Factors Affecting Combustion of Organic Materials in High-Pressure Environments

Spray Ignition of Aliphatic Hydrocarbons

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Samples of *n*-hexane, *n*-hexadecane, and squalane were used in initial studies of factors affecting combustion of aliphatic hydrocarbons in a high-pressure injection system. Factors considered were temperature, sample size, pressure, catalytic effects, and chemical structure. Ignition delay as a function of these factors was studied. Information on spontaneous ignition (self-ignition) temperatures also is presented. Ignition delay as a function of temperature was the most significant measurement. Relative activation energies were calculated from the data by the Arrhenius theory of reaction rates. Reactant sample size affected the ignition delay at specified pressures and temperature. Under the conditions studied, increasing sample injection pressure and leaving the reactor tube pressure constant decreased ignition delay. Catalytic effects, if any, were not detected and ignition delay increased with the molecular weight of the aliphatic hydrocarbons.

Studies were made of the combustion mechanism in high-pressure systems containing commercial lubricating oils (*1*, *3-6*, *8*, *9*) and show that under certain conditions a deposit of oil in a high-pressure air system may become heated and ignite spontaneously. The experiments, however, were performed in high-pressure systems without regard to fuel composition or the relationship of pressure and temperature to the ignition point. Commercial lubricants of mixed chemical structure were used; thus, the establishment of the controlling factors was on a qualitative rather than on a quantitative basis.

A series of studies using aliphatic, cyclic, and aromatic liquids and their derivatives is underway in this laboratory to show quantitatively some factors affecting combustion in high-pressure systems. Three types of high-pressure systems are being used: an injection system; a static bomb system; and a flow system. In the first system, a measured volume of sample is sprayed into a high-pressure air chamber at a present temperature. By the second system, a measured volume of fluid is vaporized in a high-pressure air chamber as the temperature is slowly increased and, in the last, a measured volume of liquid is vaporized into a flowing pressurized air stream at a preset temperature.

This paper describes the initial work on the factors affecting the combustion of aliphatic organic liquids in a high-pressure injection system. The hydrocarbons used are *n*-hexane, *n*-hexadecane, and squalane. Factors of interest are the effects of temperature, sample size, pressure, catalysts, and chemical structure.

Two general areas of combustion phenomena are expected to exist: the preignition range in which exothermic reactions take place but reaction rate is slow and does not reach explosive velocity, or become self-sustaining without a system change; and the self-ignition range in which the reaction range is rapid and does reach explosive velocity. Only the self-ignition range will be considered here. Results in the preignition range are difficult to reproduce as small changes in the environment cause large changes in the outcomes.

EXPERIMENTAL

The high-pressure injection apparatus consisting of a driver gas section, an injection section, and an electrically heated injector tube as described by Marzani and McQuaid (*5*) was used. The reactor tube consists of a section of $^{15}/_{16}$-in. i.d., Type 304 stainless steel tubing, $12^{11}/_{16}$ in. long. The apparatus is instrumented to control initial reactor temperature and to measure temperature and pressure before, during, and after reaction. Its function is to inject as a spray, by air pressure, a measured sample of liquid into a reaction zone of known pressure and temperature. Ignition was determined by the rate of change of temperature and pressure with time. The ignition, if it occurs, is shown by a sharp rise in temperature and pressure, both of which then slowly decrease. Characteristically, the penetration of the fluid sample into the pressurized air in the reactor tube is limited. Consequently, the reaction site is in the vicinity of the injection nozzle (*5*).

Measurement of ignition delay and spontaneous ignition (self-ignition) temperature and pressure was possible and the injection system pressure and reactor tube temperature and pressure could be measured before, during, and after reaction. Peak temperature and pressure measurements in the reactor tube were not utilized as the data were not reproducible. The ignition-delay measurements were the most important and most easily reproduced data. The ability of this apparatus to reproduce these results in the region of short ignition delay (less than 10 sec) was ±3 sec. For ignition delays of greater than 10 sec, reproducibility decreased in direct proportion to the ignition-delay times. The relative activation energies of the various reactions were calculated from these data by the Arrhenius theory of reaction rates.

