Modeling of Knock in Spark-Ignition Engines

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ABSTRACT

The chemical kinetic modeling of end gas autoignition leading to knocking behavior in spark ignition engines is discussed. The demands placed upon kinetic models by the conditions of temperature and pressure are examined, and the construction of both highly detailed and of more global or reduced kinetic models is outlined. Methods for including the influences of such factors as fuel molecule size and molecular structure are described for both types of knock model. The results of both types of model analyses are presented, and the strengths and weaknesses of each are discussed.

INTRODUCTION

Engine knock represents an important limit to the efficiency of the familiar spark-ignition internal combustion engine. In order to increase the thermodynamic efficiency of combustion, the compression ratio of the engine can be steadily increased; however, as the compression ratio is increased, eventually knocking behavior will begin to occur. Since knocking performance can lead to engine damage and other adverse operating conditions, the compression ratio cannot be increased beyond the knock limit.

There are several operational strategies which are commonly employed to inhibit the onset of knock. In the past, addition of antiknock compounds such as tetra-ethyl lead (TEL) made it possible to increase the operational compression ratio. However, environmental concerns have led to the elimination of such antiknock compounds. Another strategy used to permit higher compression ratios is the blending of hydrocarbon species including aromatic species to increase the effective octane number rating of the automotive fuel. Unfortunately, these higher octane fuels are more expensive to produce than older conventional gasolines.

Another practical factor involved in knocking tendency is the problem presented to the oil company which is producing automotive fuels. The blending of mixtures of hydrocarbon species and the prediction of the octane number of the resulting mixtures are difficult theoretical problems, and the availability of a proven computational model to assist in this process would be extremely useful. Such a model must be able to predict the knocking tendency of a wide range of pure component fuels, and be able to deal accurately with mixtures of the same fuels.

In order to provide insight into the details of the knock process, and to attempt to develop strategies for reducing the problems associated with engine knock, a variety of numerical modeling approaches have been developed to describe knock. These models have several interdependent goals. The first goal is to provide detailed chemical information about the specific kinetic factors which lead to and promote knock. A second goal is to provide a knock submodel which can be incorporated into multidimensional fluid mechanical models of engine combustion. Another goal is the development of strategies to reduce the tendency of a given group of fuels to knock.

In the following sections of this paper, we will describe the current modeling approaches to descriptions of the kinetics of engine knock. We will also indicate the types of approaches which are used to examine kinetic fuel modifications which can lead to reduced or even enhanced knock tendencies. We will also indicate those types of fuels and fuel additives for which current kinetic models are completely inadequate, and for which a great deal of further research is needed in order to provide a useful model for combustion research.

KNOCK IN CONVENTIONAL SPARK-IGNITION ENGINES

The most common picture of engine knock in internal combustion engines is that the knock is provided by thermal autoignition of unburned gases in the combustion chamber. In most engines, spark ignition provides a source of combustion which initiates a flame; following ignition, this flame begins to propagate across the combustion chamber. The gases in the combustion chamber are subject to two primary influences. The first of these is the turbulent flame front which was initiated by the spark plug, while the second is the process of thermal autoignition. The compression of the unburned

gases by the piston motion, and the secondary compression of the unburned gases by the flame propagation, both tend to heat the unburned gases and promote chemical reactions. If no other factors were involved, these reactions would eventually produce thermal ignition, resulting in a rapid release of chemical energy and a pressure wave. Knock depends on the outcome of a competition in the "end gases", the last portion of the unburned mixture in the engine combustion chamber to be consumed by the flame front. Generally speaking, if the flame front consumes a sample of reactive end gas before this autoignition process is complete, then no ignition occurs and no knock is observed. In contrast, when the compression ratio is high and the adiabatic heating of the end gas is large, then autoignition can occur prior to flame consumption of these end gases, and knocking performance will be observed. A primary goal of kinetic models of engine knock is the prediction of this autoignition time delay, which can then be related to the onset of knocking performance. Kinetic modifications which lead to longer autoignition times will therefore lead to knock suppression, since the flame would be expected to consume the end gases in the interim.

KINETIC MODELING OF KNOCK OCCURRENCE

The end gases in an automotive engine chamber experience a sequence of forces during the engine cycle. At the very beginning of the cycle, these gases are nearly at atmospheric temperature and pressure, but compression due to piston motion tends to increase the temperature and pressure of these unburned gases. At some later time, the spark ignition of a portion of these gases leads to a much more rapid increase in temperature and pressure of the unburned gases. At the initial conditions, the temperature and pressure of these end gases mean that reaction rates of these mixtures are very small. However, as the temperature and pressure increase, the kinetic regimes of the overall reaction gradually change, and the rate of reaction steadily increases. At the point of maximum compression, the rates of autoignition can be quite large. A kinetic model of autoignition must be able to describe this process over the entire range of conditions which might be encountered, from the nearly room temperature and pressure conditions initially, to the high pressures (50 atm) and temperatures (900 - 1000K) which are found at maximum compression.

Kinetic analysis shows that there are several distinct kinetic regimes between room temperature and 900K. At very low temperatures, the overall rate of reaction is quite small, and the modeling of this regime is straightforward. Then, as the temperature is increased, the rate of reaction increases dramatically. Eventually, the mechanism enters a regime in which increases in reaction temperature produce a net decrease in the rate of reaction, a region of so-called negative temperature coefficient. At even higher temperatures, the rate of reaction eventually increases again, leading to explosion.

