SIZE DISTRIBUTION OF DROPLETS OF A DISPERSED PHASE AT FERMENTATION

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The size distribution of droplets for a series of batch fermentation experiments was studied by taking photographs of samples of hydrocarbon emulsion stabilized in a gelatine media in a laboratory size and at pilot-plant conditions. The time dependence, dependence on volume fraction of hydrocarbons and on the size of inocula at fermentation of hydrocarbons by use of *Candida lipolytica* 4-1 yeasts were studied. The suitability of Pearson's functions for description of the obtained distributions and the data in the literature which were characterized by a strong right asymmetry, was verified.

This contribution is related to a recent study¹ in which some momentum characteristics of size distribution of droplets in an emulsion of gas oil and n-hexadecane dissolved in a deparafined gas oil were studied. An attempt is made here to describe the size distribution of droplets by use of a suitable mathematical relation which would make possible a more accurate modelling of the fermentation kinetics in an aerated batch with two liquid phases: medium-hydrocarbon.

The present state of knowledge on modelling of fermentation operations in the considered system is given e.g. by Shah and coworkers². Erickson and coworkers³ applied for the kinetics the rectangular size distribution of droplets as the first approximation; then the distribution according to Chen and Middleman⁴

$$f_{\rm v}(x/\bar{x}_{32}) = (s_{\rm v}\sqrt{2\pi})^{-1} \exp\left[(x-\bar{x}_{\rm v})^2/2{\rm s}_{\rm v}^2\right], \qquad (1)$$

where x_{32} is the Sauter's mean, \bar{x}_v and s_v^2 is the average and the estimate of variance of the volume distribution, and $f_v(x/\bar{x}_{32})$ is the volume weighted frequency function.

Katinger⁵ has made an attempt to describe the size distribution of droplets in the considered system by use of the relation published by Schwarz and Bezemer⁶

$$f_{\rm y}(x) = a/x^2 \cdot \exp(a/X - a/x)$$
, (2)

where a and X are empirical parameters, which can be determined from the linear regression relation

$$\ln [v(x)] = k_1 - k_2(1/x). \tag{3}$$

According to relation (3) v(x) represents the cumulative volume fractions in %, and x is the size of droplets. The parameters of function (2) are related with the constants of regression (3) by the following equations

$$a = k_2, \qquad (4)$$

$$X = a[k_1 - \ln 100]^{-1} . (5)$$

Schwarz and Bezemer⁶ are also giving the relation for the frequency function of droplet sizes

$$f(x) = \exp(a/X) / [6(1 + a/X + a^2/2X^2 + a^3/6X^3)] a^4/x^5 \cdot \exp(-a/x) .$$
 (6)

Experimentally determined distributions of droplet sizes of hydrocarbons at fermentation have been published only by few authors — like Katinger and coworkers^{7,8} and Wang and Ochoa⁹. McLee and Davies¹⁰ have published distributions concerning emulsions obtained in laboratory separating funnels and thus they are not of interest for this study. Rajagopal¹¹ has applied for description of size distribution of droplets in an oil emulsion the log-normal distribution which is in general suitable for distributions with the right asymmetry. As long as the transformation

$$x = 1/c \exp(csz), \tag{7}$$

is used where c = 1/M (where M is median) and s is the standard deviation for the variable of the normalized Gaussian distribution, then for the log-normal frequency function is obtained the relation given by Gebelein¹²

$$f(x) = \lambda^{1/2} [s(2\pi)^{1/2}]^{-1} \exp\left[-(z+cs)^2/2\right], \tag{8}$$

$$\lambda = \exp\left(c^2 \cdot s^2\right) \tag{9}$$

and z is the inverse transformation to Eq. (7). Steidl¹³ has derived for the turbulent emulsion the relation for stationary distribution of drop sizes, the validity of which was verified¹⁴ in a series of experiments with mechanical mixers for coarse emulsions with drop sizes above 50 μ m.

