# No. 21.

( Published March 1927 )

# Lower Limit of Inflammability of Ethyl Alcohol, Ethyl Ether, Methyl Cyclohexane and Their Mixtures.

BY

Yoshio TANAKA, *Kôgakuhakusi,*

Member of the Institute,

Yuzaburo NAGAI, *Kôgukusi,*

and

Kinsei AKIYAMA, *Kôgakusi.*

## Abstract.

The authors described the results of their research on the lower limit of inflammability of ethyl alcohol, ethyl ether, methyl cyclohexane and their mixtures in air. The limits were determined in a glass tube of 5 cm. in internal diameter and 65 cm. long, in which inflammable mixtures were ignited from the top by electric spark. The theoretical flame propagation temperatures were also calculated from the lower limits.

The results showed that the lower limit of inflammability of ethyl alcohol, ethyl ether and methyl cyclohexane for open firing are 3 81%, 1.93% and 1.15% respectively, and that the theoretical flame propagation temperature of methyl cyclohexane are nearly the same as those of paraffin hydrocarbons, showing that the naphthene ring has no effect on the theoretical flame propagation temperatures of hydrocarbons. It was also shown that in all mixtu es examined in this reseach, Le Chatelier's rule holds well the deviation being of much the same order as the experimental error.

## Introduction.

One of the important factors, which count for the starting purposes of a motor, is the lower limit of inflammability in air of the fuel used. For the usage of alcohol as a motor fuel, it will be interesting to know the lower limit of inflammability in air of mixtures of ethyl alcohol and blending materials, such as ethyl ether or hydrocarbons.

The present work was undertaken to investigate the lower limits of inflammability of ethyl alcohol, ethyl ether, methyl cyclohexane and their mixtures. Methyl cyclohexane is one of the chief constituents of Japanese gasolines, according to Y. Tanaka and Y. Nagai's investigations.(1)

The results of the experiment show that in these limit mixtures Le Chatelier's rule holds well with a maximum deviation of one per cent., which is much of the same order as the experimental error, and that the theoretical flame propagation temperature of methyl cyclohexane is nearly the same as those of n-hexane or other paraffin hydrocarbons, showing that the naphthene ring has no influence upon the theoretical flame progagation temperature of hydrocarbons.

## Materials.

Methyl cyclohexane used in the present research was isolated by the authors from a gasoline derived from Nishiyama crude oil. It had a boiling point of 100.75—100.0° *C*, $d_{4°}^{19.8°}$ of 0.7543 and $n_D^{19.3}$ of 1.4166.

Ethyl alcohol used was pure absolute alcohol, which was dried over lime and fractionated with a Hempel still-head. It had a boiling point of 78.27° *C*, $n_D^{17.4}$ of 1.3628, $d_4^{15.0}$ of 0.7954 (corresponding

(1) Y. Tanaka and Y. Nagai, Jour. Soc. Chem. Ind. Japan, **27**, 432-446, 817-830, 1924; Jour. Fuel Soc. Japan, **3**, 637-665, 1924.

to ethyl alcohol of 99.42 per cent. by weight) and showed none of reactions of aldehyde. All values for the concentration of vapour of ethyl alcohol in gaseous mixtures, described below, have been corrected for 0.58% of water contained in alcohol used.

Ethyl ether was dehydrated over calcium chloride and metallic sodium for several days and then fractionated with a long Hempel still-head. It had a boiling point of 34.5° C, $d_{4^\circ}^{15.0^\circ}$ of 0 7195 and $n_D^{17.4}$ of 1.3541.

