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Linking Continuous and Recycle Emulsification Kinetics for In-line mixers.

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Abstract

In-line high-shear mixers can be used for continuous or batch dispersion operations depending on how the pipework is arranged. In our previous work (Carrillo De Hert and Rodgers, 2017a) we performed a transient mass balance to establish the link in-between these two arrangements; however this model was limited to the estimation of the mode of dispersed phases yielding simple monomodal drop size distributions. In this investigation we expanded the previous model to account for the shape of the whole drop size distribution. The new model was tested by performing experiments under different processing conditions and using two highly viscous dispersed phases which yield bimodal drop size distributions. The results for the continuous arrangement experiments were fit using two log-normal functions and the results for the recycle arrangement by implementing the log-normal function in the previously published mass balance. The new model was capable of predicting the $\bar{d}_{32}$ for different emulsification times with a mean absolute error of 12.32%. The model presented here was developed for liquid blends, however the same approach could be used for milling or de-agglomeration operations.

Keywords: Emulsification, In-line rotor-stator, In-line high-shear mixer, Continuous emulsification, Batch emulsification, Bimodal Drop Size Distribution

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Nomenclature

Latin symbols

$\dot{Q}$	flow rate [$\text{m}^3 \text{s}^{-1}$]
$\bar{d}_G$	logarithmic mean of the log-normal distribution [m]
$\bar{d}_{G,n,x}$	logarithmic mean of the log-normal distribution for the n th pass for: $x = L$ large and $x = s$ small drops [m]
$\bar{t}_{res,T}$	mean residence time in the tank [s]
A_i	i th fit constant [-]
B_i	i th fit constant [-]
d_i	diameter of the i th drop class [meter]
$f_{v,n,x}(d_i)$	frequency of the i th drop size after n passes for $x = L$ large, $x = s$ small or $x = T$ total distribution [-]
$f_{v,Rec}(d_i)$	frequency of the i th drop size for the recycle arrangement [-]
$F_v(d_i)$	cumulative distribution of the i th drop size [-]
Mo_n	mode of the distribution for n passes [m]

$Mo_{n,x}$	mode of the distribution after n passes for: $x = L$ large or $x = s$ small drops [m]
Mo_{Rec}	mode of the distribution in the recycle arrangement [m]
N	stirring speed [s^{-1}]
n	number of passes [-]
R^2	coefficient of determination [-]
s_G	logarithmic standard deviation of the log-normal distribution [m]
t	time [s]
V_T	volume of the vessel [meter ³]

Greek symbols

μ_d	viscosity of the dispersed phase [Pa s]
ϕ_n	volume fraction of the material for n -passes [-]
$\phi_{s,n}$	relative volume fraction of the small drops after n -passes [-]

Dimensionless numbers

Po	Power number $PN^{-3}D^{-5}\rho^{-1}$
----	---------------------------------------

Abbreviations

DSD	Drop size distribution
RS	Rotor-stator
SiOil	Silicon Oil

1 Introduction

In-line rotor-stators (RS) are one of the most promising equipments that have been implemented to intensify dispersion processes. Their increase in popularity has been due to their capacity to generate highly-localised strong energy dissipation regions. In-line RS are installed in the pipework and two different types of operation arrangements are possible depending on the direction of the outflow of the RS. (1) If the outflow is directed to a secondary vessel or process, the RS is operated in a continuous fashion; evidently the

material can be processed n number of times to cause further size reduction, “multi-pass processing” occurs when the material is processed $n > 1$ times. (2) On the other hand, if the outflow is directed to the feeding tank it is operated in a recycle arrangement and processing time and volume becomes important processing parameters. The schematic representation of both configurations is shown in Figure 1.

Figure 1: Schematic representation of (a) the continuous arrangement and (b) the recycle arrangement.

