KINETICS OF BREAK-UP AND COALESCENCE OF DROPS.

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Mathematical modeling of emulsifying in the current program is based on results of theoretical and experimental researches on breaking of droplets in turbulent flows.

Theoretical foundations for analysis and mathematical description of drop formation due to effect of micro-scale turbulence are created by the well known work of Kolmogorov [1]. and its applications to flow in pipes and mixing vessels , described by several authors (Piterskich and Valashek, Calderbank, etc.[2-4). The essence of the approach consists in describing the mean size of drops formed in different flow conditions as a function of the average values of turbulent energy dissipation rate in the flow or vessel, estimated as specific power consumption per unit of mass of media:

$$\varepsilon_{av} = P/(\rho V)$$

This approach has been used in a huge number of experimental researches and resulted in accumulation of some important practical data. On the other hand, it become clear early enough [5], that the possibilities of an approach based on the average energy dissipation are limited to qualitative evaluations only. It was found also [5], that a real progress could be achieved by analyzing the kinetics of breaking and coalescence of droplets with account to local hydrodynamic conditions. Researches based on this conclusion, resulted in development of theoretical model of breaking and coalescence of droplets in turbulent flow that provides quantitative description of the phenomena [6-10] . Starting from 1996, this model is successfully used for practical application in the program VisiMix Turbulent {see www.visimix.com}. Currently this model is used also as a base for mathematical modeling of breaking and coalescence of droplets in high shear channels of RSD devices.

1. KINETICS OF EMULSIFYING.

At the current stage of the research, the task is limited to simplified modeling of kinetics of simultaneous breaking and coalescence of droplets in the range of diameters corresponding to Kolmogorov's (non-viscous) range of linear micro-scales of turbulence. Furthermore, the mixing was assumed to be "perfect", i.e. all positions of a drop in the tank were assumed to be equally probable, and distributions of drop sizes and concentration of the disperse phase were considered uniform. The system was assumed to be mono-disperse. In such conditions, the number of drops in a liquid-liquid system with defined physical properties and constant volume fraction of the starting from some initial size, in a volume with non-uniform distribution of turbulence may be described by equation:

$$\frac{d\mathrm{d}}{d\tau} = \frac{\mathrm{d}}{3V}\int_V (N_c - N_b)dV \qquad (1)$$

To use this equation, three functions should be known. The two of them, frequencies of coalescence and breaking, N_c and N_b, depend on the drop size, physical properties of the phases and local rate of turbulent dissipation of energy, while the third - distribution of turbulent dissipation by volume - depends on design and operational regime of the emulsifying device.

2. THE FREQUENCY OF BREAKING

According to the results of recent studies in the kinetics of drop break-up in mixing vessels in the absence of coalescence a quantitative description of drops break-up may be based on the universally known Kolmogorov's stability condition for a drop in a turbulent flow. An individual act of deformation and breaking must be assumed to occur under action of an instant velocity pulsation in the vicinity of the drop on the condition that the amplitude of the pulsation exceeds a certain minimum value v*. The relation between this "critical" value and the mean square root velocity was estimated as

$$U^* = \frac{\mathrm{v}^*}{\bar{\mathrm{v}}} = \frac{0.775}{\varepsilon^{1/3}\mathrm{d}^{1/3}}(M/\mathrm{d} + \sqrt{\left[(M/\mathrm{d})^2 + \frac{10\sigma}{\rho_c \mathrm{d}}\right]}) \qquad (2)$$

where

$$M = \left|1.2\frac{\rho_d}{\rho_c}v_d - 3v_c\right| \qquad (3)$$

The linear scale of the "destroying" pulsations was estimated as *l* = 2.17 d - the minimum length of the deformed droplet, corresponding to the loss of stability. Within the framework

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of this model, the mean frequency of drops breaking in an area with the local turbulent dissipation ε may be estimated as

