Method for controlling reaction mass parameters during the synthesis of alkyd resins

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Abstract. Synthesis of alkyd resins is one of the most common technological processes for deep processing of vegetable oils. In Russia, about 700 thousand tons of alkyd resins are produced per year; so much attention is paid to improving the production process of alkyd resins. Production of synthesis of alkyd resins can be classified as fire and explosive hazardous. One of the main reasons for the high level of accidents in the synthesis of alkyd lacquers and resins is the lack of digitalization of control and management of synthesis. This paper discusses the possibility of using changes in the electrical properties of the reaction mass to control the flow of a chemical synthesis reaction. The principal difference between the proposed approach is that it is proposed to use measurements of DC values directly in the technological process.

Studies have shown that it is more promising to use the analysis of the values of the complex resistance module of the reaction mass for the purposes of synthesis control. The advantage of this solution is that the method is more informative, as observations are made in a two-dimensional space of complex values rather than in a one-dimensional one. When using high-frequency alternating current, the module and phase of the complex resistance of the reaction mass are controlled, as well as a number of other parameters (leakage current, q-factor, etc.)

1. Introduction

The duration of the process of synthesis of alkyd lacquers, the rate of chemical reaction is determined and is proportional to the technical capabilities of monitoring and controlling the synthesis process. In the absence of the possibility of automated operational control of the parameters of the synthesized resin, synthesis control can be implemented based on the long-term chemical reaction, which allows reducing the probability of negative consequences of loss of process control even with long-term one-time analyses. The consequence of these circumstances is high energy consumption, the cost of the synthesized product and excessive heat load on the environment.

Various methods are known for monitoring the characteristics of liquids using their electrical characteristics [2, 3, 4, 5]. The properties of chemical substances can be determined by electrochemical methods [1, 7, 8]. These methods are fully developed and widely used in laboratory analysis.

The methods [7, 8] are focused on laboratory studies of liquid properties and, in fact, differ little from the classical methods for analyzing synthesized alkyd resins. Moreover, the technical implementation proposed in [8] cannot be used during synthesis, as alkyd resins will inevitably polymerize in the sensor cavity and its use will be impossible. These methods assume the stability of the properties
of the studied liquid, so the state of the substance is analyzed only by one parameter and is not used to study a more complete set of electrochemical characteristics of the substance.

In the above problem statements and methods for solving them, in contrast to the one proposed in [1, 9, 11-16], the parameter of a substance that is not subject to chemical changes is analyzed. During the synthesis of alkyd lacquers, we are dealing with a complex technological process in which a new substance – alkyd resin, which is a polymer, is synthesized from a liquid mixture of various substances: vegetable oil, glycerol, pentaerythritol, phthalic and maleic anhydrides, xylene and other components during a chemical reaction. The reaction mixture undergoes profound changes. This is accompanied by changes in the phase states and properties of the substance. At the initial stage of synthesis, we solve the problem of controlling the parameters of the liquid. At the end of the synthesis, we get a polymer that approaches a solid body in its properties. During the synthesis process, reaction water appears, which also affects the intermediate measurement results. Highly volatile liquids can evaporate. These circumstances require the development of new approaches to the study of the properties of the synthesized resin by electrochemical methods.

During the synthesis of alkyds, the electrochemical properties of the reaction mass are seriously changed. At the initial and final stages, the properties of the reaction mass are close to those of dielectrics. At the end of the alcoholysis stage, the properties of the resin correspond to the characteristics of the conductor. The control methods developed by us and the technical means of their implementation are free from these disadvantages and allow controlling the synthesis of alkyds.

2. Materials and methods
To describe our experiments, we introduce the following definitions and assumptions. Let us suppose that the synthesis process is described by vectors of values of characteristic parameters that change during the reaction, which are piecewise constant functions of the discrete synthesis time:

\[
\begin{align*}
\vec{a}(t_i) &= (a_1(t_i) \ldots a_n(t_i)) ; \\
\vec{b}(t_i) &= (b_1(t_i) \ldots b_m(t_i))
\end{align*}
\]

where: \(\vec{a}(t_i)\) – vector of values of the main criteria parameters at the i-th time of synthesis; 
\(\vec{b}(t_i)\) - vector of values of additional criteria parameters at the i-th time of synthesis: 
\(t_i\) – value of the discrete time of synthesis, \(i=0, \ell\).

