Analysis and synthesis of kinetic parameters of soapstock saponification stage in sunflower oil production

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Abstract. The parametric identification of the saponification experimental process is performed as a multi-stage stationary reaction with linear kinetics, characterized by adequate model estimates. It is revealed that for the saponification reaction, the kinetic curve (the change in the saponification degree from time to time) is characterized by three stages: the first induction period, the second period of constant velocity, and the period of falling velocity. The process intensification ways are justified by reducing the induction period in the ultrasound field. Experimental numerical results on modeling the dependence of the reaction rate of constants saponification are presented as the process kinetics.

1. Introduction

The concept of creating cybernetically organized chemical and technological processes (CTP) justified by academician V. V. Kafarov is the fundamental concept of the development of modern production processes. This concept implementation is the integrated design methodology of flexible CTP and systems, which assumes the joint problems solution of optimal synthesis of CTP [1, 2].

Relevant processes are considered as the synthesis problem solution of CTP parameters at the design stage of soapstock utilization processes. The control object operation is to stabilize the optimal mode, to minimize disturbances caused by instability and non-linearity of transient processes of joint processing of oil and fat waste and flexible reconfiguration [3, 4].

Physical control theory development (academician A. A. Krasovsky), in particular, the synergetic management theory, is based on analysis of the links and factors of the waste disposal CTP, reliability, the accuracy parametric identification at the design stage, in fact:

1. Analysis of the stages of obtaining fatty acids from soapstock [5].
2. Mathematical model of a liquid-phase chemical reactor system analysis and experimental parametric identification of saponification process kinetics.
3. Mathematical modeling parameters of synergetic synthesis CTP for isolation of soapstock from fatty acids and its further decomposition [6].

In general, the mathematical model of CTP for extracting soapstock from fatty acids and further decomposing it consists of:

1) equations of reaction kinetics;
2) material balance of chemical transformations;
3) the energy balance of the reactor.
2. Problem statement

In this regard, the authors set the tasks of parametric identification of the laws of:
- temperature stabilization;
- concentration stabilization;
- vector law of concentration and temperature stabilization;
- stabilization of the target component concentration in a multi-stage reaction in an isothermal mode.

3. Research objects and methods

Let us assume that the rate constants of chemical reactions of separation and decomposition of soapstock soap are numerically determined, and a mathematical dependence is constructed for various technological modes in order to find the optimal one.

The process of obtaining fatty acids from soapstock consists of the following stages:
1) saponification of soapstock with caustic sodium, proceeding by reaction (1.1):

\[ \text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}; \]  

(1.1)

where:
- f. acid caustic sodium soap soapstock

2) soapstock daubing with caustic sodium, which proceeds by reaction (1.2):

\[ \text{C}_3\text{H}_5(\text{RCOO})_3 + 3\text{NaOH} \rightarrow 3\text{RCOONa} + \text{C}_3\text{H}_5(\text{OH})_3; \]  

(1.2)

where:
- triglyceride caustic sodium hydroxide soap glycerol soaps

3) decomposition of soapstock soap with a solution of sulfuric acid, proceeding by reaction (1.3):

\[ 2\text{RCOONa} + \text{H}_2\text{SO}_4 \rightarrow 2\text{RCOOH} + \text{Na}_2\text{SO}_4; \]  

(1.3)

where:
- soapstock soap sulfuric acid f. acid sodium sulfate

4) washing fatty acids from traces of mineral acid.

We assume that the reaction is stationary and that the soapstock saponification kinetics are linear, since there are no mass transfer processes and phase transformations in the reaction volume of the object under study. Consequently, changes in the concentrations of soapstock and sodium hydroxide are the result of only chemical transformations, and the intensity of the mass source of the i-th component can be determined as the rate of the chemical reaction for this reagent.

The speed of the chemical reaction in this case will take the form (1.4):

\[ w_i = \frac{dC_i}{d\tau}, \]  

(1.4)

where:
- \( w_i \) – the rate of the chemical reaction, mol.shares / min;
- \( C_i \) – concentration of reagents, mol.shares;
- \( \tau \) – reaction time, min.