## Apparatus.

According to Coward and Brinsley[1] a gaseous mixture can be said as inflammable *per se* at a stated temperature and pressure, if it will propagate flame indefinitely, the unburned portion of the mixture being maintained at the original temperature and pressure. This definition of inflammability is now adopted, and in order to

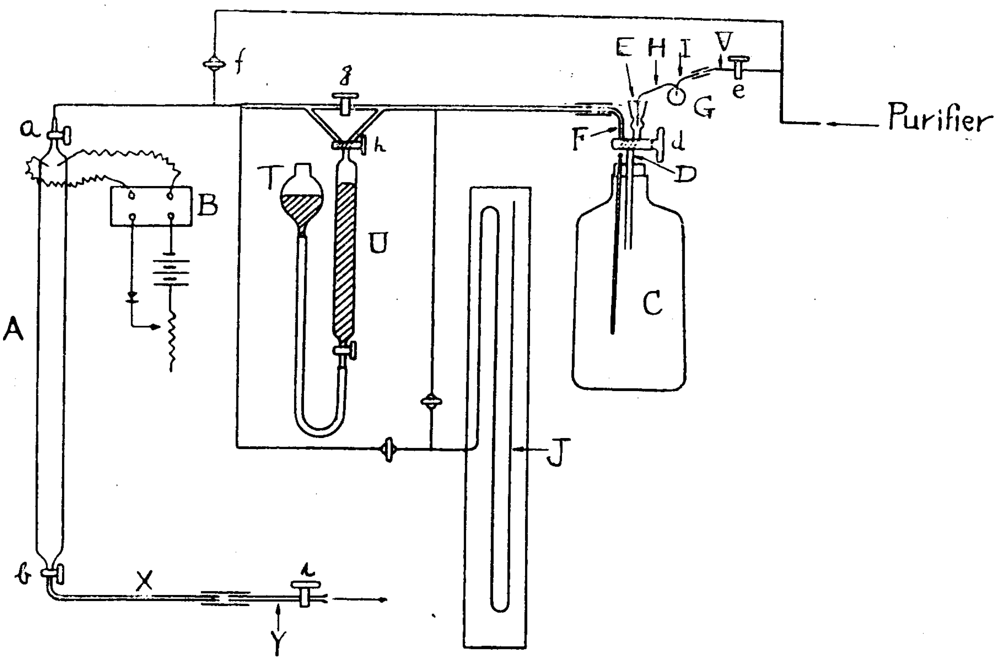


Fig. 1.

(1) Coward and Brinsley, Jour. Chem. Soc., **105** 1859, 1914.

obtain satisfactory results in the estimation of lower limits of inflammability, it is necessary to use a firing tube of such diameter that any cooling of the flame by the wall of the tube can be neglected and, moreover, of sufficient length to eliminate the influence of spark, by which ignition of inflammable mixture is effected, and to enable a sound judgement to be made as to whether a flame would propagate indefinitely or not.

In the present research, the firing tube which is shown by *A* in Fig. I., consisted of a glass tube of 5 cm. in internal diamater and 70 cm. long. Such length was found sufficient, and it can also be seen from the research of A. G. White[1] that the limit values measured in a glass tube of 5 cm. in diameter are almost free from the cooling effect of the wall. The firing tube is closed at both ends by gas-tight stopcocks *a* and *b*, the latter being of one cm. bore. Ignition was effected by passing a spark from an induction coil *B* between two electrodes of platinum wire, which are sealed near the upper end of the firing tube, and separated by an air gap of about 6 mm. The current for the firing was obtained from three of two volt accumulators.

The gaseous mixtures are made in a glass bottle *C* of five litre capacity. The bottle is closed by means of a rubber stopper, through which a mercury thermometer and an arm of the cock *d* are inserted.

The open manometer *J* is made of a glass capillary tube of two mm. in internal diameter and provided by a scale graduated on a mirror. Thus the capillary manometer was used as the free space in the tube of it was negligibly small comparing to that of the bottle *C*.

The outdoor air is purified and introduced to the bottle via a cock *e* and a sample filler *G*, or to the firing tube via a cock *f*.

(1) A. G White, Jour. Chem. Soc., **121**, 1244, 1922.

The purification of air was completed by passing it through alkali solution and soda lime and by drying successively by calcium chloride, conc. sulphuric acid, and phosphorus pentoxide and then by filtering through dried asbestos wool.

