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CHEMICAL-PHYSICAL CONCEPTION OF OVERLOAD PROPERTIES OF FUELS

From a lecture by Dr. H. Fromherz at DVL.

        The contents of this lecture are a short survey of two research paths at the I.G. Ludwigshafen high pressure experimental department.

   I. The Theoretical Explanation of Knock Limit Curves.
       (Jointly with Dr.v.Muffling and Dr. Nonnenmacher)

        It was intended to learn theoretically the inner connections between the position, shape and temperature relationship of the knock limit curve of the different kinds of motor fuels.

        Our theoretical explanation of the characteristic shape of the knock curves was based on the well known assumption, that the highest temperature in the unburned part of the cylinder charge was the cause of the beginning of knocking. This varies with changes in the temperature of the air of the charge, and the excess air number, λ, and can be computed from the final compression and combustion temperatures. When the knock limit curves are determined, changes in the maximum temperature are compensated in relation to λ in such a way by a corresponding change in the pressure of the charge, that knocking is just reproduced. Should the temperature and pressure relationships be known for the characteristic chemical reactions here involved, the knock limit curves could be calculated on the strength of these relationships. The knock limit curves for two very different hydrocarbons, iso-octane and benzol, which differ very greatly in their behavior in motors, were calculated in this way from the temperature and the pressure relationships of the self ignition reactions, in relation to the excess air number, λ, and for different air charging temperatures. The calculated curves exhibit a number of regularities:

   1.) With benzol the curves are appreciably steeper than
        with iso-octane.

   2.) When the temperature of the air of the charge is
        raised, the pressure of the charge increases
        more with benzol than with iso-octane.

   3.) The minimum of the knock curves is at a minimum
        air charge temperature of 80° C with the value
        of λ around 1.1, and with a higher value of
        in case of iso-octane than for benzol. The
        minimum is shifted with benzol towards lower
        values of λ at raised air charge temperature,
        with iso-octane towards higher λ values.

4.) The limiting knock curves are in general steeper at higher air charge temperatures, i.e. the limiting pressures are more strongly displaced in the range of excess of air, than in the richer range.

The characteristic course of the calculated curves agrees therein largely with the experimental curves. A number of simplifying assumptions have been made in order to make the computations, but the agreement indicates that the basic theory describes the actual conditions approximately correctly. On this basis, the characteristic properties of knock limit curves of substances differing chemically can be derived as a first approximation solely from the changes in the temperature of mixtures of fuel and air during the compression and combustion with different proportions of fuel:air, and the air temperature, and without any additional assumptions on the reaction mechanism of the different fuels. These conceptions permit one to understand the differences in the knock limit curves with changeable and constant ignition, and the knock limit curves with large overlapping time of valve opening.

II. Calculation of Knock Limit Curves of Fuels from the Octane Number of Gasoline and from the Aromatics Content (and Naphthene Content).

Section I shows the possibility of explaining the important regularities of the limiting knock curves entirely from considerations of temperature, and without the assumption of special reaction mechanisms. As a result, the overload behavior of mixed fuels can be calculated from the behavior of the individual compo- nents by using the rule of mixtures. This can indeed be done with an accuracy of $\mp$ 1 atm. in p_{me} for the maxima and minima of knock limit curves.

We may summarize the general rules for these calculations as follows:

1.) The maxima and minima of the limiting knock curves, in particular of the aromatic fuels, are formed (as a first approxima- tion) in accordance with the law of mixtures from the knock limit curves of the aromatic components and the knock limit curve of the residual gasoline (or the iso-octane and the residual gasoline).

2.) The maxima and minima of the knock limit curve of the residual gasoline is on a curve parallel to its motor octane number iduled by some empirical relationship.

These general rules leave out of consideration details of the effects of the naphthene contents of a residual gasoline, or the difference in behavior of the individual aromatics.

Effects of the Naphthene Content.

