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APPENDICES

Appendix A Phase Inversion Point

Phase inversion point of oil-in-water emulsion is approximate 93 vol% at oil; the drastic change in oil-in-water emulsion appearance indicated the inversion of dispersed phase from oil-in-water to water-in-oil emulsion as shown in Figure A1.

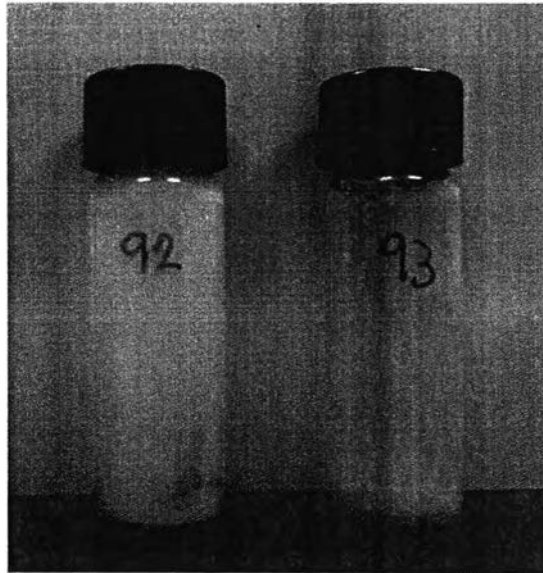


Figure A1 Oil-in-water emulsion with oil fraction at 92 vol% and 93 vol% as written on the bottles indicating significant changes due to the phase inversion.

However, there are no statistical results of viscosity change owing to viability of the rheometer. Viscosity of prepared oil-in-water emulsion is too high to measure as oil fraction gets close to the phase inversion point.

Appendix B Phase Separation Rate

The variation of height of oil-in-water emulsion was investigated as a creaming behavior of prepared emulsion was observed. Change of separated water volume was collected as a function of time and indicated the rate of separation for oil fraction at 10 vol% and 50 vol% as shown in Table B1 and B2, respectively;

Table B1 Variation of height of oil-in-water emulsion with oil fraction at 10 vol%

Observed time (hr)	Observed height (cm)	Separated region (cm)	Based on water vol.
0	0	0.00	0.0000
0.416667	3.50	0.05	2.7778
0.633333	3.45	0.10	5.5556
0.816667	3.42	0.13	7.2222
0.95	3.38	0.17	9.4444
1.283333	3.30	0.25	13.8889
1.433333	3.25	0.30	16.6667
1.983333	3.15	0.40	22.2222
2.6	3.10	0.45	25.0000
3.583333	3.02	0.53	29.4444
6.666667	2.92	0.63	35.0000
7.65	2.89	0.66	36.6667
9.833333	2.85	0.70	38.8889
23.15	2.74	0.81	45.0000
48	2.70	0.85	47.2222

Table B2 Variation of height of oil-in-water emulsion with oil fraction at 50 vol%

Observed time (hr)	Observed height (cm)	Separated region (cm)	Based on water vol.
0	0	0.00	0.0000
0.033333	1.80	1.75	76.0870
0.083333	1.70	1.85	80.4348
0.466667	1.60	1.95	84.7826
3.933333	1.55	2.00	86.9565
48	1.55	2.00	86.9565

Appendix C Micrograph Statistical Analysis

Individual droplet area of oil can be acquired from image processing software with following procedures and standards; the sensitivity analysis of adjustable analyzing tools has been examined.

Standardized operating procedures

1. Open an image: *File* → *Open*.
2. Draw a line on the scale which should be approximately the same as reference line, then set length scale as a reference: *Analyze* → *Set Scale*;
 - a. Enter value of known distance related to selected picture in the “Known distance” box and put “um” in the unit box which represents μm .
 - b. The actual length in pixels showed in “Distance in pixels.”
 - c. Check “Global” box to set the length scale for further image analysis.

