



XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov

Reception of two and three-phase combined dispersive systems with the use of centrifugal mixer

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Abstract

The article presents the theory of the formation of disperse combined systems, the greatest attention is paid to the three-phase system consisting of fine particles, gas and liquid. The authors suggest the equation describing the impact of different energies on combined particulate system. Possible conversion processes of surface energy into thermal, mechanical and chemical energy were shown. Also presents the results obtained by various dispersed systems with liquid additives and without them on the continuous mixer of centrifugal type. The study of using of volumetric ratio phases revealed major technological methods that enable to purposefully influence the ratio of different phases in order to obtain materials with the desired properties. The addition of a small amount of a liquid mixture of 4 % with a viscosity of 50 Pa sec reduces the coefficient of inhomogeneity and to reduce the segregation of the mixture obtained in the dusty area and, consequently, to increase the quality of the final product (uniformity of a three-phase system).

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Peer-review under responsibility of Tomsk Polytechnic University

Keywords: combined systems, fine components, a centrifugal mixer, mechanical mixing, adhesion, ingredients of particulate and coefficient of inhomogeneity;

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1. Introduction

The current state of the food industry is characterized by a significant increase in demand for machines and devices, allowing a small energy consumption to produce high quality products with the increased value (enriched with vitamins and biologically necessary components). Currently in food universities and research new food technologies enriched with vitamins, minerals and biological additives have been developed for a diverse population. For example, the problem of obtaining of relevant multicomponent mixtures of given quality in technology of product manufacturing and diets for astronauts, in the creation of food concentrates, including food for children, a wide range of diet and sport nutrition of balance content of essential nutrients preserving the taste qualities, development of complex food additives for confectionery, beverages and dairy products.

It is necessary to solve the similar major problem in other industries, for example, in the agro-industrial complex (feed production), in building production (production of dry mixes), pharmaceuticals (production of vitamin tablets for treatment of osteoporotic cements vertebrae), chemical (manufacture of gunpowder dry propellant).

2. Materials and Methods

Technological processes for the production of such products with the solid phases are usually performed in devices with an external supply of energy and as a rule, are the processes of mixing, dispersing, transportation, packing and breaking up.

A decisive role in these processes play a physico-chemical factor: surface effects on the interface, contact interactions between them and, therefore, the continuous formation and destruction of three-dimensional structures, aggregates of particles directly in the processes of homogeneous highly dispersed systems, i.e. the systems consisting of two phases. One of them is called a continuous dispersion medium phase, the other one is fragmented and distributed within the first phase called disperse phase.

According to the chemical nature and the intended physical properties of disperse systems with a solid phase, they are divided into three major groups⁷:

group 1 - two-phase systems such as "solid disperse phase - gas dispersion medium" (S-G);

group 2 - two-phase systems such as "solid disperse phase - liquid dispersion medium" (S-L);

group 3 - three-phase systems such as "solid disperse phase - liquid (gas) dispersion medium - gas (liquid) dispersion medium" (S-L-G).

The first group includes all powdered bulk materials, the second group includes a variety of different suspensions

and mortars. The third group of disperse systems is particularly noteworthy, which are formed in the process of removing the dispersion medium of the second group of disperse systems by thermal drying, squeezing mechanical or chemical bonding of the liquid phase and its transformation into a solid phase. These dispersions can be prepared by mixing of the particulate materials of the first group with a relatively small amount of fluid, e.g., centrifugal mixers. The obtained highly concentrated disperse system will comprise three phrases for both cases.

Important features of disperse systems as objects of colloid chemistry are heterogeneity and dispersion⁴. Combining these features, it can be concluded that the dispersion is a purely quantitative parameter characterizing the degree of fragmentation, the size of the interface. Heterogeneity also points to the qualitative characteristics of the system, since the surface tension determines the sharpness of the transition from one phase to another, the difference between the contacting phases. The lack of heterogeneity is equivalent to the lack of surface tension.

