THERMAL DRY REFORMING OF HYDROCARBONS AND OXYGENATED COMPOUNDS: A SYSTEMATIC APPROACH

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Abstract

The integration of carbon capture by dry reforming can offer a promising solution to both reduce the carbon dioxide emissions and produce valuable gases. In general, dry reforming is a catalytic process converting hydrocarbon feeds, mainly methane, into syngas over a metal-based catalyst. Although the use of catalysts allows to increase the process performance and moderate the operating conditions, deactivation phenomena represent a critical issue, even more if bio-oils, hydrocarbon by-products or heavy hydrocarbon mixtures are considered as feedstocks, due to their higher tendency to form coke. In particular, bio-oils are gaining increasing attention as feedstock for the dry reforming process, since their direct use as a fuel or chemical feedstock is hindered by the high oxygen content and instability. In this framework, this study reports an experimental and numerical investigation of the non-catalytic dry reforming of various chemicals, providing a systematic analysis of the effect of molecular structure on process reactivity. The numerical analyses were performed considering a perfectly stirred reactor while experiments were carried out in a Jet Stirred Flow Reactor, at atmospheric pressure. In particular, the focus was on C_1-C_{10} alkanes, alcohols, and aromatic species. Experimental results and numerical simulations indicate that at lower temperatures, regardless of the specific chemical, thermal decomposition and recombination reactions lead to the formation of small olefins and hydrogen, followed by CO_2 capture at higher temperatures. Methane exhibits low reactivity for dry reforming at the explored temperatures, with minimal CO_2 conversion, as it requires temperatures around 1390 K to initiate the dry reforming reaction. In contrast, methanol shows higher reactivity, with a significant improvement in CO_2 conversion, starting at around 1270 K. For heavier hydrocarbons, cracking reactions are observed, that while promoting fuel conversion, introduce competitive kinetic pathways, making dry reforming less favourable. Heavier alcohols behave similarly to hydrocarbons, with dehydration reactions dominating before oxygenated intermediates are formed.

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