A model of this complex series of responses is necessarily quite involved. We have worked for some years to be able to describe hydrocarbon oxidation over this entire range (1-8), and the results of this analysis have been quite successful. In the following sections of this paper, we will describe the details of the kinetics of this ignition phenomenon, how the mechanism changes with temperature and pressure, and how the model results relate to practical combustion systems.

Modifications of the rate of ignition, and the tendency to knock, can be made in several ways, generally intended to delay the onset of thermal ignition. This can be accomplished in the low temperature regime by reducing the rate of low temperature oxidation. This is commonly seen when fuels are blended which have low rates of low temperature reaction. A second technique for knock suppression involves addition of species which retard the rate of high temperature ignition. This usually means the introduction of additive species which remove HO_2 and/or H_2O_2 from the reactive mixture. This is the mode through which additives such as tetra-ethyl lead act (8).

There are two major trends in the modeling of the ignition of end gases. The first of these considers the fact that the fuels of interest in typical engines are very complex and involve a myriad of structural and other factors in determining their rates of reaction. Therefore, the kinetic model for the ignition of these fuels must attempt to include all of these factors. This approach has been used in several recent studies (1-8) and provides a means of dealing with many physical and chemical effects which are known to have important influences on knock onset. This approach also provides a means of assessing the effects of various anti-knock strategies such as addition of tetra-ethyl lead, blending of higher octane fuel components, and the knocking tendency of arbitrary mixtures of different hydrocarbon fuels. The second approach addresses the fact that this type of detailed kinetic modeling involves many hundreds, even thousands, of chemical species and elementary chemical reactions, and therefore is expensive to use in combustion models. For this reason, a useful model must make certain well-motivated simplifications in order to provide predictions within reasonable amounts of computer time.

KINETIC REACTION MECHANISMS

Most detailed chemical kinetic reaction mechanisms are intended to represent or predict combustion system behavior over a relatively limited range of temperature and pressure. For example, analysis of shock tube results often requires a mechanism which is appropriate for temperatures of about 1300K to perhaps 1800K. Over this range, the same family of reactions determines the rate of ignition of typical hydrocarbon fuels. Similarly, models of flame structure depend primarily on a rather small number of elementary reactions and rates (9-11).

The restricted range of temperatures in these examples means that the reaction mechanism can be qualitatively quite simple.

In contrast, the temperature and pressure ranges encountered by the end gases in knocking engines are extreme. The pressure is initially close to atmospheric, increasing to as much as 50 times its initial value at the time of maximum compression. Similarly, from room temperature at the beginning of the compression stroke, the end gases eventually reach a high pressure adiabatic flame temperature in excess of 2000K. As a result, the chemical kinetic reaction mechanism which is needed to simulate these conditions is generally quite complex. If the detailed approach is used, these reaction mechanisms can become very large even for relatively simple fuels. For example, a current mechanism for autoignition of one of the isomers of hexane, 2-methyl pentane, includes 325 chemical species and nearly 2000 elementary reactions, each with its temperature-dependent forward and reverse rate expression.

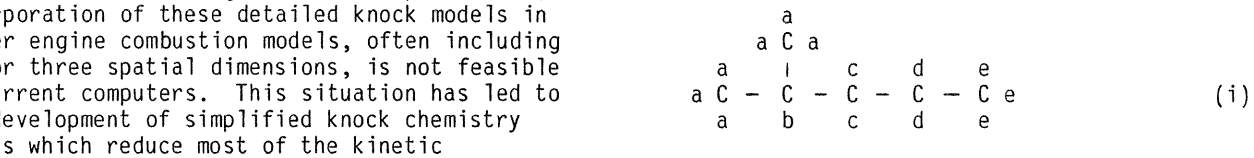
Because of the size of these reaction mechanisms, their use in computations of knock properties can be very expensive in terms of computer CPU and storage costs. In particular, incorporation of these detailed knock models in larger engine combustion models, often including two or three spatial dimensions, is not feasible on current computers. This situation has led to the development of simplified knock chemistry models which reduce most of the kinetic complexity while still retaining the most important kinetic features of the autoignition chemistry. This type of reduced kinetic model was first developed at the Shell Thornton Research Centre (12), and then refined by Cox and Cole (13) and more recently by Keck and co-workers (14,15). This approach treats autoignition as a series of global reactions, most of which represent families of individual elementary reactions. Only those reaction paths having a direct impact on the time of occurrence of autoignition are included. As a result of these simplifications, only a small number of overall reactions are needed. In the recent models of Keck (3,14,15), only 18 or 19 such global reactions are involved. Because of the much smaller size of such a reaction mechanism, it can be imbedded conveniently in multidimensional engine combustion models in an efficient manner, where the much more detailed kinetic model cannot.

A recent study by Cowart et al. (3) used both approaches to interpret a single family of engine knock data, using both n-pentane and iso-octane as fuels. This work demonstrated that, when properly formulated and calibrated, both models can provide reliable predictions of knocking engine performance. The same study also illustrated the great difference in computer CPU and storage requirements between the two types of models, nearly a factor of 100 greater for the detailed model with respect to CPU time costs.