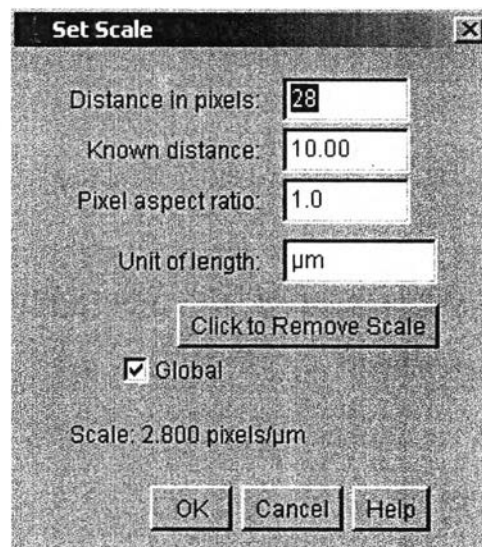


Figure C1 “Set Scale” pop-up window.

Note: 1) Our study length is usually 32 pixels per 10 μm .

2) Once this box is checked, following images are instantly affected as long as the software is running.

3) As long as you know the reference pixels/length ratio, this process can be set without drawing a line.

3. *Process* → *Sharpen*.

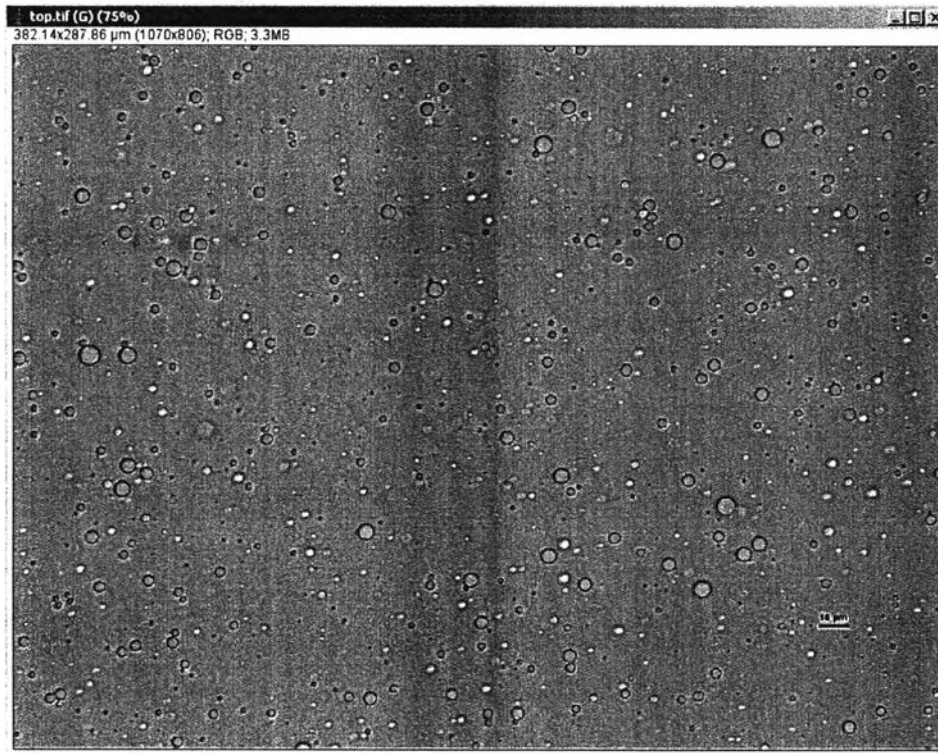


Figure C2 Sharpen image.

4. *Image* → *Type* → *8-bits*.

