COMBINING ^{13}C-NMR TRIAD SEQUENCE DATA WITH JOINT MOLECULAR WEIGHT AND COMPOSITION DATA TO ESTIMATE PARAMETERS IN A GAS-PHASE POLYETHYLENE REACTOR MODEL

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A 3-site metallocene catalyst is used in a gas-phase semi-batch reactor to produce ethylene/hexene copolymers. At the end of each batch, the polyethylene (PE) is collected from the reactor and analyzed to determine the 13C-NMR triad sequence distribution. Also, joint molecular weight and composition distribution data are obtained using GPC-IR. The current study builds on a previous model that was developed when NMR triad data were not available. In the current modelling work, differential equations are developed to predict triad sequence distributions in the final PE product. Data from 10 experimental runs are then used for kinetic parameter estimation. Using a mean-squared error (MSE) subset selection methodology, 23 of the 36 model parameters are selected for estimation using the available polymerization rate and PE characterization data. The remaining 13 parameters are held at their initial guesses to avoid overfitting of the data. Addition of the triad data to the parameter estimation problem allows for one additional parameter to be estimated and results in improved estimates of the 22 parameters that were previously estimable. For example, standard deviations of all but one of the estimated parameters decreased due to inclusion of the triad sequence data. The updated parameter estimates result in good fits for the triad sequence data as well as the joint molecular weight and composition data. In addition, the model accurately predicts four validation data sets that were not used for parameter estimation, indicating reliable predictive power of the model. The new model and its updated parameter estimates will be valuable for scaling up new polymer grades from lab-scale to commercial scale.