Detailed Kinetic Models

Our present understanding of the major chemical kinetic processes which control hydrocarbon oxidation in this intermediate temperature range was established originally by Fish (16). Many others continued to develop and refine the overall theory, and the entire subject has been reviewed by Pollard (17). Pollard summarized the available rate data for many of the major steps in what is usually termed the alkylperoxy radical isomerization theory. More recent studies have determined better rates or energy barriers to many of the kinetic processes, but the picture proposed by Fish and reviewed by Pollard remains the foundation of our present model. In a sense, our current work represents an attempt to place this theory on an accurate quantitative basis, to assign numerical values to the essential reaction rates in alkylperoxy isomerization theory and then use that model to interpret practical engine combustion data.

For purposes of illustration, in the present discussion we will use 2-methyl pentane in examples of the major factors to be considered in the development of detailed kinetic knock models. This fuel can be described schematically



(i)

where C indicates a carbon atom, and the lower case letters a, b, c, d, and e represent the structurally distinct hydrogen atoms. Of these H atoms, those labeled 'a' and 'e' are bonded at primary sites, those labeled 'c' and 'd' are bonded at secondary sites, and the H atom labeled 'b' is bonded at a tertiary site. All of the 'a' H atoms are structurally equivalent and are logically distinct from those labeled 'e'. Most of the important kinetic processes which influence the knocking tendency of a given fuel can be understood, both qualitatively and quantitatively, in terms of the types of C - H bonds in the molecule and the spatial relationships established by the structure of the molecule. The type of C - H bond is important because H atoms and molecular oxygen bond less strongly to tertiary sites than at secondary sites, and at secondary sites less strongly than at primary sites. The molecular structure is important because the rates of transfer of atoms between different sites in the molecule depend on the spatial distances between them. Both of these points will be explained further below.

Another factor which is central to understanding the kinetic influences leading to engine knock is the identification of these elementary reactions which produce chain branching, the multiplication in the size of the available radical pool, and those reactions which either maintain the radical pool or actually destroy radical species. At high temperatures, it has been very well established that the single most important chain branching reaction in combustion kinetics is the reaction

$$H + O_2 = O + OH \quad (1)$$

which consumes one radical (the H atom) and produces two radicals, O atoms and OH radicals. The variation of combustion rate with temperature and pressure, the effectiveness of various flame inhibitors and sensitizers, and other practical phenomena are easily explained in terms of the effects that such variations have on the rate of H atom production and on the resulting rate of consumption of H atoms by Reaction 1 (10,11).

Under the conditions encountered in knocking engines, however, Reaction 1 does not contribute to the chain branching properties of the reaction mechanism until the very last part of the oxidation process, when the high temperature ignition occurs. Instead, under these conditions, an entirely different series of elementary reactions is responsible for the multiplication of the radical pool. In fact, several families of reactions contribute to the rate of chain branching, and the analysis of the chain branching, propagation, and termination properties of knock mechanisms is much more involved than at the high temperatures where Reaction 1 is dominant. These reaction sequences will be described in detail below.

Under near-knocking conditions, end gas temperatures start at room temperature and peak near 900K. These temperatures are the result of compression, first due to piston motion and then due to flame propagation which compresses the unburned gases. The rates of ignition at the lower portion of this temperature range are quite small, but the residence time in this temperature range is quite large. In contrast, residence time of the end gas at the highest part of this temperature range is small, but here the reaction rates are at their largest. Accordingly, all of this range must be treated by the model.

Hydrogen atoms are abstracted from the fuel molecule by radical attack. The most important radicals for this process are OH and HO_2. The abstraction by OH is important because water is a product, and the resulting release of heat provides end gas temperature increase in addition to that provided by compressional heating (5). Abstraction by HO_2 is extremely important because of the role this reaction plays in the chain branching system. To illustrate this,

$$C_6H_{14} + HO_2 = C_6H_{13} + H_2O_2 \quad (2)$$

is followed by the thermal decomposition reaction

$$H_2O_2 + M = OH + OH + M \quad . \quad (3)$$

This simple pair of reactions starts with a single HO_2 radical and finishes with two OH radicals and an alkyl radical which leads to even more radical growth, as we will show below. Therefore, H atom abstraction by HO_2 provides chain branching, and an increase in the model values for the rates of these reactions results in a dramatic increase in the rate of autoignition and a smaller computed value for the ignition delay time. As we will discuss below, in the present model a decrease in the ignition delay time can be interpreted as a numerical prediction of a reduction in the octane rating of that fuel.

The numerical description of the process of H atom abstraction must include the fact that H atoms are bound more tightly at primary sites, followed by secondary sites and then by tertiary sites. Of course, the number of each type of H atom also contributes to the overall rate of H atom abstraction. Thus, in the above model of 2-methyl pentane, the rate of primary H atom abstraction from site 'a' is smaller, per H atom, than the rate of abstraction from the secondary 'c' site. However, since there are 6 type 'a' primary H atoms, the overall rate of abstraction of 'a' H atoms is often actually greater than the rate of abstraction of the 'c' H atoms. In Table I, the rates of H atom abstraction per C - H bond are summarized for all of the important abstracting radicals and for each type of site.