The main group includes criteria parameters related to the characteristics of the synthesized product (reaction mixture) at the i-th stage of synthesis with a high degree of confidence.

The group \(\vec{b}(t_i)\) \(i=1, \ell\) includes parameters that characterize additional features of the synthesis process or its stages. The values of these parameters may not be related to the characteristics of the synthesized product (reaction mixture), but the nature of their changes may give technologists additional information about the course of the synthesis reaction. In particular, information about at what stage, active phase, or completion phase of the chemical reaction the synthesis is. The entire range of synthesis time (synthesis stage) is divided into \(\ell\) segments, within each of which changes in the parameters of the synthesized product can be estimated as insignificant. Let us assume that for the realized synthesis of a particular type of resin, for each i-th time interval \(t_i(i=0, \ell)\) the values \(\vec{a}(t_i)\) and \(\vec{b}(t_i)\) are uniquely determined from experimental data and characterize the corresponding synthesis interval. It is quite natural to assume that the synthesis and the values of the parameters \(\vec{a}\) and \(\vec{b}\) are determined, including the initial values of these parameters \(\vec{a}_0 = \vec{a}(t_0), \vec{b}_0 = \vec{b}(t_0)\), which characterize the feedstock loaded into the reactor before the synthesis begins. These values can vary from synthesis to synthesis and their value can determine the initial position of the curves \(a(t_i)\) and \(b(t_i), \ i=1 \ldots \ell\). In order to take into account the initial values of the characteristics of the feedstock before the start of synthesis, it is quite natural to go to the relative normalized values of the parameters \(\vec{a}\) and \(\vec{b}\) namely:
\[
\begin{align*}
\tilde{a}_i(t) &= \frac{a_j(t_i) - a_j(t_0)}{a_j(t_0)}, \quad i = 1, \ldots, \ell, \quad j = 1, \ldots, n; \\
\tilde{b}_s(t) &= \frac{b_s(t_i) - b_s(t_0)}{b_s(t_0)}, \quad j = 1, \ldots, n; \quad s = 1, \ldots, k.
\end{align*}
\] (2)

It can be assumed that this will increase the compatibility of the results, as it will lead to a combination and visibility of the initial control points. In the problem under consideration, the parameters \(\tilde{a}\) and \(\tilde{b}\) are the electrochemical characteristics of the synthesized alkyd resin, as well as the values that are functionally related to them. These parameters are supposed to be determined at the characteristic frequency selected at the stage of preliminary studies using an algorithm similar to that described in [8] for each \(i\)-th \((i=1,\ell)\) synthesis segment.

To determine the characteristic frequency on the \(i\)-th \((i=1,\ell)\) segment of the synthesis of the corresponding type of resin, a sample of the reaction mixture is taken. The frequency is determined by the results of the analysis of this sample. It is natural to assume that each \(i\)-th segment will have its own value of the characteristic frequency. With this assumption, we pass from the value of the characteristic frequency introduced in [8] to the characteristic function \(\zeta(t_i) = 1, \ell\) or its continuous approximation \(\zeta = \zeta(t) = \zeta(t_0, \ldots, t_{max})\).

The schematic diagram of the contact resistivity sensor \(Z\) is shown in Fig. 1.

![Figure 1. Contact resistivity sensor Z: 1, 4 – Exciting electrodes; 2, 3 – measuring electrodes; 5 – dielectric element; 6 – variable signal source; 7 – monitoring and data processing device; 8 – comparison device.](image_url)

3. Results and discussion
The primary goal of our work is to develop methods for controlling the synthesis parameters of the synthesized resin. The objectives of the control are:

- control of the end of the stages of interesterification for the passage of the alcoholysis reaction;
- monitoring the polyesterification stage in order to determine the parameters of the synthesized resin, in particular the viscosity.