N_b = *mean frequency of pulsations of the scale l* x *relative frequency of pulsations l with amplitudes* $v' \geq v^*$ x *probability of one or more droplets residing in an area of the scale l*,

or

$$N_b = f_l P(v' \geq v^*)(1 - P(0)) \qquad (4)$$

where $$f_l = \frac{1}{l^3}\frac{\varepsilon^{1/3}}{l^{2/3}} \qquad (5)$$

$$P(v' \geq v^*) \cong \sqrt{2/\pi}\int_{U^*}^{\infty} \exp(-U^2/2)dU \qquad (6)$$

and $$P(0) \cong 1 - \exp(-19.6\varphi) \qquad (7)$$

3. THE FREQUENCY OF COALESCENCE

The act of coalescence is usually assumed to occur (see for instance [11]) if (1) two droplets approach each other and collide and (2) the collision happens to be "efficient", i.e. the amplitude of the fluctuation is high enough to overcome the resistance of a liquid film separating the drops:

N_c = *frequency of collisions* x *efficiency of collisions*

It seems, however, that the individual acts of collision and junction of the drops must not necessarily occur due to the same random turbulent fluctuation. The necessary condition of coalescence of two droplets may thus be assumed to consist in their being in contact as the fluctuation occurs. The term "in contact" here means that the distance between the drops' centers is practically equal to the drop diameter, *d*, and their surfaces are separated by a thin layer of ions existing on the water-oil boundary, water side. According to the postulates of the DLFO-theory [12], the interfacial boundary is surrounded with a "double layer" of ionized liquid. Due to inter-action of these layers, the neighboring surfaces are kept from junction by electrostatic repulsive pressure, *p*. The value of this pressure depends on the chemical composition of substances. For "pure" oil - distilled water couple, the theoretically estimated value is about 20 Newtons per sq. m; it increases in emulsions stabilized with detergents, and decreases in solutions of flocculants and multivalent electrolytes. The coalescence only happens if the squeezing pulsation pressure is high enough to overcome the repulsive pressure. The condition for a random turbulent pulsation to be "efficient" may thus be formulated as

$$v'_n \geq v_c{*} = \sqrt{(2p \ / \rho_c)} \tag{8}$$

where v'_n is the constituent of the pulsational velocity v'_λ, normal to the contact surface, and

$\lambda \cong d$ is the linear scale of the "coalescing" pulsations.

According to this model, mean frequency of coalescence may be defined as

N_c = *mean frequency of pulsations of the scale* λ x *relative frequency of pulsations with amplitudes satisfying the condition* $v'_n \geq v_c{*}$ x *probability of the presence of two or more drops in an area of the scale* λ*,*

or

$$N_c = f_\lambda P(v_n' \geq v{*})(1 - P_\lambda(0) - P_\lambda(1)), \tag{9}$$

where $$f_\lambda = \frac{1}{\lambda^3}\frac{\varepsilon^{1/3}}{\lambda^{2/3}} \tag{10}$$

$$P(v_n' \geq v_c{*}) = \frac{1}{\sqrt{2\pi}}\int_{V*}^{\infty}(1 - \frac{V'}{V*})\exp(-V'^2/2)dV' \tag{11}$$

$$V{*} = \frac{v_c^*}{\bar{v}} = \frac{\sqrt{(2p/\rho_c)}}{\varepsilon^{1/3}\lambda^{1/3}} \tag{12}$$

and $$V' = v'_\lambda / \bar{v}_\lambda \tag{13}$$

The term $(1 - \frac{V'}{V*})$ in Eq. 11 accounts for the fact that v_n is a component of pulsation velocity normal to the contact surface.