Previous study: continuous arrangement

In one of our previous studies (Carrillo De Hert and Rodgers, 2017a), we installed a pump at the feed of the RS to control the flow rate $\dot{Q}$ and studied the emulsification kinetics using a 10 cSt silicon oil (SiOil). The 10 cSt SiOil yielded monomodal drop size distributions (DSD). The characteristic measure of central tendency used was the mode Mo_n of the DSD, where the sub-index refers to the n th pass. For a RS working at given stirring speed N , the multi-pass data for the continuous arrangement was well correlated by

$$Mo_n = A_1 \left(\frac{n}{\dot{Q}} \right)^{-1/5} N^{-6/5} \quad \text{for } n = 1, 2, \dots, n-1, n \quad (1)$$

23 where $(n/\dot{Q})$ is proportional to the residence time of the material inside the
 24 RS. We attribute the effect of mean residence time to the internal recirculation
 25 or fluid re-entrainment inside the RS, this has been reported by authors such
 26 as Özcan-Taskin et al. (2011) and Mortensen et al. (2017) using particle
 27 image velocimetry and by Xu et al. (2014) using laser Doppler anemometry.
 28 Therefore the lower $\dot{Q}$ the more times the emulsions re-enters the region where
 29 drop breakup occurs.

30 We did not do experiments at different scales, however there is strong
 31 evidence that the characteristic volume of the RS is its swept volume (Hall
 32 et al., 2013). Hall et al. (2011) did not find a correlation in-between the
 33 coarse emulsion ($n = 0$) and the one at the outlet of the RS, therefore in
 34 the continuous arrangement all the information of the coarse emulsion is lost
 35 after one pass is completed.

In a second study (Carrillo De Hert and Rodgers, 2017b), we extended
 Equation 1 to account for the effect of the viscosity of the dispersed phase μ_d
 by doing experiments using SiOils in the 10 cSt-30 000 cSt range. We found
 that SiOils thicker the 350 produced bimodal DSD. The mode of the large
 $Mo_{n,L}$ and the mode of the small $Mo_{n,s}$ drops were used to characterise the
 drop sizes of the emulsion, for the same geometry used in (Carrillo De Hert
 and Rodgers, 2017a) the following correlations were obtained for the SiOil in
 the 10 cSt-2760 cSt range

$$Mo_{n,L} = 1.18 \times 10^5 \mu_d^{0.365} N^{-1.05} \left(\frac{n}{\dot{Q}} \right)^{-1/5} \quad (2)$$

$$Mo_{n,s} = 1.69 \times 10^3 \mu_d^{-0.365} N^{-1.05} \quad (3)$$

36 Furthermore we correlated the DSDs using a simple mixing rule

$$f_{v,n,T}(d_i) = (1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i) \quad (4)$$

37 where $f_{v,n,T}(d_i)$ is the total drop size distribution; $f_{v,n,L}(d_i)$ and $f_{v,n,s}(d_i)$ are
 38 the drop size distribution of the large and small drops respectively; and $\phi_{s,n}$
 39 is the volume fraction of the small drops for the n th pass through the RS. We
 40 further used Generalised Gamma probability density functions for $f_{v,n,L}(d_i)$
 41 and $f_{v,n,s}(d_i)$ and the power-law function below for $\phi_{s,n}$

$$\phi_{s,n} = C_{\phi,0} \mu_d^{C_{\phi,\mu_d}} N^{C_{\phi,N}} \left(\frac{n}{\bar{Q}} \right)^{C_{\phi,\bar{t}}} \quad (5)$$

42 *Previous study: recycle arrangement*

43 In the recycle arrangement (see Fig. 1b) a coarse emulsion ($t = 0$) is
 44 pumped through the RS and back into the its feeding vessel. For $t > 0$ it is
 45 expected to have a mixture of material that has passed n times, the fraction
 46 of each material ϕ_n is a function of time t , volume of the vessel V_T and of $\dot{Q}$.
 47 As can be expected, the DSD distribution of the coarse emulsion is important
 48 in this arrangement until its complete consumption.

49 In Carrillo De Hert and Rodgers (2017a) we did a transient mass balance
 50 to obtain ϕ_n as a function of the aforementioned variables, the expression for
 51 ϕ_n reads

$$\phi_n = \frac{1}{n!} \left(\frac{t}{\bar{t}_{res,T}} \right)^n \exp \left(-\frac{t}{\bar{t}_{res,T}} \right) \quad (6)$$