The saponification reaction proceeds in multiple stages as a result of differences in the transfer mechanism of reagents in the reaction mixture. In this case, it is necessary to operate with the concept of the chemical reaction flow rate stage using (1.5):

\[ w_i = \sum_{j=1}^{m} \alpha_{ij} \cdot r_j, i = 1, n \]  

(1.5)

where:
- \( \alpha_{ij} \) – the reaction stoichiometric coefficient;
- \( r_j \) – the chemical reaction stage rate.

The chemical reaction stage rate is (1.6):
\[ r = k \prod C_i^{a_i}, \quad (1.6) \]

where \( r \) is the substance stoichiometric coefficient or the order of multistage reactions.

Since formal kinetics stoichiometric equations are based on the final results of a chemical reaction without taking into account elementary stages flow reflect the true mechanism of the process, stoichiometric coefficients often do not coincide with the exponents in kinetic equations. Then, when determining the rate of a chemical reaction, we are talking about the order of the reaction.

Given the equations (1.4-1.6), we have a differential equation (1.9) describing the kinetics of the chemical reaction:

\[ k_i \prod j C_j^{a_j} = \frac{dC_i}{d\tau}, \quad (1.7) \]

It follows that the determination of the chemical reactions rate constants and further verification of the adopted suitability kinetics equation are carried out using integral methods based on the use of integral dependencies that link the concentration of the reacting substance with the process parameters and the time of its flow.

The soapstock saponification stage reaction is described by a second-order kinetic dependence [7]. The kinetics of the second-order process equation (1.8), the second order were determined by the equation from the degree of saponification (1.9):

\[ \frac{dx}{d\tau} = r = k \cdot C_{i0} \cdot (1 - x)^2, \quad (1.8) \]

\[ x = (C_{i0} - C_i) / C_{i0}, \quad (1.9) \]

where \( x \) is the degree of saponification, mol.shares; \( C_{i0}, C_i \)– initial and current fat concentration, Kmol / m\(^3\); \( k \) – reaction rate constant, min\(^{-1}\); \( \tau \)– reaction time, min.

Solution of the integral equation (1.10), from which the constant in the time axis was determined by the equation (1.11):

\[ \frac{1}{C_{i0} (1 - x)} - \frac{1}{C_{i0}} = \frac{x}{C_{i0} (1 - x)} = k\tau, \quad (1.10) \]

\[ k = \frac{x}{\tau \cdot C_{i0} (1 - x)}, \quad (1.11) \]

For a second-order reaction, the value of the constant is constant in the time axis. In view of this, the average value of the reaction rate constant is used in the calculations (1.12):

\[ k = \frac{\sum_{i=1}^{N} k_i}{N}, \quad (1.12) \]

where \( N \) – the number of experiments.

The value of the chemical reaction rate constant does not depend on the concentration of reagents and is constant for the selected conditions. The dependence on the temperature regime for the rate of chemical reaction is described by the Arrhenius equation (1.15):
\[ k = k_0 \exp \left( -\frac{E}{R \cdot T} \right), \] (1.15)

where \( k_0 \) - the pre-exponential multiplier; \( E \) - the activation energy, \( \text{j/mol} \); \( R \) is the universal gas constant, \( \text{j/(mol*K)} \); \( T \) - the temperature, \( \text{K} \); the \( k_0 \) is determined numerically.

Logarithmizing the Arrhenius equation, we get the equation (1.16):
\[ \ln k = -\frac{E}{R \cdot T} + \ln k_0, \] (1.16)
and substituting in it the found average rate values of the chemical reactions \( k_{60} \) and \( k_{80} \) at temperatures \( T_{60} = 60 ^\circ \text{C} \) and \( T_{80} = 80 ^\circ \text{C} \), respectively, we get a system of equations (1.17):
\[
\begin{align*}
\ln k_{60} &= -\frac{E}{R \cdot T_{60}} + \ln k_0, \\
\ln k_{80} &= -\frac{E}{R \cdot T_{80}} + \ln k_0,
\end{align*}
\] (1.17)
\[
\ln \frac{k_{60}}{k_{80}} = -\frac{E}{R \cdot T_{60}} + \frac{E}{R \cdot T_{80}} = \frac{E(T_{60} - T_{80})}{R \cdot T_{80} \cdot T_{60}},
\] (1.18)
\[
E = \ln \frac{k_{60}}{k_{80}} \cdot \frac{R \cdot T_{60} \cdot T_{80}}{(T_{60} - T_{80})}. \] (1.19)

Solving the system of equations (1.17), we have found the activation energy for (1.19).