Expression for Distribution of Drop Sizes in Emulsion

Together with the frequency function f(x) defined e.g. by relation

$$\mathrm{d}n = f(x) \,\mathrm{d}x\,,\tag{10}$$

where dn is the number of drops with dimensions satisfying condition $x \in (x, x + dx)$, the so-called weighted frequency functions are also frequently used giving the distribution of volumes or surface areas of particles. In this case *e.g.* the volume weighted frequency function $f_v(x)$ is defined by

$$dv = f_v(x) \, dx = k_v x^3 \, dn \,. \tag{11}$$

In Eq. (11) k_v is the shape factor for volume of particles (for spherical drops in an emulsion it can be accepted $k_v = \pi/6$). Recalculation of frequencies from the volume weighted frequency function (without considering the functional transformation) is affected by a great error. If Δn is the absolute error of frequencies corresponding to a finite interval of size Δx (which is a quantity

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proportional to the relative error of the frequency function (10), from relations (10) and (11) results

$$\Delta n / \Delta x \approx dn / dx = f(x) = f_v(x) (k_v x^3)^{-1}$$
. (12)

For illustration are in Fig. 1 given, for one typical experiment, the ranges limited by 10% error of the frequency function f(x) — the region limited by solid lines (error at direct determination of frequencies). Dashed lines are limiting the region of fluctuating frequencies at their recalculation from the volume function $f_v(x)$ which is affected by the same relative deviation of 10%. It is obvious that frequencies of fine particles which are of great importance in fermentation cannot be reliably determined at all from the course of the function $f_v(x)$. For this reason we have not studied the suitability of the volume distribution according to Chen and Middlemann (Eq. (1)).

Verification of Relations Published for Frequency Functions

Analysis of suitability of frequency functions for drop sizes which had been derived on basis of physical models of formation of an emulsion and the review of which is *e.g.* given by Shah and coworkers² or by Steidl and Ludvík^{13,14} was negative. These functions include² a great number of parameters of emulsion which can be determined with a great difficulty or which are not suitable due to their shape. Also the log-normal distribution which is based on a quite general model of particle desintegration is not satisfactory for our experimental data. On basis of the relation for the moments about origin of log-normal distribution as given by Gebelein¹²

$$\mu_{\rm r}(x) = c^{-r} \lambda^{r^2/2} , \qquad (13)$$

can be derived relations for the coefficient of asymmetry S_k

$$S_{k} = m_{3} s^{-3} = (\lambda + 2) (\lambda - 1)^{0.5}, \qquad (14)$$

where m_3 is the central moment of the third order and s is the standard deviation. For the coefficient of excess E_k then results

$$E_{\mathbf{k}} = (m_4 s^{-4}) - 3 = [\lambda^6 - 4\lambda^3 + 6\lambda^{3/2}c^{-1} - 3]/$$

/[$c^{-4}\lambda^2(\lambda^4 - 4\lambda^3 + 6\lambda^2 - 5\lambda + 1)$] - 3. (15)

Comparison of coefficients S_k and E_k , as detemined from the empirical moments and across the parameters of log-normal distribution (see Eqs (7), (9) and (14), (15), is for illustration given for two examples: The empirical values of coefficient of skewness S_k 2·24 and 2·42 correspond to the log-normal value 2253·0 or 118·2. For the coefficient of excess E_K the corresponding empirical values were 4·98 and 6·14 and from the log-normal distribution both were – 2·997. The difference in the momentum characteristics S_k and E_k according to the log-normal distribution in comparison with the empirical values is characteristic for the majority of experimental data¹ and confirms that the log-normal frequency function is not suitable for our purposes.

The distribution according to Schwarz and Bezemer (Eqs (2) or (6)) was not directly verified due to negative results with testing of regression dependence (3), the linearity of which determines suitability of this distribution for the given data. In Figs 2 to 4 logarithms of empirical cumulative volumetric fractions are plotted for the experiments of Katinger⁸ (Figs 2 and 3) and for one series of our own data in Fig. 4. Dependences for other original data have an analogical character. In these Figs are further plotted the regression dependences according to Eq. (3). From given Figs





Error of Frequency Function for Selected Experiment (Exp. 68b (ref.^{15,16}))

f(x), ---- lines limiting the region $f(x) \pm 0.1.f(x)$, ---- lines of relative deviations according to Eq. (12).





