Research on the shaping process of PKR-2 catalyst for a high-temperature N_2O decomposition with using capillary rheometry

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PKR-2 catalyst for N_2O abatement in HNO_3 plants is shaped by an extrusion process, from a mixture of catalyst powder and plasticizing additives. The catalyst mass composition, allowing for its trouble-free shaping on an industrial extruder and producing catalyst extrudates with the best mechanical parameters, was opimized using capillary rheometry.

Keywords – N_2O emission abatement, secondary catalyst, ammonia burner, rheological properties, PKR-2 catalyst mass, capillary rheometry, catalyst extrudates.

Introduction

New Chemical Syntheses Institute developed PKR-2 catalyst for a high-temperature N_2O decomposition. One of the important unit operations in the manufacturing technology of this catalyst is shaping by an extrusion. For a better control of catalyst production, it is necessary to assess the rheological properties of the mass, from which the catalyst extrudates are formed. The rheological properties describe the mass flow behaviour and constitute the material reaction to the shear stresses, leading to its deformation during the extrusion process. These properties depend on:

- mass composition, i.e. the type and amount of plasticizers, the content of batch water, grain size distribution of the catalyst powder,
- operating conditions of the extrusion process, i.e. temperature and extrusion velocity.

The rheological properties of PKR-2 catalyst mass were studied with using capillary rheometry. Formability and apparent viscosity of the examined mass samples were determined, depending on the mass composition and extrusion conditions.

The aim of the rheological studies was the optimization of PKR-2 catalyst mass composition in terms of producing the extrudates of a required mechanical strength and simultaneous ensuring a good mass formability. Te optimization involved the selection of batch water content, the type and amount of plasticizers. The Benbow-Bridgewater equation (Eg. 1) was used to indentify the main flow resistances of PKR-2 catalyst masses and to determine their rheological parameters [1]:

$$P_c = 2\,ln\left(\frac{D_0}{D}\right)(\sigma_0 + \alpha V) + \frac{4L}{D}(\tau_0 + BV) \qquad (1)$$

where:

D_0 i D – barrel and capillary diameter,

L – capillary length,

V – extrussion velocity,

$(\sigma_0+\alpha V)$ – plasticity dependent on the extrusion velocity,

$(\tau_0 +\beta V)$ – shear stress, associated with a mass friction against the capillary wall.

Based on the extrusion pressure (P_c), measured at different extrusion conditions, the mass flow resistances, associated with the mass deformation at the capilary inlet $(\sigma_0+\alpha V)$ and mass friction against the capillary wall $(\tau_0 +\beta V)$, were determined.

Experimental

PKR-2 catalyst masses were prepared by mixing powdered catalyst precursor, batch water and plasticizers. Various plasticizers were tested, such as: inorganic acid, cellulose derivative, polyalcohol and polyglycol. The rheological properties of the catalytic masses were tested using the capillary rheometer CEAST SR20 Instron by measuring the total extrusion pressure and pressure in the capillary at different extrusion velocities and for two capillary lengths. Shaped masses were dried and calcined at a temperature of about 500°C, and then the mechanical strength of the extrudates was determined.

In the first stage, the optimal content of inorganic acid, organic plasticizers and batch water in PKR-2 catalyst mass was determined, allowing for trouble-free mass shaping in the continuous mode and producing extrudates of a required mechanical strength. The results shows, that the addition of inorganic acid in the amount of <1.5 wt.% (calculated on a dry mass weight) has a beneficial influence on the mechanical strength of the catalyst extrudates. The addition of organic plasticizer in the amount of 1 wt. % increases the plasticity of the mass, limits the liquid phase migration the during the extrusion process and increases the green strength of the shaped mass (extrudates). The content of batch water (≤ 35 wt.% calculated on the dry mass weight) was determined so as to obtain the mass of a good formability, without simultaneous lowering the mechanical strength of PKR-2 catalyst below the accepted level.

In the next step, the influence of various organic plasticizers addition on the rheological properties of the catalyst mass and mechanical strength of the final product, was investigated. The mass samples were prepared using the same amount of batch water and inorganic acid (determined in preliminary studies), while the amount of organic plasticizer/s was no greater than 1 wt. %. Based on the results of the rheological studies, carried out at different shear rates and for two capillary lengths, the parameters of the Benbow-Bridgewater equation, were calculated (Table 1).

Table 1 Benbow-Bridgewater parameters, calculated for PKR-2 catalyst mass with different combinations of plasticizers (M1 – cellulose derivative+inorganic acid, M2 – polyalcohol+ inorganic acid, M3 – polyglycol+inorganic acid, M4 - polyalcohol+cellulose derivative+inorganic acid) and mechanical strength of produced catalyst extrudates (W)

		PKR-2 catalyst mass			
		M1	M2	M3	M4
Benbow-Bridgewater parameters	σ_0	0.287	0.515	0.193	0.162
	α	$9,0\cdot10^6$	$6.0\cdot10^7$	$8.0\cdot10^6$	$3.4\cdot10^4$
	τ_0	0.014	0.295	0.009	0.026
	β	3.2	490.2	$1.2\cdot10^4$	1.1
	n	0.25	0.79	0.99	0.14
W [N/mm]		4.2	5.2	4.3	5.2

In the case of all studied PKR-2 catalyst masses, the greatest extrusion resistances generates the plastic mass deformation at the capillary inlet, whereas in the area of capillary mass flows easily ($\alpha>\beta$). The highest value of $(\sigma_0+\alpha V)$ was obtained for the mixture of polyalcohol and inorganic acid. On the other hand, the presence of these two plasticizers improves the mechanical strength of the catalyst extrudates. The lowest flow resistances at the capillary inlet were observed for the mass with the addition of polyglycol. However, in this case, the highest mass flow resistances in the capillary area were observed (mass friction against the capillary wall). This can be related to the mass dewatering during its formation in the capillary.