The parts of the apparatus connected by glass capillary tubes are shown by single lines.

## Procedure of experiment.

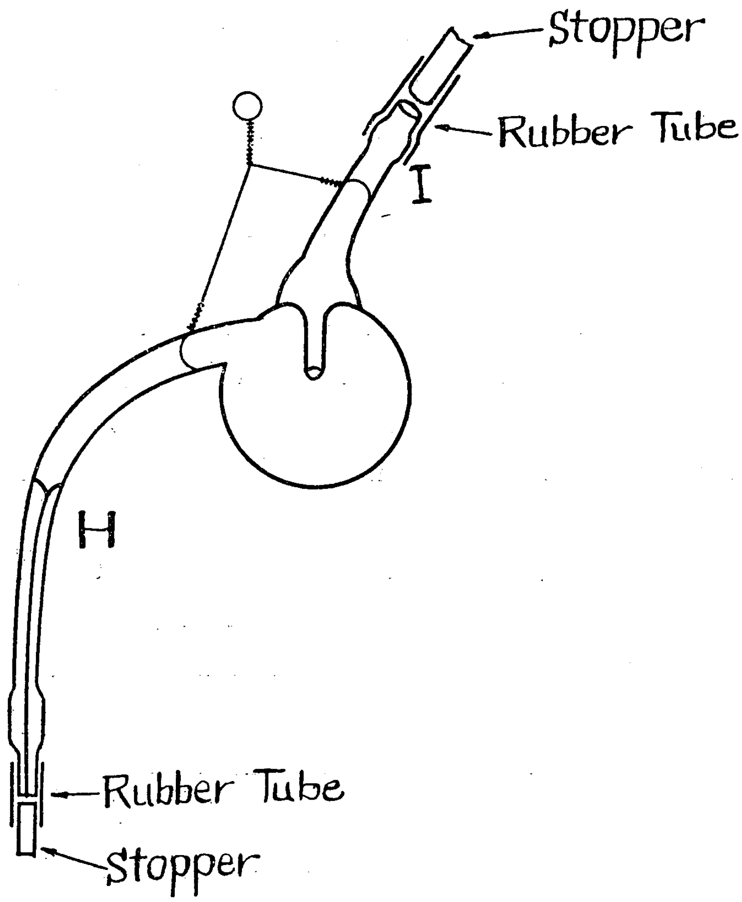


Fig. 2.

The combustible mixture was made by exhausting the bottle and allowing air to sweep a known weight of the combustible liquid from the filler *G* (Fig. 2.), which was of about four cc. capacity. Connection between the arm *H* of the filler and the arm

*E* of the cock *d* was made by a ground-glass joint and furnished with a mercury seal.

When all of the liquid in the filler was evaporated, cock *d* was turned by 180° and the required amount of air was introduced from the tube *F*, pressure in the bottle being read by means of the manometer *J*. When it was necessary to raise the pressure in the bottle up to above atmospheric, cock *g* was closed, and a mercury reservoir *T* was lowered, air being drawn into the glass tube *U*, which was of 35 mm. in diameter and 30 cm. long. Then cock *h* was turned by 180°, mercury reservoir raised, the air in the tube *U* was pressed into the bottle. This procedure was repeated until the required amount of air was introduced. When this was done, the pressure and the temperature of the combustible mixture in the bottle was measured, from which the concentration of vapour of the liquid was calculated, from the volume of the bottle and the molecular weight of the liquid, assuming the gas law. When a mixture of several combustible liquids was evaporated from the filler into the bottle, the mean molecular weight of the mixture was taken for the calculation. In order to obtain the homogeneous gaseous mixture, the bottle was taken appart from the other parts of the apparatus and was shaken, by which the gaseous mixture was stirred up by several blades of aluminium, previously put into the bottle.