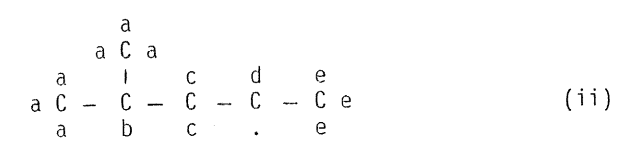
Table I

Rate expressions for H atom abstraction
(per C - H bond)
Rates are given in cm^3-sec-kcal units

OH	1.75×10^9	$T^{0.97} \exp(-1.59/RT)$	primary
	2.30×10^7	$T^{1.62} \exp(-0.04/RT)$	secondary
	5.70×10^{10}	$T^{0.51} \exp(-0.06/RT)$	tertiary
HO_2	1.34×10^{12}	$\exp(-19.4/RT)$	primary
	1.22×10^{12}	$\exp(-17.0/RT)$	secondary
	2.16×10^{12}	$\exp(-14.4/RT)$	tertiary
H	9.33×10^6	$T^{2.00} \exp(-7.70/RT)$	primary
	4.50×10^6	$T^{2.00} \exp(-5.00/RT)$	secondary
	1.26×10^{14}	$\exp(-7.30/RT)$	tertiary
O	7.33×10^6	$T^{2.40} \exp(-5.50/RT)$	primary
	2.35×10^5	$T^{2.50} \exp(-2.23/RT)$	secondary
	1.10×10^{13}	$\exp(-3.28/RT)$	tertiary
CH_3	2.17×10^{11}	$\exp(-11.6/RT)$	primary
	1.98×10^{11}	$\exp(-9.50/RT)$	secondary
	1.00×10^{11}	$\exp(-7.90/RT)$	tertiary

Abstraction of H atoms occurs at all ranges of temperatures and pressures. Only at very high temperatures, such as those encountered in high temperature shock tubes (18), where the thermal decomposition of the fuel molecule contributes a significant fraction of the total rate of fuel consumption, does any other process provide any amount of fuel consumption. Abstraction by O, H, and CH_3 is often very important at higher temperatures and under pyrolysis conditions, but for knock conditions the abstractions by OH and HO_2 are most important. One of the keys to the alkylperoxy isomerization theory is its explanation of the many reaction paths which lead to OH and HO_2 production.

The alkyl radicals produced by H atom abstraction are then consumed. At high temperatures, such as in flames or shock tubes, these radicals decompose into olefins and smaller alkyl radicals. However, under the lower temperatures and higher pressures of engine environments, the major alkyl radical reaction is the addition of molecular oxygen, O_2, to the alkyl radical. This is a reversible addition reaction, and its equilibrium constant plays a major role in determining the computed rate of autoignition. One of the alkyl radicals from 2-methyl pentane, produced by abstraction of one of the 'd' H atoms, can be denoted as dC_6H_{13} and shown schematically by



(ii)

The thermal decomposition of this radical, dominant at high temperatures but still important at the lower temperatures in the end gas, would proceed via β-scission to produce C_3H_6 and iC_3H_7 radicals. Decomposition of the iso-propyl radical would then produce C_3H_6 and an H atom. As a result, this decomposition route is a chain propagation sequence, starting with the one radical that abstracted the 'd' H atom from the fuel, and ending with the H atom. In the same manner, the other alkyl radical decomposition paths can be shown to represent chain propagation sequences. Addition of molecular oxygen to the dC_6H_{13} radical, however, leads to chain branching through several possible reaction paths. Beginning with the addition of O_2

$$dC_6H_{13} + O_2 = dC_6H_{13}O_2 \qquad (4)$$

these possible paths consist of:

a) Abstraction of H atoms (usually from the fuel molecule) by this alkylperoxy radical

$$RH + dC_6H_{13}O_2 = R + dC_6H_{13}O_2H \qquad (5)$$

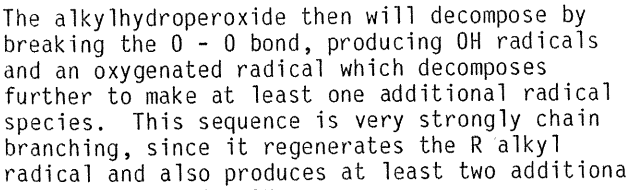
The alkylhydroperoxide then will decompose by breaking the O - O bond, producing OH radicals and an oxygenated radical which decomposes further to make at least one additional radical species. This sequence is very strongly chain branching, since it regenerates the R alkyl radical and also produces at least two additional radicals including OH.

b) The alkylperoxy radical can abstract an H atom from another location in the radical itself. Formally an isomerization reaction, this process is actually an abstraction of an H atom by a radical site in the same species, with the net result being the creation of a species with a Q - O - O - H structure, where Q represents a potential olefin species. There are two major considerations which control the rate of this internal H atom abstraction. The first of these is the type of site from which the H atom is abstracted. That is, the energy barrier to primary H atom abstraction is greater than that for secondary abstraction, and abstraction of tertiary H atoms is easier than either primary or secondary. The second factor of importance is the distance between the O - O radical site and the H atom to be abstracted. This factor is termed the ring strain energy and reflects the fact that abstraction of H atoms which are close to the abstracting site requires the radical to bend itself rather tightly in order to get the two sites close enough together for the transfer to occur. This energy barrier is largest for abstraction of a "nearest neighbor". In terms of the example species above, for the $dC_6H_{13}O_2$ radical

(iii)