Cumulative Volume Fractions According to Eq. (3)

• Empirical values (Exp. K 1, Table I), ----- regression dependence.





Cumulative Volume Fractions According to Eq. (3)



FIG. 4

Cumulative Volume Fractions According to Eq. (3)

• Empirical values (Exp. 106 (ref.^{15,16})) ------ regression dependence.

| Conditions | of Expe | riments | and Re- | sults of Ca | lculations | | | | | | | | |
|--------------------------|------------------|--|---------|----------------|-------------|----------------|-------|------------|------------|-------------|---|---------|----------------------------------|
| | | Non-contraction of the second second second second | | Pear | rson's | | | D | istributio | n parameter | s | | |
| | r ^a h | ϕ^{p} | | types of d | listributio | SU | typ | e X | type | s XII | (type | 1II)° | Note |
| see ref ^{15,16} | • | h | E | ain | altern | ative | s | Y_0 | М | B | | N^{q} | |
| | | | type | χ ² | type | x ² | | | (C) | (b) | (V) | | |
| 32a | 0.5 | 0-03 | XII | 90-1 | × | 161-2 | 11-96 | 61.3 | 0-668 | 5.14 | | 766 | time dependence, inoculum |
| 325 | 3.0 | 0.03 | ШЛ | C'9C1 | > | 746.0 | 1.2.7 | 05.3 | 0.814 | 13.6 | | 1 167 | $X_0 = 0.5 \mathrm{g/l}$ |
| 32c | o, o o o | 0.03 | IIX | 171.8 | ×× | 261-0 | 7.88 | 5.86 | 0-815 | 2.65 | | 1 218 | |
| 32c' | 5.5 | 0-03 | × | 164.1 | 1 | | 6.76 | a Managara | 1 | I | and the second se | 1 166 | |
| 32c″ | 5-5 | 0-03 | × | 136-6 | Weaton | - | 6.68 | I | | 1 | I | 1 043 | |
| 32d | 8.0 | 0-03 | × | 176.5 | 1 | 1 | 7-76 |] | 1 | | | 1 249 | |
| 32d' | 0·8 | 0-03 | x | 151-5 | 1 | 1 | 8·12 | | - | NOTION | - | 1 319 | |
| 32e | 10.5 | 0.03 | × | 182.6 | 1 | ļ | 6·28 | 1 | - | - | I | 1 358 | |
| 32e' | 10.5 | 0-03 | × | 159-0 | I | I | 5.78 | I | | 1 | 1 | 1 410 | |
| 32f | 23-5 | 0.03 | | 278-9 | ШX | 141-7 | 7-99 | 100.7 | 0.722 | 3·20 | ł | 965 | |
| 14a | 1.5 | 0.03 | IIX | 24·3 | × | 6.99 | 10-44 | 49·1 | 0.703 | 4-30 | - | 579 | time dependence, |
| | | | | | | | | | | | | | inoculum $X_2 = 0.8 \text{ g/l}$ |
| 14b | 4·0 | 0-03 | ШX | 1.16 | III | 105.6 | | 120.6 | 0.787 | 2-47 | 1 | 1 189 | - io - 0. |
| | | | | | | | | (123-9) | (0-261) | (-0.181) | (3-14) | | |
| 146′ | 4-0 | 0.03 | ХШ | 76-7 | Х | 137.6 | 6·12 | 142.6 | 0-832 | 1-96 | I | 1 460 | |
| 14c | 6-5 | 0-03 | ШX | 71.8 | III | 49-4 | ŗ | 180-7 | 0.821 | 1-67 | ł | 1 453 | |
| | | | | | | | | (203.3) | (0.318) | (-0-354) | (2.03) | | |
| 14c′ | 6:5 | 0.03 | ШX | 49-4 | II | 51.3 | 1 | 157-1 | 0.831 | 1-75 | | 1 419 | |
| | | | • | | | | | (182-0) | (0-283) | (-0.401) | (2·11) | | |
| 14c″ | 6.5 | 0.03 | ШX | 97-0 | III | 54.4 | [| 178-4 | 0·802 | 1.68 | I | 1 297 | |
| | | | | | | | | (190-4) | (0.353) | (-0.259) | | | |

