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Conversion of Hydrocarbons for Fuel-Cell Applications

Part I: Autothermal Reforming of Sulfur-Free and
Sulfur-Containing Hydrocarbon Liquids

Part II: Steam Reforming of n-Hexane on Pellet
and Monolithic Catalyst Beds

Maria Flytzani-Stephanopoulos
Gerald E. Voecks

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ABSTRACT

In support of the Department of Energy (DOE) Fuel Cell Program, aimed at operating fuel cells on middle distillate petroleum liquids in the near term and coal-derived hydrocarbon liquids in the near future, experimental work has been conducted on improving the autothermal and steam reforming processes. Autothermal reforming (ATR) tasks have been directed toward understanding the different mechanisms by which various fuel component hydrocarbons (related to both heavy petroleum and coal-derived liquids) are converted to hydrogen without forming carbon. Steam reforming tasks have been directed toward examination of monolithic catalysts with higher available active surface area and better thermal conductivity than conventional pellet beds, making it possible to steam reform fuels heavier than naphtha without sacrificing efficiency.

Experimental ATR results obtained in the previous phase of this work with sulfur-free pure hydrocarbon liquids are summarized here. Catalyst types and configuration used were the same as in earlier tests with No. 2 fuel oil to facilitate comparisons. Fuel oil has been found to form carbon in ATR at conditions much milder than those predicted by equilibrium. Reactive differences between paraffins and aromatics in ATR, and thus the formation of different carbon precursors, have been shown to be responsible for the observed carbon formation characteristics (fuel-specific). The types of carbon formed in the reformer were identified by SEM and XRD analyses of catalyst samples and carbon deposits. From tests with both light and heavy paraffins and aromatics, it is concluded that high boiling point hydrocarbons and polynuclear aromatics enhance the propensity for carbon formation in ATR.

Effects of olefin (propylene) addition on the ATR performance of benzene are described in this report. The amount of propylene that can be added at the inlet of the reformer before carbon begins to be formed is higher than what can be added at locations within the steam reforming region of the bed.

In ATR tests with mixtures of paraffins and aromatics (n-tetradecane and benzene) synergistic effects on conversion characteristics were identified. Thus, the mixtures' propensity for carbon formation was intermediate between that of the pure hydrocarbon component fuels under similar operating conditions.

Comparisons of the No. 2 fuel oil data with the experimental results from this work with pure (and mixed) sulfur-free hydrocarbons indicate that the sulfur content of the fuel may be the limiting factor for efficient ATR operation, i.e., low oxygen-to-carbon ratios and low preheat temperature. Exploratory tests with sulfur-containing paraffins and aromatics are described here in which the conversion and degradation effects of the sulfur additive (thiophene) in ATR were examined. At the low preheat temperatures and steam-to-carbon ratios used here, the front part of the catalyst was deactivated by sulfur-catalyst interaction, while the propensity for carbon formation was enhanced.

Steam reforming of hydrocarbons in conventional reformers is heat transfer limited. Steam reforming tasks performed in this work have included performance comparisons between conventional pellet beds and honeycomb monolith catalysts. The same fuel, n-hexane, was used in all cases. Metal-supported

monoliths were examined in this phase of the work. These offer higher structural stability than ceramic supports, which were found to disintegrate under the steam reforming conditions used in previous work in this laboratory. Moreover, metal monoliths offer the advantage of higher thermal conductivity.

Data from two metal monoliths of different catalyst (nickel) loading have been compared to pellets under same operating conditions. Improved heat transfer and better conversion efficiencies than for the pellets were obtained with the metal monolith of the higher catalyst loading. Experimental results are indicative of surface-gas interaction throughout the length of the monoliths.

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