It was found, that after adding to the mass more than one organic plasticizer, the flow resistances, related both to the deformation of the mass at the capillary inlet and mass flow through the capillary, can be reduced. This synergistic plasticizers interaction was observed for the plasticizing additives mixture: polyalcohol+cellulose derivative+inorganic acid. The addition of this plasticizers mixture has a positive influence on the mass formability and rheological stability of PKR-2 catalyst mass (see Table 1, M4).

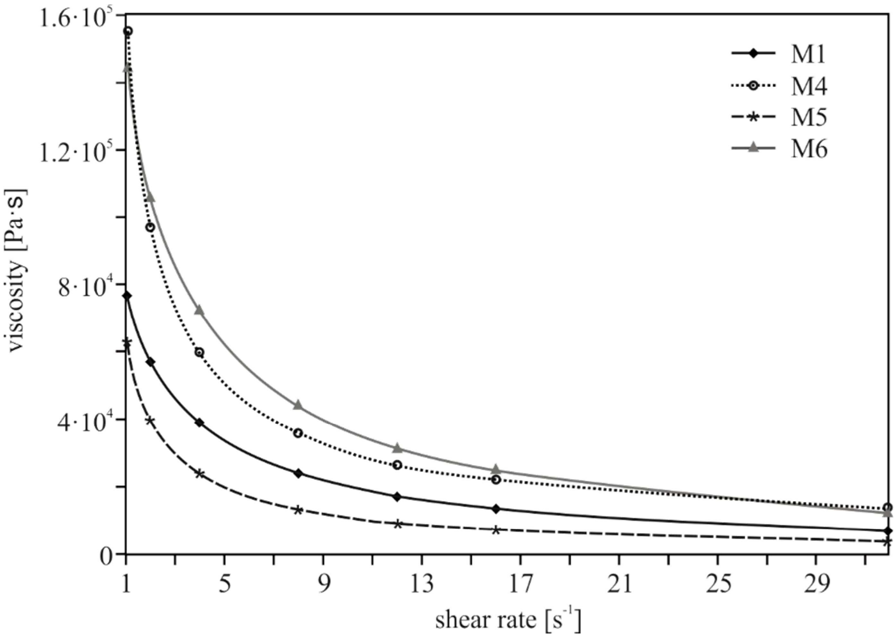

Fig. 1 Viscosity curves obtained for PKR-2 catalyst masses, containing different plasticizers mixtures (extrusion termperature = 56°C, capillary length = 10 mm): M1 (cellulose derivative + inorganic acid), M4 (polyalcohol + cellulose derivative + inorganic acid), M5 (polyglycol + cellulose derivative + inorganic acid), M6 (polyalcohol + polyglycol + cellulose derivative + inorganic acid).

In Figure 1, the viscosity curves, obtained for PKR-2 catalyst masses with the addition of various organic plasticizers mixtures, are shown. The results indicate, that regardless of the used plasticizing additives combination, the catalyst masses have complex rheological properties, clasyfying them as the pseudoplastic shear-thinning fluids. Various plasticizers have different influence on the mass flow properties and mechanical parameters of the catalyst extrudates. The addition of polyglycol in a mixture with another organic plasticizer (sample M5), increases the relative humidity of PKR-2 catalyst mass, significantly improves its formability and rheological stability. However, it leads to the production of catalyst extrudates with a lower mechanical strength (Table 2). The addition of polyalcohol (M4, Fig. 1), improves the mechanical strength of the catalyst extrudates (Table 2), but simultaneously deteriorates the mass formability, to the greater extent, the higher is its content in the catalyst mass. The reseaches show, that the mechanical properties of the catalyst can be improved, without significant deterioration of the mass formability, using a mixture of plasticizing additives: cellulose derivative + polyglycol + polyalcohol + inorganic acid+water. Polyglycol in mixtures with polialcohol plays a role of cross-linking agent, promoting the aggregation of polyalcohol macromolecules, surrounding the solid phase grains. This leads to an increase in the catalyst mass density and, as a consequence, to the increase of extrudates mechanical strength.

Table 2 Mechanical strength of catalyst extrudates (W), obtained from PKR-2 catalyst mass with different combinations of plasticizers: M1 (cellulose derivative+ inorganic acid), M4 (polyalcohol+cellulose derivative+inorganic acid), M5 (polyglycol+cellulose derivative+inorganic acid), M6 (polyalcohol+polyglycol+cellulose derivative+inorganic acid).

PKR-2 catalyst mass	*W* [N/mm]
M1	4.8
M4	5.2
M5	4.0
M6	6.4

Conclusion

Rheological studies of PKR-2 catalyst masses, with using capillary rheometry, showed, that they have complex rheological properties, clasyfying them as pseudoplastic shear-thinning fluids. Increasing the amount of batch water or polyglycol in the mass, improvess its formability, but has a negative influence on the mechanical strength of the catalyst extrudates. The mechanical properties of the catalyst can be improved by the additon of inorganic acid and polyalcohol. It was found, that mass flow resistances and mechanical strength of the final product, increase with the the molecular weight of organic plasticizer, contained in PKR-2 catalyst mass: polyglycol<cellulose derivative<polyalcohol. A positive synergistic effect of the addition of polyglycol and polyalcohol mixture was observed, consisting in improving the mass formability and its rheological stability, limiting a liquid phase migration and increasing the mechanical strength of the shaped catalyst. During the researches, the following optimal combination of the plasticizing additives was determined: polyalcohol+polyglycol+cellulose derivative+inorganic acid.

References

[1] J. J. Benbow, J. Bridgewater, Paste Flow and Extrusion, Clarendon Press, Oxford, 25, 1993.