52 where $\bar{t}_{res,T} = V_T/\dot{Q}$ is the mean residence time of the material in the tank.
 53 Equation 6 was tested by (1) measuring the depletion of the coarse emulsion as

a function time, as the $n = 0$ and $n > 0$ materials produced two very distinct peaks and by (2) predicting the mode of the distribution of the mixture of the $n > 0$ drops Mo_{Rec} . Provided that the continuous arrangement experiments showed that the DSD for $n > 0$ were monomodal and had the same shape, a mixing rule to estimate the Mo was used

$$Mo_{Rec} = \sum_{n=1} \frac{\phi_n}{1 - \phi_0} Mo_n \quad (7)$$

Substituting Equation 1 and 6 in Equation 7 lead to

$$Mo_{Rec} = \frac{A_1 \dot{Q}^{1/5}}{N^{6/5} \left[\exp \left(\frac{t}{\bar{t}_{res,T}} \right) - 1 \right]} \sum_{n=1} \frac{1}{n^{1/5} n!} \left(\frac{t}{\bar{t}_{res,T}} \right)^n \quad (8)$$

Equations 8 is limited to monomodal distributions and to the calculation of the mode, in this study we will expand our two previous studies (Carrillo De Hert and Rodgers, 2017a,b) to systems yielding bimodal drop size distributions, which are common for highly viscous dispersed phases.

Materials and equipment and methods

Materials

Two 200 Silicone Fluid (dimethyl siloxane, Dow Corning, Michigan, USA) of 350 cSt and 1000 cSt nominal kinematic viscosity were used as dispersed phases. Their relevant properties are listed in Table 1. The specific gravity s was taken as given by the provider and the μ_d were obtained using a DV2T Viscometer (Brookfield Viscometers, Essex, UK).

As continuous phase 1 wt.% of sodium laureth sulfate (SLES) in water was

used; SLES is the surfactant, in Texapon N701 (Cognis, Hertfordshire, UK) at 70wt.%. The surfactant concentration was approximately 120 times the critical micellar concentration found by El-Hamouz (2007) for Texapon N701. The interfacial tension in-between the dispersed phases and the continuous phase σ are also shown in Table 1; these were obtained using a K11 Mk4 Tensiometer (KRUS, Hamburg, Germany) and a KRUS platinum-iridium standard ring.

Table 1: Relevant properties of the Silicon Oils used at 25 °C. These same properties have been previously reported in Carrillo De Hert and Rodgers (2017a,b)

SiOil [cSt]	s [-]	μ_d [Pa s]	σ [N m]
350	0.965	3.279×10^{-1}	9.129×10^{-3}
1000	0.970	9.474×10^{-1}	9.172×10^{-3}

Equipment

The same L5M-A Laboratory Mixer (Silverson Machines, Chesham, UK), rotor, screen and peristaltic pump in Carrillo De Hert and Rodgers (2017a,b) were used for this study. The characteristics of the rotor and the screen are listed in Table 2.

Table 2: Geometrical characteristics of the rRS.

Rotor		Screen	
Diameter	3.0 cm	Inner diameter	3.2 cm
Number of blades	4	Outer diameter	3.4 cm
Height	1.0 cm	Stator height	2.0 cm
Blade thickness	0.5 cm	Hole arrangement	6x40, pitched
Maximum speed (nominal)	133 s^{-1}	Number of holes	240

84 *Methods*

85 The coarse emulsions were prepared using an unbaffled cylindrical vessel
 86 with diameter of 25 cm and a 8-blade Rushton turbine with a diameter of
 87 6.62 cm. After dissolving the SLES completely (1.0wt%), the stirring speed
 88 was fixed to the desired stirring speed and the SiOil was poured (1v.%). The
 89 systems were stirred for 24 h to ensure that all drop break-up was due to the
 90 RS and not to the impeller in the vessel.

91 For the continuous arrangement, the coarse emulsion was fed to the RS at
 92 the experimental conditions specified in Table 3. After the volume in feeding
 93 tank was consumed, the connecting tubes were rinsed with fresh water and
 94 purged. The tanks were swapped and the process was repeated for n number
 95 of passes. Samples were taken after the whole volume was processed while
 96 the tank was being stirred.

97 The recycle arrangement experiments were performed at the same $\dot{Q}$ and
 98 N as for the continuous arrangements under the conditions specified in Table
 99 3. Samples were taken for different t .

Table 3: Experimental conditions of experiments performed. The number inside parenthesis indicate the number of samples taken at different times.

	350 cSt	1000 cSt
Arrangements-Shared		
$\dot{Q}$ [m ³ s ⁻¹]	2.90×10^{-5}	9.08×10^{-9}
Impeller N [s ⁻¹]	11.9	11.7
RS N [s ⁻¹]	50.00	166.7
Continuous		
n [-]	0-7	0-7
Recycle		
V_T [m ³]	13×10^{-3}	10×10^{-3}
t [s]	0-4544 (8)	0-10 000 (8)

100 Sampling was done approximately 5 cm below the liquid level. The samples
101 were stored and analysed as soon as the previous sample was analysed.

