The EVM (Error-in-Variables-Model) framework is a combination of parameter estimation and design of experiments procedures for the reactivity ratio estimation problem. It provides more reliable reactivity ratios for any copolymerization system (and multicomponent systems in future extensions).

Reactivity ratios are very important parameters in copolymerization studies, for describing chain microstructure and hence determining polymer chain composition and sequence length.

For several decades, copolymerization reactivity ratios have been estimated incorrectly. In addition, there has been poor or no statistical design at all in the experimental trials conducted to collect the required data.

The biased and unreliable database of reactivity ratios clearly underlines the fact that this whole area requires a complete overhaul. It is time to start employing “state of the art” parameter estimation approaches and design of experiment strategies.

Error-in-Variables-Model (EVM) is a parameter estimation approach suitable for problems where all the variables are subject to error; dependent and independent variables are not distinguishable. Hence, EVM is the perfect method for estimating reactivity ratios in multicomponent copolymerizations.

This poster will illustrate the procedure of the EVM framework with the intention of addressing questions regarding its requirements, and mainly its mathematical implementation and numerical steps.

**Further reading**


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**Tips and Prescriptions for Numerical Implementation of the EVM Framework for Copolymerization**

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The iterative nature of the EVM algorithm requires a set of initial reactivity ratio values that can often be found in related literature.

The system model in the Direct Numerical Integration (DNI) approach consists of a step by step integration of the differential copolymer composition equation:

\[
\frac{df_i}{dx} + f_i - f_i = \frac{1}{x} - x
\]

EVM relates measurement values to their true values with respect to error

\[
x = x^*(1 + Ke)
\]

The EVM algorithm finds parameter estimates and true values of the variables by minimizing

\[
\phi = \frac{1}{2} \sum_{i=1}^{n} (x_i - \xi_i) (x_i - \xi_i) = (x_i - \xi_i)
\]

Reactivity ratio estimates are accompanied by their joint confidence regions, which reflect level of uncertainty.

One step further from the commonly used initial design of experiments is to design the next sequential experiment, using the prior information.

The sequential EVM design criterion is

\[
\text{Maximize } \sum_{i=1}^{n} \left( \frac{1}{2} (x_i - \xi_i)^2 \right) \left( \frac{1}{2} (x_i - \xi_i)^2 \right)
\]

Considering the feasible region, the sequential optimal feed composition is marked in Figure 2.

This iterative procedure stops when the reactivity ratio estimates have a satisfactory level of reliability.

The improvement in the precision of results can be shown by comparing corresponding joint confidence regions, as shown in Figure 3.

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![Figure 1: Initial design criterion surface](image1.png)

![Figure 2: Inverse of the sequential design criterion vs. feed composition](image2.png)

![Figure 3: JCRs of reactivity ratio estimation of initially and sequentially designed experiments](image3.png)