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A surrogate model for acid functional group conversion in alkyd reactor

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ABSTRACT

Due to lack of detailed kinetic model, the alkyd resin polymerization reactor problem has been a subject of extensive theoretical, simulation and experimental studies, given the demand of processes with better compromises between safety, productivity and quality, and the development of control methods. In this study, a novel linear integral kinetic model for the conversion of acid functional group have been developed for predicting the progress of the reaction in the alkyd batch reactor on the basis of empirical third-order rate model, wave propagation theory and discrete delayed measurements. The new approach when tested, using an alkyd reactor calibration problem was found to be much more reliable. The model was able to approximate the motion and the trajectory of the polyesterification reaction process such that the desired properties were kept within specification.

1. Introduction

Gmelina seed oil (GSO) is a non-edible saturated vegetable oil extracted from *Gmelina arborea* fruit, available naturally throughout greater part of India, Vietnam, Nigeria, Sierra Leone, Malaysia, China, Laos and Thailand etc. Over the years, a tonne of research have been directed towards discovering the economic importance of this highly available non-edible oil. The potentials of the gmelina seed oil resource have been explored in the fields of; medicine and pharmacy (Sankh and Ashalatha, 2015; Oguwike and Offor, 2013; Ingole, 2013), bio-diesel production (Ingole, 2013; Sanjay, 2013; Sanjay et al., 2012, 2014), and production of lubricants (Oseni et al., 2013). From the available literature, it seems that no significant work have been directed towards exploring the potentials of the gmelina seed oil in alkyd resin synthesis which have important application in coating industry. Gmelina seed oil have been classified as saturated oil (Sanjay, 2013; Uzoh et al., 2014) which implies that neither the oil nor its derivatives can undergo auto-oxidation. This makes the oil a less prospective raw material for coating application where drying properties are considered of prime importance. It is pertinent to expand research, especially on tropical seed plants oils, to replace industrial seed oil that constitute food source with inedible ones. An oxy-polymerizable alkyd resin have been synthesized through green chemistry (epoxidation, hydroxylation, dehydration and polyesterification) (Uzoh, 2015). Hence, this opens avenues for further investigation on the potentials of the highly available gmelina oil in commercial processing of coating resins. One major issue identified in the course of the study (Uzoh, 2015) was the difficulty in predicting the kinetics of the alkyd polymerization process which basically allows for enhanced monitoring/control of the reaction progress and product quality. The need to address this problem motivates an elaborate study on the kinetics of polycondensation process in the batch stirred-alkyd reactor applied in this study.

The basic industrial batch reactor monitoring system depends on operator's experience supported with on-line measurements of conversion and the end-use properties including molecular weight and viscosity of cold product for predicting or estimating reaction progress and product quality in alkyd polymerization processes. This implies that the treatment of

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industrial alkyd kinetics prediction-estimation problem basically involves intensive laboratory testing and on-line reactor calibration effort which usually involves considerable experimental delay time. Thus the results obtained at any given time reflect the state of the reactor motion at certain time in the past and the measurements are said to be discrete-delayed. A Proper monitoring/control of the batch reactor and process design, therefore, requires both present time and time-ahead prediction of reaction progress/product quality. In this regard, the usual practice in the industry involves interpolation/extrapolation on log–log viscosity-conversion chart. This practice guides batch operators reasonably well to certain acceptable level of success (driven by operator's experience) in industrial alkyd reactor monitoring. The major concern of the present work is to develop an effective and automated batch monitoring scheme which on the basis of a model driven by discrete-delayed measurements yields an adequate prediction of the reaction progress, product quality or end-use properties up to and possibly beyond the critical gel point.

