MODELING STUDIES OF THERMAL CRACKING IN A TUBULAR REACTOR AND IN A DIRECT HYDROCARBON SOLID OXIDE FUEL CELL: REACTOR SIMULATION, KINETICS AND EQUILIBRIUM

by

RAJEEV KUMAR

DEPARTMENT OF CHEMICAL ENGINEERING

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Thermal cracking

CERTIFICATE

This is to certify that the thesis entitled "**MODELING STUDIES OF THERMAL CRACKING IN A TUBULAR REACTOR AND IN A DIRECT HYDROCARBON SOLID OXIDE FUEL CELL: REACTOR SIMULATION, KINETICS AND EQUILIBRIUM** " being submitted by **Rajeev Kumar Garg** to the Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by him under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

To the best of our knowledge, the results contained herein have not been submitted in part or in full, to any other University or Institute for the award of any degree.

(**Dr V. V. Krishnan**)
Assistant Professor
Department of Chemical Engineering
Indian Institute of Technology, Delhi
New Delhi -110016

(**Prof. V. K. Srivastava**)
Professor
Department of Chemical Engineering
Indian Institute of Technology, Delhi
New Delhi -110016

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Rajeev Kumar

Rajeev Kumar

ABSTRACT

Ethylene is a vital feed stock in the production of petrochemicals. The production of ethylene is accomplished by using cracking of petroleum based feeds along with the production of a number of by-products. Thermal cracking of naphtha and ethane, to produce ethylene and other olefins, is accomplished by a tubular reactor in a furnace, where the product distribution is controlled by temperature, pressure and residence time. Modeling studies for thermal cracking are mostly based on plug flow model disregarding the radial variations in the tubular reactors.

In this work, a 2-D *r-z* model for a tubular reactor is used to simulate the conditions inside the thermal cracker where the cracking chemistry is described by a set of molecular reactions involving eight species (instead of free radical reactions). The model is solved numerically by backward difference finite difference scheme followed by the validation of the numerical scheme. Assuming constant transport properties (independent of temperature and composition), simulations for the reactor have been carried out for dilute ethane feedstock. On comparison of the simplified 2-D model predictions with those from plug flow model, the conversion from the former (2-D model) is found to be higher than that from the latter (plug flow) model due to the consideration of the radial gradients.

The rigorous 2-D model, consisting of simultaneous momentum, mass and energy balances, is applied for a concentrated ethane feed stream. The predictions are validated against experimental results available in literature. The product distribution throughout the reactor shows that certain species achieve maxima within the reactor due to the reaction chemistry. The rigorous model is applied for both the heat transfer conditions i.e. constant wall temperature and constant heat flux at the wall. The parametric study to

evaluate the effect of operational conditions on the reactor operation like space time, wall temperature/heat flux etc. has been done.

Detailed reaction chemistry is available for some hydrocarbon species. The mechanism for the thermal cracking of methylcyclohexane has been taken from literature. The mechanistic model consisting of free radical mechanism reactions along with plug flow reactor model, leading to a set of ODEs, has been used to simulate the reactor output conditions. The system of stiff ODEs has been integrated along the reactor length and the simulated values are found to be in error as compared to the experimental values available for thermal cracking of methylcyclohexane. The results have been optimized by manipulating the pre-exponential factors for the various reactions using Lavenberg-Marquardt method. A run for the simulation optimization strategy considering the reported conversion and yield as the objective functions has been successfully done.

Hydrocarbons are potential feeds for Solid Oxide Fuel Cells (SOFC) and may be fed directly to the anode (Direct Hydrocarbon SOFCs), leading to a combination of several reactions. Due to the high temperatures encountered at the anode the hydrocarbon feed molecules undergo dissociations (cracking), steam reforming and electrochemical oxidation to give a wide range of product species. Due to large number of reaction pathways, the Nernst potential can not be modeled based upon a single reaction. This is a problem involving multi-reaction equilibria. The behaviour of this reaction system will dictate the Nernst potential values and V-I characteristics of the SOFC.

The equilibrium state of the SOFC at the open circuit condition (Nernst potential) has been calculated based on reaction combinations involving species like hydrogen, syngas, methane etc. The dilution of reactant stream with the reaction products due to reaction upstream of the location under consideration is taken in terms of pre-conversion. The predicted Nernst potential is in good agreement with the experimental results of OCV

for hydrogen, syngas and methane as a feed to SOFC in literature. The effect of operational conditions on Nernst potential has also been investigated. At open circuit, for methane as a feed, the operational conditions that describe the onset of coke formation are examined. At lower temperatures, coking tendency is found to be higher as compared to that at higher temperatures. This has been explained based on thermodynamic behaviour of the various reactions involved.

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