The probability for the centers of the two drops to be in the area of the scale λ was estimated approximately as

$$1 - P_{\lambda}(0) - P_{\lambda}(1) \cong 1 - (1 + \varphi)\exp(-\varphi)$$

(14)

Applicability of these equations for quantitative description of drop breaking / coalescence phenomena has been confirmed with experimental researches, related mainly to mixing equipment [9,10]. Some of these results are presented in the Figures 1 and 2. Mean diameter of droplets is presented in these graphs as a function of maximum local value of energy dissipation in the mixing vessel.

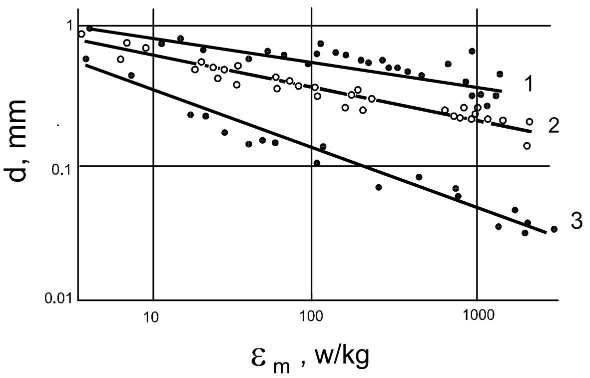

Figure 1. Mean drop diameter vs. ε_m .

1 - P = 20 Pa; 2 - P = 7 Pa; 3 - P →∞ (fully stabilized). Solid lines correspond to calculations by equations 1-14.

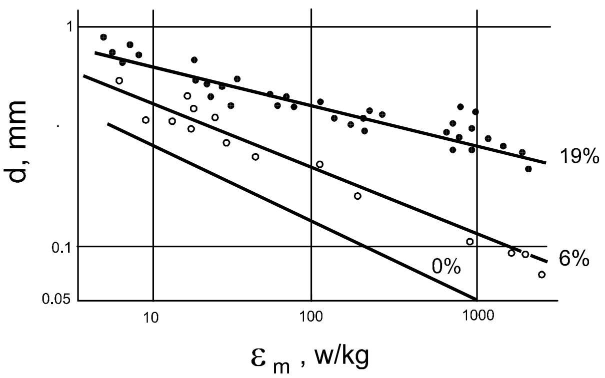

Figure 2. Mean drop diameter vs. ε_m . The effect of the concentration of the disperse phase. Solid lines correspond to calculations by equations 1-14.

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4. APPLICATION OF THE THEORETICAL MODEL FOR RSD DEVICES

The system of equations described above serves as a base of mathematical model of emulsifying in the current program. For practical application it is completed with data on turbulent energy dissipation in RSD channels and on residence time distribution of droplets in these channels that are provided with other sections of the program (see Attachments 1 and 2).

Results of mathematical modeling have been verified with laboratory research. Experiments on emulsifying were performed in laboratory vessels, from 0.2 t0 1.5 liter by volume. A wide variety of stators and rotors with different dimensions and geometry used in experiments. Characteristics of the most often used rotors and stators are shown is shown in the Tables 1 and 2.

Table 1. Dimensions of experimental stators.

Stator sizes			Stator slots		
Designation	Internal diameter, mm	External diameter, mm	Number of slots	Width, mm	Height, mm
1	44	50	12	3	10
2			12	3	5
3			24	1	10
4			24	1	5
5			6	3	10
6			12	1	10
7	44	46	12	3	10
8	34	40	12	3	8
9	34	40	6	3	10
10	44	46	12	3	10
11	44	50	12	5	10
12	44	50	8	8	10

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13	52	64	18	3	10
14	52	60	18	3	10
15	52	60	36	1	10
16	52	64	36	1	10
			Stator perforations		
			Number	Diameter	
17	44	50	64	3	
18	44	50	144	1	

Table 2. Dimensions of experimental cylindrical rotors.