102 The experimental conditions listed in Table 3 were chosen to provide an
103 example where the DSD for $n = 0$ and for $n > 0$ were close (350 cSt) and an
104 example where these were more separated (1000 cSt) within the experimental
105 range where the correlations obtained in Carrillo De Hert and Rodgers (2017b)
106 have been proven.

107 The DSDs were analysed using the Mastersizer 3000 (Malvern Instruments,
108 Malvern, UK). The complex refractive index used was $1.399 + 0.001i$ and
109 the details of the Standard Operation Procedure used has been previously
110 detailed in Carrillo De Hert and Rodgers (2017a) and Carrillo De Hert and
111 Rodgers (2017b).

112 **Log-normal fits for previous work in Carrillo De Hert and Rodgers** 113 **(2017b)**

114 The data exported by the Mastersizer 3000 is presented as a cumulative
115 frequency histogram where $\sum f_v(d_i) = 100$. In our previous work (Carrillo De
116 Hert and Rodgers, 2017b) we normalized the DSD exported from the Master-
117 sizer by making the area under the curve equal 100%, this was done in order
118 to transform the cumulative frequency histogram into a probability density
119 distribution. After normalizing, the DSD were fit using probability density
120 functions. However, the integration and normalisation of the experimental
121 data is not required if the difference between the cumulative frequency of the
122 i th drop diameter $F_v(d_i)$ and the one of the $(i - 1)$ th drop diameter $F_v(d_{i-1})$

123 is used

$$f_v(d_i) = F_v(d_i) - F_v(d_{i-1}) \quad (9)$$

124 The DSD were fit using a mixing rule (Eq. 4) and we used two Generalised
125 Gamma functions (GGf) to fit our results in Carrillo De Hert and Rodgers
126 (2017b). The GGf has three parameters: one that controls its scale, another
127 that controls its broadness and a third one that affects the symmetry (low
128 values yield skewed distributions, the opposite is true for large values) of the
129 distribution. A large value for the latter was chosen and was kept constant
130 for all our fits.

131 In this investigation it was shown that log-normal distributions are also
132 adequate to describe the shape of the DSD and also give a good estimation
133 of the $\bar{d}_{32}$. The equation of the cumulative function reads

$$F_v(d_i) = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left(\frac{\ln d_i - \bar{d}_G}{\sqrt{2}s_G} \right) \quad (10)$$

134 where $\bar{d}_G$ is the logarithmic mean of the DSD and s_G the logarithmic standard
135 deviation.

136 In this section we provide the new fit parameters for the simplified fit-
137 scheme based on two log-normal cumulative distributions. The fit to the DSD
138 was performed using a power-law function for $\bar{d}_G$ (Eq. 11 below), the indexes
139 are known from the analysis of variance (ANOVA) done for the modes in
140 Carrillo De Hert and Rodgers (2017b) and the only parameter for $\bar{d}_{G,L}$ and
141 $\bar{d}_{G,s}$ obtained using the method of the least squares were the pre-exponentials

142 $C_{G,L}$ and $C_{G,s}$

$$\bar{d}_G = \ln \left[C_G \mu_d^{C_{G,\mu}} N^{C_{G,N}} \left(\frac{n}{\bar{Q}} \right)^{C_{G,\bar{t}}} \right] \quad (11)$$

143 The standard deviations of the distributions ($s_{G,L}$ and $s_{G,s}$) were also obtained
 144 using the method of the least squares but these were considered to be indepen-
 145 dent of μ and the processing conditions. The coefficient obtained using the
 146 least square method for Equation 11 and the standard deviations are listed in
 147 Table 4. If this table is compared with Equation 2 and Equation 3 it can be
 148 seen that the value of $C_{G,N}$ was changed from -1.05 to -1.2. The former value
 149 was obtained directly from the ANOVA in Carrillo De Hert and Rodgers
 150 (2017b); however changing its value to -1.2 produces no significant variation
 151 in the goodness of the fit (within our experimental range 50-166.67 s⁻¹) while
 152 being in agreement with the well-know theory developed by Hinze (1955).