Knowing the activation energy, we determine the natural logarithm of the pre-exponential multiplier \( \ln k_0 \) at temperatures \( T_{60} = 60 ^\circ \text{C} \) and \( T_{80} = 80 ^\circ \text{C} \), which should be equal to (1.20):
\[
\begin{align*}
\ln k_0 &= \ln k_{60} + \frac{E}{R \cdot T_{60}}, \\
\ln k_0 &= \ln k_{80} + \frac{E}{R \cdot T_{80}}.
\end{align*}
\] (1.20)

The adequacy of the constructed model was checked using the relative deviation (1.21) and the standard error (1.22):
\[
D^k = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( k_i - k_{\text{calc},i} \right)^2} \cdot 100\%,\] (1.21)
\[
S^k = \frac{1}{n} \sum_{i=0}^{n-1} \left( k_i - k_{\text{calc},i} \right)^2,\] (1.22)

where \( D^k \) - the relative error, \% ; \( S^k \) - the standard error; \( k, k_{\text{calc}} \) - the chemical reaction rate of constant’s experimental and calculated values.

To identify saponification process kinetics, laboratory studies were performed isolation fatty acids from soapstock on this stage. The process was carried out in a reactor unit equipped with a mixing device and ultrasonic emitters. When modeling a reactor, we assume the following assumptions:

1) the system is homogeneous at any time, i.e. there is no concentration gradient in the reactor;
2) in the chemical conversion process, the number of reagents moles does not change;
3) the temperature in reactor at any point is evenly distributed, i.e. there is no temperature gradient in the reactor;

4) there is no heat loss to the environment.

4. Results and discussion

The soapstock saponification experiment was performed on the model systems "sunflower soapstock-caustic soda" at temperatures of 60 °C and 80 °C when stirring with a frame agitator at a constant speed and identically, but in the field of ultrasound.

For the saponification reaction, the kinetic curve (the change in the saponification degree over time) is characterized by three stages: 1) the induction period, 2) the constant velocity period, and 3) the falling velocity period.

Table 1. The reaction kinetics saponification. Experimental values at the temperature of $T=60\ ^\circ\mathrm{C}$

| Timer, min | Concentration of alkali $C_{NaOH}, \text{mol} / l$ | Saponification degree $x$, mol. shares | The rate constant for reaction $k$, l/mol·min | Relative error $D^k$, % | RMS error $S_k^k$ |
|-----------|---------------------------------|---------------------------------|---------------------------------|----------------|----------------|
| Mixing with a frame agitator | | | | | |
| 0 | 1.426 | - | - | - | - |
| 5 | 1.047 | 0.266 | 0.051 | -7.24% | 1.32·10$^{-05}$ |
| 15 | 0.628 | 0.560 | 0.059 | 8.32% | - |
| 25 | 0.492 | 0.655 | 0.053 | -2.38% | - |
| The first period | | | | | |
| Mixing with a frame agitator + ultrasonic action | | | | | |
| 5 | 0.9579 | 0.328 | 0.069 | -3.93% | 7.44·10$^{-05}$ |
| 15 | 0.6115 | 0.571 | 0.062 | -14.38% | - |
| 25 | 0.3606 | 0.747 | 0.083 | 14.05% | - |
| Mixing with a frame agitator | | | | | |
| 35 | 0.201 | 0.859 | 0.122 | 5.31% | - |
| 45 | 0.160 | 0.888 | 0.123 | 6.35% | - |
| 60 | 0.142 | 0.901 | 0.106 | -9.00% | - |
| 80 | 0.102 | 0.928 | 0.113 | -1.88% | 3.37·10$^{-05}$ |
| 100 | 0.083 | 0.942 | 0.114 | -1.32% | - |
| 120 | 0.069 | 0.951 | 0.114 | -1.00% | - |
| The second period | | | | | |
| Mixing with a frame agitator + ultrasonic action | | | | | |
| 35 | 0.12 | 0.916 | 0.218 | 1.57% | - |
| 45 | 0.0957 | 0.933 | 0.217 | 0.91% | - |
| 60 | 0.0728 | 0.949 | 0.217 | 1.20% | 9.62·10$^{-06}$ |
| 80 | 0.0563 | 0.961 | 0.23 | -0.65% | - |
| 100 | 0.0453 | 0.968 | 0.214 | -0.42% | - |
| 120 | 0.0388 | 0.973 | 0.209 | -2.73% | - |