Rotor sizes			Rotor slots		
	Internal diameter, mm	External diameter, mm	Number of slots	Width, mm	Height, mm
1	36	42	12	3	8
2	36	42	6	3	8
3	34	40	12	3	8
4	34	40	6	3	8
5	24	30	12	3	8
6	24	30	6	3	8
7	34	42	12	5	8
8	34	42	24	1	8
9	40	42	12	3	8
10	42	50	12	3	8

The tests were performed with oil-in water emulsions. Oil phase was resented by vegetable oil+CCL4, vegetable oil+kerosene+CCL4 and kerosene+CCL4 solutions with different viscosity. Batch duration was from 15 min to 6 hours. Diameter of droplets was kept in experiments within the range 30- 7.5 mcm, it was defined using digital microphotography.

Additionally, applicability of the program was confirmed with production scale tests using 3 – and 4-stage RSD dispersers produced by IKA (Germany). Emulsion of paraffin in water was produces at temperature about 90deg.C, with flow rate from 10 to 50 liter per min. Mean drop size in the final emulsion attained at different conditions was from 5 to 10 microns and was in good correspondence with the calculated values.

Results of the main (batch) experiments have been used for some adjustment of the theoretical predictions. They confirmed that drop sizes of the emulsions obtained at different conditions are dependent mainly on the average energy dissipation (specific power) in the RSD channels, defined on the starting stages of modeling (see option SHEAR CHARACTERISTICS OF RSD CHANNELS in the Calculate menu). However, in some cases influence of radial slots or perforations can also be significant. As it follows from the data presented in the Figures 3 and 4, application of stator with smaller width of radial slots or perforations usually results in smaller values of mean drop diameter.

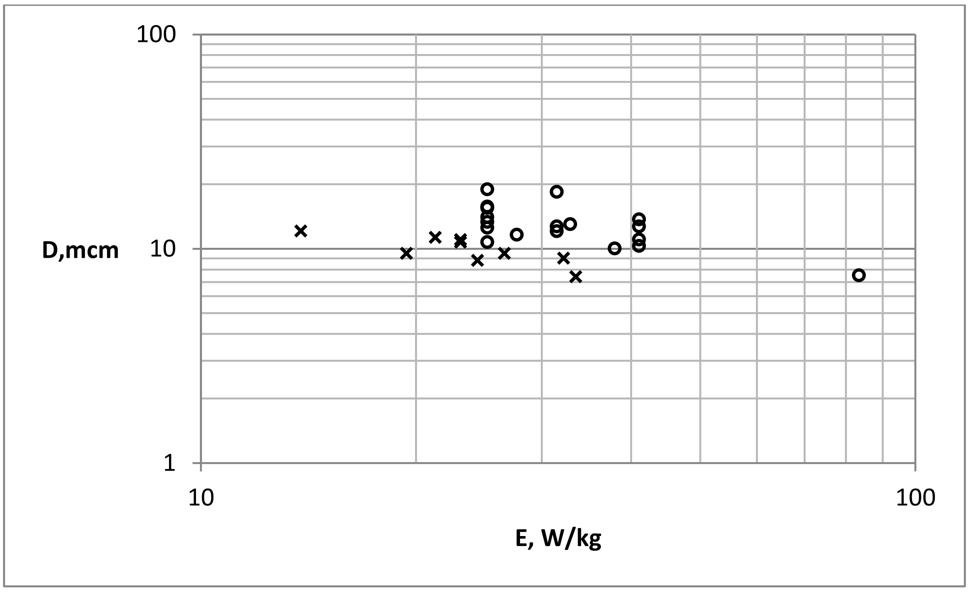

Figure 3. Influence of width of radial slots in stator on mean drop size. Stabilizer –Tween, 3%.

Stator diameter 50 mm, thickness 3 mm. E – specific power in channel.

O -width of slots 3 mm, ×- width of slots 1 mm.