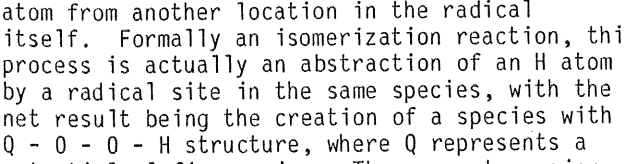
this would refer to the internal transfer of one of the 'c' H atoms to the O atom site. Benson (19) asserts that, for internal H atom transfer in alkyl radicals, this ring strain energy falls to essentially zero for ring structures with six or more C atoms. Following many other authors, we assume that the same trend should be expected to alkylperoxy radicals as for alkyl radicals. However, because direct kinetic evidence is scarce for these processes, there is still some uncertainty about whether ring structures larger than six members (or atoms) also have zero strain energy, or if the six-membered ring structure represents the minimum energy barrier with seven-membered and larger ring structures possessing higher strain energy barriers.

Following internal H atom abstraction, the resulting radical species can react in several ways. The two most important of these consist of cyclization to produce an epoxide species and an OH radical, and addition of another O_2 molecule to produce a dihydroperoxy radical. To illustrate the first alternative, if the above radical had transferred the 'c' H atom to create



(iv)

then the products of cyclization would be

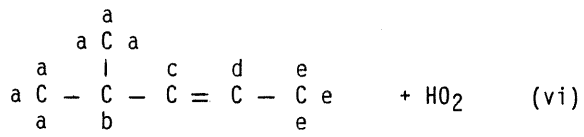


(v)

in which the epoxide consists of 2-methyl,3-isopropyl oxiran. Even for this single fuel, if all of the possible alkyl radicals are included, there 11 possible epoxide

species which can be produced. Although formally a propagation sequence, these reaction paths are found to have an accelerating influence on the overall rate of ignition, because they rapidly convert an alkyl radical to a very reactive OH radical and a relatively reactive epoxide species.

There is another product possible following the isomerization of some of the RO_2 radicals. For those cases in which the internal H atom is abstracted at the site adjacent to the O - O bond as in (iv) above, then it is possible for the C - O bond to be broken. The products of such a process would be



(vi)

Somewhat surprisingly, this sequence is found computationally to retard the overall rate of autoignition. This is due to the fact that the subsequent reaction of HO_2 radicals

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (6)$$

followed by

$$H_2O_2 + M = OH + OH + M \qquad (7)$$

produces one OH radical for each alkyl radical consumed. The difference between this sequence and that producing epoxide species is that the process producing HO_2 also makes very stable olefin species, while the epoxides produced in the earlier sequence are more reactive than the olefins. Our numerical models are quite sensitive to the ratio of these two families of RO_2 isomerizations, the first of which produces epoxides + OH while the second produces olefins + HO_2.

c) Finally, if a second O_2 molecule adds to the isomerized QOOH species, then the most common reaction sequence leads to at least three radical species, two OH radicals and another olefin or oxygenated radical species. As a result, this sequence of reactions tends to accelerate the overall rate of autoignition.

The above families of reactions are quite involved and lead to complicated system behavior. The equilibrium constants for the addition of molecular oxygen to alkyl radicals have a large dependence on temperature. There is a "ceiling" temperature (20) above which the RO_2 radicals decompose rapidly. Recall that most of the reaction sequences which begin with the addition of O_2 to alkyl radicals provide chain branching, so reduction in the concentration of RO_2 radicals as temperature is increased retards the rate of reaction. This phenomenon is responsible for the so-called negative temperature coefficient, in which increases in temperature actually lead to a decrease in the overall rate of reaction. Under atmospheric pressure conditions, the ceiling temperature for typical hydrocarbon fuels would be less than 900K, but these reaction rates and the equilibrium constants vary with pressure, and these addition steps are still very important at peak end gas temperatures.

Global Kinetic Models

This model consists of nineteen reactions, most of which represent families of elementary reactions. Some of the species, including OH, O_2, HO_2, H_2O_2, and the fuel are "real" chemical species, while others represent families or groups of species such as a generic alkyl radical R and alkylperoxy radical RO_2. A few of the reactions represent actual detailed model reactions, including reactions (6) and (7) discussed above for the detailed model. Other reactions represent averages of actual groups of elementary reactions, such as

$$RH + OH = R + H_2O \qquad (8)$$

which does not distinguish between primary, secondary, and tertiary rates of abstraction.

The most important reaction in the global model is the isomerization of the RO_2 radical,

$$RO_2 = ROOH \qquad (9)$$

a reaction which is approximately equilibrated under most conditions. Although the rate of the reverse reaction is always the same, regardless of fuel, the rate of the forward reaction is used to calibrate the model for each different hydrocarbon fuel. Historically, this calibration was originally carried out through comparisons between computed results and experimental data from rapid compression machines. However, the recent study by Cowart et al. (3) showed that engine knock data were required in some cases to establish the appropriate forward reaction rate for Reaction (9) in the global model. Once this calibration was accomplished, the global reaction mechanism could be used with confidence to analyse engine knock data.

It is clear that a considerable variety of kinetic factors, involving molecular size and structure, are being combined together into a single forward rate constant, and it should not be surprising to find situations in which the rate of Reaction (9) in the global model is assigned a rate which is inconsistent with the rate of isomerization in the detailed model. However, it is found that, even in those cases, the computed results are still reliable. A careful analysis of the reduced model structure shows that the quantity which is being adjusted is really the overall rate of chain branching, and this can be done in several places in the global model. The general reason that the global mechanism gives results which agree both with the detailed kinetic mechanism and with experiments is that it includes all of the essential elements of any chain reaction, initiation, propagation, branching, and termination.

