Diesel Fuels (According to Heinze, Marder, and Veidt)

Spaltgasoel = Cracked gas oil

Zusatz = Additive

Braunkohlenoel = Lignite oil

Steinkohlenschweloel = Anthracite carbonization oil

Amylnitrat = Amyl nitrate

Amylnitrit = Amyl nitrite

| | | |
|---|---|---|
| Aethylnitrat | = | Ethyl nitrate |
| Tetralinperoxyd | = | Tetralin peroxide |
| Nitrosomethylurethan | = | Nitrosomethylurethane |
| Diaethyltetrasulfid | = | Diethyl tetrasulfide |
| Trinitrotoluol | = | Trinitrotoluene |
| Benzoylaceton | = | Benzoyl acetone |
| Cyclohexanonoxim | = | Cyclohexanonoxim |
| Nitrosodimethylanilin | = | Nitrosodimethyl aniline |

Table 61 - Temperature Degrees

| | | |
|---|---|---|
| Abs. Temp. | = | Absolute temperature |

Table 62 - Density and API Degrees (Specific Weight 60°F/60°F = 15.6°C)

Table 63 - Viscosity Degrees

| | | |
|---|---|---|
| Kinem. Visk. | = | Kinematic viscosity |
| Grad Engler | = | Degree Engler |
| Saybolt Sek. | = | Saybolt sec |
| Redwood Sek. | = | Redwood sec |
| Weiterhin gelten folgende Umrechnungsformeln: | = | In addition, the following conversion formulas apply: |
| Diese Umrechnungsformeln sind oberhalb einer Zaehfluessigkeit von 50 cSt brauchbar | = | These conversion formulas can be used above a viscosity of 50 cts. |

Table 64 - Tank and Barrel Capacity

If d denotes the diameter, r the radius, and h the height, the capacity of cylindrical tanks is calculated as follows:

$$r^2 \pi h = \left(\frac{d}{2}\right)^2 \pi h$$

In partially filled upright cylinders, the charge is simply determined by plumb lines. In partially filled horizontal cylinders (tank cars, horizontal tanks) the level of the liquid s with respect to the cylinder diameter z is determined by plumb lines and the factor f is read from the following table for the quotient s/d. The total capacity I of the cylinder multiplied by f will then furnish the corresponding charge.

If d denotes the diameter of the barrel bottom in bulging barrels, and D the diameter of the bulge, the content of the barrel will be as follows:

$$\pi h (2 D^2 + d^2)/12$$

The capacity of spherical vessels will then be $0.5236 \, d^3$.

Table 65 – Logarithmic Table with Four-Place Mantissa

Nat. Zahl = Natural logarithm

Table 66 – Engine Data

Verdichtung = Compression

Drehzahl (U/min) = Rotational speed (rpm)

Kolbengeschw. = Piston speed

Arbeitsdruck = Working pressure

Hubraumleistung = Piston-displacement power

Leist.gew. kg/PS = Power weight kg/hp

Brennstoffverbrauch g/PSh = Fuel consumption g/hp/hr

Wirk.grad = Efficiency

Ottomotoren = Otto-cycle engines

Kraftraeder = Motorcycles

2 Takt, bis 250 ccm = 2-stroke, up to 250 cc

ob. gesteuert = Top control

unten gesteuert = Bottom control

[illegible] = Racing car

Personenwagen = Automobile

Sportmodelle = Sports models

Rennmodelle = Racing models

Lastkraftwagen = Truck

Flugmotoren = Aircraft engines

luftgekuehlt, 200 PS = Air-cooled, 200 hp

wassergekuehlt = Water cooled

Schnellflugzeuge = High-speed aircraft

Gluehkopfmotoren = Glow mixed-cycle engines

Dieselmotoren = Diesel engines

in LKW und Triebwagen = In trucks and railroad engines

in Flugzeugen = In aircraft

in Luftschiffen = In airships

in ortsfesten Anlagen u. auf Schiffen = In stationary systems and on ships

Kolbendampfmaschinen = Piston steam engines ortsfest = Stationary

Lokomotiven = Locomotives

Dampfturbine = Steam turbine

Wasserturbine = Water turbine

Elektromotor = Electromotor

Fig. 1 - Mixed Octane Numbers

falsche Interpolation = Wrong interpolation

Benzol = Benzene

i-Paraffin = i-paraffin

Polymerbenzin = Polymeric benzine

Zusatz = Addition

Fig. 2 - Boiling Curve of Alcohol-Free and Alcohol-Containing Benzine

Siedetemperatur = Boiling temperature

Menge Destillat = Amount of distillate

Fig. 3 - Q-Fluid Addition to Knocking Benzines for Producing Octane Ratings of 74

