

3D03: DETAILED CHEMICAL KINETIC MODELING OF THE EFFECTS OF C=C DOUBLE BONDS ON THE IGNITION OF BIODIESEL FUELS

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A detailed chemical kinetic reaction mechanism previously developed to study combustion of soy and rapeseed oil methyl ester biodiesel fuels is used to simulate combustion of many other biodiesel fuels derived from different vegetable oils and animal fats. All of these biodiesel fuels consist of unique mixtures of the same five individual, single-component methyl esters, including methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and methyl palmitate. The stearate and palmitate molecules are saturated, while the oleate, linoleate and linolenate have one, two and three C=C double bonds, respectively. Each plant- or fat-derived biodiesel fuel that is made from the same five components has variations in combustion properties that depend on differences in the relative fractions of these five components. The present study focuses on ignition properties of these oil- and fat-derived biodiesel fuels and in their cetane numbers (CN), which measure relative ignition rates under diesel engine operating conditions. A key factor determining differences in ignition properties and CN of the many methyl ester diesel fuels is shown to be the number of C=C double bonds in the long carbon chains of each component molecule, with each C=C double bond reducing the CN value by a significant amount. Each C=C double bond provides allylic sites where H atoms are easily abstracted, but these allylic radical sites are shown to be weak bonding sites for molecular oxygen that do not support subsequent isomerization reactions that lead to low temperature reactivity and ignition. This reduced rate of low temperature reactivity is responsible for the reductions in CN due to the presence of these C=C double bonds. The amount of reduction in low temperature reactivity is roughly proportional to the number of C=C double bonds in each biodiesel fuel molecule, relative to the saturated components of biodiesel fuel.

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