MODEL RESULTS

There are three groups of model results which represent tests of this type of approach. The first of these is the recent study by Cowart et al. (3) in which both the detailed and the global mechanisms were used to examine engine knock data. The global model required calibration by adjusting the rate of Reaction (9) for n-pentane, one of the fuels used in the study, while rate parameters for iso-octane were unchanged from previous studies. The detailed kinetic mechanisms for the same two fuels also required some refinements. Once the two sets of kinetic data were established, the computed results compared well with experimental data.

This is illustrated by the results of comparisons for both n-pentane and iso-octane mixtures in a test engine which was operated under knocking conditions. For a series of engine cycles, the pressure-time histories were recorded and used to drive the numerical model. The only variable in these engine cycles is the variability from cycle-to-cycle which is always present in actual operation. Because of this variability, each cycle knocks at a different time. We assume that the pressure-time history for each cycle contains those factors which led to engine knock at these different times.

This can be seen in Fig. 1, where the predicted or computed time of knock occurrence is plotted against the observed time of knock occurrence, for a range of engine cycles. Both the detailed mechanism results and the global mechanism results are shown, and results for both fuels fall along the diagonal line, indicating good agreement with experiment for both models.

Both the detailed and global model results were very sensitive to the rates of alkylperoxy isomerization. The detailed mechanism also showed great sensitivity to the rate of addition of molecular oxygen to the alkyl radicals and to the rate of H atom abstraction by HO_2 radicals. This study showed that, under controlled conditions, both models can interpret and predict experimental knock results. The global or reduced model required one calibration using engine data, but it then provided very reliable results and was very economical in terms of computer resources. The detailed mechanism did not require calibration to simulate the engine knock data, but it was computationally very expensive. Both mechanisms described only single-component fuels; because of the ways in which the mechanisms were developed, the detailed mechanism would be expected to be able to describe autoignition of mixtures of these fuels, while the ability of the reduced mechanism to predict knock in such mixtures would be uncertain.

Westbrook et al. (1) used the present approach to simulate the autoignition of mixtures of primary reference fuels, n-heptane and iso-octane, under engine conditions. By definition, n-heptane has an octane rating of 0, while iso-octane has an octane rating of 100. Mixtures of these two fuels have an octane rating

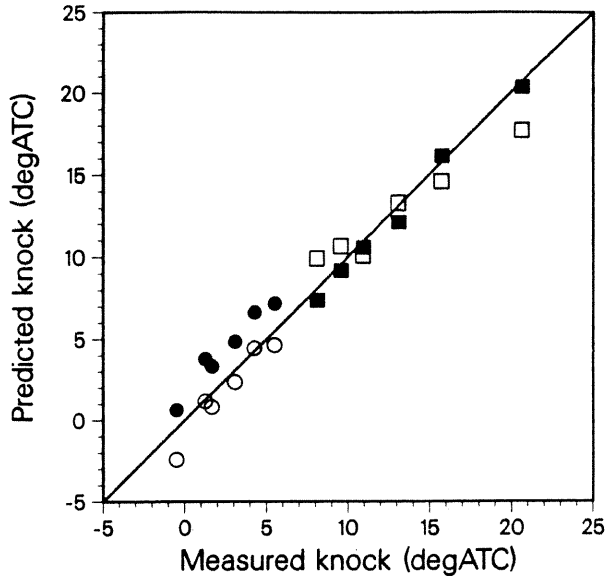


Figure 1

Predicted and observed times of knock occurrence Open symbols are global model results, solid symbols are detailed model results, cirles refer to iso-octane and squares to n-pentane.

equal to the percentage of the fuel mixture which consists of iso-octane. Thus a fuel mixture of 75% iso-octane and 25% n-heptane defines a mixture whose octane rating is 75. The octane rating of arbitrary fuels and fuel mixtures are evaluated by comparing their knocking behavior to mixtures of these primary reference fuels.

Primary reference fuel mixtures were the computational end gases in an engine cycle that was driven by a measured engine pressure history. This engine history was taken (22) from an engine operating close to its knock limit with a 90 octane number primary reference fuel mixture. Therefore, if a fuel with a lower octane rating were used in this same engine, knock ought to occur. As the octane rating is reduced below 90, knock should occur at steadily earlier times. Conversely, knock would not be expected for fuels with octane ratings greater than 90, using this same pressure history. The end gas temperature corresponding to this experimental end gas pressure history is given by the solid curve in Fig. 2.