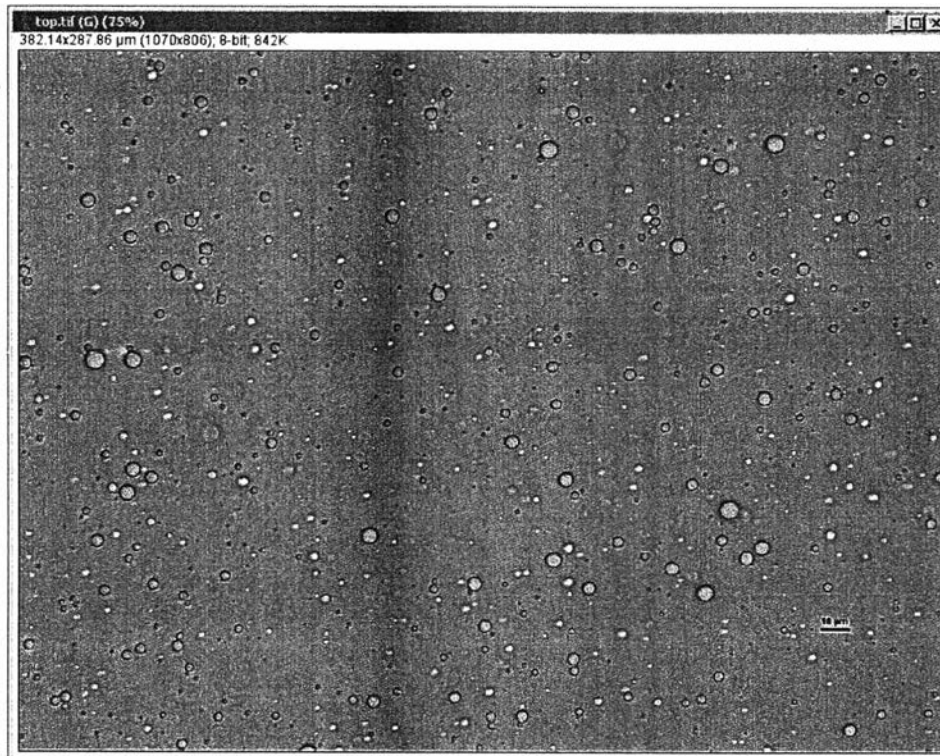


Figure C3 8-bits applied image.

5. Select *Image* → *Adjust* → *Threshold*. To adjust the threshold of droplets in order to obtain fine droplets shape, the droplets should be fully covered by small red dots and then click apply.

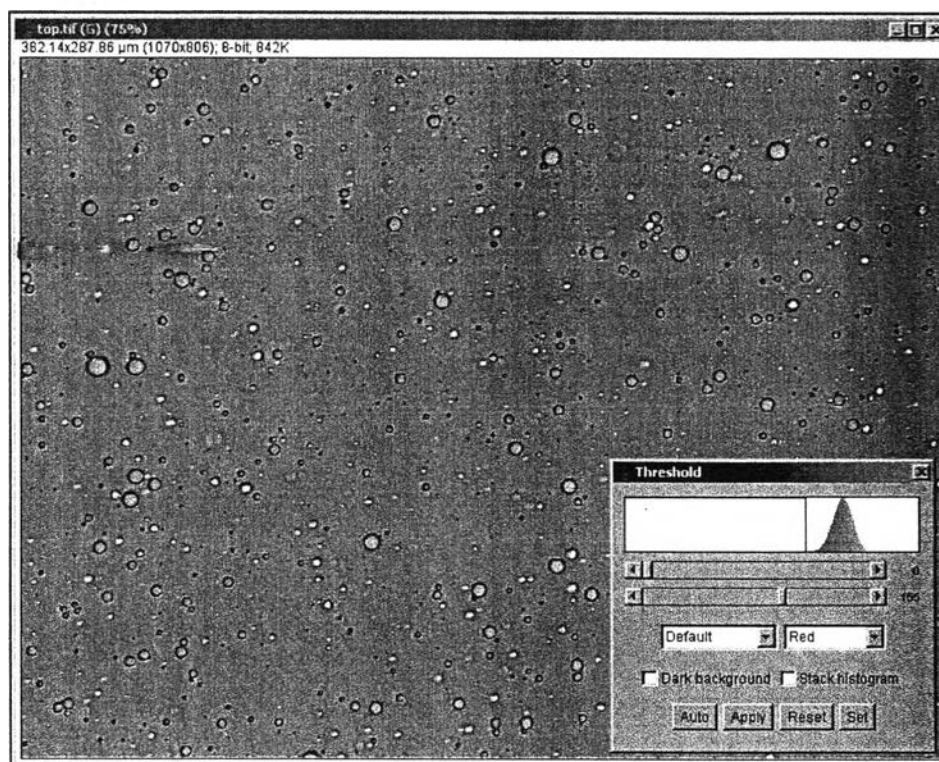


Figure C4 Threshold adjusted image.