Multiplication of the surface tension σ on the surface area S gives the surface energy:

$$\Delta G = \sigma \cdot s \quad (1)$$

Thus, any individual dispersion system will have inherent value of the surface energy predetermine mainly particulate solids^{5,9}.

For any heterogeneous system the combined equation of the first and second laws of thermodynamics, which

includes the main types of energy can be written in the following form:

$$\Delta G = -SdT + VdP + \sigma \cdot dS + \sum \mu_i \cdot dn_i + \varphi dq \quad (2)$$

where G - Gibbs energy; S - entropy; T - temperature; V - volume; P - pressure; σ - surface tension; S - surface area; μ_i - chemical potential of component i ; n_i - the number of moles of component i ; φ - the electric potential; q - the amount of electricity.

This equation expresses the increment of the Gibbs energy of the system through the algebraic sum of the increments of other forms of energy, and it implies five possible surface energy conversion processes¹⁰:

- 1 - to the Gibbs energy;
- 2 - thermal energy;
- 3 - to chemical energy;
- 4 - into mechanical energy;
- 5- into electrical energy.

In turn, the Gibbs energy change ΔG ($P = \text{const}$) and the Helmholtz free energy ΔF ($V = \text{const}$) are related to each other:

$$\Delta G = \Delta H - T\Delta S = \Delta U + p\Delta V - T\Delta S = \Delta F + p\Delta V \quad (3)$$

where U - internal energy of the system;
 ΔH - enthalpy change.

Intuitively, this relation can be presented by the scheme shown in fig. 1. Equation (3) as well as (2) is based on the combined equation of the first and second laws of thermodynamics with the difference that in the relation (3) shows the relationship between the basic thermodynamic functions, as in (2) shows the possible mutual transitions of various types of energy in the dispersed system.

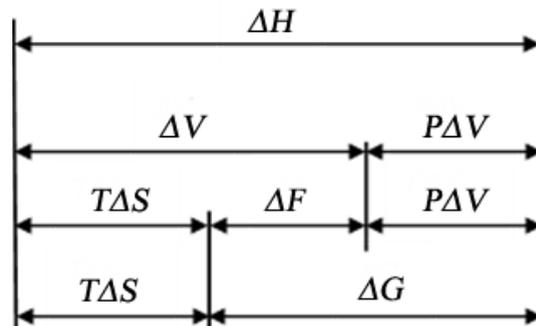


Fig. 1. The relationship between the basic thermodynamic functions

Based on the above mentioned, it can be said that the laws of thermodynamics indicate possible effects on the path of dispersed systems in order to obtain the desired result. For example, the maximum free energy change ΔF can be further achieved by performing various types of work: mechanical, electrical, chemical, work with using surface forces.

When considering the processes associated with the use of two (S-L) - or three-phase (S-L-G) systems, it is necessary to consider the adhesion of fluids and wetting process.

Adhesion is a spontaneous process with leakage when the system tends to reduce the surface energy. Gibbs energy change and the work of adhesion W_a linked with the Dupre equation, reflecting the law of conservation of

energy for adhesion:

$$\Delta G = Wa = \sigma_{lg} + \sigma_{sg} + \sigma_{lg} \quad (4)$$

where lg – liquid-gas system index; sg – solid-gas system index;

The adhesion process is completed by intermolecular interaction of phases, which is the minimum surface energy.

Adhesion and wetting the same phenomenon, that occurs when fluid contacts with a solid surface. Adhesion causes the interaction between a solid and a liquid and wetting is the result of this interaction.

Wetting occurs at the interface of the three phases, one of which is solid and the other two are liquid and gas. The degree of wetting is characterized by the cosine of the contact angle or wetting angle θ . At equilibrium between all components of the force vectors of the surface energy the ratio known as Young's law is observed:

$$\sigma_{sg} = \sigma_{lg} + \sigma_{lg} \cdot \cos \theta \quad (5)$$

Dupre equation alone is almost never used to calculate the work of adhesion due to the difficulty in determining the surface tension of solids on the border with gas and liquid. Convenient formula for the calculation of this value can be obtained by a combination of the laws of Dupree and Young:

$$W_a = (1 + \cos \theta) / \sigma_{lg} \quad (6)$$

Since the adhesion of the liquid is due to the molecular interactions occurring at the interface of liquid – solid phase, the work of adhesion can be determined not only by the formula (6), but also on the basis of the molecular nature of adhesive interaction⁸. The work required to overcome the molecular interaction between two flat hard surfaces can be calculated by the following formula:

$$W_a = -A / (12\pi H^2) \quad (7)$$

where, A - molecular interaction constant or constant of Vander - Waals ($A = (2\div 3.5) \cdot 10^{-19}$ J. for the interaction of the water layer with a solid surface);

H - the distance between the contacting bodies, m.

Formula (7) can be used to determine the adhesion of the liquid to the solid state, but it is obtained on the basis of the assumption that the adhesion is determined by the molecules on the surface of the boundary phase. Taking into account the intermolecular interactions of not only surface but deep molecules, the formula for calculating the adhesion of the liquid to the solid surface was determined:

$$W_a = -0.6A / (\pi H^2) \quad (8)$$

It more accurately defines adhesive interaction of liquids with solid surfaces taking into account of dispersion forces. In this equation, the value of the constant A refined in⁷ is $(2\div 3) 10^{-21}$ J.

The analysis of adhesive interaction process of liquid and solid phases shows that reduction of the gap between the solid particles interacting through the interlayer of a liquid phase leads to a decrease in the free energy of the system and, consequently, to increase of the stability of the disperse system. This conclusion is important for the processes of mixing of finely systems used in the manufacture of dry and wet food combined.

For obtaining of various two-or three-phase dispersed systems the change in the quantitative ratio of the separate phases of these systems. Relative mass and specific characteristics were widely used to assess the quantitative

relationship between the separate phases; but they have one very significant drawback - they do not give a clear and definite representation of the quantitative content of the gaseous phase, which is an equal partner in a two-phase (S + G) or three-phase system (S + L + G).

Therefore, for the characteristics of quantitative ratio of different phases in the dispersion media, along with the above mentioned and it is advisable to use a volume content of phases, as long as in this case the presence of the dispersed phases of the whole system is equally considered. Indicating the fraction of the volume occupied by a given phase by K with the corresponding index (s – solid, l – liquid, g – gas), we have:

$$K_s + K_l + K_g = 1 \quad (9)$$

In some cases, using K_g the relative density of the solid phase system is characterized according to¹¹. Volume concentration of the solid phase is determined from the ratio of the apparent density of the particle layer ρ_g to the true (t index) density of the material of particles ρ_t :

$$K_s = \rho_s / \rho_t \quad (10)$$

The presence of liquid of the dispersion system leads to an increase of the apparent density of the particle layer and in this case, a total apparent density of the layer is following:

$$\rho_{total} = \rho_s (1 + W_a) \quad (11)$$

where W_a - absolute moisture of the material expressed in relative units (by analogy with water-solid ratio).

Based on the numerous studies of disperse systems (powders of berries, milk and whey, molding compounds) it was found that the use of absolute humidity (or absolute moisture content expressed in kg water / kg dry matter) has several advantages when using of W_{rel} relative humidity, which are linked by the relation:

$$W_{rel} = W_a / (1 + W_a); W_a = W_{rel} / (1 - W_{rel}) \quad (12)$$

If the material has a moisture W_a , then the bulk moisture of the material W_{vol} or volume concentration of liquid phase can be calculated by the formula:

$$K_l = W_{vol} = \rho_s \cdot W_a \quad (13)$$

If any other liquid with a density ρ_l is used instead of water ($\rho_l = 1 \text{ g} / \text{m}^3$), the equation will be presented in the following way:

$$K_l = W_{vol} - W_a \cdot \rho_s / \rho_l \quad (14)$$

The volume content of the gaseous phase can be obtained from equation (9) as the difference of values:

$$K_g = 1 - K_s - K_l = 1 - \rho_s / \rho_t - W_a \cdot \rho_s / \rho_l \quad (15)$$

With certainty it can be argued that the volume proportion of phases according to equation (9) is a fundamental

characteristic of disperse systems, since it is based on the physical characteristics such as mass, volume and density. Using of volumetric ratios of phases allows us to study the behavior of disperse systems, for example, when they are mixed, to identify the quantitative ratio of the phases during impact and to identify the main technological methods that enable to purposefully influence the ratio of different phases in order to obtain materials with the desired properties.