Table 4: Constants obtained for the log-normal distributions for the large and small type of drops for Eqs. 11 and 10.

Parameter	Large	Small
C_G	2.10×10^5	3.40×10^3
$C_{G,\mu}$	0.365	-0.365
$C_{G,N}$	-1.2	-1.2
$C_{G,\bar{t}}$	-0.2	0
s_G	0.400	0.843

153 Simultaneously the ϕ_s for each distribution were “freely fit”. As recognized
 154 in our previous work (Carrillo De Hert and Rodgers, 2017b), this is the most
 155 difficult parameter to obtain a correlation for. The power-law function shown

below was also used to correlated the data

$$\phi_s = C_\phi \mu_d^{C_{\phi,\mu}} N^{C_{\phi,N}} \left(\frac{n}{\dot{Q}} \right)^{C_{\phi,\bar{t}}} \quad (12)$$

The ANOVA for Equation 12 yielded $C_{\phi,\mu} = 0.025 \pm 85.2\%$ and a p -value of 0.0223, therefore the effect of μ_d was considered negligible due to its low statistical significance. Under these considerations, the ANOVA yielded the values listed in Table 5. The mean absolute error obtained for ϕ_s was 3.89%.

Table 5: ANOVA results for Eq. 12 for $C_{\phi,\mu} = 0$. The percentages represent the 95% confidence interval.

Parameter	Value	p -value
C_ϕ	$1.23 \times 10^{-1} \pm 19.7\%$	6.10×10^{-27}
$C_{\phi,N}$	$2.53 \times 10^{-1} \pm 15.6\%$	1.01×10^{-18}
$C_{\phi,\bar{t}}$	$4.90 \times 10^{-2} \pm 36.4\%$	8.64×10^{-7}

The authors recognise the limitations of using a power-law function to parametrise ϕ_s , as these function can yield values higher than unity; however within the experimental range studied it was not possible to correlate our results using a function that runs from 0 to 1 (such as a cumulative log-normal distribution).

Extended model

As proven in Carrillo De Hert and Rodgers (2017a), the mode of an emulsion produced in the recycle arrangement for $t > 0$ consists of a mixture of materials that have passed n number of times through the RS. The DSD at any given time $f_{v,Rec}(d_i)$ should equal the sum of the distribution of its

171 composing materials

$$f_{v,Rec}(d_i) = \sum_{n=0} \phi_n f_{v,n}(d_i) \quad (13)$$

172 where ϕ_n can be obtained by Equation 6 and $f_{v,n}(d_i)$ is the frequency of the
 173 i th drop size for the material that has passed n number of times through the
 174 RS.

The examples that will be given in Section 5 consist of bimodal coarse emulsions and bimodal DSD for any $n > 0$. Using the mixing rule in Equation 4, the following equation can be derived

$$\begin{aligned} f_{v,Rec}(d_i) &= \phi_0 f_{v,0}(d_i) + \sum_{n=1} \phi_n f_{v,n}(d_i) \\ &= \phi_0 [(1 - \phi_{s,0}) f_{v,0,L}(d_i) + \phi_{s,0} f_{v,0,s}(d_i)] + \\ &\quad \sum_{n=1} \phi_n [(1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i)] \end{aligned} \quad (14)$$

where $\phi_{s,n}$ is the relative volume fraction of the small drops of the material that has passed n -times through the RS and, $f_{v,n,L}(d_i)$ and $f_{v,n,s}(d_i)$ are the frequency of the i th drop size of the material for n -passes for the large and small types of drops respectively. Substituting Equation 6 in 14 yields

$$\begin{aligned} f_{v,Rec}(d_i) &= \exp\left(-\frac{t}{\bar{t}_{res,T}}\right) \left\{ [(1 - \phi_{s,0}) f_{v,0,L}(d_i) + \phi_{s,0} f_{v,0,s}(d_i)] + \right. \\ &\quad \left. \sum_{n=1} \frac{1}{n!} \left(\frac{t}{\bar{t}_{res,T}}\right)^n [(1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i)] \right\} \end{aligned} \quad (15)$$

175 As seen in Section 5, $f_{v,n,L}(d_i)$ and $f_{v,n,s}(d_i)$ can be given by cumulative
 176 log-normal distribution difference and $\phi_{s,n}$ by a power-law function.