Temperature and pressure records were made of many samples of *n*-hexane, *n*-hexadecane, and squalane (2,6,10,15,19,23-hexamethyl tetracosane), introduced into the apparatus at a variety of preset temperature and pressure conditions. These liquids are examples of saturated, aliphatic hydrocarbons. *n*-Hexane contains a 6-carbon chain; *n*-hexadecane, a 16-carbon chain; and squalane, a 22-carbon chain with branching methyl groups.

The first group of runs was made with extremely pure (chromatographic grade) *n*-hexane, *n*-hexadecane, and squalane, obtained from the British Drug Houses, Ltd., Liverpool, England. The next group used liquids from Eastman Organic Chemicals to test the necessity for using reagents of high purity. The *n*-hexane was a purified grade, b.p. 65° to 67° C; the *n*-hexadecane was a practical grade, m.p. 17° to 18° C; and the squalane was "highest purity" grade (4% unsaturated). Comparison of the runs between the extremely pure and less pure grades showed that this ignition system could not differentiate between them. For reasons of economy, the less pure grades of chemicals were used.

RESULTS

Effect of Temperature. High-pressure combustion reactions in the gas phase probably proceed by a complicated process involving many elementary reactions. Frequently, free radicals are formed in the system. When this occurs to a sufficient extent, the total number of free radicals in the system may increase rapidly, so that steady-state conditions no longer hold; the reaction occurs almost simultaneously with free radical formation, and an explosion results. An elementary reaction producing an increase in the total number of free radicals is known as a "branching reaction"; the complete process is known as a "branching process." The following is a free radical mechanism which could occur in the combustion process of hydrocarbons:

$$R_1H + O_2 \rightarrow R_1{-}O{-}O^{\bullet}{-} + H^{\bullet} \quad (1)$$

$$R_1{-}O{-}O^{\bullet}{-} + RH \rightarrow R{-}O{-}O{-}H + R_1^{\bullet} \quad (2)$$

$$R_1^{\bullet} + H^{\bullet} \rightarrow R_1H \quad (3)$$

$$R_1^{\bullet} \rightarrow \text{destruction on walls} \quad (4)$$

$$H_1^{\bullet} \rightarrow \text{destruction on walls} \quad (5)$$

$$2\,H_1^{\bullet} \rightarrow H_2 \quad (6)$$

$$H_2 + {}^1/_2\,O_2 \rightarrow H_2O \quad (7)$$

Below the minimum self-ignition temperature for specified pressures and sample size, the mixture will not ignite explosively in the reactor tube. Above this minimum, the ignition delay will decrease with increasing temperature until it becomes instantaneous by measurement.

Figure 1 shows the curves representing ignition delay *vs.* temperature for *n*-hexane, *n*-hexadecane, and squalane at the conditions of temperature, pressure, and sample size specified. Figure 2 shows another curve for *n*-hexadecane at other conditions.

Each curve shows an exponential type of increase in ignition delay with decreasing temperature. The vertical dashed lines represent points of infinite ignition delay and the curves approach these lines asymptotically. The lines determine the minimum self-ignition temperatures.

The natural logarithm of the ignition delay of these three compounds plotted against $1/T$ (Kelvin) gives an approximate straight line (Figure 3–5) which can be related to the Arrhenius reaction rate theory (*2*).

The Arrhenius reaction rate theory equation is

$$k = Ae^{-E/RT} \quad (8)$$

where

k = reaction rate
A = frequency factor
E = activation energy
T = absolute temperature
R = universal gas constant from the ideal gas law.