After any required mixture was thus made, the bottle *C* was connected to a tube *W* by a rubber tube. The firing tube *A* and the tube connecting *A* and *C* were exhausted and washed several times using a small portion of the gaseous mixture under the test. Then the gaseous mixture was introduced into the firing tube and the pressure in it was made to be higher than the atmospheric by 3 to 4 mm. by means of the tube *U*, as above mentioned. Then the tube *X*, 1 cm in dia., was taken apart from the tube *Y*, cock *b* being opened, and the cock *a* was removed and spark passed to effect the ignition. Observation was made as to whether the flame would propagate down to the lower end of the firing tube. In some measurements, spark was passed, both ends of the firing tube being kept closed. These are specially noted in the following as "closed firing". If noted as "open firing" or not specially remarked, the both ends of the firing tube were opened before ignition, as above described. In all limit mixtures tested, the velocity of flame propagation was about ten cm. per second, and the passage of the flame could de easily followed by eyes. Several observations were repeated with the same gaseous mixture in order to make sure the determination.

The manometer was tapped with the fingers each time before the reading was made. The readings were also corrected for the capillary depression of mercury of the manometer. Another correction was always made for the vapour present in the air above the liquid in the filler.

Thus the errors in the values for lower limits obtained in the present research were kept below 0.5 per cent. The lower limit values of ethyl alcohol and ethyl ether obtained agree very well with those obtained by A. G. White.[1]

## Results of experiment and discussion.

The results obtained in the present investigation are shown in the following tables. In all cases, the temperture of combustible mixtures before the ignition was $19°C \pm 3°$.

---

(1) A. G. White, Jour. Chem. Soc. **121**, 1244, 1922.

## Table I.

Lower Limit of Inflammability of Pure Combustibles in Air and Theoretical Flame Propagation Temperatures.

| Combustible. | Percentage of combustible in lower limit mixtures. | | Theoretical flame propagation temp. °C. |
|---|---|---|---|
| | Open firing. | Closed firing. | |
| Ethyl ether | 1.93 | 1.89 | 1450 |
| Ethyl alcohol | 3.81 | $\ngtr$ 3.80 | 1440 |
| Methyl cyclohexan | 1.15 | $\ngtr$ 1.14 | 1480 |

In the above table, the theortical flame propagation temperature is the calculated temperature of flame propagated in lower limit mixture, the heat loss from the flame being neglected and moreover assuming that the chemical reactions in the flame have been completed. In this calculation, the values for specific heat at constant pressure, obtained by Holborn and Henning[1], were used for nitrogen, carbon dioxide and steam. The molecular value for oxygen was taken to be equal to that of nitrogen.

From Table I, it can be seen that the theoretical flame propagation temperature of methyl cyclohaxane is nearly equal to those of ethyl ether and ethyl alcohol, and that these values are also nearly equal to those[2] given to ethane, pentane and other lower members of paraffin hydrocarbons. This shows that the naphthene ring has very little effect on the theoretical flame propagation temperature of hydrocarbons.

(1) Holborn and Henning, Ann. Physique, **18**, 739, 1905; **23**, 809 1907.
(2) A. G. While, Jour. Chem. Soc., **125**, 2387. 1923.

## Table II.

Lower Limit of Inflammability of Mixtures of Combustibles in Air.

(A) Mixtures of ethyl alcohol and ethyl ether.

| Composition of combustibles in mixture by mol per cent. | | Lower limit. | Percentage of combustibles in limit mixture. | | $\Sigma \frac{n_1}{N_1}$ |
|---|---|---|---|---|---|
| Ethyl alcohol | Ethyl ether. | | Ethyl alcohol. | Ethyl ether. | |
| 100 00 | 0 | 3.81 | 3.81 | 0 | — |
| 82.53 | 17.47 | 3.27 | 2.699 | 0.571 | 1.004 |
| 61.86 | 38.14 | 2 79 | 1.726 | 1.064 | 1.004 |
| 34.95 | 65.05 | 2.34 | 0.818 | 1.522 | 1.003 |
| 0 | 100.00 | 1.93 | 0 | 1.93 | — |