We noted earlier that knocking occurs in an engine when the autoignition of the end gas takes place before the premixed flame can consume it. In the computational model, the flame propagation is included only through its influence on the pressure history. As a result, it is necessary to establish a reference time for the model which corresponds to the time at which the flame would be expected to complete end gas consumption. Based on extensive experience with the engine from which these pressure histories were taken, Leppard (21) found that when threshold knock was observed, it would appear at approximately 58 msec after bottom dead center. This time was thus adopted as the reference time of knock occurrence for the 90 octane rating engine

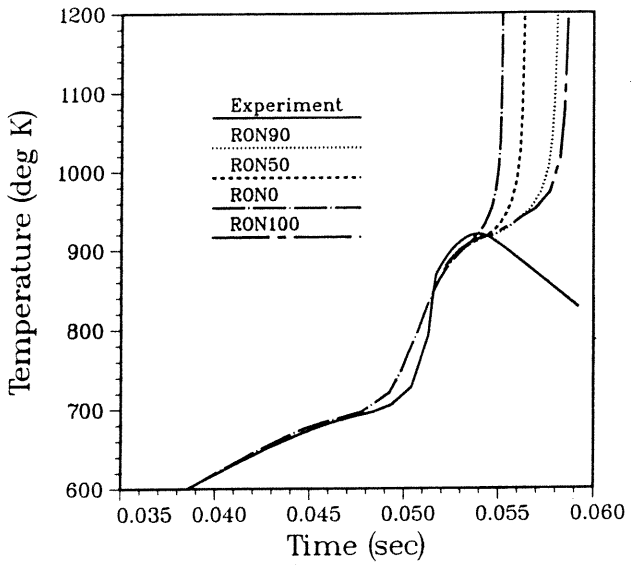


Figure 2
Temperature histories for primary reference fuel mixtures

cycle. With this in mind, the autoignition model, with the detailed kinetic mechanism for the mixtures of primary reference fuels, was calibrated so that a mixture of 90% iso-octane and 10% n-heptane (by definition 90 octane) ignited at 58 msec after bottom dead center. This calibration was made by varying the rate of end gas heat transfer in the numerical model. Once this heat transfer coefficient was determined it was left unchanged while the fuel composition was varied systematically over its entire range from octane rating 0 (i.e. 100% n-heptane) to 100 (100% iso-octane). The computed times of autoignition were found to depend monotonically on the octane rating of the fuel mixture, from an earliest ignition time of 55.0 msec for octane rating 0, with ignition at 58 msec for octane rating 90, to ignition at 58.8 msec for octane rating 100. Again, it should be noted that, for the octane rating mixture of 100, autoignition would not be expected at all, since the flame in the engine chamber would have consumed the end gases at a time of 58 msec, terminating the approaching autoignition before it had released any noticeable energy. This study demonstrated that the present kinetic treatment includes all of the major factors that are responsible for determining the rates of autoignition of these primary reference fuel end gases. It also shows that a detailed mechanism can indeed treat mixtures of different fuels.

A final example of the capabilities of the present approach is provided by a study which has examined the autoignition properties of a rather large family of related fuels, the structural isomers of pentane and hexane. We used one of these isomers earlier in this paper to illustrate the kinetic pathways included in the detailed modeling approach, 2-methyl pentane (i). The entire family of these 8 fuels is shown in Fig. 3. The octane ratings (Research Octane Number RON) for these fuels are also indicated, ranging from a very low value of 25 for n-hexane to a maximum of 99 for the highly branched fuel 2-3,dimethyl butane. These fuels include a variety of primary, secondary, and tertiary C - H bonds, a range of fuel sizes, and therefore provide a very demanding test of the modeling approach.

The present model has been used to simulate the autoignition of each of these fuels, and the detailed analysis of the results will be published in the near future. However, the computed results can be summarized here to indicate the current ability of the approach to describe this type of complex knock behavior. The computed times of autoignition for the C_5 and C_6 isomers, shown in order of octane rating, are

Table II

Computed autoignition times

Fuel	autoignition time (msec)	octane rating RON
n-hexane	55.0	25
n-pentane	55.9	62
2-methyl pentane	55.5	73
3-methyl pentane	57.2	74
2,2-dimethyl propane	56.4	86
2-methyl butane	59.1	92
2,2-dimethyl butane	59.9	92
2,3-dimethyl butane	58.1	99

Overall the agreement between computed and experimentally determined octane ratings is quite good. The fuels which ignite earlier than 58 msec are indeed those with octane numbers smaller than 90, while those which ignite later are those with octane numbers larger than 90. In most cases the relative times of autoignition also correlate with octane rating, with n-hexane being the earliest to ignite, followed by n-pentane and 2-methyl pentane. Similarly, the branched fuels are generally slower to ignite than the straight chains.

Perhaps even more significant, the model shows which factors are particularly important in determining the time of autoignition. One key factor is the observation, based on the detailed kinetic histories for all of the fuels, that virtually no fuel consumption has taken place prior to the time of maximum pressure at about 53.7 msec. There is a fairly long period of time during which the pressure is relatively constant at close to its maximum value and the temperature is approximately 900K. Therefore the entire process of fuel consumption must occur over a relatively short period of time. In the cases in which the octane rating is less than 90, fuel consumption requires less than about 4.3 msec, between 53.7 msec and 58.0 msec. This also means that the dominant kinetic regime is that which is most important at about 900K, and that one can use this temperature to make estimates of reaction rates and other kinetic properties.