From these positions two - and three-phase disperse systems were investigated, which are the main objects of study in this paper.

According to the research^{1,2} it was found that the most promising mixers for such systems are centrifugal mixers (CM), which are characterized by high intensity of the mixing process by the directing traffic organization of sparse thin layers which provide reliable input ripple of smoothing material flows. In CMs, it is possible to combine mixing and dispersion in order to receive a mixture of good quality with a large ratio of the blend components and it is one of their main advantages.

In the case when particle sizes of the key component with respect to the other differ by up to 40 times, and their mixing ratio is 1:400 or more, to obtain a biphasic system S + G (ready-mix) with well-defined properties becomes virtually impossible due to the occurrence of segregation in the space above the centrifugal rotary mixer due to the high rotational speed of the rotor. By centrifugal force, the prepared mixture begins to flake, not having time to form a clear two-phase system. As long as a part of the components with high dispersion rise over in the rotor dusty space and remain there in a suspended state, and the other part is removed from the CM with the main component. As a result of this, the prepared mixture loses some valuable components, thus becoming unsuitable for its ultimate purpose.

To resolve this problem (segregation phenomenon), we proposed to enter a small amount of liquid with different viscosities (syrops, extracts, etc.) into the system, i.e. up to the obtaining of the three-phase system with the aim of strengthening of intermolecular cohesive forces between the particles of fine components.

The implementation of the mixing process is advantageously carried out in a single unit with the highest exposure to intense mechanical working body on the material. As such, it is proposed to use the original design of the continuous mixer centrifugal type⁶ (fig. 2) designed for the preparation of granular mixtures with strongly differing dispersion of particles, and with the possibility of the liquid phase entering. Increasing of process efficiency is achieved due to spraying of the liquid phase flow in a thin layer of loose components and mixing in two stages.

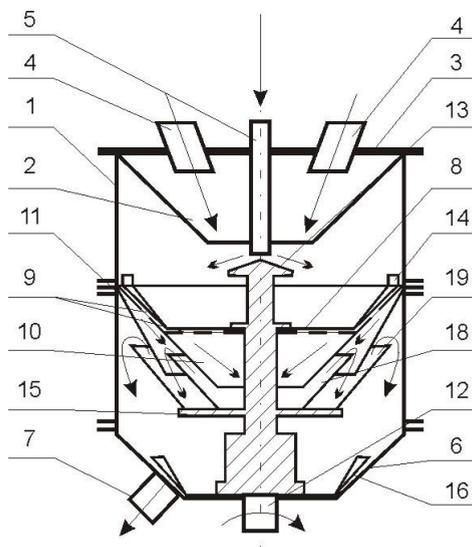


Fig. 2. Centrifugal mixer (patent № 2191063)

1 - cylinder course, 2 - guide funnel, 3 – cover, 4 - loading tubes, 5 - a connection for feeding the liquid phase, 6 - a bottom, 7 - discharge pipe, 8

- receiving and dispensing device, 9 - the dispenser openings 10, 11 - hollow guide cone, 12 - shaft, 13 - a disc for spraying the liquid phase 15 - rotor disc, 16 - unloading blades 18 - the inner cone, 19 - outer cone.

At this CM to determine the effect on the quality of the mixture ratio of the particle size of the primary and key components $D=d_0/d_k$, the amount of moisture introduced by C , % and its viscosity μ , Pa \times s, a full factorial experiment was planned and implemented. Vitamins (A, D₃, B₁, B₂, B₃, B₅, B₁₂) included in the mixture in lesser amounts were used as key components. Mixing quality was assessed by inhomogeneity coefficient V_C due to key components:

$$V_C = \frac{S}{\bar{C}} \cdot 100\% \quad (16)$$

where S – sample standard deviation key component of the content in the samples taken from the mixture; \bar{C} – selective mean concentration of the key component in the samples.