177 Results and discussion

178 Continuous arrangement results

179 The results obtained for both SiOil are shown in Figure 2. The same
 180 trends found in Carrillo De Hert and Rodgers (2017b) were observed: (1) no
 181 steady-state DSD was found for $n = 7$ and (2) the large drops are n -dependent
 182 while the small drops are n -independent (see Fig. 3).

Figure 2: DSD obtained for $n = 1, 2, \dots, 7$ passes in the continuous arrangement for the (a) 350 cSt SiOil and (b) 1000 cSt SiOil.

Figure 3: Modes of the DSDs shown in Fig. 2 as a function of n for both SiOils.

183 The DSD were fit using the cumulative log-normal distributions. Never-
 184 theless, the parametrization was only done as a function of n for each set of
 185 experiments to prove the extended model (Sec. 4) in Section 5.2 with the
 186 most accurate accurate parameters.

187 The fit for the coarse material was fit independently of the $n > 0$ distribu-
 188 tions, as no correlation in-between these was found in this work nor by Hall
 189 et al. (2011). The logarithmic mean of the large drops of the coarse emulsion
 190 $\bar{d}_{G,0,L}$, their logarithmic standard deviation $s_{G,0,L}$ along with these parameter
 191 for the small drops $\bar{d}_{G,0,s}$ and $s_{G,0,s}$ and their volume fraction $\phi_{s,0}$ are listed
 192 in Table 6 for the coarse emulsions obtained for both SiOils.

193 For the $n > 0$ distributions, the large drop sizes are n -dependent and, as
 194 shown in Figure 3 and in Carrillo De Hert and Rodgers (2017b), these are
 195 well-correlated by $n^{-0.2}$, the following model was proposed for the logarithmic
 196 mean of the large drops

$$\bar{d}_{G,n,L} = \ln(B_1 n^{-1/5}) \quad (16)$$

197 The rest of the parameters of the log-normal cumulative distribution for the
 198 large and small drops were considered constant and were not parametrised,
 199 however $\phi_{s,n}$ was, because it is n -dependent (Carrillo De Hert and Rodgers,
 200 2017b)

$$\phi_{s,n>0} = B_2 n^{B_3} \quad (17)$$

201 The values of all the variables for the large and small drops for $n > 0$ are also
 202 displayed in Table 6, while two examples of the appearance of the fits are
 203 shown in Figure 4.

Figure 4: Examples of fits: (a) 350 cSt SiOil for $n = 4$ and (b) 1000 cSt SiOil for $n = 2$.

Table 6: Fit parameters for the dual log-normal cumulative distribution fit for the 350 cSt and 1000 cSt SiOils.

Parameter	350 cSt	1000 cSt
$\bar{d}_{G,0,L}$	5.69	6.51
$s_{G,0,L}$	0.432	0.443
$\bar{d}_{G,0,s}$	4.43	5.53
$s_{G,0,s}$	0.650	0.855
$\phi_{s,0}$	0.878	0.595
B_1	139	56.6
$s_{G,n>0,L}$	0.44	0.45
$\bar{d}_{G,n>0,s}$	3.59	1.90
$s_{G,n>1,s}$	0.861	0.792
B_2	0.628	0.234
B_3	-0.0688	-0.111

204 *Recycle arrangement results*

205 Figure 5 shows the DSDs obtained using the recycle arrangement for the
206 same $\dot{Q}$ and N used for the continuous arrangement for different processing
207 times. Figure 5a provides an example where the DSD decreases progressively

208 and the consumption of the coarse emulsion cannot be tracked directly. As
 209 will be shown later, the progressive size reduction is due to the close proximity
 210 in-between the DSDs obtained for $n = 0$ and the $n > 0$ (see Fig. 2a). In
 211 Figure 5b the consumption of the coarse emulsion is more evident because
 212 the DSDs of the coarse emulsion and the material that has passed through
 213 the rotor-stator are further apart.

Figure 5: DSDs for the recycle arrangement for different times for the conditions listed in Table 3 for (a) the 350 cSt SiOil and for (b) the 1000 cSt SiOil.

214 Equation 15 was combined with Equations 9, 10 and with the fit constants
 215 obtained for the continuous arrangement experiments listed in Table 6 to fit
 216 the recycle arrangement DSDs shown in Figure 5.