Were we to replace a certain percentage of naphthenes in a gasoline (for instance, in a residual gasoline) with the same

amount of paraffinic gasoline of the same octane number (by the motor method) as of the naphthenes removed, the knock limit curve will be changed as follows:

    a) p_{me} (min.) (with $\lambda = 1.2$) will not be changed, as a first approximation.

    b) p_{me} max. (at $\lambda = 0.8$) will be lowered by 0.65 at. for every 10% naphthene removed and replaced by a paraffinic gasoline of the same octane number.

Different Behavior of the Aromatics.

    A very careful comparison of a large number of corresponding knock limit curves showed certain aromatics of a higher boiling point than toluene to have a better knock behavior in supercharged engines than lower boiling aromatics.

    A detailed investigation permitted us to realize, that aromatics with side chains of at least 2 C atoms in the side chain possessed a particularly favorable overload behavior. The C-C bond between the first and the second carbon atoms in the side chains are known to be the weakest. The presence of such weak spots evidently results in a favorable effect upon the knock and overload behavior, similar to the double bond of the olefines.

. . . .

    The above process of approximate prediction of the knock limit curves and overload behavior from the aromatics content and the antiknock value of the residual gasoline can be used successfully to answer quantitatively the very important practical question of the proportion of suitable materials (iso-octane, alkyl-octane, alcohol gasoline or aromatics) to be added to a given gasoline to bring it up to the C_3 or C quality.

    We may particularly emphasize in conclusion, that the present paper is based on preliminary information, which can not be considered to be based on any well defined laws, and are more in the nature of working hypotheses.

    They offer us nevertheless a now, during war time, some valuable help where it is important to be able to solve quickly important question for the prosecution of the war and to take the proper steps when there is no time to set up any long-term investigations.

/Signed/ Fromherz.

Supplement to Section II, 1) and 2).

Example of Computations for an Approximate Preliminary Computation of $p_{me}(max)$ and $p_{me}(min)$ in Atm. of the Overload Curve of the DVL Process.

The gasoline contains: 40% aromatics,
40% residual gasoline (O.N. 74)
20% iso-octane 100 (O.N. 100)

The octane number of the total residual gasoline (residual gasoline + iso-octane) can be calculated from the law of mixtures as

$$\frac{40 \times 74 + 20 \times 100}{40 + 20} = 82.6$$

The curve in the appendix gives $p_{me}(max) = 16.1$ atm for a gasoline with an octane number 82.6 ($\lambda = 0.8$); and $p_{me}(min) = 10.7$ atm ($\lambda = 1.2$). The values $p_{me}(max) = 32$ and $p_{me}(min) = 13.5$ atm. are always used as the characteristic values for aromatics. The law of addition gives for the maximum and minimum p_{me} of the gasoline,

$$p_{me}(max) = \frac{40 \times 32 + 60 \times 16.1}{100} = 22.5 \text{ atm and } p_{me}(min) =$$

$$= \frac{40 \times 13.5 + 60 \times 10.8}{100} = 11.9 \text{ atm.}$$

actual determination gave $p_{me}(max)$ 23 - 23.5 (extrapol.) and $p_{me}(min) = 11.8$ atm.

The perfect agreement between the calculated and experimental $p_{me}(min)$ is accidental. Section II shows that the limits of error are ± 1 atm in the value of p_{me}.

