Hydrocarbon Burning Velocities Predicted by Thermal Versus Diffusional Mechanisms

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The maximum burning velocities for 36 hydrocarbon-air mixtures are predicted by the semi-empirical thermal equation of Semenov and compared with N.A.C.A. experimental velocities and those predicted by the semi-empirical Tanford and Pease diffusion equation, as previously calculated. Both correlations are based on the assumption that the specific reaction rate constant for the chemical reactions controlling the respective mechanisms is independent of hydrocarbon. Like the diffusional theory, the thermal correlation also shows that the combustion mechanism for the majority of the hydrocarbons is strikingly similar. For example, if a constant frequency factor is assumed in the Semenov equation, a variation of less than five per cent. in the activation energy brings the thermal result into line with experimental velocities for all mixtures except ethylene and acetylene.

Recently Simon showed the maximum burning velocities for 35 hydrocarbons to be consistent with the active particle diffusion theory of flame propagation, as postulated by Tanford and Pease. However, as is recognized by Simon, the correlation is chiefly one involving the equilibrium flame temperature since the calculated radical concentrations depend primarily on this variable. It would, therefore, appear likely that a thermal mechanism which also depends primarily on the flame temperature might give a correlation with burning velocity equally as good as the active particle diffusion theory.

For the semi-empirical thermal correlation the general equation of Semenov, assuming a biomolecular reaction to be the controlling step, is used. The use of this thermal equation for evaluation of the burning velocities of a series of hydrocarbon compounds is tenable if the basic assumption is made that for all of the hydrocarbon-air mixtures considered, heat capacity, diffusivity, density and thermal conductivity and the variation of these properties with temperature can be described solely by the properties of air. Considering the fact that for all hydrocarbons studied the quantity of fuel in the mixture extends over the limited range from 2 to 10%, the thermal properties of the gaseous mixtures do not deviate appreciably from those of air. This is particularly true since the more a hydrocarbon's properties deviate from those of air, the lower, usually, is its percentage composition in the hydrocarbon-air mixture. Using the same temperature approximations as employed by Daguer, who simplified the Semenov equation for a propane-air mixture, the following general equation applicable to all hydrocarbons is obtained

\[
\mu_{\text{r}} = \sqrt{\frac{n_{1}}{n_{2}}} \left( K \left( \frac{T}{T_{0}} \right)^{2} \right) \left[ \frac{T_{0}^{2}T_{1}^{2}e^{-E/RT_{1}}}{(T_{1} - T_{0})^{1/2}} \right]^{1/2}
\]

where

\[
\frac{n_{1}}{n_{2}} = \text{mole reactants/mole products by stoichiometric equation}
\]

\[
K = \text{a frequency factor}
\]

\[
E = \text{activation energy}
\]

\[
T_{0} = \text{initial mixture temperature}
\]

\[
T_{1} = \text{calculated equilibrium flame temperature}
\]

The first three terms of equation (1) are essentially temperature independent and solely properties of the hydrocarbon-air mixtures. The term \(n_{1}/n_{2}\), of course, is easily calculated for each mixture and is taken into account. Unlike the simplified diffusional equation which has only one unknown, the specific reaction rate constant, the simplified thermal equation has two unknowns, the frequency factor and the activation energy for combustion initiation. If the thermal equation is to be used for predicting relative flame velocities, it is necessary to assume both unknowns independent of fuel-air mixture. In essence the hypothesis that the frequency factor and activation energy are constants in the thermal equation implies that the specific rate constant for the chemical reactions involved in the thermal mechanism are invariant for all hydrocarbons. That this may have some justification as an initial assumption is seen from the fact that Simon found the specific reaction rate constant in the diffusional equation virtually independent of hydrocarbon. This was interpreted as an indication of a similar reaction mechanism for all hydrocarbons.

Since activation energy is also involved in the temperature dependent part of equation (1), it is necessary to select a reasonable activation energy for the correlation. Limited experimental data which have been found on activation energies for low temperature hydrocarbon oxidation (ethane, propane, pentane and ethylene) yield values from 38 to 42 kcal./mole. If a value of 40 kcal./mole is then assumed for the heat of activation of all hydrocarbon-air mixtures and \(K\) is taken as a constant, the relative values of burning velocity may be expressed by the following form of equation (1)

\[
\mu_{\text{r}} = \frac{n_{1}}{n_{2}} \sqrt{T_{1}^{2}T_{0}^{-E/RT_{0}}/(T_{1} - T_{0})^{1/2}}
\]

where \(n_{1}/n_{2}\) and \(T_{1}\) pertain to the hydrocarbon in question. The relative values of burning velocity for 36 hydrocarbon-air mixtures at room temperature, 300°K., are then converted to absolute values by using the maximum experimental velocity of


(10) Heats of activation were also found for methane and benzene, but these compounds are known to give anomalous oxidation results and higher heats of activation than the other members of the hydrocarbon series. Therefore, they were not considered in selecting a mean activation energy for the hydrocarbons.