(B) Mixtures of ethyl ether and methyl cyclohexane.

| Composition of combustibles in mixture by mol per cent. | | Lower limit. | Percentage of combustibles in limit mixture. | | $\Sigma \frac{n_1}{N_1}$ |
|---|---|---|---|---|---|
| Ethyl ether. | Methyl cyclohexane. | | Ethyl ether. | Methyl cyclohexane. | |
| 100.00 | 0 | 1.93 | 1.93 | 0 | — |
| 79.89 | 20.13 | 1.70 | 1.358 | 0.342 | 1.001 |
| 57.30 | 42.70 | 1.50 | 0.860 | 0.640 | 1.002 |
| 31.17 | 68.83 | 1.32 | 0.412 | 0.909 | 1.003 |
| 12.81 | 87.19 | 1.22 | 0.156 | 1.064 | 1.006 |
| 0 | 100.00 | 1.15 | 0 | 1.15 | — |

(C) Mixtures of ethyl alcohol and methyl cyclohexane.

| Composition of combustibles in mixture by mol per cent. | | Lower limit. | Percentage of combustibles in limit mixture. | | $\sum \frac{n_1}{N_1}$ |
|---|---|---|---|---|---|
| Ethyl alcohol | Methyl cyclohexane. | | Ethyl alcohol. | Methyl cyclohexane. | |
| 100.00 | 0 | 3.81 | 3.81 | 0 | — |
| 91.04 | 8.96 | 3.18 | 2.895 | 0.285 | 1.008 |
| 74.93 | 25.07 | 2.43 | 1.821 | 0.609 | 1.008 |
| 50.25 | 49.75 | 1.79 | 0.900 | 0.891 | 1.011 |
| 23.26 | 76.74 | 1.39 | 0.323 | 1.067 | 1.012 |
| 0 | 100.00 | 1.15 | 0 | 1.15 | — |

(D) Mixtures of ethyl alcohol, ethyl ether and methyl cyclohexane.

| Composition of combustibles in mixture by mol per cent | | | Lower limit. | Percentage of combustibles in limit mixture. | | |
|---|---|---|---|---|---|---|
| Ethyl alcohol. | Ethyl ether. | Methyl cyclohexane. | | Ethyl alcohol. | Ethyl ether. | Methyl cyclohexane. |
| 47.54 | 30.00 | 22.46 | 2.11 | 1.003 | 0.633 | 0.474 |
| 77.95 | 12.61 | 9.44 | 2.86 | 2.229 | 0.361 | 0.269 |
| 24.87 | 63.20 | 11.93 | 2.01 | 0 500 | 1.271 | 0.240 |
| 27.42 | 17.30 | 55.28 | 1.57 | 0.431 | 0.272 | 0.868 |

In the above tables, $\sum n_1/N_1$ is the left side of the equation of the Le Chatelier's rule, which is

$$\frac{n_1}{N_1}+\frac{n_2}{N_2}+\cdots\cdots\cdots\cdots\cdots=1$$

where $n_1$, $n_2$,......are the percentages of combustibles in limit mixtures and $N_1$, $N_2$,......are the percetages of the same combustibles to give limit mixtures when each is mixed with air separately.

The lower limit of inflammability of mixtures of ethyl ether and ethyl alcohol was studied by A. G. White and Price(1) and again by A. G. White.(2) In the former the Le Chatelier's rule holds well with maximum deviation of 3 per cent., while in the latter more closely with that of 0.7 per cent. In the present research (Table II. (A)) the rule holds exceedingly well with the deviation of as small as 0.5 per cent, which is of the same order as the experimental error.

From Table II., it can be seen that in all mixtures $\sum n_1/N_1$ is nearly equal to unity and therefore Le Chatelier's rule holds again very well.