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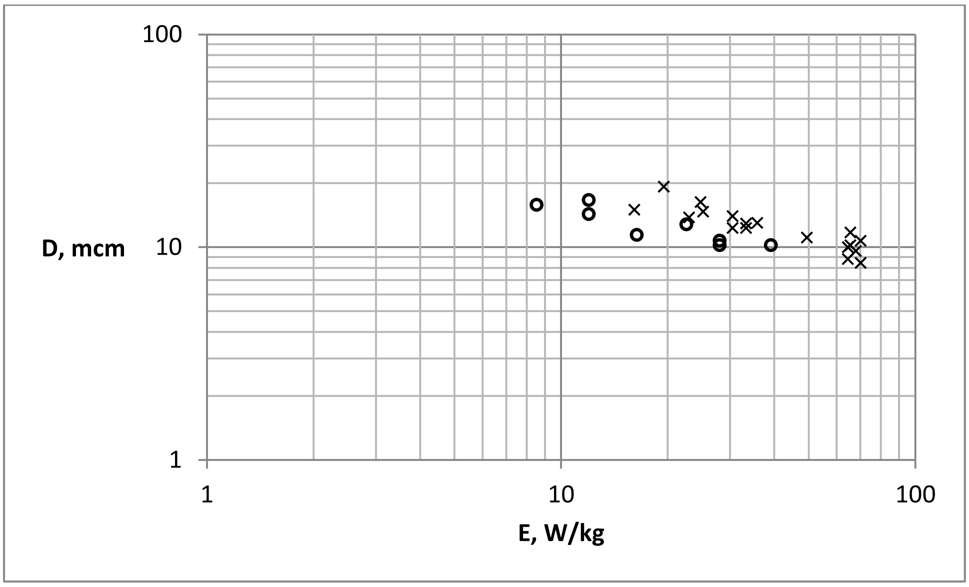

Figure 4. Influence of width of radial slots in stator on mean drop size. Stabilizer –Tween, 3%.

Stator diameter 40 and 60 mm, thickness 3 and 4 mm. E – specific power in channel.

O -width of slots or perforations 3 mm, ×- width of slots or perforations 1 mm.

A more detailed study of this dependence have shown (Figure 5), that the effective value of local turbulent dissipation in the drop breaking area is a function of relation between length and width of the slots or perforations in the RSD stator.

The corresponding adjustment has been introduced into the calculation algorithms. Degree of correspondence between results of mathematical modeling and experimental results in batch laboratory tests is illustrated in the Figures 6 and 7.

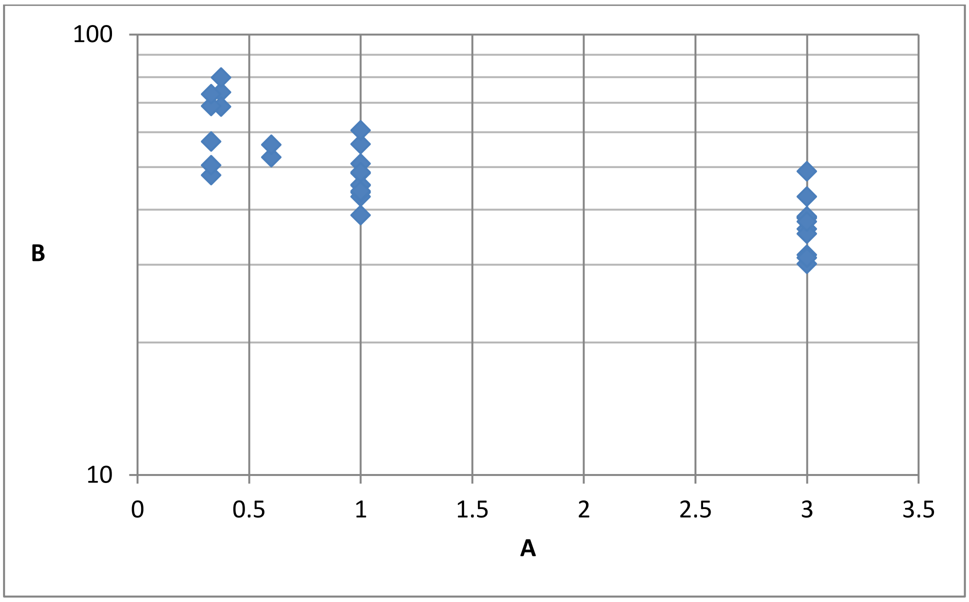

Figure 5. Influence of relative width of slots on mean drop diameter.