217 Examples of the fit are shown in Figure 6. Figure 6a shows an example of
 218 the composition of each of the drop size distributions for $t > 0$. As can be
 219 seen in this figure, the coarse emulsion has not been completely consumed
 220 and the contribution of the materials that has passed $n = 1, 2, 3$ are the main
 221 responsible for the change in the shape of the DSD. On the other hand, Figure
 222 6b shows the total fit for three different times, it can be seen that the model

is accurate in predicting even very complex DSD.

Figure 6: Examples of the fit using the new model. (a) Shows the contribution of the different materials for the DSD obtained for $t = 358$ s for the 350 cSt SiOil; (b) shows the total fit for the 1000 cSt SiOil experiment for three different times.

The goodness of the fit was assessed by comparing the experimental and predicted $\bar{d}_{32}$. The obtained coefficient of determination R^2 obtained were 0.997 and 0.980 for the 350 cSt and 1000 cSt SiOils respectively, while the mean absolute error were 12.32% and 9.51%. The experimental and predicted $\bar{d}_{32}$ as a function of time in log-log scale are shown in Figure 7, where it can be seen that the models follow the complex trend reasonably well.

Conclusions and recommendations for future work

The transient mass balance derived in our previous work Carrillo De Hert and Rodgers (2017a) can be used to predict the evolution of the DSD with time by using the mixing rule in Equation 14. The mixing rule could be implemented to bimodal DSD. As shown in the examples presented, future study of multiphase systems in RSs has to be done preferably (if not

Figure 7: Experimental and predicted $\bar{d}_{32}$ as a function of time for both SiOils.

exclusively) using the continuous arrangement to remove misleading mass balance features. The authors consider that the models presented in Carrillo De Hert and Rodgers (2017a) and in this investigation provide a strong fundamental basis to extrapolate continuous arrangement results to recycle systems, provided that the vessel is well-mixed.

There have been multiple studies (Badyga et al. (2008); Padron et al. (2008); Özcan-Taskin et al. (2009, 2016) among others), which have used the recycle arrangement to study the de-agglomeration of nano-particles. These authors have explained breakup in terms of shattering, rupture or erosion mechanisms. Figure 5a resembles the rupture mechanism for nanoparticles while Figure 5b resembles the shattering one. However, we have shown that the trends in these figures are due to mass balance features and by the proximity in-between the DSD of the coarse and processed materials. Future work on breakup mechanism require the separation of the break-up inside the rotor stator and mass balance effects. Ideally experiments with the continuous arrangement should be used.

The semi-empirical model for emulsification in the continuous arrangement

253 presented here and in our previous work (Carrillo De Hert and Rodgers,
 254 2017a,b) (Eqs. 1, 2 and 3) consider that the drop sizes are proportional to the
 255 mean residence time inside the RS which is further proportional to $\left(n/\dot{Q}\right)^{-1/5}$;
 256 this can be explained by the internal recycling inside the RS (reported by
 257 Özcan-Taskin et al. (2011); Mortensen et al. (2017); Xu et al. (2014) among
 258 others). However it is unknown if the $-1/5$ index is universal or depends on
 259 the geometrical characteristics of the RSs. Hall et al. (2013) reported indexes
 260 of -0.148 and -0.043 for 10 cSt and 350 cSt SiOils respectively, but their
 261 results were correlated to the $\bar{d}_{32}$ and their emulsions were produced using a
 262 double-rotor-double-stator geometry. The lower residence time dependency
 263 reported by Hall et al. (2013) for the thickest oil is most likely due to the
 264 small daughter drops which make the $\bar{d}_{32}$ trend smoother because these are
 265 mean residence time-independent. To our knowledge there is no other work
 266 in literature which uses the mode or the maximum drop diameter to know
 267 the mean residence time dependency.

268 The drop size dependency with N has more theoretical basis as its index
 269 is in agreement with the mechanistic models developed by Hinze (1955) and
 270 Shinnar and Church (1960) even though these were postulated for steady-state
 271 systems. Finally the study on the μ_d dependency in (Carrillo De Hert and
 272 Rodgers, 2017b) (Eqs. 2 and 3) is unique as most of the correlations found
 273 in literature use the $\bar{d}_{32}$ and do not track the individual drop size change
 274 nor the relative volume fraction of each type of drop produced which makes
 275 comparison with other work in literature virtually impossible. Future work
 276 should also focus on analysing the whole DSDs and not only the $\bar{d}_{32}$, specially
 277 for highly-viscous dispersed phases which tend to produce bimodal DSD.

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