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Changes of P_{me} (max) and P_{me} (min) of a residual gasoline with the octane number. (motor method)
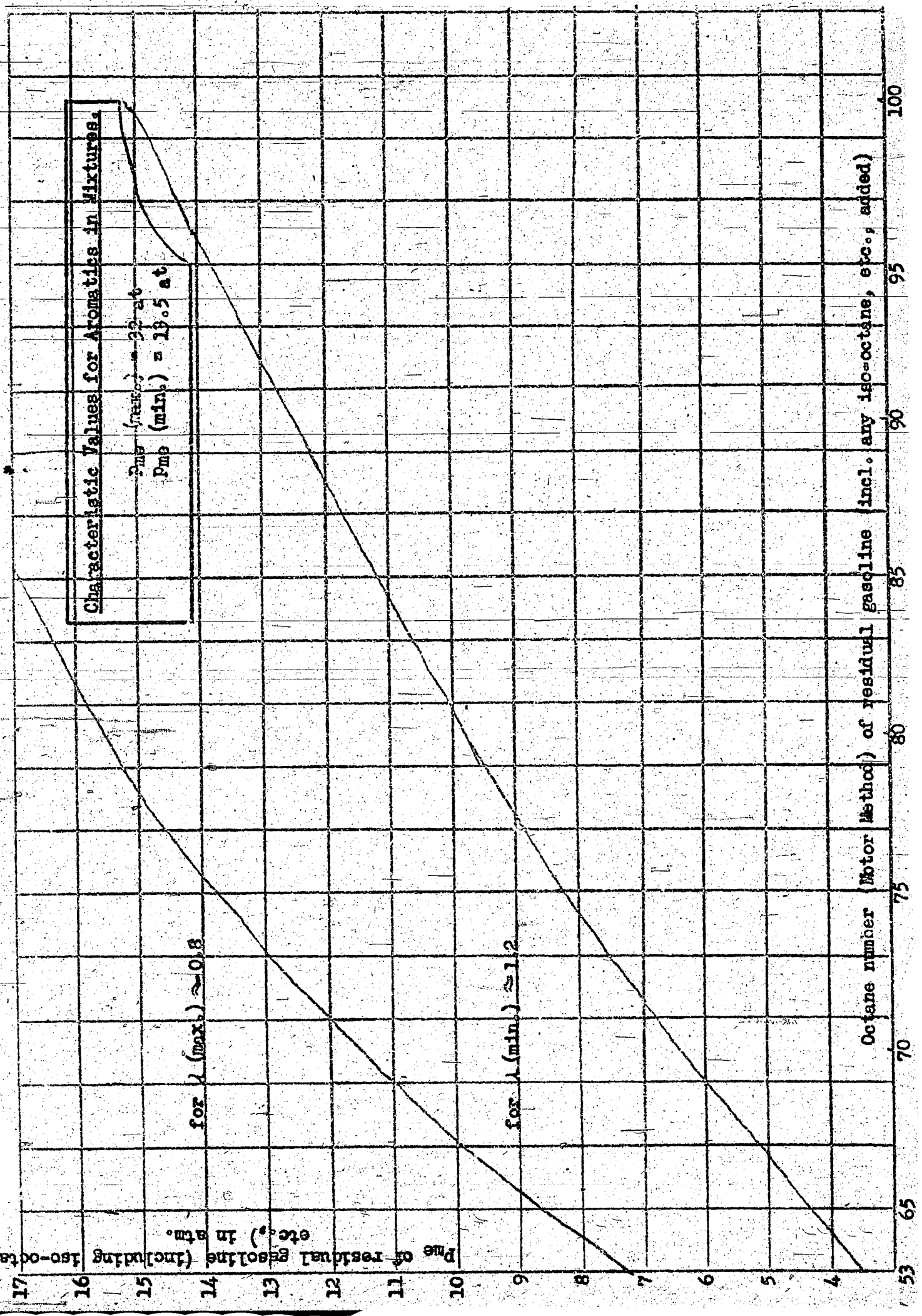
Characteristic Values for Aromatics in mixtures. (values for mixtures)

P_{me} (max.) = 32 at
P_{me} (min.) = 18.5 at

for λ (max.) ≈ 0.8

for λ (min.) $\leqq 1.2$

P_{me} of residual gasoline (including iso-octane, etc.,) in atm.

Octane number (Motor Method) of residual gasoline (incl. any iso-octane, etc., added)

53   65   70   75   80   85   90   95   100

4   5   6   7   8   9   10   11   12   13   14   15   16   17

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