A = S/W, where S is thickness of stator and W is width of slots or diameter of perforations.

B= $D*E^{0.4}$, where D is mean drop diameter, mcm, and E is calculated value specific power in the RSD channel.

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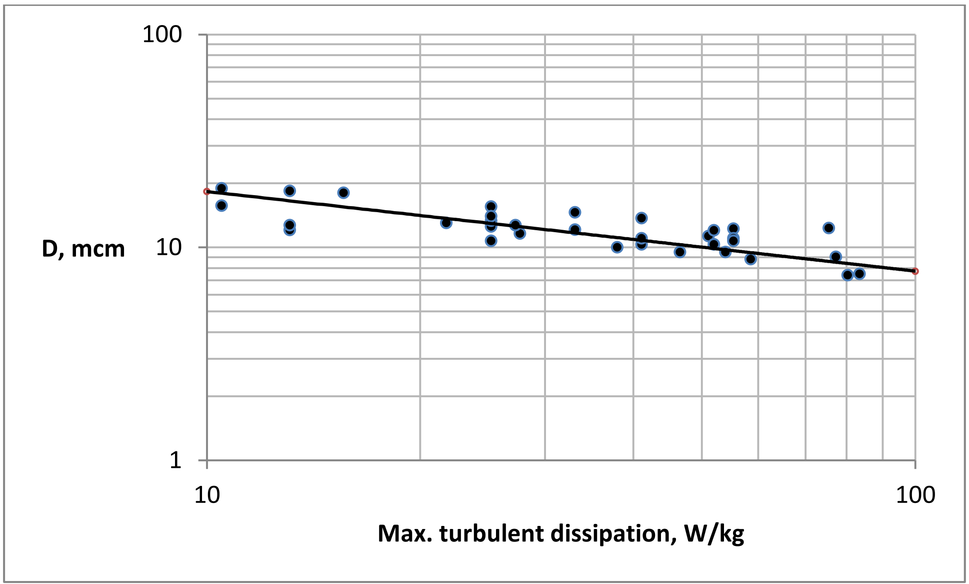

Figure 6. Mean drop diameter as a function of calculated value of maximum local energy dissipation.

External RSD diameter – 50. Oil phase viscosity 1.7cSt. Stabilizer – Tween, 3%.

Points – experimental, solid line – calculated.

