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## Improved prediction of alkyd reactors via infrequent-delayed observations

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### ABSTRACT

The problem of alkyd reactor polycondensation kinetics has been addressed. This was enhanced through a novel mechanistic approach and discrete-delayed measurements. The predictor provides adequate empirical-analytical basis for evaluating and operating alkyd batch reactor based on the present performance in order to monitor, control, correct the reactor and ensure prompt termination of the batch such that the final product quality index is maintained within specification. The current proposal considers modification of the existing models to include certain adjustable parameters whose values must be computed numerically such that the error measured between the actual and the predicted results are adequately minimized. The new approach was tested and validated in a reasonable number of reactions. The results were found to be reliable than the conventional approach. Further detailed comparison of the results achieved through the error dynamics and RMSE revealed a significant overall improvement in the studied reactor calibration problems.

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## 1. Introduction

Due to the stringent industrial specification that today's alkyd resin must meet, the need for fine tuning their properties through a more effective reactor operation is more acute than ever. For instance, in order to produce alkyd resin offering a combination of both desired drying time, chemical and mechanical properties, the molecular weight, viscosity, conversion and some instance, undesirable side product concentration must be controlled within limits that would not damage the industrial or end-use requirements (Lin and Hsieh, 1977). These alkyd resin property variables, in most instance, are difficult or impossible to measure on-line, specifically, viscosity. Thus, it is very difficult to control the alkyd resin product quality when all that is available is infrequent and delayed-offline laboratory measurements. One major problem facing the study of alkyd polycondensation processes up to the present time is the difficulty in modeling the reaction kinetics (Lin and Hsieh, 1977; Aigbodion and Okeimen, 1996). Due to the complexity of alkyd polymerization mechanism, and other reasons related to the uncertainty of the monomer structure, detailed kinetics model capable of yielding accurate prediction of reaction motion and product quality in alkyd reactor is basically lacking. This problem has been well-emphasized in reaction engineering

literatures and no satisfactory solution has been reported. However, previous works intended to address this problem only achieved certain levels of compromise between the observable outcome and the desired result. The earlier alkyd kinetics studies report kinetics models whose prediction accuracies degrade either at high or low conversions (Lin and Hsieh, 1977; Aigbodion and Okeimen, 1996). In a consistent effort to address this problem, works abound in literature where the state estimation methods (Alvarez and Lopez, 1999), system identification/recursive parameter estimation (Araromi and Adegbola, 2014) and nonlinear model predictive control (Valeel and Georgakis, 2002; Eaton and Rawlings, 1992; Castellanos and Zaldo, 2015; Bachir et al., 2005–2008) were recommended for the treatment of the alkyd kinetics prediction–estimation problem. The nonlinear state estimation method due to its compatibility with discrete-time system seems to be a preferred choice for handling monitoring and control problems in polycondensation processes. However, reports (Bachir et al., 2005–2008; Buruaga et al., 2003; Patton, 1962) show that the lack of reliable kinetics models preclude direct application of the standard state estimation methods such as extended Kalman filter (Bequette, 1991; Wang et al., 1997) and Luenberger-type model-based observer (Deza et al., 1992; Ciccarella et al., 1993) to alkyd reactors. Further attempts to overcome this problem led to the development of geometric estimation method

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(López et al., 2000; Hernández and Alvarez, 2003; Henerndez-Escoto et al., 2010) which attempts to reconstruct the kinetics uncertainties via a dynamic observer driven by discrete-delayed measurements. The method basically involves designing a compensator network (or matrix of gain functions) that could be linked to the available kinetics models to allow them perform within specification. The level of success attainable with this method remains a major breakthrough in the history of alkyd kinetics studies.

Optimal estimation is a process of extracting information concerning a parameter or function from noise corrupted observation. Considering model based and estimator based kinetic study of the polycondensation process, it is seen that model based kinetic study utilizes analytical models which often comes with unknown parameters. These unknown parameters, usually, are difficult to estimate but can be estimated using experimental data. However, prediction of the reactor parameter based on empirical-analytical model often introduces some unavoidable error in the results due to observed delay from measurement time. The present value of the measured quantity actually reflects value at certain time in the past since reasonable time is devoted to experimentation. To accurately predict the reaction motion over the entire course of the reaction requires an appropriate online sensor capable of time ahead prediction of the reaction based on previous or current data. This online sensors are equally referred to as dynamic data processor (DDP) (Henerndez-Escoto et al., 2010). This is usually achieved using a well-constructed estimator which acts as a process filter. In order to apply the technique of estimation theory to a particular engineering problem, an appropriate mathematical model must be found for the system of interest. Most chemical engineering processes, due to their highly non-linear nature, cannot be readily modeled and thus defining control strategies become cumbersome. Since the implementation of estimation algorithm is based primarily on system state observation or function thereof, the use of well-constructed filter based on third-order rate model have assisted in parameter estimation and model development; given that a measure of the accuracy of the model is directly obtainable (Hernández and Alvarez, 2003).