Note: The proper threshold is around 160. Still, threshold depends on droplets density appeared on micrograph.

6. Analyze the particles on micrograph by: *Analyze* → *Analyze Particles*, set the area range to be from 0.5 to $\infty \mu\text{m}^2$ and choose show “Outlines” in drop-down box. Also, “Display results” and “Summarize” should be checked for required results. Moreover, “Clear results” can be optionally checked in order to clear all the result after analysis.

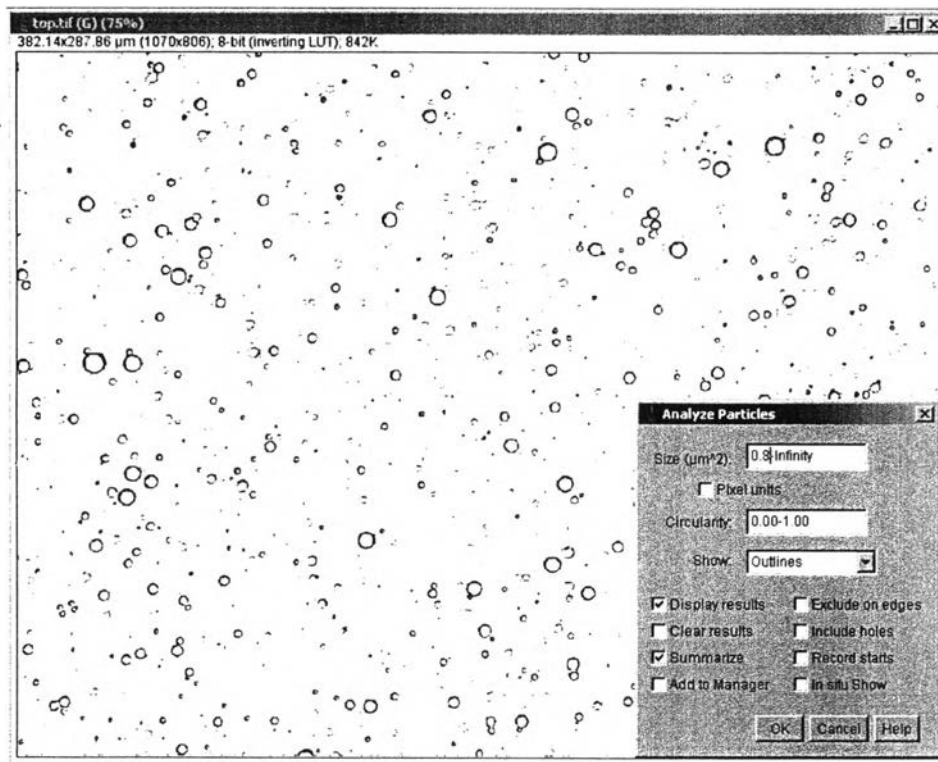


Figure C5 Threshold adjusted image with analyze particles window.

After click OK, the outlines will show up as following figure. Additionally, the results and summarize are also shown in two separated windows.

