A-117

Promotion of Hydrogen Production via the Thermal Decomposition of Piperylene in the Presence of By-Product Light Hydrocarbons

S. Miyamoto[1], Y. Katsuragawa[1], H. Ueda[2], M. Asahara[2], T. Watanabe[2], S. Ohta[2], T. Miyasaka[2]
[1]Gifu University, Graduate School of Natural Science and Technology, Gifu, Japan, [2]Gifu University, Department of Mechanical Engineering, Gifu, Japan

The effective utilization of refinery- and steam-cracking-derived by-product hydrocarbons is important for sustainable supplies of fuels, chemicals, and carbon carriers. Piperylene (1,3-pentadiene, C_5H_8), a C5 diene generated in petroleum refining and cracking processes, is a reactive unsaturated hydrocarbon and a potential feedstock for hydrogen production via non-catalytic thermal decomposition. Ideally, complete dehydrogenation and carbonization of piperylene is expressed as $C_5H_8 \rightarrow 5C + 4H_2$, corresponding to a theoretical maximum of 4 mol H_2 from 1 mol piperylene. In practice, however, pyrolysis proceeds through complex radical reactions forming C_2–C_4 hydrocarbons, aromatics, and coke precursors.

In this study, non-catalytic gas-phase piperylene pyrolysis was investigated using detailed chemical kinetic analysis with CHEMKIN-PRO. Piperylene single-feed pyrolysis was used as the reference system, and co-pyrolysis with refinery-derived light hydrocarbons, including propane, ethane, methane, ethylene, propylene, allene/propyne, and acetylene, was compared to evaluate their effects on hydrogen production and product distribution. The analysis focused on piperylene conversion, H_2 formation rate, H_2 yield, H_2 selectivity, hydrogen yield per supplied carbon atom, and the formation of acetylene, benzene, and cyclopentadiene as representative coke precursor species.
The reference piperylene/Ar system showed that increasing temperature and residence time enhanced piperylene conversion and hydrogen formation. In the intermediate temperature region, C_2–C_4 hydrocarbons such as ethylene, propylene, and 1,3-butadiene were dominant, whereas higher temperatures promoted acetylene, cyclopentadiene, and benzene formation, indicating a transition toward aromatic and carbon precursor chemistry.
Among the coexisting hydrocarbons, propane is expected to show the strongest promoting effect. Its thermal decomposition generates H, CH_3, C_2H_5, and C_3H_7 radicals, which can accelerate hydrogen abstraction and decomposition of piperylene. Thus, propane-assisted co-pyrolysis is expected to increase both piperylene conversion and H_2 formation rate under identical conditions. In contrast, methane is expected to provide limited promotion owing to its high thermal stability. Allene/propyne and acetylene may accelerate decomposition but also enhance aromatic and coke precursor formation through propargyl-related pathways.
The novelty of this study is the use of coexisting light hydrocarbons not simply as diluents or fuels, but as radical sources for promoting hydrogen-oriented pyrolysis of refinery-derived C5 hydrocarbons. This kinetic analysis aims to identify gas compositions and operating conditions that maximize hydrogen production while suppressing aromatic and coke precursor formation, contributing to efficient hydrocarbon upgrading and hydrogen production processes.