Potential Vorticity (PV) is used as a diagnostic tool to explore the three-dimensional dynamical and thermodynamical structure of the Madden-Julian Oscillation (MJO) and its initiation in comparison to equatorial waves. PV of the MJO is distinct from those of the equatorial Kelvin and Rossby waves in their zonal scales and spatial structures. PV generation of the MJO is dominated by MJO diabatic heating acting on planetary vorticity and interaction between diabatic heating and relative vorticity of non-MJO components. From a PV point of view, thus, the MJO is maintained by a combination of self-sustaining and scale-interacting processes. Over the tropical Indian Ocean, PV generation of the MJO during its initiation is featured of strong pre-existing anticyclonic PV associated with negative anomalies of diabatic heating prior to positive anomalies of diabatic heating emerges. This suggests a possible precursor for prediction of MJO initiation.