The exponential factor, $\exp(-E/RT)$, is a measure of the probability of the occurrence of the activated state. For simple bimolecular reactions at low pressures, A is the frequency of collisions between the reacting molecules. The reaction rate is inversely proportional to the reaction time, which should be related to the activation energy as follows:

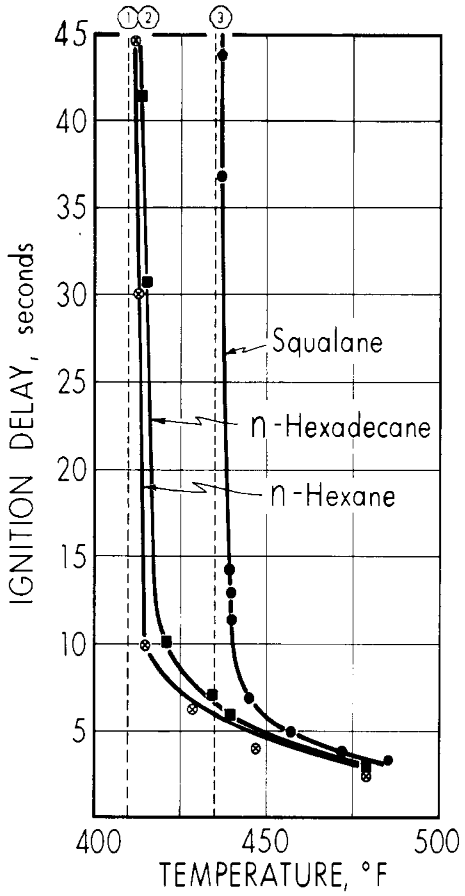

Figure 1. Curve; ignition delay for *n*-hexane, *n*-hexadecane, and squalane vs. temperature

Injection pressure, 3000 psi; reactor tube pressure, 2000 psi; sample size 0.30 ml

$$\ln \tau = A' + E/RT \quad (9)$$

Accordingly, a plot of ln τ (the natural logarithm of the ignition delay) *vs.* $1/T$ should give a straight line with a slope equal to E/R. The Arrhenius plot should be regarded as a rough approximation as the Arrhenius equation describes a simple bimolecular reaction at low pressures where the molecules are small and considered to be spheres. Therefore, the slopes of the least square-fitted straight lines of Figures 3–5 are a rough measure of the activation energy for ignition and may be used to indicate approximate relative differences in activation energies between the fluids. The data for *n*-hexane (Figure 3) show small dispersion from a straight line. The data for *n*-hexadecane (Figure 4) follow a straight line plot closely. However, the data for squalane (Figure 5) show considerable scatter from a straight line. It is not determined whether this large dispersion may be attributed to the fact that the squalane is a much larger molecule with branching methyl groups or to possible changes in reaction mechanism.

On the basis of the slopes of these curves, the activation energies for *n*-hexane, *n*-hexadecane, and squalane are 17.5, 19.9, and 27.8 kcal per mole, respectively, for the experimental conditions used.

The activation energy of *n*-hexane of 17.5 kcal per mole under the conditions of the experiments (pressure between 2000 and 3000 psi) is less than the value of 25.0 kcal per mole obtained for the ignition of *n*-hexane at 1 atm of pressure by Johnson *et al.* (*2*). This would be predicted since the ignition temperature is lower at the elevated pressure.

Effect of Sample Size. The sample size of the injected fluid has a complicated effect on the ignition delay at

