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Microscopic pyrolysis mechanism and kinetics of model biodiesels: Methyl butanoate, ethyl propanoate, and propyl acetate

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Abstract

Biodiesel is a promising alternative fuel that can help reduce fossil fuel consumption and mitigate environmental pollution.

In this study, we employed reactive molecular dynamics (ReaxFF MD) simulations to investigate the isothermal pyrolysis behavior of model biodiesel fuels: methyl butanoate (MB), methyl iso-butyrate (MiB), ethyl propanoate (EP), propyl acetate (PA), and iso-propyl acetate (iPA). Elevating the temperature facilitates the observation of chemical reactions at the microscopic scale. The reaction temperatures ranged from 2000 to 2900 K, with intervals of 300 K. The CHO-2016 combustion force field [1], which has been widely used in biofuel research, was adopted for our simulations.

During the initial decomposition stage, the ester group (R-C(=O)-O-R') exhibited two carbon-oxygen single bonds that were the most susceptible to cleavage. The primary pyrolysis pathways identified were MB/MiB/PA/iPA → $CO_2 + C_2H_4 + 2CH_3$ and EP → $CO_2 + 2C_2H_5$. Secondary reaction channels included MB/MiB/PA/iPA → $CO + C_2H_4 + CH_3 + CH_3O$ and EP → $CO + C_2H_5 + CH_2O + CH_3$. The pyrolysis processes produced significant amounts of gaseous products, with CO_2 yields following the order: iPA > EP > PA > MiB > MB. Methane production peaked at 2600 K, with yields decreasing at both lower and higher temperatures. C_2H_6 exhibits relatively low sensitivity to temperature, yielding nearly constant production across all temperature conditions. Regarding intermediate radical species, MB, MiB, PA, and iPA all generate a significant amount of CH_3 radicals, with branched fuel molecules producing even more. In contrast, EP predominantly produces C_2H_5 radicals. Additionally, we analyzed detailed reaction mechanisms, including decomposition, combination, hydrogen abstraction reactions, and soot inception pathways. Based on reactant consumption profiles, kinetic parameters were extracted. Among the fuels studied, iPA showed the highest consumption rate within the given temperature range. The calculated activation energies for MB, MiB, EP, PA, and iPA were 52.6, 48.1, 40.6, 42.5, and 34.0 kcal/mol, respectively, indicating the difficulty of thermal decomposition for each fuel.

The above pyrolysis mechanisms and kinetic studies provide theoretical support for the utilization of biodiesel.

References

[1] Ashraf C, Van Duin ACT. Extension of the ReaxFF Combustion Force Field toward Syngas Combustion and Initial Oxidation Kinetics. Journal Physical Chemistry A. 2017;121:1051–68.

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