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TABLE I

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| 512 | • - | 100 | | | 011 | 0. | *** 0 P | 1010 | , | | | | | | | | | | | | | | | | | | | | | |
|-------|-------|----------|-------|-------|--------|------------------|----------------------------------|----------|-------|-------|-------|-------|-------|-------|-------|-------|------------------|-------------|-----------------|-------|--------|----------------|-------|--------|-------|-------|----------------|-------------------------|----------|-------|
| | | | | | | time dependence, | inoculum $X_0 = 1.5 \text{ g/l}$ | > | | | | | | | | | effect of volume | fraction of | dispersed phase | | | | | | | | fermentor with | volume 1 m ³ | | × |
| 1 306 | I 520 | 1 318 | 1 318 | 1 435 | 1 214 | 1 349 | | 1 988 | 1 576 | 1 626 | 1 729 | 1361 | 1 694 | 1 493 | 1 352 | 1 302 | 1 538 | | | 1 329 | 1 606 | | 2 217 | 1 704 | 1 548 | 1 374 | 962 | | 1 167 | 1 041 |
| 1 | - | (1-89) | 1 | | I | (4·274) | | (3-00) | - | | I | - | 1 | Manan | I | - | - | | | | | (3.60) | - | | 1 | | ١ | | W | Į |
| 1.67 | 1.65 | (-0.158) | 1.42 | 1.38 | 1.34 | (0.017) | | (-0.156) | - | 1.60 | 1.45 | 1-09 | 1-45 | 1.74 | 1-76 | 1.68 | 2.01 | | | 2.48 | 2.76 | (-0.061) | 2-47 | 3-61 | 4.03 | 3-44 | 1.89 | | 1.97 | 2.39 |
| 0.817 | 0-811 | (0·442) | 0.828 | 0.802 | 0.810 | (0.238) | | (0·281) | - | 0.777 | 0-835 | 0-821 | 0.814 | 0-804 | 0.815 | 0-819 | 0.828 | | | 0.812 | 0.766 | (0·261) | 0.810 | 0.790 | 0.762 | 0.818 | 0-838 | | 0·842 | 0-801 |
| 165.6 | 208·1 | (230·3) | 184·3 | 240-4 | 199-5 | (117-5) | | (220-7) | ļ | 267-9 | 226-2 | 256-9 | 251-0 | 196-7 | 164.8 | 161-6 | 151-1 | | | 116.9 | 182-6 | $(31 \cdot 1)$ | 197-5 | 117-2 | 109-5 | 83-9 | 94.4 | | 106.1 | 101.0 |
| 4-96 | 4.68 | 4·12 | 4·32 | 3.96 | 3.92 | 8-46 | | 6-51 | 4.61 | 4.36 | 4.25 | 3.28 | 4-30 | 5.00 | 5.24 | 5-04 | 6.18 | | | | WARANA | | 7-44 | ****** | | - | 5-97 | | l | 9.90 |
| 78.3 | 69-5 | 48.1 | 68-3 | 127-0 | 86.7 | 132-3 | | 181.2 | 1 | 84.5 | 90-4 | 128-4 | 100.0 | 77-5 | 95.7 | 67-4 | W ARM | | | - | 72.0 | | 292-8 | | - | | 215-9 | | ***** | 211-7 |
| XII | ШX | III | XII | XII | ХΙΙ | III | | III | | ШX | IIX | XII | XII | XII | IIX | ШX | Manage 1 | | | - | III | | × | 4 | I | I | × | | ł | IIX |
| 63.2 | 85.5 | 34.5 | 52-3 | 90·6 | 63·6 | 134·3 | | 105-3 | 49.7 | 49.5 | 88.4 | 49-9 | 81.6 | 79.6 | 118-7 | 65-5 | 109-3 | | | 75-2 | 46.0 | | 282-8 | 52.0 | 41.0 | 48.0 | 180.8 | | 133-1 | 164-5 |
| × | × | × | X | × | x | × | | X | × | × | × | × | × | × | × | × | × | | | IIX | IIX | | ХП | ШΧ | ШX | ЯΠ | ШX | | ШX | × |
| 0.03 | 0.03 | 0-03 | 0·03 | 0.03 | 0·03 | 0.03 | | 0.03 | 0.03 | 0-03 | 0-03 | 0.03 | 0.03 | 0-03 | 0-03 | 0-03 | 0.015 | | | 0.015 | 0.03 | | 0.05 | 0.10 | 0.10 | 0.10 | 0.10 | | 0·10 | 0.108 |
| 9.5 | 9.5 | 9.5 | 9.5 | 12.5 | 12.5 | 0.75 | | 3.5 | 6.75 | 6-75 | 6-75 | 9.5 | 9.5 | 12.5 | 12.5 | 12.5 | 4.5 | | | 4.5 | 5.0 | | 6.0 | 6-0 | 6.0 | 7.0 | 6-0 | | 6.0 | 5-0 |
| 14d | 14ď | 14d" | 14d‴ | 14e | . 14e' | 13a | | 13b | 13c | 13c' | 13c″ | 13d | 13d' | 13d | 13e′ | 13e″ | 68a | | | 68b | 106 | | 102 | 62a | 62b | 121 | 47a | | 47b | 48 |