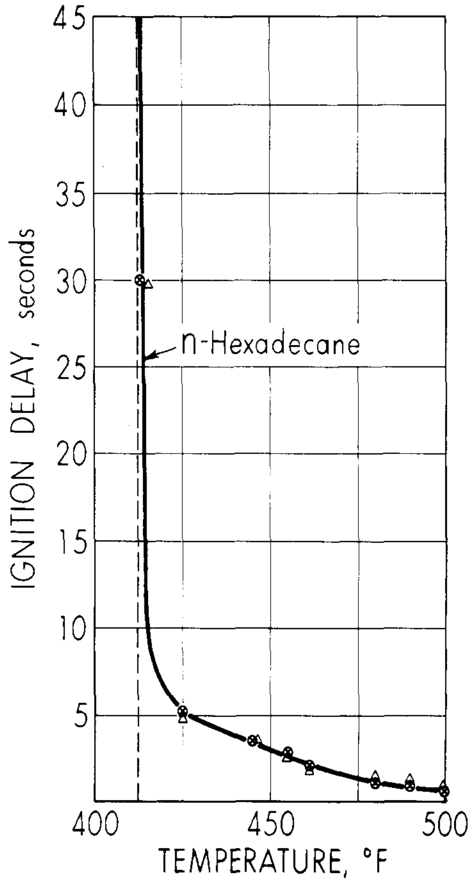

Figure 2. Curve; ignition delay for *n*-hexadecane *vs.* temperature

Injection pressure, 2000 psi; reactor tube pressure, 1500 psi; sample size, 1.5 ml

⊗ Without catalyst △ With catalyst

a specified temperature and injector and reactor tube pressure. As the sample size increases (from 0.1 to 2.0 ml), the ignition-delay time decreases, passes through one or more maximum or minimum points, and then increases. With small sample sizes, near 0.1 ml, the fuel/air mixture is "lean." With sample sizes near 2.0 ml, the fuel/air mixture is "rich."

Ignition delay *vs.* sample size data for *n*-hexane are shown in Figure 6. Curves A and B at temperatures of 400° and 420° F, respectively, have long delay times at small sample sizes and then pass through two minima and a maximum before increasing to longer delay times. The second minimum is the lowest in both cases. Curve C at 460° F falls slowly until it reaches a minimum delay time at 0.75 ml; then the curve rises very slowly to longer delay times.

As another illustration, the sample size of the reactant *vs.* ignition delay is plotted for squalane at 450° F (Figure 7). For a sample size of 0.20 ml, squalane fires with a delay of 10 sec. At 0.45 ml, the curve for ignition delay *vs.* sample size reaches a minimum, and then for 1.00 ml the delay time rises to 7 sec. This curve shows that there is a minimum ignition-delay time at a specified temperature, injector, reactor tube pressure, and sample size.

The results for *n*-hexane and squalane and previous data on commercial mixtures (*1*, *5*) show that there is an optimum sample size for every combustible liquid that can be expected to ignite at some minimum temperature under a given set of system conditions and geometry.

Pressure Effect. This was explored by varying the sample injection pressure into the preheated pressurized reactor tube initially set at 1500 psi. Sample injection pressures of 2000, 3000, and 3500 psi were used. The equilibrium pressure following injection and before ignition was recorded. A 0.45-ml sample of squalane and a reactor tube temperature of 450° F were used in the results for Figure 8. These suggest a reduction in ignition delay with an increase

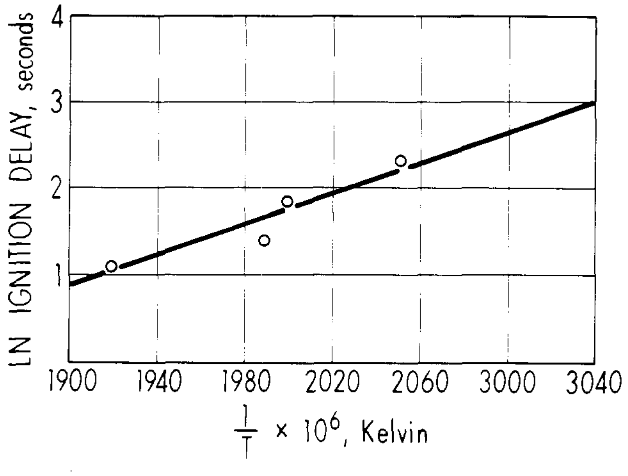

Figure 3. Curve; Arrhenius plot of *n*-hexane data

Injection pressure, 3000 psi; reactor tube pressure, 2000 psi; sample size, 0.30 ml

