

Development of Information System for Extrusion Forming Process of Catalyst Pastes

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Abstract

Evolution of theoretical basis of extrusion paste forming processes will raise the solution of several problems in the technology of catalysts, which are used in different branches of chemical, automobile (block ceramic overburning catalysts) and petrochemical industries. Taking into account the importance of this problem on the department of cybernetics of chemical technological processes we developed the information system which allow us to find initial concentrations of catalyst paste components for obtaining target product with predefined properties (mechanical strength and porosity). User of this system can specify desired values of target product specifications (such as mechanical strength, porosity of catalyst) or intermediate ones without dealing with experiments., i.e. specify the values of rheological parameters of catalyst pastes (viscosity, plastic strength, elasticity) on the catalysts preparation stage. As a result of interaction with this system end-user will receive a set of recipes (component mass compositions) for catalyst paste preparation and the ram extruder which can be used for production of catalyst with user defined properties.

Keywords: [extrusion, catalyst pastes, information system]

1. Introduction

By means of extrusion forming it is possible to obtain various materials: catalysts with different form (from cylinder to figured grains and honeycomb blocks), ceramic materials, food materials (noodles, candies, etc.).

Obtaining of materials, based on $\alpha\text{-Fe}_2\text{O}_3$ is considered in this work. Following stages are contained in the process of wide class materials obtaining (including new ones): synthesis, mixing, flowing through an extruder, drying and firing. The obtained materials should have a series of the given properties: appearance, durability, porosity, water absorption, etc.

Extrusion is one of the processes, where the process of paste's particles agglomeration is unwelcome, as it leads to turn for the worse of the paste's properties. Therefore, this paper is devoted to investigation and mathematical simulation of catalyst pastes

preparation with taking into account formation of solvate films, which prevent the agglomeration of particles. At this stage, the solid carrier ($\alpha\text{-Fe}_2\text{O}_3$) is being mixed with the water solutions of surfactants (in or case, these are solutions of PVA and MC). Addition of these substances makes the forming paste plastic. The substances keep the dispersed phase in a bounded condition, counteracting the factors, which disintegrate the structure.

The most important problem at preparation of catalyst pastes is a problem of evaluation and prediction of their forming properties with help of their rheological properties, where the plastic strength and viscosity are two general ones.

The properties of pastes start getting their properties at the preparation stage. According to representations of physical chemical mechanics, plastic forming pastes present themselves a system of rigid particles, surrounded by the solvate films. Cross-linking of such dispersed systems happens in the result of molecular coupling of dispersed phase particles by the most lyophobic areas of surface, which are the least protected by the solvate films of media. Thickness of solvate films significantly determines the system's technological parameters, including its formability.

2. Experimental

A series o experiments were carried out, where the pastes with different composition were being prepared by varying the concentration of continuous phase (PVA and MC) and the content of a solid phase (table 1). Each paste was being prepared in a mixer for about 30 minutes, then it was being matured for 24 hours. Plastic strength was being determined after 30 minutes and after 24 hours by means of Rebinder's conic plastometer by the cone penetration method under action of a constant weight [1]. Viscosity was being determined after 24 hours by means of capillary viscosimeter at the shear strain, equal to 10 s^{-1} .

Table 1. Experimental values of rheological characteristics of catalyst pastes.

N exp.	α_2^0	C_1^0	C_2^0	η^a	P_m^b	P_m^c
1	0,502	0,012	0,06	41,20	2059	3658
2	0,460	0,012	0,06	0,78	84	298
3	0,500	0,012	0,018	6,61	566	1304
4	0,458	0,012	0,018	0,36	25	82
5	0,501	0,0012	0,06	15,85	3031	3536
6	0,459	0,0012	0,06	1,12	74	192
7	0,499	0,0012	0,018	0,31	173	318
8	0,457	0,0012	0,018	0,24	32	65
9	0,492	0,0075	0,04	19,01	727	1755
10	0,476	0,0075	0,04	14,79	507	1221
11	0,477	0,00375	0,06	5,75	496	875
12	0,454	0,00375	0,06	0,66	105	180
13	0,484	0,01125	0,02	4,68	289	742
14	0,462	0,01125	0,02	0,56	63	186

^a When $\dot{\gamma} = 10 \text{ s}^{-1}$.

^b After 30 minutes.

^c After 24 hours.

Experimental values of plastic strength and viscosity are presented in the table 1. Behaviour plastic strength in time was observed for some experiments. The graph of plastic strength in time comes out to plateau (see figure 1), what means the system's stabilization. Only two limiting values of plastic strength are presented in table 1: after 30 minutes and after 24 hours. But even these two values are enough to get convinced in importance of taking into account the maturing stage. For 24 hours plastic strength doubles for almost all the experiments, and for the experiment 3 it even quadruples. Structurization of the system happens for this time, the paste becomes more dense and rigid.

