Kinetic description of heterogeneous processes using surface tension as an information parameter

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Abstract. We evaluate the possibility of using surface tension as the main information parameter for determining the order of the polycondensation reaction in the main reagent occurring in the “glyoxal-bark”. Surface tension was calculated according to the method of Owens, Wendt, Rabel and Kaelble (OWRK). In addition, the identified minus the first order of the polycondensation reaction may be due to the fact that the limiting stage occurs in the diffusion region. In this case, blocking the free reactive surface centers of the plant component of the mixture by products of the primary interaction leads to a slowdown of the process, despite an increase in the concentration of glyoxal. The unit modulus of the reaction order means that one molecule of glyoxal is involved in an elementary act of interaction of glyoxal with the structural units of the lignin macromolecule. This confirms both the working hypothesis on the mechanism of structure formation in “glyoxal-bark” system, and the possibility of using surface tension for the kinetic description of heterogeneous processes.

1. Introduction
Preliminary studies have shown that the chemical interaction of glyoxal with lignin substances of mechanically activated bark [1, 2] can lead to the formation of derivative compounds that make it possible to create a periodic colloidal structure resistant to temperature and humidity based on aluminium silicate colloid-dispersed soils [3]. It was hypothesized that the mechanism of the structure formation in the “glyoxal-bark” system is as follows: glyoxal binds the structural units of the lignin macromolecule, which have phenolic hydroxyl and carbonyl (carboxy) groups as substituents of the aromatic ring [4].

To confirm the working hypothesis, it is necessary to study the kinetics of formation of such a structure. This will allow to control the polycondensation reaction of glyoxal in the investigated organic-mineral system and optimize the modifier composition.
Since the sandy soil is a dispersed system, and the formation of the periodic colloidal structure with the introduction of the organic-mineral additive is associated with a change in surface characteristics, the polar component of the surface tension was chosen as the main integral information parameter for the kinetic process description. This parameter, determined by the non-destructive OWRK method [5-11], takes into account transformations in the kinetic and diffusion interfacial regions in a heterogeneous system.

The interaction process of glyoxal with finely dispersed bark is a complex heterogeneous reaction that proceeds in several stages with the formation of a number of intermediate products (intermediates). However, if we consider the interaction of glyoxal and structural units of lignin (guaiacyl propanoic groups) as a separate stage of a complex reaction, the order of the reaction can be equated to its molecularity. To calculate the ratio of reagents, literature data on the content of functional groups of the lignin macromolecule were used [12].

The paper evaluates the possibility of using surface tension as the main parameter for determining the order of the polycondensation reaction in the main reactant occurring at the interface in the “glyoxal-bark” system.

2. Method

The polycondensation reaction order in glyoxal was determined by traditional physicochemical methods based on the law of mass action using the Ostwald isolation method to eliminate the interfering effects of other reactants and the Van't Hoff's differential method. The rate of the process is determined indirectly through the rate of change of surface tension \( \nu, \text{mN/(m·min)} \) (equation (1))

\[
\nu = \pm \frac{d\sigma^p_S}{d\tau}
\]

where \( \sigma^p_S \) is the polar component of the surface tension, mN/m; \( \tau \) is time, min.

Pinus sylvestris bark was preliminarily prepared to its constant weight under the temperature of 40 °C. To activate surface centers of lignin, the bark was ground in the planetary ball mill Retsch PM100 using the dry mechanical dispersion method. Optimal dispersion parameters presented in the Table 1 were selected experimentally to obtain a finely dispersed system and achieve a metastable state of the surface.

| Stage | Grinding jar size, ml | Grinding balls, diameter, mm / quantity, pcs | Sun wheel speed, rpm | Grinding time, min |
|-------|-----------------------|---------------------------------------------|---------------------|-------------------|
| 1     | 500                   | stainless steel alloy 20/18                | 420                 | 10                |
| 2     | 50                    | stainless steel alloy 5/150                | 420                 | 20                |

To study the kinetics of the structure formation in the “glyoxal-bark” system, samples with an excess reactive groups of bark lignin and variable glyoxal content were fabricated. The amount of glyoxal (by the mass of the dissolved substance) in the system was taken 5-15 times lower than the mass content of the reactive phenyl-propane units of the organic polymer. To obtain a homogeneous mixture, glyoxal was introduced in the form of an aqueous solution. The amount of the water phase \( W \) was taken to be the same for all compositions, based on the specific water absorption of the bark \( B \) with the optimum dispersion \( W/B=1.5 \).

The components having been mixed thoroughly and compacted on a PLG-20 hydraulic press at a pressure of 1 MPa, samples were kept in natural conditions at a temperature of 25±2 °C. The diameter of the samples was 30 mm and the height was 18 mm. The contact angle of wetting was determined at different time intervals (0.5; 2; 4; 6; 8 hours) on the DataPhysics OCA 35 automatic device. Service fluids were ethylene glycol, ethanol (96 %), decane and water. The set of experiments consisting of three mandatory parallel measurements with a maximum allowable difference in contact angle of wetting values (no more than 2°) having been completed, corresponding functional dependencies were
plotted and the polar component of the surface tension was calculated at specified time intervals for each composition. Then, functional dependencies of the polar component of the surface tension on time (kinetic curves) were constructed by differentiating which with respect to time the initial rates \((v_0)\) of the polycondensation reaction for each composition were obtained. The time interval used for calculating the initial rates was equal to the duration of the active stage of the polycondensation reaction and averaged 8 hours regardless of glyoxal content.