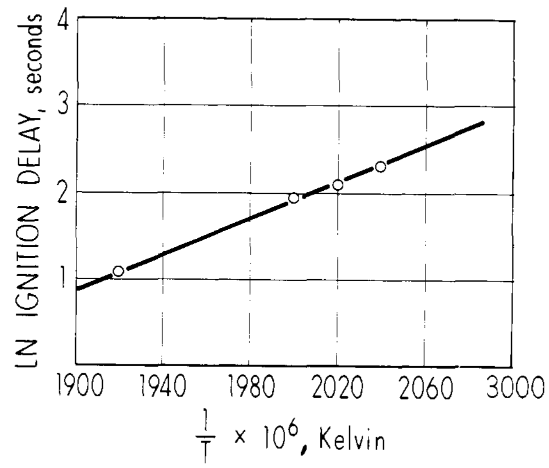

Figure 4. Curve; Arrhenius plot of *n*-hexadecane data

Injection pressure, 3000 psi; reactor tube pressure, 2000 psi; sample size, 0.30 ml

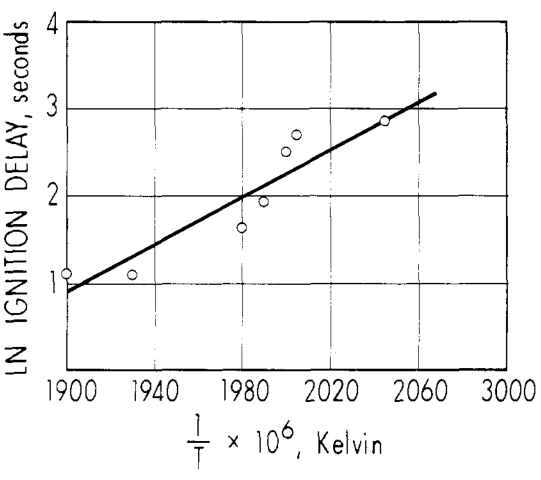

Figure 5. Curve; Arrhenius plot of squalane data

Injection pressure 3000 psi; reactor tube pressure, 2000 psi; sample size, 0.30 ml

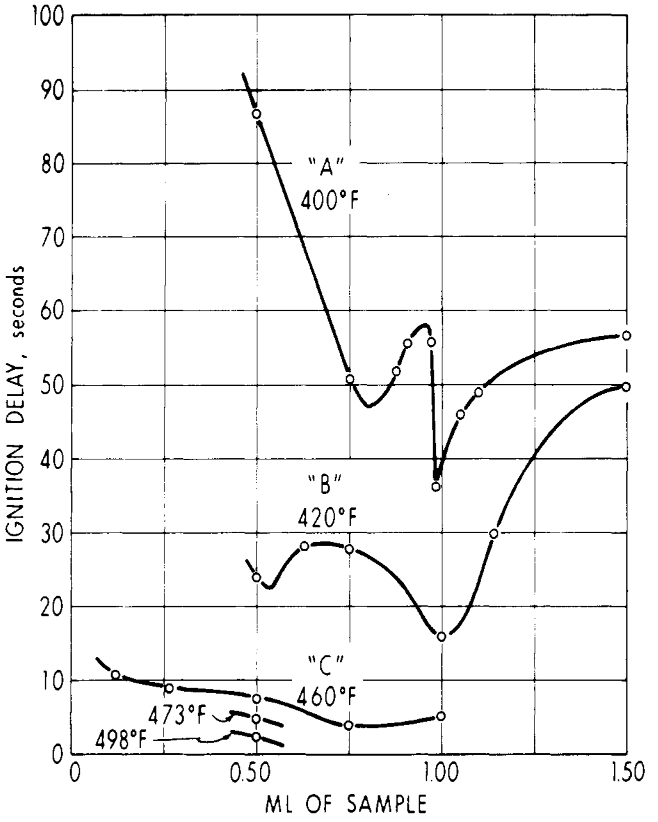

Figure 6. Curve; ignition delay for *n*-hexane vs. ml of sample
Injection pressure, 3000 psi; reactor tube pressure, 2000 psi