3. Results and Discussion

Extended matrix experimental design and results are presented in table 1.

Table 1. Variable parameters of the experiment

№	The amount of moisture	Particle size ratio	Viscosity of liquid	Coefficient of inhomogeneity
	C, %	$D=d_0/d_k$	μ , mPa·sec	Vc, %
1	2	3	4	5
1	2	10	10	7.16
2	2	10	70.0	6.76
3	2	10	130	8.44
4	2	25	10	8.79
5	2	25	70.0	7.22
6	2	25	130	8.48
7	2	40	10	9.21
8	2	40	70.0	8.39
9	2	40	130	10.12
10	4	10	10	6.76
11	4	10	70.0	6.26
12	4	10	130	7.73
13	4	25	10	7.97
14	4	25	70.0	6.73
15	4	25	130	10.47
16	4	40	10	9.23
17	4	40	70.0	7.31
18	4	40	130	10.89
19	6	10	10	7.85
20	6	10	70.0	7.38
21	6	10	130	10.49
22	6	25	10	10.33
23	6	25	70.0	9.32
24	6	25	130	16.25

25	6	40	10	22.89
26	6	40	70.0	20.52
27	6	40	130	27.71

These results indicate that our design CM allows obtaining a good quality of the mixture with $D = 10$, the amount of moisture introduced by $C = 4\%$, and its viscosity varying from 40 to 70 Pa \times sec, since V_c does not exceed 6 \div 7%. In other cases the quality of the mixture can be considered satisfactory ($V_c = 8 \div 11\%$). The large value of $V_c = 20 \div 28\%$ is due to the fact that the ratio of the dispersion composition of the blend components was very large $D = 10$, the amount of introduced moisture being $C = 6\%$, and the viscosity being varied from 70 to 130 mPa \times sec.

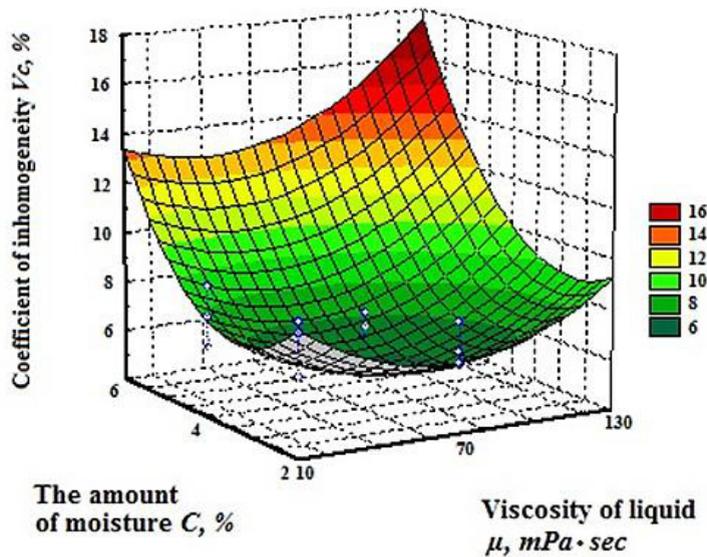
This is due to the fact, that by adding 4% moisture intermolecular the cohesive forces between the particles reach their maximum values, while keeping the three-phase system mixable components, and the resulting mixture is obtained with a good quality and has a homogeneous structure. When you enter a 6% moisture, cohesion for particles which are mixed violated as a result of this highly-components begin to stick together to form small aggregates, deteriorating quality of the obtained three-phase system.

