KINETICS OF THERMAL CRACKING OF HYDROCARBONS BY PULSED MICRO REACTOR

by

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ABSTRACT

Kinetic studies on thermal cracking of hydrocarbons have been mostly conducted in empty tubular reactors, and design of industrial crackers based on such laboratory studies has not been very successful. Though packed bed micro reactor technique under steady-state operations has been extensively used for evaluation of kinetics for many gas phase reactions, it has not been successful for thermal cracking because of the obvious reason of unavoidable carbon formation in such a reactor. More recent trend of application of pulsed technique with packed bed micro reactor for evaluation of kinetics has not been reported so far for thermal cracking of hydrocarbons. The present investigation is an attempt to evolve a more accurate picture of hydrocarbon cracking kinetics by use of pulsed micro reactor technique.

LPG, a mixture of ethane, propane and butanes, marketted in India as 'Indane' by Indian Oil Corporation has been used as the raw material for study. A stainless steel micro reactor system was specially developed for the purpose. Kinetics studies have been conducted under atmosphere of hydrogen and nitrogen with the reactor

packed with quartz as well as with stainless steel particles. For comparison, a set of runs was also conducted with the empty reactor. The data on runs, conducted under pulsed feed conditions, were analysed on the basis of isothermal plug flow integral reactor assuming first order reaction rate on carbon conversion basis. Effect of surfaces was studied by varying surface to volume ratio of the packing inside the reactor. Runs were conducted in the temperature range of 550 to 780°C with residence times varying between 0.5 and 2.0 seconds.

The study revealed that quartz surface had some inhibitory effect on the reaction. In presence of hydrogen, the inhibitory effect could be quantified in the following form:

$$-\ln(1-x_H) = [k_v + k_s\ (S/V)]t$$

with the assumption of two parallel first order reactions, one on the basis of void volume of the bed and the other on the surface. However, in presence of nitrogen, the inhibitory effect was negligible, and the reaction rate could be expressed in terms of purely homogeneous first order reaction.

The empty tube reactor data yielded activation energy figure (47 K.cal./mole) very close to but slightly

less than that in a quartz packed reactor (51 K.cal./mole) The activation energies with stainless steel packed reactor, however, were found to have much lesser values (24-36 K.cals/mole) to be considered as those in a catalytic reaction. Also, some inconsistancy in results were observed while using different sizes of stainless steel packings in the reactor.

Kinetic parameters were also evaluated in terms of individual hydrocarbons as well as formation of products. The results generally agreed with those published in literature. The yield and selectivity were evaluated in all the cases, and the optimum values of experimental parameters for formation of ethylene and propylene were defined.

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