SOME STUDIES ON HYDROCARBON CRACKING AND COMPUTATIONAL ASPECTS OF VAPOR-LIQUID EQUILIBRIA FOR SEPARATION OF HYDROCARBON MIXTURES

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CERTIFICATE

This is to certify that the thesis entitled "SOME STUDIES ON HYDROCARBON CRACKING AND COMPUTATIONAL ASPECTS OF VAPOR-LIQUID EQUILIBRIA FOR SEPARATION OF HYDROCARBON MIXTURES" being submitted by Mr. Doddipatla Veeranna to Indian Institute of Technology, Delhi, for the award of Doctor of Philosophy in Chemical Engineering, is a record of bonafide research work carried-out by him. Mr. Doddipatla Veeranna has worked under our guidance and supervision and has fulfilled the requirements for the submission of thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any Degree or Diploma.

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ABSTRACT

The present work consists of i) development of an experimental facility to study the thermal cracking of hydrocarbons at controlled conditions, and ii) study of computational aspects of vapor-liquid equilibrium (VLE) calculations for hydrocarbons and related compounds, which are essential for the design and operation of cracking plants for the production of olefins.

A tubular flow reactor, heated by fluidised bed combustor, was built to study the thermal cracking of hydrocarbons. The reactor diameter was 10 mm and length 2500 mm. A number of experiments were conducted with hexane in the temperature range 660 - 780°C using steam as diluent. Hexane flow rate was varied from 70 to 700 g/h. The hydrocarbons in the reaction products were analysed by gas chromatography while hydrogen and oxides of carbon were analysed by Orsat analysis. The observed conversions were compared with kinetic data from i) tubular reactor, and ii) pulse microreactor published in literature.

With widely used equation of state approach for VLE calculations of hydrocarbon mixtures, there are certain computational difficulties such as trivial solutions, false convergences etc. It was shown that these problems exist for all types of VLE calculations. These were illustrated with three popularly used equations of state : i) Starling-Han generalised correlation (SHGC), ii) Soave modification of Redlich-Kwong equation (SRKE), and iii) Peng-Robinson equation (PRE). It was shown that in phase boundary calculations, these problems are caused by poor initial values of temperature/pressure while initial K values do not play any important role. Empirical correlations were developed to calculate the initial estimates using true critical temperature and pressure. Kreglewski and Kay method was modified to improve the prediction of true critical pressure.

In isothermal flash calculations, the relative importance of initial estimates of K values and vapor fraction depends on the calculation scheme. In the scheme with material balance equation in the inner loop, the success of convergence depends on the initial K values. With the material balance equation in the outer loop, the convergence is sensitive to initial vapor fraction. Poor estimate of vapor fraction leads to a trivial solution.

In addition to trivial solutions, there are other computational problems like false convergences and maximum and minimum on convergence curve. Algorithms, for phase boundary and isothermal flash calculations, were proposed to avoid these problems by using the following physical constraints :

i) for a given mixture, along the phase boundary, vapor density is maximum and liquid density is minimum at the critical point

ii) vaporisation increases with increasing temperature and decreasing pressure in the normal region and reverse in the retrograde region.

Pressure-temperature envelopes were calculated for several hydrocarbon mixtures, where experimental data are available, using the three models. The predictions for low pressure are nearly same from the three models. At high pressures, the deviations with the SHGC are large. For wide boiling mixtures the SHGC fails to predict complete pressure-temperature envelope. The large deviations between experimental and predicted dew-point loci, especially at low pressures, were shown to be due to inherent experimental error.

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