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propane–air, 30.0 cm/sec, as the reference mixture, and the results are presented in Table I. A comparison of the burning velocities as predicted by the Tanford and Pease and by the Semenov equations with the experimental results show that for the straight chain alkane, the agreement is, for the most part, good. That the Semenov equation predicts too high a burning velocity for methane is expected since the heat of activation of methane–air mixtures is reputed to be considerably higher than 40 kcal./mole. For the branched-chain alkanes and alkenes both the thermal and diffusional equations predict burning velocities that are too high. The diffusional theory appears to predict high values because the specific reaction rate constant for branched-chain compounds is somewhat lower than the average value assumed for all hydrocarbon–air mixtures. The thermal equation predicts a still higher value, probably due to deviations in the frequency factor and heat of activation from the average. An indication of a deviation in activation energy was expected since branched chain compounds do have higher ignition temperatures and, therefore, higher energy than the straight chain counterparts. For normal alkenes the values predicted by the two equations are in relatively good agreement with experimental results except for ethylene. It is particularly interesting that both the thermal and diffusional equations predict very nearly the same velocity for ethylene. Certainly both mechanisms substantiate the belief that the ethylene–air combustion reactions are quite different from other hydrocarbons. The burning velocities predicted for the normal alkenes are in relatively good agreement with experiment except for acetylene, which deviates markedly. Its deviation is expected when predicted by the thermal equation since the heat of activation of acetylene has been shown to be considerably lower than 40 kcal./mole. However, a deviation also in the reaction mechanism for acetylene is indicated by the considerable difference between the diffusional equation and experimental results.

In general, the diffusional equation predicts the burning velocity of the room temperature hydrocarbon mixtures more closely than does the thermal equation. Examination of the two equations does indicate, however, that the thermal equation is more sensitive to a given percent change in the reaction rate constant than is the diffusional equation.

![Graph](image)

**Fig. 1.** Correlation between burning velocity and equilibrium flame temperature.

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**Table I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vol. %</th>
<th>Flame velocity, cm/sec</th>
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<tbody>
<tr>
<td>Methane</td>
<td>9.06</td>
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<td>Ethane</td>
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<td>Propane</td>
<td>4.54</td>
<td>2251</td>
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<td>Butane</td>
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<td>Pentane</td>
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<td>Hexene</td>
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<td>2241</td>
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<td>Heptane</td>
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<td>2235</td>
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<td>2-Methylpropane</td>
<td>3.48</td>
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<td>2,2-Dimethylpropane</td>
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<td>2-Methylbutane</td>
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<td>Benzene</td>
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<td>2307</td>
</tr>
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</table>

+ Equilibrium flame temperature calculated by authors.

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Therefore, the assumption of an invariant rate constant, if incorrect to any degree, would result in a
temperature correlation that is not as satisfactory as a
diffusional correlation. However, beyond this
point it is impossible to state whether the difference
in correlation is due to the fact that either the reac-
tion rate constant in the thermal equation is more
affected by hydrocarbon or that the thermal me-
chanism less closely predicts the true combustion
phenomenon.

Simon⁵ has plotted the variation in burning veloc-
ity solely as a function of flame temperature and
has remarked on the good correlation obtained. It
is interesting to note that equation (2) predicts di-
rectly the variation in burning velocity with flame
temperature if the mole ratio, n₁/n₂, is assumed in-
dependent of hydrocarbon–air mixture. This is a
justifiable approximation since, near the stoichio-
metric mixture where maximum burning velocity
occurs, the ratio rarely varies by more than two per
cent. from the mean. Figure 1, then, is a log–log
plot of burning velocity predicted by equation (2),
using the experimental value of propane as a basis,
versus the calculated equilibrium flame tempera-
ture with n₁/n₂ a constant. The equation plots es-
tentially as a straight line predicting that the burn-
ing velocity varies approximately as the 4.9 power
of the flame temperature. Disregarding the burn-
ing velocities of ethylene and acetylene, which give
anomalous results with both theories, the rate of
change of burning velocity with equilibrium flame
temperature is satisfactorily predicted by the modi-
fied Semenov equation. It is not certain whether
the fact that the predicted rate of change is not
quite as great as actually occurs is due to the choice
of a slightly low average activation energy, to a
progressive increase of the frequency factor with
decreasing chain length of the alkynes or to an ac-
tivation energy for the alkynes that is progressively
lower than the assumed value. However, it would
not seem to be due to the selection of a low average
activation energy for two reasons. First, the trend
of the alkynes with decreasing chain length appears
to be toward lower activation energy and higher
frequency factor, as is exemplified in acetylene.
Second, since the activation energy value selected
was from available data on low temperature hydro-
carbon oxidation, it would be expected that the
value would be too high rather than too low when
applied to activation at combustion temperatures.

A variation of less than 5% in activation energy
will bring the calculated burning velocities, as
shown by the modified Semenov equation, in line
with experimental values for all mixtures except
ethylene and acetylene. This is an indication that
the initial assumption of the constancy of the fre-
cency factor and activation energy was justifiable.
Furthermore, it again stresses the fact that both
thermal and diffusional theories indicate a marked
similarity of most hydrocarbons for the combustion
reaction.

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