Abstract

Methanol as an alternative fuel has gained significant attention in India under the vision of the Methanol Economy for the enhancement of energy security and reduction of emissions from industrial and transportation sectors. Methanol, which can be produced primarily from coal, natural gas, and biomass, is an octane booster, as it can be blended with gasoline in different ratios for utilization in spark-ignition engines. Fuel Quality parameters such as density, viscosity, thermal conductivity, diffusivity, etc. indicate the macro physicochemical properties, but the properties need to be understood at molecular levels for finding out the optimum blend ratio of methanol-gasoline mixture, macroproperties related to molecules effect, and input of molecular properties to injection and spray characteristics of the engine.

This study mainly focuses on predicting the physicochemical properties (density, viscosity, bulk modulus, thermal conductivity and diffusivity) using the COMPASS force-field potential, and critical properties and phase-transition behaviour using the TraPPE–UA force-field potential of methanol–gasoline blends (M15 and M85). In addition, injection and spray characteristics (dynamic injection timing, spray penetration length and breakup length) in a constant volume chamber were studied with the input data obtained from MD simulation. Density, viscosity, thermal conductivity, and bulk modulus increased with an increase in pressure due to reduced intermolecular distance and stronger non-bonded molecular cohesion, while these properties decreased with temperature due to weakened non-bonded (van der Waals and electrostatic) interactions. Bonded interactions (bond stretching, angle bending, dihedral torsion, and improper deformation) governed molecular deformation, whereas mutual diffusivity showed the opposite trend due to enhanced molecular mobility at higher temperatures and reduced mobility under compression. Compared with M15, M85 exhibited stronger hydrogen-bonding and electrostatic interactions due to its higher methanol content, leading to shorter intermolecular distance, stronger molecular interaction, lower free volume, and higher bulk modulus. Therefore, density, viscosity, thermal conductivity, and bulk modulus were more strongly influenced by non-bonded cohesion in M85, whereas M15 showed weaker polar association and relatively higher hydrocarbon-dominated dispersion behaviour.

The bonded interactions governed intramolecular deformation, whereas the difference between M15 and M85 was primarily controlled by non-bonded van der Waals and Coulombic interactions. Energy analysis showed that M15 had higher bonded-energy contribution due to its hydrocarbon-rich molecular structure, whereas M85 was governed by stronger non-bonded van der Waals and electrostatic interactions arising from methanol-rich hydrogen-bonded molecular networks. The critical temperature, critical density, and critical pressure were 540 K, 246.35 kg/m^3, and 3.734 MPa for M15, and 510 K, 263.56 kg/m^3, and 6.442 MPa for M85, respectively. At the critical point, the increased intermolecular distance weakened cohesive interactions, causing the liquid-vapor density difference and phase interface to disappear. Under subcritical conditions (500 K and 20 bar), distinct liquid and vapor phases were observed due to sufficient van der Waals and Coulombic cohesion. Clear O-H and O-O RDF ordering in M85 confirmed the persistence of hydrogen-bonded methanol clusters.

In the final phase, MD-predicted molecular properties are linked with injection characteristics. M85 showed a higher bulk modulus than M15 because stronger hydrogen bonding and electrostatic cohesion reduced the intermolecular distance. At 100 bar injection pressure, dynamic injection timing increased from 23.98 s for gasoline to 25.19 s for M15 and 29.48 s for M85 due to stronger molecular cohesion. The breakup length decreased with higher chamber pressure and fuel temperature. M85 had a longer breakup length than M15 due to its stronger hydrogen-bonding and electrostatic cohesion, which preserved the intact liquid core over a longer axial distance. For M15, it decreased from 11.3742 to 5.0841 mm at 100 bar when the chamber pressure increased from 1 to 5 bar, while for M85, it decreased from 11.6633 to 5.2136 mm under the same conditions. Increasing fuel temperature from 323 to 373 K at 100 bar injection pressure reduced the breakup length from 10.3780 to 8.7301 mm for M15 and from 10.6033 to 8.9167 mm for M85. The notable conclusions that emerged from this study's results indicate that force-field potentials such as COMPASS and TraPPE–UA strongly influence the physicochemical and critical properties of methanol–gasoline blends (M15 and M85), with the M85 blend showing stronger hydrogen bonding, higher intermolecular cohesion, and stronger electrostatic interactions, resulting in more pronounced variations in physicochemical and critical properties compared to M15.