In the initial (induction) period, the reaction value rate depends on the specific contact phases' surface, which the interaction of the fat and alkali molecules occurs, which in physical terms are heterogeneous systems that are poorly soluble in each other.

At the initial moment of time, the phases contact surface of such systems is small, so in practice, to accelerate the reaction, the fat-alkali system is emulsified using intensive reagents mixing, as a result of the interaction of the initial components, surface-active substances are formed, which contribute to fine emulsification and increase the reaction speed. When the soap formation in an amount of 15-20% is achieved, it is sufficient for an intensive reaction in the second period (constant speed). Reducing
the induction period can be achieved in several ways:

1) increasing the reaction temperature, however, this may contribute to the fine emulsion destruction, resulting in a decrease in the rate;

2) introducing a small number of surfactants into the reaction mixture, which are used as catalysts (emulsifiers) and can serve as a "seed" for the formation of soap [8].

For the chemical and technological processes intensification, ultrasonic technologies are currently widely used, which allow efficient implementation of high-energy processes in liquid media due to cavitation that occurs in the liquid as a pressure reduction result during the passage of an acoustic wave. In this regard, research on the use of ultrasound in saponification and neutralization processes is relevant.

A saponification reaction series experiments were performed at temperatures T=60 °C and T=80 °C, with stirring by a frame agitator and an ultrasonic field (V=22 kHz, N=30 W / dm³), the average values of which are presented in tables 1-2.

| Time, min | Concentration of alkali $C_{NaOH}$, mol / l | Saponification degree $x$, mol. shares | The rate constant for reaction $k$, l/mol·min | Relative error $D_k$, % | RMS error $S_k$ |
|-----------|-------------------------------------------|--------------------------------------|-----------------------------------------------|------------------------|----------------|
| 0         | 1.426                                     | "                                    | "                                             | "                      | "              |
| 5         | 1.057                                     | 0.259                                | 0.049                                         | 0.050                  | -1.58%         | 3.44 - 10^{-07}|
| 15        | 0.69                                      | 0.516                                | 0.050                                         | 0.050                  | 0.26%          | 1.28%          |
| 25        | 0.51                                      | 0.642                                | 0.050                                         | 0.050                  | 1.28%          |

Table 2. Reaction kinetics saponification of the experimental values at the temperature of $T=80$ °C

As a saponification process kinetics parametric identification result, the temperature dependences of the saponification reaction rate constants were obtained when stirring with a frame agitator (1.23 - 1.24) and using ultrasonic action (1.25 - 1.26) for the I and II periods, respectively:
\[ k = 0.014 \exp \left( -\frac{3761}{8.314 \cdot T} \right), \]  \hspace{1cm} (1.23)  

\[ k = 1.48 \exp \left( -\frac{7049}{8.314 \cdot T} \right), \]  

\[ k = 0.091 \exp \left( -\frac{683}{8.314 \cdot T} \right), \]  

\[ k = 1.114 \exp \left( -\frac{4554}{8.314 \cdot T} \right), \]  \hspace{1cm} (1.26)  

It was found that ultrasonic exposure increases the reaction rate constant more than 1.8 times.

5. Conclusion
1. The parametric identification experimental process is performed saponification as a multi-stage stationary reaction with linear kinetics, characterized by adequate model estimates.
2. It is revealed that for the saponification reaction, the kinetic curve (the change in the saponification degree from time to time) is characterized by three stages: the first induction period, the second period of constant velocity, and the period of falling velocity.
3. The process intensification ways are justified by reducing the induction period in the ultrasound field.
4. Experiments numerical results on modeling the dependence of the reaction rate constants saponification are presented in the process kinetics.

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