A comprehensive review of the literature reveals that detailed kinetics models capable of giving reliable prediction of reaction motion in alkyd polymerization process are basically lacking. The existing alkyd kinetics studies report simplified or lumped-condensation-type kinetics models which are valid either at high or low conversion (Lin and Hsieh, 1977; Aigbodion and Okeimen, 1996). The treatment of this problem led to the application of nonlinear state estimation techniques (Alvarez and Lopez, 1999), system identification/data-based regressive models (Araromi and Adegbola, 2014) and nonlinear model predictive control methods (Valeel and Georgakis, 2002; Eaton and Rawlings, 1992). Although the state estimation method due to its compatibility with discrete-time system seems to be a preferred choice for handling, monitoring/controlling the problems in polycondensation processes in recent polymer reaction engineering literature, yet, reports (Bachir et al., 2005–2008; Buruaga et al., 2003; Patton, 1962) show that the lack of reliable kinetics model occasioned by the complexity of alkyd polymerization mechanism, and other reasons related to the uncertainty of the monomer structure preclude the direct application of the standard estimation methods such as extended Karman filter and Luenberguer-type model-based observer to alkyd reactors (Bequette, 1991; Wang et al., 1997; Deza et al., 1992; Ciccarella et al., 1993). Various attempts to overcome this problem led to the development of geometric estimation framework (López et al., 2000; Hernández and Alvarez, 2003; Henerndez-Escoto et al., 2010), where the kinetics uncertainty is robustly reconstructed via a dynamic observer driven by discrete-delayed measurements. While these reports established the possibility of resolving the alkyd reactor prediction-estimation problem via geometric estimation technique, they also reveal that such a method may not be appropriate for studying the system as a distributed delay system where the measurements are more conveniently taken at variable time intervals. Moreover, the implementation of the geometric estimation method in the form reported in the referenced articles is strictly challenged by:

i. The difficulty in realizing the robust convergence criterion which involves highly rigorous estimator construction (with proof of convergence), and complicated turning procedure that involves trial and error selection of the tuning parameters
ii. The task involved in manipulating the observability matrix of the estimator is a serious mathematical endeavor that progressively becomes cumbersome as the size of the matrix or the indices of the problem increases

In a decisive effort to simplify the alkyd reactor prediction–estimation problem and all monitoring/control problems associated with it, a novel linear integral model for conversion of acid functional group was developed in this study for predicting the progress of reaction in a typical batch operation based on empirical third-order rate model and wave propagation theory. The development of the new conversion model employs the knowledge that on the basis of a model augmented with wave particle behavior and driven by online measurements, the kinetics uncertainty could be robustly reconstructed via successive linearization and indefinite integration of the adjusted model. That is, with proper adjustment of parameters, the third-order rate model (1a) could be integrated analytically to obtain a generalized integral conversion model of the form (7) which could be linked to existing kinetics laws to yield adequate prediction of the entire reactor motion and the emerging product quality Except for the present work, the idea of using a kinetics model, modified based on wave propagation theory as a compensator network to approximate the motion and the trajectory of reaction in alkyd polymerization process has not been reported. 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.

2. Materials and methods

2.1. Material

The gmelina fruits were collected locally from a forest in ministry of forest reserve, Anambra State in Nigeria. It was soaked in water for 8 days so as to easily separate the fruit pulp from the seed (de-pulp). The seeds were sun-dried and crushed mechanically using corona blender. The oil was extracted using soxhlet extractor. Analytical grade glacial acetic acid, H_2SO_4, phthalic anhydride, maleic anhydride, acetic acid, sodium bicarbonate, lithium oxide and glycerol were obtained from commercial sources (Merck Chemicals, BDH Chemical Limited, Poole, England and May and Baker Limited, Dangeham, England) and used without further purification.

2.2. Methods

2.2.1. Chemical modification of the GSO

The raw GSO was chemically modified (desaturation) according to the method described in (Odetoye et al., 2012).

2.2.2. Synthesis of GSO modified alkyd resin

Alkyds were prepared with GSO using lithium oxide as catalyst. The reactions were carried out in a three necked round bottom flask titled with a motorized stirrer, a dean-stark trap titled with water-cooled condenser and nitrogen in let tube at