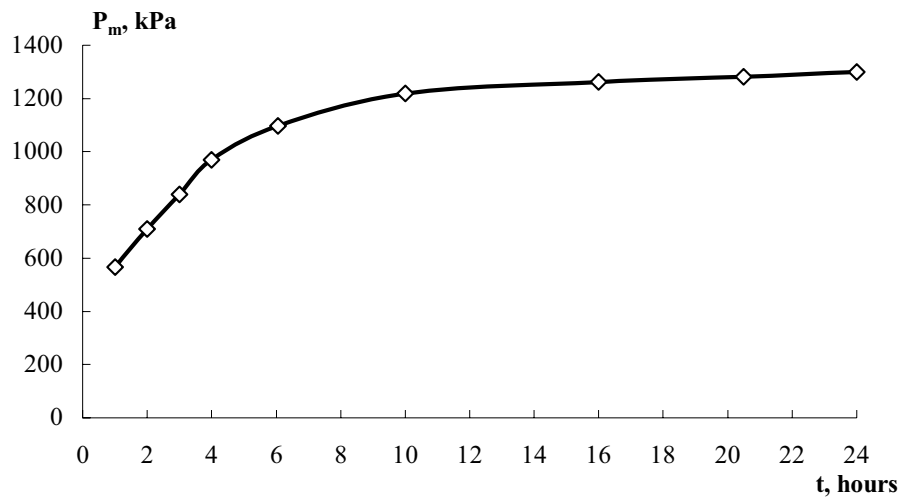


Figure 1. Experimental dependency of plastic strength from time for the experiment 3.

3. Results

3.1 Obtaining of functional dependencies

The mathematical model for the stage of catalyst paste mixing was built on a base of application of heterogeneous media mechanics apparatus and colloid chemistry. This model allows calculation of $\alpha\text{-Fe}_2\text{O}_3$ particle-size distribution density at any moment of time on solvate films thicknesses.

Multicomponent two-phase system is considered at the stage of paste preparation in a mixing apparatus. First phase is continuous, the second one consists of solid $\alpha\text{-Fe}_2\text{O}_3$ particles. Components of continuous phase are: water, PVA and MC. We consider that in the process of mixing, particles of $\alpha\text{-Fe}_2\text{O}_3$ get covered by the solvate film. Properties of this film depend on composition of continuous phase.

The mathematical model of a catalyst pastes mixing stage is constructed on a base of application of heterogeneous media mechanics and methods of colloid chemistry. The model allows to calculate a distribution density of Fe_2O_3 particles number for any moment of time on solvate films thickness and includes the following equations:

- balance equation of α -Fe₂O₃ particles number, predicting the number of particles in any moment of mixing and storing, having solvate film; predicting the medium size of solvate film:

$$\frac{\partial f}{\partial t} + \frac{\partial f\mu}{\partial r} = 0 ; \quad (1)$$

- dependency for the solvate film growth rate:

$$\mu = \frac{dr}{dt} = 4\pi l^2 [K_1 C_1 C_3 + K_2 C_2 C_3^2 + K_3 C_3] ; \quad (2)$$

- particles mass change at the expense of solutions' components income of continuous phase:

$$\psi = \frac{dm}{dt} = 4\pi l^2 [\rho_{11} K_1 C_1 C_3 + \rho_{12} K_2 C_2 C_3^2 + \rho_{13} K_3 C_3] ; \quad (3)$$

- equation of liquid phase density changing:

$$\frac{d\rho_1}{dt} = - \int_0^{R_m} f\psi dr ; \quad (4)$$

- equation of components concentrations changes for liquid phase:

$$\rho_1 \frac{dC_i}{dt} = - \int_0^{R_m} \rho_{1i} f\mu_i dr + C_i \int_0^{R_m} f\psi dr , \quad (5)$$

where $\mu_1 = 4\pi l^2 K_1 C_1 C_3$, $\mu_2 = 4\pi l^2 K_2 C_2 C_3^2$, $\mu_3 = 4\pi l^2 K_3 C_3$.

Volume content of a solid phase is determined on a base of these equations (1-5):

$$\alpha_2 = \alpha_2^0 + \int_0^{R_m} r f dr \quad (6)$$

Unknown kinetic constants of the mathematical model (1-6) are K_1 , K_2 , K_3 . For the definition of kinetic constants we took the data, represented in a paper of Yu. Mosin [2]. Following values of kinetic constants were found in the result of this search:

$K_1 = 10,5 \cdot 10^{-10} (m s^{-1})$, $K_2 = 0,66 \cdot 10^{-10} (m s^{-1})$, $K_3 = 0,2 \cdot 10^{-10} (m s^{-1})$.