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Size Distribution of Droplets

| | | | | Реаг | rson's | | | D | istribution | parametei | rs | | |
|----------------------|---------------|----------------------------|------------------------|----------------|------------------------------|----------------|----------|-------------|-------------|--------------|--------------|---|--|
| | <i>r</i> ª, h | ${oldsymbol{\Phi}}^{p}$ | L " | Types of c | listributior | IS | tyı | pe X | type J | XII | (type I | 11) ^c | Note |
| Run No | | | E | ain | altern | ative | S | Y_0 | W | B | | N^{q} | × |
| | | | type | x ² | type | x ² | | | (ک | (<i>I</i>) | (<i>V</i>) | | |
| WI | | | III | 52-0 | | | Name of | (172-8) | (0.549) | (4·72) | (10-42) | - | W1-600 r.p.m. ⁹ |
| W2 | | Processo I | III | 54.0 | [| 1 | I | (193-8) | (0.739) | (3.79) | (6.48) | | W2-800 r.p.m. ⁹ |
| W3 | 1 | 1 | III | 54.0 | 1 | ł | I | (187-6) | (0.884) | (4.09) | (5.76) | | W3 - 1000 |
| KI | l | vename | XII | 24.0 | | I | 1 | 224.8 | 0.966 | 0.164 | | The second se | r.p.m. ⁹ K1-mechanically |
| | | | | | | | | | | | | | agitated fermentor ⁷ |
| K 2 | l | 1 | IIX | 63-0 | × | 67-0 | 2.70 | 137.6 | 0·772 | 1.98 | | 1 | K2-mechanically |
| | | | | | | | | | | | | | agitated fermentor ⁷ |
| K 3 | ł | 1 | Ш | 18-0 | | I | ļ | (212·6) | (0.637) | (2·19) | (5.00) | l | K3-mechanically |
| | | | | | | | | | | | | | agitated |
| | | | | | | | | | | | | | lermentor |
| <i>a t</i> is the ti | me from | the beg $\frac{1}{N}$ is 1 | ginning c he size o | of ferment | ation. ^b Ø nle | is the vo | lume fra | ction of th | e dispersed | phase. | Values of p | paramet | ers for type III are |
| 3 | | | | | | | | | | | | | |

TABLE I (Continued) 2 to 4 is obvious that the regression dependence (3) for fermentors intensively agitated by mechanical agitators does not fit the empirical values and distributions according to Schwarz and Bezemer thus are not suitable for the cases considered by us. Of all the studied systems it is suitable only for the bubble-type fermentor according to Katinger⁵.