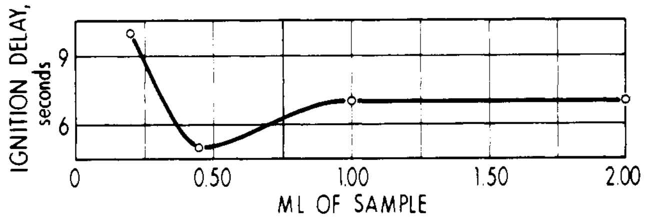

Figure 7. Curve; ignition delay for squalane vs. ml of sample
Injection pressure, 2000 psi; reactor tube pressure, 1500 psi at 450° F

in sample injection pressure. The same ignition-delay reduction effect with increasing injection pressure was obtained by Marzani and McQuaid (*5*) with commercial fluids.

Catalysts Effect. The catalytic effects of charcoal, platinum, and Hopcalite (a complex mixture of cuprous oxide, cupric oxide, and manganese dioxide prepared by alkaline precipitation of the respective oxides) were examined. The method was to place catalysts in the reaction tube at the reaction site close to the nozzle. The platinum samples (Harshaw Chemical Co.) were 1.0-g cylindrical granules, ⅛-in. diam and ⅛ in. high, consisting of 95% aluminum oxide and 5% platinum. The Hopcalite samples (Tiltrol Corp.) were 1.0-g. granules, approximately ⅛ in. diam. The carbon consisted of 1.0 g samples of animal charcoal obtained from Fisher Scientific Co. Samples of *n*-hexadecane (1.50 ml) at 200 psi were injected into the reaction tube at a pressure of 1500 psi. The ignition-delay data with a catalyst were compared with ignition-delay data without a catalyst. The ignition-delay data with and without a catalyst are plotted in Figure 2.

The catalysts produced no noticeable effects on ignition delay, temperature or pressure rise, or self-ignition temperature. Therefore, the effects, if any, of these catalysts could not be determined with the present apparatus and technique used.

Chemical Structure Correlation. Because only three structurally similar molecular species of aliphatic hydrocarbons with molecular weights ranging from approximately 86 to 423 were examined, correlation was sought only with the effect of their molecular weight on ignition delay. Figure 9 shows the plot of ignition delay *vs.* molecular weight. At the lower temperatures, increased molecular weight of the sample resulted in increased ignition delay. However, for high temperatures, the ignition-delay times for these hydrocarbons approach zero and the effect of molecular weight cannot be differentiated. These findings are consistent with those on commercial fluids (*5*).

DISCUSSION

In this initial examination, it appears that, with respect to ease of ignition, *n*-hexane > *n*-hexadecane > squalane. On the basis of Figure 1, minimum self-ignition temperatures are 412° for *n*-hexane, 415° for *n*-hexadecane, and 435° F for squalane. Available data (*7*) give values at atmospheric pressures for the minimum spontaneous ignition temperatures of 453° for *n*-hexane and 401° F for *n*-hexadecane. Thus, there appears to be a reversal in ordering with respect to ease of ignition. Whether this reversal is due to the effect of pressure or other factors operating in each of these experiments is not known.

The idea of a minimum spontaneous ignition temperature for a material also deserves some comment. This work and Marzani and McQuaid (*5*) show that a minimum spontaneous ignition temperature for a material will vary, at least, according to sample size, pressure, and initial temperature. A true or absolute value for minimum spontaneous ignition temperature requires exploring the behavior of a material over a considerable range of variables such as sample size, pressure, etc., and developing relationships from which such true values can be derived. Materials may have more than one minimum spontaneous ignition temperature value, as suggested by Figure 6, and the choice of materials for a particular application may require choosing which of the values presents the proper definition hazard expected in the use of the material.