Following functional dependencies were obtained by comparing data, obtained with help of the mathematical model (for example, volume content of catalyst, taking into account the presence of a solvate film; average values of solvate films thicknesses) with the experimental data on plastic and rheological properties of pastes:

- dependencies for the plastic strength:

$$P_m = 10^3 \exp(-14,792 + 1,77 \cdot 10^6 h + 8,1 \cdot 10^{12} h^2 + 15,207 \alpha_2 + 61,113 \alpha_2^2 - 2,547 \cdot 10^7 h \alpha_2) ; \quad (7)$$

- dependencies for viscosity of catalyst paste:

$$\eta = \eta_0 \exp(98\alpha_2 - 36,8) \left(\frac{45,12 \cdot 10^{-7}}{h} - 3,7 \right) \quad (8)$$

3.2 Information systems

The Information System (IS) allows user to find paste composition for specified input parameters. Search results consist of a set of pastes, so user need to choose one of them. At the moment the IS applicable only to catalytic paste based on ferric oxide α -Fe₂O₃ and consists of four modules.

First module represents a database of rheological, deformation properties of catalyst pastes and target product parameters. This database was built using the mathematical model of the mixing stage within the catalyst preparation process. This model takes into account formation and growth of adsorption solvate shells on solid phase particle. Rheological and deformation properties of catalyst pastes were generated by equations for plastic strength (7) and viscosity (8). Target product parameters were put into database from equations for mechanical durability and porosity of target product. This module allows one to choose automatically the composition of catalyst paste, which satisfy user demands (fig. 2).

Second module is the database of ram extruder parameters, including unit geometry, manufacturer's name and address (at the moment the system contain information about ram extruder, but it is possible to put other types of extruders there).

In the third module system calculates extruder load for chosen catalyst paste forming. Calculations are based on mathematical model for catalyst paste flow in extruder.

Fourth module of information system allows us to choose ram extruder from industrial units database depending on calculated in the second module extruder load. By using the assurance factor when choosing the unit we can expand search range for the system.

The screenshot shows a software window titled "Result of Selection". It contains several input fields and a table of results.

Composition of Paste:

- Weight of iron oxide (g): 667
- Weight of solution MC(g)(%wg): 57 (3.38)
- Weight of solution PVA(g)(%wg): 83 (10.75)
- Composition of Paste: 7 (dropdown menu)

Rheological property of Paste:

- Plastic strength(kPa): 1305.377
- Humidity(%): 15.868
- Viscosity(Pa*s): 3064.98

Property of Product:

- Mechanical strength(MPa): 1.075
- Porosity: 0.52

Table of Results:

N	Weight of iron oxide(g)	Weight of sol. MC(g)(%wg)	Weight of sol. PVA(g)(%wg)	Plastic strength(kPa)	Humidity(%)	Viscosity(Pa*s)	Mechanical strength(MPa)	Porosity
6	667	83 (2.35)	57 (14.92)	1307.942	15.868	3063.76	1.075	0.52
7	667	57 (3.38)	83 (10.75)	1305.377	15.868	3064.98	1.075	0.52
8	667	30 (6.25)	110 (8.333)	1296.052	15.868	3069.283	1.075	0.52
9	800	110 (1.78)	57 (14.92)	1064.324	16	3659.28	1.083	0.519
10	800	83 (2.35)	83 (10.75)	1063.879	16	3659.425	1.083	0.519
11	800	57 (3.38)	110 (8.333)	1061.97	16	3659.922	1.083	0.519

Figure 2: The results after we chosen the paste.

Work sequence for this system include several stages:

- Query definition for calculation of paste composition
- Database preparation for rheological properties dependency on paste composition
- Calculation of extrusion process parameters for ram extruder
- Extrusion equipment vendor selection from database
- Equipment selection from unit database basing on calculation results

In order to determine paste composition in is necessary to specify following parameters:

- catalyst powder nature, type and its dispersity
- temporary technological linkage information (quantity and type of technological linkage used)
- rheological and deformation properties of paste (plastic strength, humidity and viscosity)
- target product parameters (mechanical strength and porosity)

Data is input by ranges. For the plastic strength it is needed to specify more exact value. From the data obtained the program automatically choose appropriate catalyst paste compositions from database, from which user can select one item satisfying his demands. Then user chooses extruder type for this selected paste composition. Extrusion pressure calculations are performed using user specified ram extruder parameters. If extruder load does not suit user needs, it is possible to get back to previous stage and choose another paste composition. Then the same procedure executed for the new paste. As a result, user selects one of computer-proposed paste compositions, which satisfies not only demanded rheological and deformation properties, but also extruder load wanted. After this stage program look for suitable equipment for the selected paste in the database. In order to run this user should input geometry parameters of the unit and assurance factor. Additionally, you can use this module apart from others, but in that case you need to specify manually all unit parameters for database search. At the last stage you can print the report for all stages of calculation with this system. This report can be saved in a file or printed.

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Acknowledgements

This work was supported by grants RFBR № 02-03-32215, № 03-01-00567, RFBR-NSFC grant № 02-03-39003 and Ministration of Education Russian Federation T 02-09.4-2936.