EXPERIMENTAL

The laboratory fermentor is a cylindrical vessel with radial baffles having a volume 1.51, intensively agitated (speed of rotation of the impeller 1000 min^{-1}) by a non-standard turbine mixer situated in a cylindrical drought tube. Description of the mixer (modified mixer according to Waldhof) together with the detailed description of the apparatus and conditions of the fermentation experiments and properties of the used substances are given in the earlier publications of this series^{15,16}. Numbering of experimental runs in all these publications is identical. Several experiments were performed with a pilot-plant fermentor of 10001 volume. This fermentor was mixed by several mixers with drought tubes¹⁷. In both experimental units the samples were taken from the region of the mixer and in the pilot-plant fermentor also from the circulation part of the vessel.

The complete description of the experimental method for determination of the drop size distribution by stabilization of samples in gelatine is given in the preceding paper of this series¹⁸. The fermentation experiments were performed batchwise. In three experiments has been studied the time dependence of distribution for different sizes of inoculus of the yeast culture. Further the effect of fraction of the hydrocarbon phase in the dispersion was studied. The conditions of the experiments are given in Table I together with the calculation results.

FREQUENCY FUNCTIONS ACCORDING TO PEARSON

Because of the negative results with the until now published relations for the frequency function for drop sizes in emulsion and due to great complexity of the given system, an attempt has been made to find a new empirical relation. The system of frequency functions¹⁹ according to Pearson was chosen because of its universal application. This system includes 13 types of frequency functions whose parameters can be determined through the first four moments about origin of the system. The details of calculation are not presented here, they can be found *e.g.* in the monography by Elderton and Johnson¹⁹ and for their realization the program published by Chisman²⁰ has been modified. Preliminary results of tests of all types on about 10 experiments made by us have demonstrated that types II, IV and VIII are not suitable for mathematical reasons. Further on, the frequency functions of types I, V, VII, IX, XI and the normal distribution have completely unsuitable dependences with respect to the empirical frequency function. Therefore the selection of types of Pearson's functions has been narrowed to the types III, X, and XII.

The number of drops fitting the frequency function of type III can be determined from the relation

$$n_0 = Y_0 (1 + x/A)^{\rm P} \exp(-Gx) . \tag{16}$$

Parameters of distribution Y_0 , A, P, and G can be determined from following relations

$$Y_0 = N \cdot G(P+1)^{P} / [\exp(P+1) \cdot \Gamma(P+1)], \qquad (17)$$

$$A = (P + 1)/G$$
, (18)

$$P = 4B_1 - 1 , (19)$$

$$G = 2m_2/m_3$$
, (20)

$$B_1 = t_3^2 / t_2^3 . (21)$$

In Eqs (17) to (21) m_2 and m_3 are the central moments of the second and third order, N is the size of sample, B_1 is the coefficient asymmetry due to Pearson, t_2 and t_3 are the transformed central moments for the grouped empirical frequencies $\{x_i, n_{ie}; \Delta x\}$ which for the case of equidistant classes of drop sizes ($\Delta x = \text{const}$) can be determined from the relation

$$t_{j} = m_{j} / (\Delta x)^{j} . \tag{22}$$

Frequency for the type X are defined by the relation (negative exponential curve)

$$n_0 = N\{\exp[-(x/s) - 1]\}/s.$$
 (23)

This function has a single parameter - the standard deviation s.