Although the possibility of resolving the alkyd reactor prediction–estimation problem using the geometric estimation technique is well established in literature, yet, there are indications that the accuracy of such a method fluctuates considerably in the reaction path (especially in the low conversion range <90%). Other major issues associated with the implementation of geometric estimation method as inferred from the referenced articles include;

- i. Conditional stability of the iteration process: setting of the tuning parameters required to achieve adequate convergence to the experimental data is based on trial and error, and the stability of the computation process is not always guaranteed at all trial settings of the tuning parameters. This makes the task involved in realizing the convergence criteria a bit difficult.
- ii. Low dimensional integrity: the task involved in describing the non-linear gain functions which determine the performance of the estimator progressively becomes cumbersome as the dimension of the problem increases.

In a decisive effort to simplify the alkyd reactor prediction–estimation problem, a pure mechanistic approach to the solution of the problem was introduced in this paper. An integral conversion model was developed based on the empirical third-order rate model. The development of the integral conversion model follows from the knowledge that with proper adjustment of parameters, the third-order rate model Eq. (1a) could be integrated analytically to obtain a generalized integral conversion model of the form Eq. (7); which could be linked to existing kinetics laws to yield adequate prediction of the entire reactor motion and the emerging product quality. The performance of the proposed method in yielding the present-time estimate of the key reactor variables that are related to product quality including; conversion viscosity, molecular weight, was compared with that of the standard geometric estimation method using data taken from the results of a laboratory scale synthesis of

alkyd resin from oxy-polymerizable gmelina seed oil, palm stearin and a published data (Nanvae et al., 2013).

## 2. Mathematical modeling of the alkyd kinetics

The following relationships are already known in coating industry for modeling the kinetics of polycondensation processes:

- i The empirical third-order reaction rate model for conversion of acid functional group (Lin and Hsieh, 1977; Henerndez-Escoto et al., 2010)

$$r = \rho(c, k, ce) := k(1 - c)(c_e - c)^2 \quad (1a)$$

- ii Viscosity-conversion expression in a form suggested by free-volume theory (Odetoye et al., 2011)

$$v = \mu(c, p_\mu) := a_\mu e^{b_\mu/(c_\mu - c)}, \quad p_\mu = [a_\mu, b_\mu, c_\mu]' \quad (1b)$$

- iii Average molecular weight conversion—relationship (Patton, 1962)

$$M = \eta(c, p_\eta) := \frac{1 + a_\eta c}{b_\eta + c_\eta c + d_\eta c^2} \quad (1c)$$

$$p_\eta = [a_\eta, b_\eta, c_\eta, d_\eta]'$$

The third-order rate equation  $[k(1 - c)(c_e - c)^2]$  in its basic form is nonlinear with respect to conversion. Thus, it is less possible to integrate the equation analytically. To overcome this problem, it was conceived in this study, that, instead of searching for an appropriate numerical integration scheme (which has also been proven difficult from earlier study (López et al., 2000)), a possible linearization scheme could be imposed on the empirical third-order rate model. This was fully developed in this paper via the following steps.

- (i) Substitution of relevant parameter of the third-order rate model with an arbitrary parameter  $\chi$ .
- (ii) Approximating  $\chi$  with a linear integrable function with some useful tuning parameters. This involves trying some basic linear, trigonometric, polynomial, exponential and logarithmic function for adequacy bearing in mind that:
  - (a) the most appropriate fitting function, must be able to predict  $\chi = 1 - c/ce$  adequately, over the entire reaction course,
  - (b) the approximation function must have tuning parameters that would allow for improvement of the model performance in any given data set,
  - (c) the tuning scheme need to be systematic for easy implementation.

Considering these three points, an approximating polynomial of the form  $q(t) = \alpha t^n + \beta t^{(n-1)} + \dots + \gamma t + \psi$  was considered most appropriate for the following reasons;

- (1) The  $q(t) = \alpha t^n + \beta t^{(n-1)} + \dots + \gamma t + \psi$  function is linear integrable,
- (2) Adequate fit to the value of  $\chi$  resulting from the experimental data can be obtained by mere selection of the parameters of the function,
- (3) Adjustment could be made easily in any new data set.

The application of Eqs. (1a)–(1c) in modeling reaction kinetics for a given batch process requires that the unknown set of model parameters  $k$ ,  $p_\mu$  and  $p_\eta$  are known. Basically,  $p_\mu$  and  $p_\eta$  are evaluated by fitting the calibration models to appropriate empirical data, while  $k$  are determined following standard linearization scheme. This study noted that unadjusted model(s) resulting from direct application of the third-order reaction rate model (1a) lead to poor prediction of the reactor variables at certain conversion range. Hence, in advanced kinetics modeling, the reaction rate model (1a) is usually forced to adequately describe the

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