Oktanzahl = Octane number

Fig. 4a - Oppau Alignment Chart

Oktanzahl = Octane number

ccm Bleitetraaethyl/Liter = cc tetraethyl lead/liter

Fig. 4b - Mathematical Lead Sensitivity (According to Hammerich)

Ethylfluid = Ethyl fluid

$E_n$ CFR Motor-Methode = $E_n$ CFR engine method

Ordinate: Gehalt an Bleitetraaethyl in Vol % = Ordinate: content in tetraethyl lead in vol %

Nullpunkt Research Methode = Origin research method

Nullpunkt Motor Methode = Origin engine method

Abscisse Research Methode = Abscissa: research method

Abscisse: Erhoehung der $OZ_0$ in % = Abscissa: increase in octane rating $CR_0$ in %

~~Abscisse: Motor-Methode~~ = Abscissa: engine method

Motor-Methode = Engine method

Research-Methode = Research method

$cm^3$ in U.S. Gallons = $cm^3$ in US gallons

Fig. 5 - Power Increase and Fuel Consumption in Aircraft Engines with Fuels of Increased Octane Number

Leistungssteigerung = Power increase

Kraftstoffverbrauch = Fuel consumption

g/PS/h = g/hp/hr

OZ = CR

Fig. 6 -

F = Aviation benzine
A = Automobile benzine
BA = Benzine-alcohol mixture
BB = Benzine benzene
S = Heavy benzine
P = Petroleum

Siedemengen = Distillation quantities

Fig. 7 - Evaporation Curves of Several Light Fuels

Normalbenzin = Ordinary benzine

Reinbenzol = Pure benzene

Alkohol, abs. = Alcohol, abs.

Leunabenzin + 20% Alkohol = Leuna benzine + 20% alcohol

Leunabenzin = Leuna benzine

Verdunstungszeit b.45°C, 80 mm Hg n. Wawrzinick = Evaporation period at 45°C, 80 mm Hg according to Wawrzinick

Fig. 8 - Vapor-Pressure Curves of Several Liquid Substances

Oktan = Octane

fluessige Phase = Liquid phase

Wasser = Water

Aethanol = Ethanol

Benzol = Benzene

Hexan = Hexane

Pentan = Pentane

Aether = Ether

Dampf phase = Vapor phase

Fig. 9 - Vapor-Pressure Curves of Several Fuels

Fig. 10 - Apparatus for Determining the Saturation Pressure (According to Wawrzinick)

Fig. 11 - Apparatus According to Stelling, Freeze-Point Determination by Ether Evaporation

Fig. 12 - Sulfur Determination according to Grote and Krekeler

zur Pumpe = To the pump

Fig. 13a - Aniline Point and Boiling Points or Boiling Cross Sections of Hydrocarbons and Their Mixtures

Dekalin = Decaline

Schwelbenzin = Carbonization benzine

Benzin-Benzol-Gemische = Benzine-benzene mixtures

Cykloolefine = Cyclo-olefins

Naphtene = Naphthenes

Autobenzine = Automobile benzines

n-Paraffine = n-paraffins

i-Paraffine = i-paraffins

Fig. 13b - Diagram by Garner for Determining the Naphthene Content of Benzines

Siedepunkte = Boiling points

Paraffine = Paraffins

Naphtene = Naphthenes

Fig. 14 - Boiling Level and Refraction of Hydrocarbons and Automobile Benzine

Aethanol = Ethanol

n-Paraffine = n-paraffins

Isoparaffine = Isoparaffins

Olefine = Olefins

Cykloparaffine = Cycloparaffins

60% Benzin + 40% Benzol = 60% benzine + 40% benzene

Cykloolefine = Cyclo-olefins

Aromaten = Aromatic compounds

Fig. 15a - Combustion Course at Knock-Free and Knocking Combustion (according to Schnauffer)

nicht klopfend = Not knocking

klopfend = Knocking

Fig. 15b - Pressure-Time Diagram of Knocking and Knock-Free Combustion in the Otto-Cycle Engine

oberer Totpunkt = Top center

klopfend = Knocking

nicht klopfend = Knock-free

unterer Totpunkt = Bottom center

Fig. 16 - Influence of Mixture Preheating on Power of the Otto-Cycle Engine (according to Hubendick)