The frequencies according to type XII have the form

$$n_0 = Y_0 (s\beta^+ - x)^{M} (s\beta^- + x)^{-M}, \qquad (24)$$

as long as the third central moment is positive $(m_3 > 0)$ and

$$n_0 = Y_0 (s\beta^+ + x)^M (s\beta^- - x)^{-M}, \qquad (25)$$

as long as $m_3 < 0$. The empirical parameters in Eqs (24) and (25) can be calculated from relations

$$\beta^+ = (3 + B_1)^{1/2} + B_1^{1/2}, \qquad (26)$$

$$\beta^{-} = (3 + B_1)^{1/2} - B_1^{1/2}, \qquad (27)$$

$$M = [B_1/(3 + B_1)]^{1/2}, \qquad (28)$$

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$$Y_0 = N / [B \cdot \Gamma(1+M) \Gamma(1-M)], \qquad (29)$$

$$B = 2[m_2(3 + B_1)]^{1/2}, \qquad (30)$$

in which the $\Gamma(a)$ is the complete gamma function value of argument *a*. Frequencies calculated from relations (16), (23), (24) or (25) were corrected by relation

$$n_{\rm t} = n_0 \, . \, N/N_0 \, , \tag{31}$$

where N and N₀ are sums of empirical and theoretical frequencies respectively. By this arrangement the normalization of calculated frequencies is obtained *i.e.* $\sum_{i} n_{ie} = \sum_{i} n_{it}$.

For the graphical comparison of results the empirical and theoretical frequency functions were calculated

$$f(x_i) = n_i / \Delta x \sum_i n_i , \qquad (32)$$

where Δx is the width of the size interval of empirical distribution of drop frequencies (grouped distribution). The agreement of empirical and theoretical distributions has been considered according to the uncorrected value χ^2 of the criterion of goodness of fit which is defined by relation

$$\chi^{2} = \sum_{i} \left[(n_{it} - n_{ie})^{2} / n_{it} \right].$$
(33)

Neither grouping of frequencies in calculation (33) nor other goodness tests of fit have been used.

RESULTS AND DISCUSSION

In Table I is presented the summary of results of distributions according to Pearson both for our own data as well as for data by Katinger^{7,8} and by Wang–Ochoa⁹. As the main is always considered the type of distribution with the minimum value of χ^2 criterion. As long as for one of the considered types the value of χ^2 is smaller then the twice of χ^2 value for the main type, the given distribution is considered as an alternative type. In the other part of the Table are given parameters of the considered types. Mostly the types X and XII* are concerned. The values of parameters for the type III are denoted by an asterisk. In Table I is also given the size of samples from which the parameters were calculated.

^{*} In all considered cases hold $m_3 > 0$ so that the type XII was calculated from the relation (24).





Distribution According to Pearson of the Types X and XII (exp. 14a (ref. 15,16)) \odot Empirical frequency function, ----

Pearson's type X distribution, Pearson's type XII distribution.



Fig. 7



• Empirical frequency function (K_2 , Table I), \odot Pearson's type XII frequency function.



FIG. 6

Relative Deviations (δ_y , %) of Frequency Functions of the Types X and XII (exp. 14a (ref.^{15,16}))

• Type X, • type XII; t = 12.5 h, 2 t = 9.5 h, 3 t = 1.5 h.



Fig. 8

Pearson's Type III Distribution

• Empirical frequency function (K₃, Table

I), O Pearson's type III frequency function.

Size Distribution of Droplets

The time dependence. From Table I is obvious that for the sets of drops formed at the beginning of fermentation for small values of inocula $(X_0 = 0.5 \text{ and } 0.8 \text{ g/l})$, the type XII seems to be more suitable then the type X which is suitable for systems at the end of fermentation and for larger values of inocula. This trend is in agreement with the change of the coefficient of excess E_k (see¹). The type XII is suitable for systems with smaller peakedness. The graphical comparison of distributions of types XII and X with the empirical frequency function for the system from the beginning of fermentation is in semi-log coordinates given in Fig. 5. In these coordinates the type X is linearised and thus it is stressed that this type is not suitable for the given conditions. For illustration of selection between the types X and XII and for graphical localisation of deviations for one selected experiment are in Fig. 6 also given the relative deviations between the empirical and theoretical frequency functions (distributions according to Pearson of types X and XII) ∂_{y} for various times from the beginning of fermentation. If we neglect the deviations in the region of large particles (above 20 μ m) which, due to the small interval frequencies are not statistically significant, it can be said that the deviations dependence on the size of drops are for both types analogical and differs with the type only in magnitude.