Both of these tasks are solved at the final stage of the corresponding synthesis stages. Therefore, in a practical setting, their solution can be divided into two parts:

- control of the output to the final stage of the synthesis stage;
- control of parameter values at this stage.

The implementation of the above tasks is based on the properties of the synthesized alkyd resins, namely, changes in the electrical conductivity of the reaction mass depending on the stage of the syn-
thesis reaction. The possibility of using these properties was indicated in [10]. As in [7], the possibility of using changes in the electroconductive properties of the reaction mass to control the course of the chemical synthesis reaction was noted. The principal difference between the approach discussed in [10] is that it is proposed to use measurements of DC values flowing through the sample for analysis. Detailed studies of potential practical applications for the purposes of real-time synthesis of alkyds are not given in [7,10].

The conducted studies [1] showed that it is more promising to use the analysis of the values of the complex resistance module of the reaction mass for the purposes of synthesis control. The advantage of this solution is that the method is more informative, as observations are made in a two-dimensional space of complex values rather than in a one-dimensional one. When using high-frequency alternating current, the module and phase of the complex resistance of the reaction mass are controlled, as well as a number of other parameters (leakage current, q-factor, etc.). Our proposed approach has the following important advantages of high-frequency measurement methods:

- the possibility of implementing a scheme that allows controlling contamination or oxidation of the electrodes,
- possibility of galvanic isolation of the measuring device from the controlled product,
- a significant reduction in the probability of distortion of measurement results by induced potentials.

In [10], the following mechanism for changing the electroconductive properties of the reaction mass during the synthesis of alkyds is described. An increase in the permittivity of the medium occurs due to the characteristics of the chemical reaction. During the reaction, fatty acid radicals are replaced by hydroxyl groups, and an asymmetry of molecules occurs, which leads to an increase in the polarity of the ion dissociation system, and consequently to an increase in the electrical conductivity of the solution.

These properties are shown in measurements using not only direct current, but also alternating current. Graphs of the registered values of the parameters of the complex resistance of the reaction mass during the synthesis of alkyd resin (for example, resin 90) are shown in Fig. 2. The graphs show the curves of changes in the values of the complex resistance module of the reaction mass (CSRM)-Z, the phase of the CSRM-Fiz and the active projection of the vector CSRM-Rp. These parameters are most susceptible to changes when observing synthesis processes. The graphs were registered using the developed hardware complex for monitoring the synthesis of alkyd lacquers and resins (TC 28.99.39-001-04156963-219).

Rp and Fiz undergo the most characteristic changes. The change in Rp corresponds to the one described in [1]. Initially, the Rp value corresponds to the characteristic of the dielectric, which is vegetable oil and reaches values close to the upper limit of measurement of the device “Immitans meter E7-30”- up to 10 GOhm. After loading pentaerythritol, soda and exposure to the synthesis temperature, the measured Rp value decreases sharply to the values of 30-100 kOhm, typical for a conductor (resistor). At the stage of reducing the temperature before loading phthalic anhydride, the property of the synthesis-reversibility reaction is manifested. As a result, the Rp values increase slightly. After loading and raising the synthesis temperature, the Rp values again rush to the lower value. As the polymer is formed, the hydroxyl groups are replaced and the Rp values gradually increase. These changes are accompanied by a similar change in Z values, a change in Fiz from -90 degrees to 0 (stage 1) and then to -90 at the end of polymerization.
4. Summary
The dependence of the Rp parameter and the viscosity of the synthesized resin was experimentally established. At the final stage of synthesis, this dependence can be approximated by a linear function whose coefficients are different for different types of synthesized resins. It should be noted that the figures shown in Fig. 2 the graphs reflect the typical dependencies that we have repeatedly recorded in the synthesis of alkyd lacquers PF 060, PF-053, AF 033, and others. The graphs were obtained using the hardware synthesis control complex (TC 28.99.39-001-04156963-2019). The experience of practical application and testing showed the operability of the hardware complex and control methods.

5. References
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