Because of the structural diversity in biofuels, owing to functional groups such as ethers (R–O–R), alcohols (R–OH), carbonyls (R–C(=O)–R), and esters (R–C(=O)–C–O–R), peroxy radical-driven reaction mechanisms that underpin autoignition chemistry are dependent heavily on molecular structure. Labile hydrogen atoms, enhanced ring-opening reaction rates, and the influence of resonance-stabilization are some of the characteristics that functional groups impose. The impact on autoignition chemistry arises from alterations in initial radical distributions as well as R + O₂ reaction pathways relative to analogous alkane species. The present work provides a review of low-temperature oxidation chemistry of biofuels with a particular emphasis on initiation steps via reaction with hydroxyl (OH), hydroperoxyl (HOO), and methyl (CH₃) radicals, elementary reactions of QOOH including cyclic ether formation, and ignition delay times. Included in the review are quantum chemical studies and experimental studies using flow reactors, shock tubes and rapid compression machines.

keywords: biofuel, QOOH, peroxy radicals, autoignition, chemical kinetics