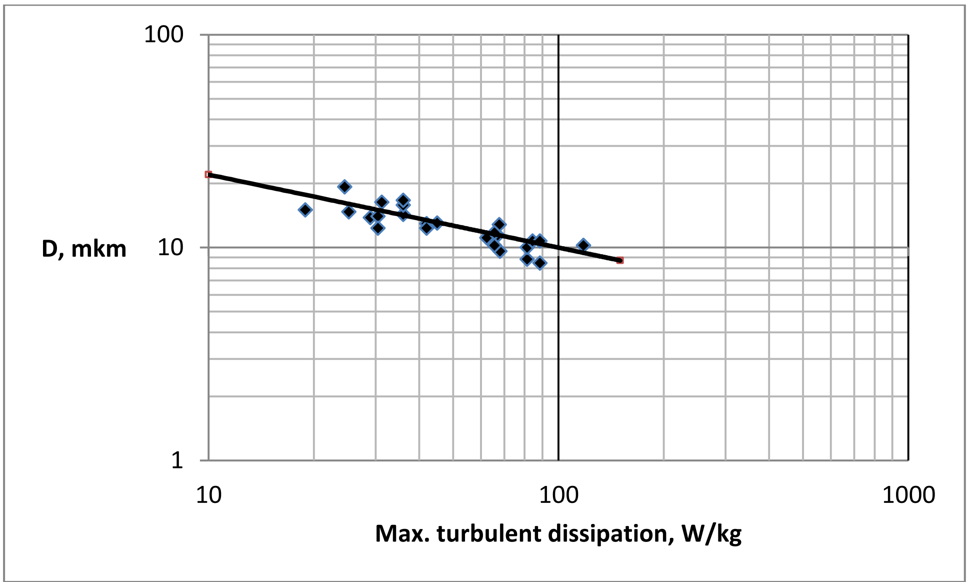

Figure 7. Mean drop diameter as a function of calculated value of maximum local energy dissipation.

External RSD diameter – 40 mm , 46 mm, 60 and 64 mm. Oil phase viscosity 1.2 cSt. . Stabilizer – Tween, 3%.

Points – experimental, solid line – calculated.

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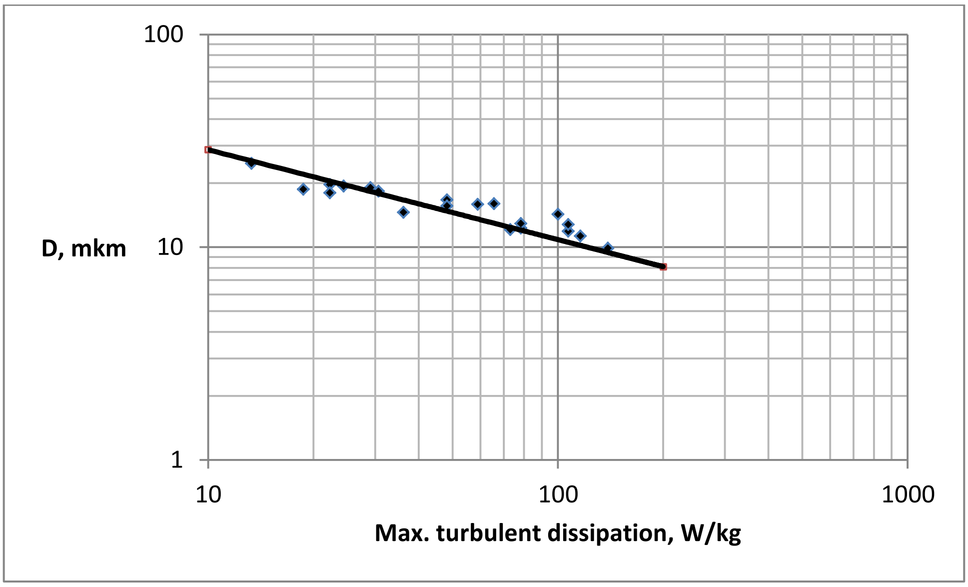

Figure 8. Mean drop diameter as a function of calculated value of maximum local energy dissipation.

External RSD diameter – 50 mm and 60 mm. Oil phase viscosity 1.25 cSt. Stabilizer – Tween, 1%.

Points – experimental, solid line – calculated.

Applicability of the models and calculation method for continuous flow emulsifying has been confirmed with production of paraffin emulsion in water. Emulsifying was performed with in-line 3-stage and 4-stage RSD homogenizers produces by IKA (Germany). Flow rate of emulsion varied from 10 to 50 liter per min. Mean drop diameter of the final emulsions varied at different conditions from 1.5 to 20 mcm and was in a good correspondence with the calculated values.

NOMENCLATURE

N_b, N_c - frequencies of breaking and coalescence

$\bar{v}$ - mean sq. root pulsational velocity

φ - volume fraction of the disperse phase

ν_c, ν_d - kinematic viscosity of the continuous and disperse phases

ρ_c, ρ_d - density of the continuous and disperse phases

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