During the regression equation in coded and natural forms, reflecting the impact of our selected parameters and the quality of the liquid mixture was received.

$$Y=10.395+3.232 \cdot X_1+3.19 \cdot X_2+0.756 \cdot X_3+3.335 \cdot X_1 \cdot X_2+0.958 \cdot X_1 \cdot X_3+3.35 \cdot X_1^2+1.37 \cdot X_2^2+2.26 \cdot X_3^2 \quad (17)$$

$$V_c=-118.94-1.473 \cdot C-0.198 \cdot D-0.0165 \cdot \mu+0.095 \cdot C \cdot D+0.00686 \cdot C \cdot \mu+1.43 \cdot C^2+0.0749 \cdot D^2+0.03221 \cdot \mu^2 \quad (18)$$

The analysis of the coefficients of the regression equations leads to the following conclusions. The greatest impact on the quality of the three-phase systems have the number of injected fluid and particle size ratio of the main and key components, as well as their combined effect. To achieve the best quality values of the mixture it is necessary that the ratio of the particle size does not differ by more than 10 times, and the amount of the injected fluid does not exceed 4 % by volume of the resulting mixture. Viscosity of the fluid has the least impact on the quality of the mixture, but it must be borne in mind that the greater its value, the higher specific energy costs. It should be noted that at higher input fluid it is necessary to increase the viscosity, and the average particle size of the mixture must not be less than 40 microns. For a visual display of the impact of the above mentioned factors on the quality of the mixture the response surface is represented in fig. 3 corresponding to equation (18).

Fig. 3. Response surface with $D=d_o/d_k=10$

We used the Fisher criterion F_m for assessing the adequacy of the obtained equations. F criterion for equation (18) was 5.47, and the value of Fisher's exact test was $F_m = 5.82$. Thus, we can conclude that the obtained equation adequately describes the process of obtaining of three-phase systems, as long as $F < F_m$.

For comparison we have performed the additional experiments to minimize the effect of segregation on the quality of two-and three-phase systems by addition of liquid to the CM⁶, allowing to mix materials with dispersion of particles in the range of several micrometers up to $3 \div 4$ mm, providing the productivity up to 1000 kg / hr (at a diameter of 400 mm and a machine speed of the rotor $10 \div 15$ s⁻¹). Specific energy consumption is $200 \div 300$ J/kg.

At this CM the vitaminized flour and the whole milk substitutes supplemented with 4% liquid and without³ it were received. Bulk concentration of key components (vitamins) in the mixtures was varied $C_{K.K.} = 0.25 \pm 6\%$. Rotor speed was taken to be $n = 12.5$ s⁻¹. The experimental results are shown in Table 2.

Table 2. The experimental data of the effect of the concentration of the key component of the mixture on its quality in the CM

The main component of the mixture	The concentration of the key component $C_{K.K.}, \%$	Coefficient of inhomogeneity $V_c, \%$	
		no addition of liquid	liquid additives
Wheat flour	0.5	9.81	9.2
	1	8.38	8.04
	2	5.2	4.75
	4	3.49	3.02
	6	3.23	2.92
Powdered milk	0.25	10.15	9.14
	1	8.31	8.09
	2.5	4.96	4.85
	4	3.05	2.9
	6	2.91	2.85

The table shows that the CM allows us to receive the mixture of high quality components at a ratio of 1 to 100, since the value of the coefficient of inhomogeneity V_c mixture does not exceed $6 \div 7\%$. When the ratio of the components is in the range $1: 100 \div 1: 400$ the mixture has a satisfactory quality ($V_c \approx 9 \div 10\%$). Adding a small amount of fluid with a viscosity of $4\% \cdot 50 \text{ Pa}$ to the mixture with a viscosity of $4\% \cdot 50 \text{ Pa}$ helps to reduce the coefficient of segregation and the heterogeneity of the mixture obtained in the dusty area and, consequently, to increase the quality of the final product (uniformity of the three-phase system).

4. Conclusions

From the results of the studies we can conclude that while a liquid entering on the preparation stage of dry combined products the obtained systems became more homogeneous in their composition, and the quality improved by 1.5 times and the effect of segregation actually reduced to zero.

Acknowledgements

We thank Kemerovo Institute of Food Science and Technology that have allowed using laboratories materials, equipment which are necessary for the success of this study.

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