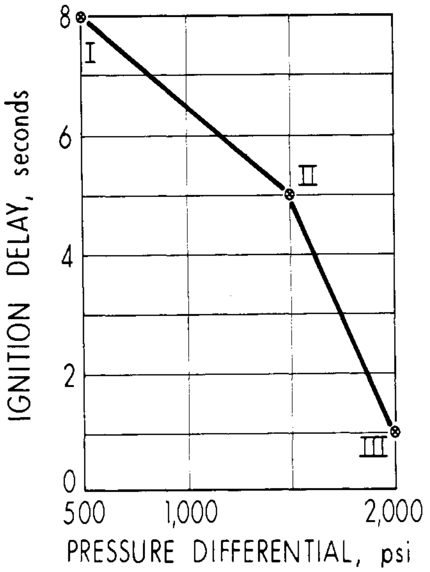

Figure 8. Curve; ignition delay for squalane vs. pressure
Sample size, 0.45 ml at 450° F

	Injection Pressure, psi	Reactor Tube, psi	Equilibrium Pressure, psi
I	2000	1500	1700
II	3000	1500	2150
III	3500	1500	2350

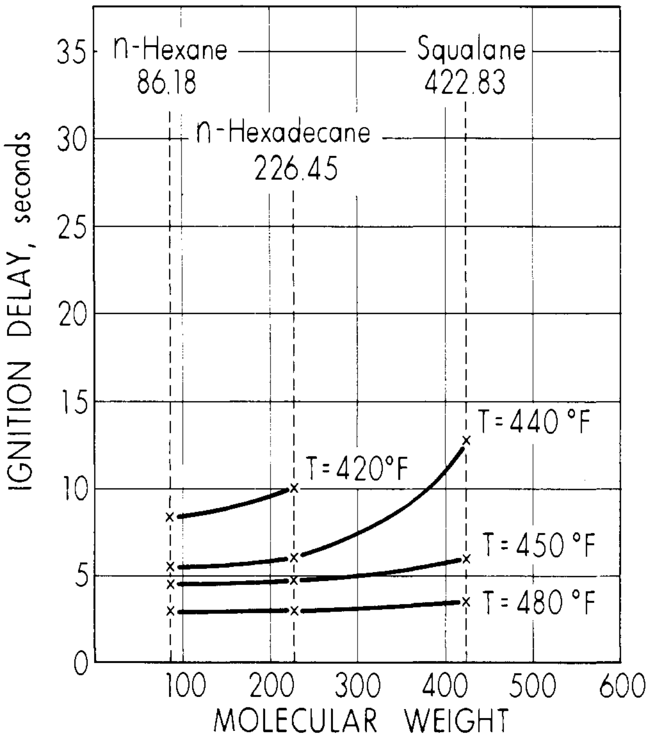

Figure 9. Curve; ignition delay for *n*-hexane, *n*-hexadecane, and squalane *vs*. molecular weight

Ignition pressure, 3000 psi; reactor tube pressure, 2000 psi; and sample size, 0.30 ml

More data must be accumulated to provide the basis for the selection of materials with respect to relative safety from high-pressure combustion.

CONCLUSIONS

Increases in system temperature decrease the ignition delay. There is a temperature at which the ignition delay becomes infinite and this is a measure of the minimum self-ignition temperature of the material under the test conditions.

Sample size has a complicated effect on ignition delay, suggesting optimum sample sizes for combustion or non-combustion in the range from "lean" to "rich" fuel/air mixtures.

The effect of increasing the sample injection pressure decreases the ignition delay.

Catalytic effects, if any, could not be observed under the conditions used.

At lower temperatures, increasing sample molecular weight resulted in increased ignition delay. At higher temperatures, the effect of molecular weight could not be observed.

The data suggest that for every material there exists a minimum self-ignition temperature near the region of infinite delay which is a function of temperature, pressure, and sample size.

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