Luftmangel = Air deficiency

Luftueberschuss = Air excess

Fig. 17 - Influence of Operating Conditions on Engine Knocking (according to Singer)

Klopffestigkeit = Knock resistance

wird groesser = Becomes larger

wird kleiner = Becomes lower

um Oktanwerte = By octane values

U/min = rpm

Verdicht.-Verhaeltnis = Compression ratio

Vorzuendung = Preignition

Belastung = Load

Luftfeuchtigk. = Air humidity

Lufttemperatur T (Kuehlung) = Temperature T (cooling)

Luftueberschuss = Air-excess coefficient

Fig. 18 - Bouncing-Pin Apparatus with Adjustable Bar Spring

1 Steel membrane
2 Bouncing pin
3 Rod spring
4 Bouncing-pin contact
5 Countercontact
6 Slotted screw
7 Knurled screw
8 Ring screw
9 + contact
10 Ground contact
11 Protective hood

Fig. 19a - Knock Indication by Cathode-Ray Oscillograph (according to Wawrzinick)

Fig. 19b - Oscillogram (According to Wawrzinick)

Klopfen = Knocking

T.P. = Dead center

Fig. 20a - Oscillogram (According to Schmidt and Generlich)

Iso-Oktan = Iso-octane

Normal Heptan = Normal heptane

Dollberger Benzin = Dollberg benzine

Standard Benzin = Standard benzine

Krackbenzin = Cracked benzine

Fig. 20b - Oscillogram (According to Schmidt and Generlich)

Standard-Benzin = Standard benzine

10% Benzol = 10% benzene

Fig. 21 - Knock Intensity and Boost (According to Schmidt)

Fig. 22 - Critical Values for Knocking (According to Seeber)

Verdichtungsverhaeltnis = Compression ratio

Luftueberschuss = Air excess

Fig. 23 - $n_D$ of Benzine and Pure Benzene Blends

Fig. 24 - Boiling Curves of Petroleum (P) and Gas Oil (G,H)

n-Paraffine = n-paraffins

Naphtene = Naphthenes

Aromaten = Aromatic compounds

Fig. 25 - Nomogram by Beale and Docksey

Abgelesene Siedetemp. bei jeweil. Vakuum mm HS = Read boiling temperature at corresponding vacuum mm Hg berichtigte Siedetemperatur auf 760 mm QS = Corrected boiling temperature to 760 mm Hg

Vakuum mm QS = Vacuum mm Hg

Fig. 26a - Filterability of Diesel Oils at Low Temperatures (According to Hagemann and Hammerich)

Fig. 26b - Filterability of Diesel Fuels (According to HWA and Hammerich)

Fig. 27 - Conradson Coking Test

Fig. 28 - Heat Value (cal/ℓ or cal/kg) of Heavy Fuels

cal u. H = Calorie, lower calorific value

Fig. 29 - Relations between Boiling Cross Section (BC), Aniline Point, Refraction, Density, and Cetane Rating according to Harder in Fractionation of Diesel Fuels (According to Kadmer)

Anilin Punkt = Aniline points

Cetanzahlen = Cetane ratings

Fig. 30 - Pressure Curve (p) and Ignition Lag (Z,Z') in a Diesel Engine

ob. Totpunkt = Top center

Fig. 31 - Decrease of Ignition Lag with Increase in Compression

Kompression = Compression

Fig. 32 - Engine Cetane Rating (EOR) and Cetane Rating (CaR)

CaZ = CaR

= ECR

Fig. 33 - Ratio of Suction Subpressure and Cetene Number in HWA Test Diesel (Compression Constant 1 : 14.5)

Saugunterdruck = Suction subpressure

Cetenzahl = Cetene No.

Fig. 34 - Calibration Diagram IG Test Diesel (Ignition Constant 13° [illegible])

Cetanzahl = Cetane rating

Verdichtungsstellung = Compression setting

Fig. 35 - Density of Cetene Number (CFR Method) of Diesel Oils (According to Heinze and Marder)

Cetenzahl = Cetene No.

Fig. 36 - Cetene-Number Nomogram by Tannenberger

Fig. 37 - Family of Curves of the Boiling Characteristic 200 - 330 in the Field between $d_{20}$ CeR (According to Heinze and Marder)

Cetenzahl = Cetene No.

Fig. 38 - Nomogram by Best (bibl. 143)