Volume fraction of hydrocarbon phase. The volume fraction Φ has been varied from 1.5 to 10 vol. %. The time in which the samples were taken was about the first third of the total time of fermentation¹. We came to the conclusion that at higher concentrations of the hydrocarbon phase the suitability of the type XII was prevailing.

Data of other authors. Katinger^{7,8} has studied emulsification of the gas oil (volume fraction 10%). For the fermentor with a mechanical mixer the Pearson's distribution of the type XII is suitable (Fig. 7) while for a less intensively agitated bubble-type



Pearson's Type III Distribution, Data No. W 1 to W 3



fermentor is more suitable the type III (Fig. 8). Wang and Ochoa⁹ are presenting distributions of n-hexadecane in the media with yeasts obtained at various mixing intensities with a standard turbine mixer. These distributions of drop sizes obtained by sedimentation were before evaluation normalized as they have not fulfilled the condition for the frequency function $\int_x f_e(x) dx = 1$. Distribution according to these authors has a considerably lesser peakedness and can be described regardless of the mixing intensity by the Pearson's type III (Fig. 9).

Finally, it can be concluded that the system of frequency functions according to Pearson has been found suitable for distributions of drop size at fermentation of hydrocarbons. By this way quite different shapes of frequency functions can be described which are characterized by a different skewness and asymmetry. Some new information were obtained concerning the usability of individual types under certain fermentation conditions. Correlation of distribution parameters with the conditions will require additional experiments.

REFERENCES

- Prokop A., Ludvík M. in the book: Proc. lst. Internat. Symp. Advances in Microbiol. Engn. (B. Sikita, A. Prokop, M. Novák, Eds); Biotechnol. Bioeng. (Symp. No 4), 349 (1973).
- 2. Shah P. S., Fan L. T., Kao I. C., Erickson L. E.: Advan. Appl. Microbiol. 15, 369 (1972).
- 3. Erickson L. E., Fan L. T., Shah P. S., Chen M. S. K.: Biotechnol. Bioeng. 12, 713 (1970).
- 4. Chen H. T., Middleman S.: A.I.CH.E. J. 13, 989 (1968).
- 5. Katinger H.: Private communication.
- 6. Schwarz N., Bezemer C.: Kolloid Z. 146, 139 (1956).
- 7. Katinger H., Nobis A., Meyrath J.: Experientia 26, 565 (1970).
- 8. Katinger H.: Biotechnol. Bioeng. (Symp. No 4), 485 (1973).
- 9. Wang D. I. C., Ochoa A.: Biotechnol. Bioeng. 14, 345 (1972).
- 10. McLee A. G., Davies S. L.: Can. J. Microbiol. 18, 315 (1972).
- 11. Rajagopal E. S.: Kolloid-Z. 162, 85 (1959).
- 12. Gebelein H.: Mitteilungsbl. Math. Statistik, München 1950, 155.
- 13. Steidl H.: This Journal 33, 2191 (1968).
- 14. Ludvík M., Steidl H.: This Journal 35, 1480 (1970).
- 15. Prokop A., Erickson L. E.: Biotechnol. Bioeng. 14, 571 (1972).
- 16. Prokop A., Erickson L. E., Paredes Lopez O.: Biotechnol. Bioeng. 13, 241 (1971).
- 17. Prokop A., Ludvík M., Erickson L. E.: Biotechnol. Bioeng. 14, 587 (1972).
- 18. Kvasnička J.: Czechoslov. Pat. 136 438 (1970).
- 19. Elderton W. P., Johnson N. L.: Systems of Frequency Curves. Univ. Press, Cambridge 1969.
- 20. Chisman J. A.: *The Pearson Generalized Statistical Distribution*. Bulletin No 111 (1968), College of Engineering, Clemson Univ., South California.

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