To determine the polycondensation reaction order in glyoxal, the dependence \(\ln v_0 = f(\ln C_0)\) was plotted, where \(C_0\) is initial glyoxal concentration. The tangent of slope angle of this dependence is equal to the reaction order in glyoxal.

3. Results
Temporal changes in the values of the polar component of the surface tension for compositions with different initial glyoxal concentrations are presented in the Table 2.

Table 3 contains the experimental data to calculate polycondensation reaction order in glyoxal.

The functional dependence \(\ln v_0 = f(\ln C_0)\) for the determination of the polycondensation reaction order in glyoxal is shown on the Figure 1. The mathematical expression is represented by equation (2).

Table 2. Temporal changes in the values of the surface tension for different compositions.

| Time, \(\tau\), min | Surface tension \(\sigma_s^p\), mN/m for compositions with different initial glyoxal concentrations \((C_0, \text{mol/g})\) |  |
|-----------------|-------------------------------------------------|---|
|                 | composition 1 \((5.1 \cdot 10^{-5})\) | composition 2 \((3.1 \cdot 10^{-5})\) | composition 3 \((2.4 \cdot 10^{-5})\) | composition 4 \((2.1 \cdot 10^{-5})\) | composition 5 \((1.7 \cdot 10^{-5})\) |
| 45              | 54.76                                          | 56.26                                | 51.48                                | 46.57                                | 52.21                                |
| 134             | 47.45                                          | 47.22                                | 48.66                                | 31.08                                | 47.31                                |
| 257             | 45.57                                          | 36.44                                | 39.92                                | 27.79                                | 36.10                                |
| 382             | 44.48                                          | 30.73                                | 34.15                                | 13.47                                | 21.05                                |
| 490             | 33.34                                          | 24.65                                | 2.32                                 | 1.99                                 | 3.88                                 |

Table 3. The values of the initial glyoxal concentration and the initial rates of the polycondensation reaction in the “glyoxal-bark” system.

| Composition | Initial glyoxal concentration, \(C_0; 10^{-5}\), mol/g | Coefficients of the equation for the functional dependence \(\sigma_s^p = f(\tau)\) | Correlation coefficient, \(R\) | Reaction rate, \(v_0; 10^{-2}\), mN/(m·min) |
|-------------|--------------------------------------------------------|---------------------------------|-------------------|---------------------------------|
| 1           | 5.1                                                    | -0.041                          | 55.37             | 0.90                            | 4.10                             |
| 2           | 3.1                                                    | -0.074                          | 57.89             | 0.98                            | 7.40                             |
| 3           | 2.4                                                    | -0.109                          | 65.17             | 0.91                            | 10.90                            |
| 4           | 2.1                                                    | -0.094                          | 49.29             | 0.98                            | 9.40                             |
| 5           | 1.7                                                    | -0.105                          | 60.55             | 0.99                            | 10.50                            |
Figure 1. Functional dependence $\ln \nu_0 = f(\ln C_0)$ for the determination of the polycondensation reaction order in glyoxal.

\[
\ln \nu_0 = -0.90 \ln C_0 - 12, \; R=0.94
\]  

4. Discussion

The obtained values of the polar component of the surface tension for compositions with different initial glyoxal concentrations decrease with time, which does not contradict the kinetics laws.

To calculate the rate of the reaction, the kinetic dependencies $\sigma_s^P = f(\tau)$ were approximated by various mathematical formulas. Analysis of the results showed that linear equations (3) have the largest correlation coefficient ($R=0.95\pm0.05$)

\[
\sigma_s^P = a \cdot \tau + b
\]  

where $a$ and $b$ are the coefficients presented in the Table 3.

Differentiation of these equations made it possible to calculate the initial polycondensation reaction rate ($\nu_0$). When the glyoxal concentration is increased, the rate of the reaction decreases. This indicates a complex polycondensation reaction mechanism. Glyoxal acts as an inhibitor, slowing the formation of a hydrophobic structure.

It is established that the polycondensation reaction order in glyoxal is negative (minus first). This fact, in our opinion, may be due to the fact that the limiting reaction stage is the stage occurring in the diffusion region. In this case, the free reactive surface centers of the plant component of the mixture are blocked by the products of the primary interaction. As the result, the process is slowed down, despite an increase in the glyoxal concentration. However, it should be noted that the modulus of the reaction order is “1”, that is, one glyoxal molecule participates in the elementary act of interaction of glyoxal with structural units of the lignin macromolecule. This confirms the working hypothesis on the mechanism of structure formation in the “glyoxal-bark” system.

Thus, based on the conducted kinetic studies, it can be concluded that the surface tension takes into account the change in the composition of the heterogeneous system and can be used as an information parameter to determine the polycondensation reaction order in the main reactant that proceeds at the interphase in the “glyoxal-bark” system.

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\[
\ln \nu_0 = -0.90 \ln C_0 - 12, \; R=0.94
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