Generally, if any mixture of air and vapours of several combustibles, which have the same theoretical flame propagation temperature, satisfies a relation represented by the equation $n_1/N_1+n_2/N_2+\ldots\ldots=1$, then this gaseous mixture can be considered as a final mixture of $n_1/N_1$ volumes of lower limit mixture of the first substance and $n_2/N_2$ volumes of that of the second and so on. Therefore the calculated flame temperature of this final mixture must be the same as that of each component limit mixture, which is equal to each other, according to the above assumption. As the all combustibles considered here have the same theoretical flame propagation temperature, the flame temperature of this final mixture will be just sufficient fo propagate flame. Therefore this final mixture must be a limit mixture, or in any lower limit mixture of air and the vapours of several combustibles, which have the same theoretical flame propagation temperature, Le Chatelier's rule must hold.

(1) A. G. White and Price, Jour. Chem. Soc., 1462, 1919.
(2) A. G. White, Jour. Chem. Soc., 2561, 1922.

## Summary.

(1) Lower limits of inflammabibility of ethyl alcohol, ethyl ether, methyl cyclohexane and their mixtures in air have been investigated.

(2) Le Chatelier's rule holds well in any lower limit mixture of air and the vapours of ethyl alcohol, ethyl ether and methyl cyclohexane.

(3) Le Chatelier's rule must hold in any limit mixture of air and vapours of combustibles which have the same theoretical flame propagation temperature.

(4) Lower limit of inflammability of methyl cyclohexane in air measured in a 5 cm. glass tube, flame being propagated downwards, is 1.15 per cent. and the theoretical flame propagation temperature calculated is 1480°*C.*, which is nearly equal to those of ethyl alcohol, ethyl ether and the lower members of paraffin hydrocarbons. Therefore it can be seen that the naphthene ring has very little effect on the theoretical flame propagation temperature of hydrocarbons.

# 第二十一號

昭和二年三月發行

# 抄　　録

## アルコール、エーテル、メチルサイクロヘキサン混合物の火焔傳播の低極限に就て

所員　工學博士　田中芳雄
工學士　永井雄三郎
工學士　秋山金正

適當なる可燃物の蒸氣と空氣との混合氣體に點火する時は火焔は其處から凡ての方向に傳播する、而して此の混合氣體中の可燃物の濃度を次第に減少する時は火焔の傳播速度は又次第に減少して終には全く火焔が傳播することが出來なくなる。此の火焔が傳播するに必要なる可燃性蒸氣又は氣體の最低の濃度を該可燃物と空氣との混合氣體に於ける火焔傳播の低極限(或は該物質の火焔傳播の低極限)と云ふ。低極限が小くて蒸氣壓が大きい物質を燃料として用ふれば內燃機關の始動は容易であつて此の低極限の大小は燃料の始動能力に關聯して極めて重要である。

ガソリン、アルコール、エーテルの混合物は種々の點から內燃機關用燃料として興味あるものである。而して本邦產ガソリンの主要部をなす成分の一つとしてメチルサイクロヘキサンがある事は既に著者等の研究に依て明かである。其處で著者等はメチルサイクロヘキサン、エチルアルコール、エチルエーテルなる三種の蒸氣と空氣との混合氣體中に於ける夫々の火焔傳播の低極限を測定した。蓋し從來メチルサイクロヘキサン又は之れを含んだ混合物の低極限を實驗的に定めたものがなく、又ナフテン環連鎖が低極限に如何に影響するかに就ても未だ充分詳かでない。此の實驗は斯かる意味からも必要な事である。而して本研究の結果之等の三物質の混合物は火焔傳播の低極限に關して1%の誤差以內でLe Chatelierの法則に從ふ事、Le Chatelierの法則は同じ理論火焔傳播溫度を有する可燃物と空氣との凡ての低極限混合物に於て適合す可きこと、メチルサイクロヘキサンの低極限は1.15%で、又其の理論火焔傳播溫度は1480°Cなること、並にナフテン環連鎖が低極限に特別な影響を與へない事等が明かになつた。