There are also some areas in which the model results do not agree particularly well with the

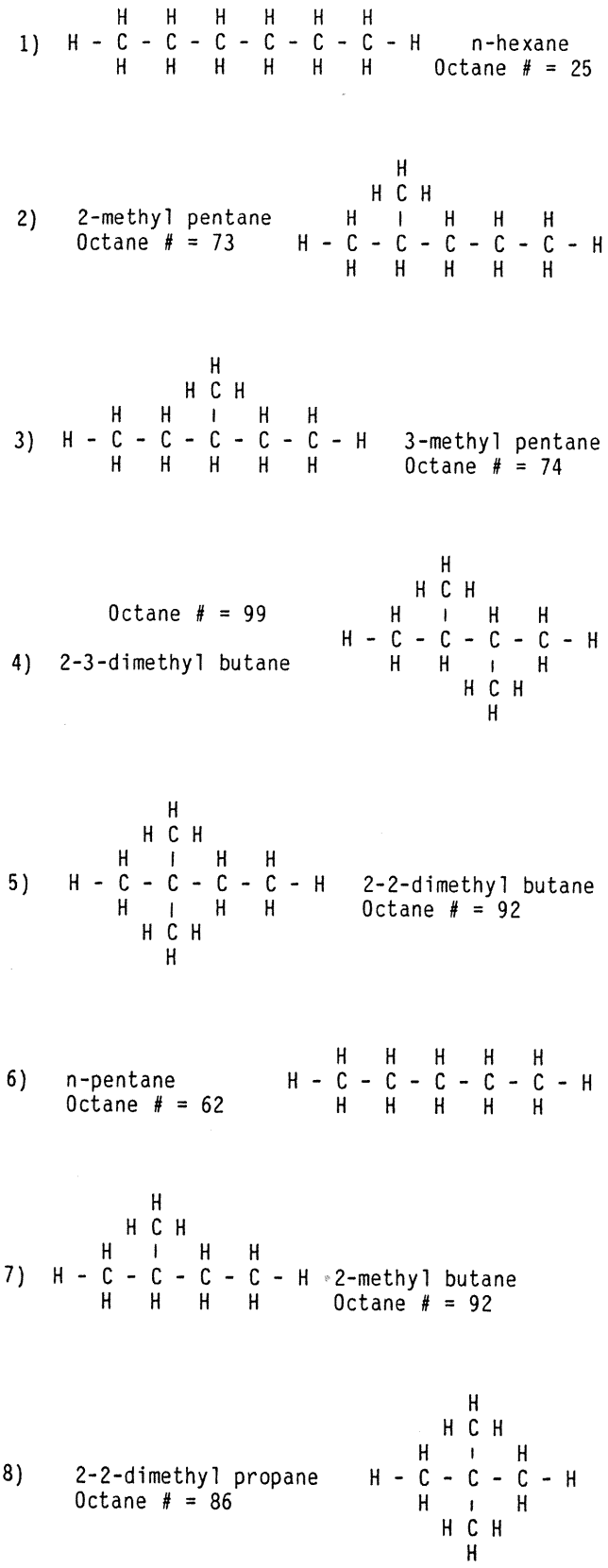


Figure 3
Schematic diagrams of hexanes and pentanes

experimental observations. The computed results for 2-methyl pentane and 3-methyl pentane are quite different, although both predict autoignition earlier than 58 msec, but the octane ratings of these two fuels are virtually identical and their structures are very similar. In addition, the fuel with the largest octane rating, 2,3-dimethyl butane, does not have the longest computed autoignition delay time, although the computed result indicates it does ignite later than 58 msec and therefore has an octane number greater than 90.

There are several areas in which the present model can be refined to improve the model performance and utility as a predictive tool. First, continued analysis of the elementary reaction rate information, product information, and modifications will improve the reaction mechanisms. There are experimental studies in the literature which examine the intermediate temperature slow oxidation of many of these fuels, and this information can be used to test the mechanisms. Future plans include extensions of the present approach to isomers of heptane and octane, which will provide an even more extensive validation and test series for the model.

Another refinement which may help to improve the model is the use of more than a single pressure history to drive the model. That is, the present study uses only a pressure history (and its implied temperature history) which is accurate for a 90 octane number primary reference fuel. It is possible that small changes in the compression history for different octane numbers might lead to quantitatively different results.

Another related consideration is that the numerical model assumes that all of these fuels starts at exactly the same initial temperature and pressure. This neglects any effects of differences in heat of vaporization, flame propagation in the engine chamber, and other thermochemical parameters. Methods for consideration of these effects and incorporating them into the model must be developed.

CONCLUSIONS

At the present time, there are two approaches commonly employed to model and predict the onset of knocking performance in spark-ignition engines. A global, reduced mechanism can be calibrated and used economically in large engine models and will provide reliable estimates of the rate of autoignition as various engine operating parameters are varied. This reduced mechanism includes the important qualitative reaction steps which produce knock, and the calibration constant, the rate of alkylperoxy radical isomerization, corresponds to a very sensitive parameter in the detailed kinetic mechanism. The ability of the reduced mechanism to deal with more complex situations, including fuel mixtures, additives to increase or decrease the knocking tendency, and significant changes in other operating conditions, is not yet established.

The second type of kinetic model for engine knock kinetics is the detailed reaction mechanism, which has been outlined in the present discussion. The mechanisms are particularly sensitive to several types or classes of reactions, and these have been identified. The detailed approach has been shown to apply to pure component and mixed fuels, and the applicability to treat antiknock and proknock additives has been established. Finally, the two types of kinetic models, the reduced and the detailed mechanisms, have been shown to agree well with each other in comparable situations, so that it is possible to use either one reliably, depending on the degree of detail, and the total computing costs, which are appropriate.

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