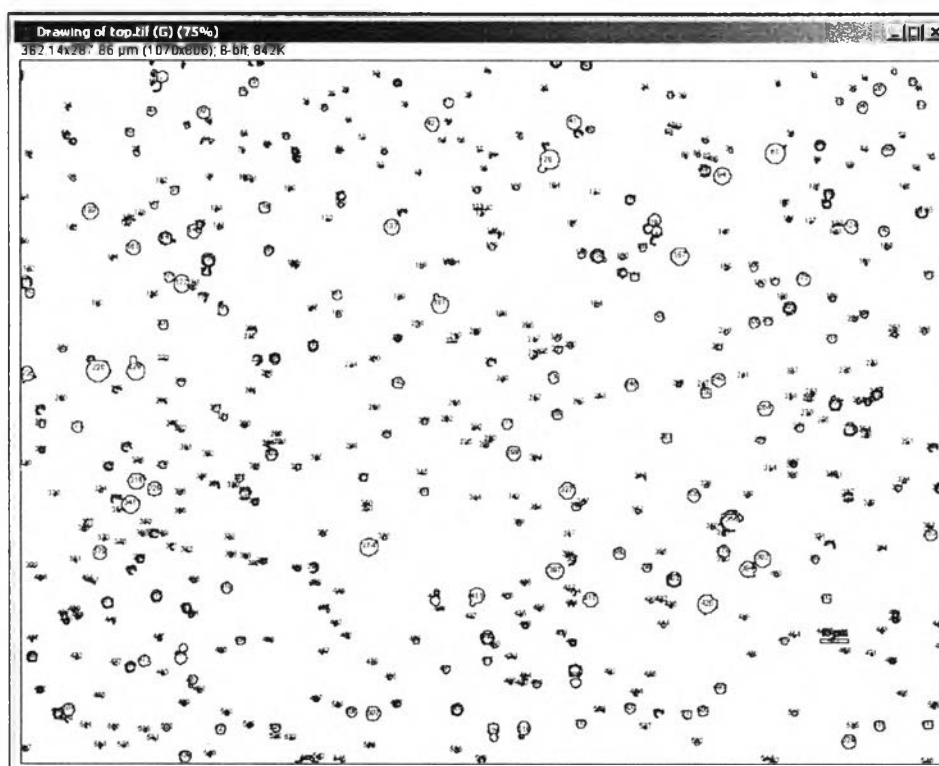


Figure C6 Analysed image; each droplet is identified by red number counting up all presented droplets on micrograph.

7. Copy the data in the “Results” dialog to an excel spreadsheet for further analysis using MATLAB.

Individual droplet area can be obtained from previous procedures. Consequently, lots of data points were produced depending on each micrograph since several sets of sample were taken at five different positions. Therefore, the results from one position were showed in Table C1.

Table C1 Individual droplet areas from one position on micrograph

No. of Droplet	Area	No. of Droplet	Area	No. of Droplet	Area
1	14.648	3	6.445	5	0.879
2	63.086	4	1.27	6	3.516

Table C1 Individual droplet areas from one position on micrograph (cont'd)

No. of Droplet	Area	No. of Droplet	Area	No. of Droplet	Area
7	1.367	46	1.66	85	4.98
8	6.152	47	1.66	86	2.93
9	9.668	48	4.785	87	7.617
10	8.496	49	14.16	88	1.172
11	6.641	50	1.367	89	63.672
12	2.246	51	1.562	90	3.613
13	4.688	52	9.766	91	8.301
14	4.98	53	1.074	92	10.156
15	1.074	54	1.855	93	33.105
16	3.223	55	17.383	94	10.547
17	0.879	56	27.832	95	1.953
18	65.137	57	38.086	96	5.859
19	13.477	58	4.883	97	17.773
20	16.113	59	3.32	98	1.172
21	2.93	60	1.855	99	18.164
22	30.176	61	3.32	100	1.562
23	20.898	62	0.879	101	1.953
24	7.324	63	0.879	102	3.418
25	3.125	64	1.562	103	16.309
26	30.273	65	2.246	104	3.32
27	46.582	66	27.246	105	3.027
28	4.102	67	25.781	106	1.758
29	7.52	68	1.66	107	3.711
30	1.172	69	64.062	108	16.504
31	11.816	70	4.102	109	7.715
32	5.859	71	6.152	110	4.297
33	17.969	72	5.566	111	4.004
34	4.102	73	4.883	112	5.664
35	4.98	74	5.273	113	32.52
36	0.879	75	5.859	114	23.438
37	1.172	76	13.867	115	4.883
38	4.297	77	8.984	116	57.617
39	5.664	78	2.344	117	2.734
40	1.66	79	0.977	118	4.102
41	93.652	80	2.344	119	9.766
42	3.125	81	25	120	41.895
43	48.926	82	0.977	121	3.125
44	1.855	83	16.211	122	4.785
45	4.199	84	91.699		

Appendix D DSD and Volume-based Mean Diameter Calculation

MATLAB is used to further calculate individual droplets diameter on spherical droplets basis, then analyzed the DSD in each micrograph for certain droplet size ranging from 0.5 to 15 micrometers. Relative frequency of given diameter range is eventually obtained from this analysis.

Droplet size distribution

Following MATLAB codes consist of two main parts; first convert the droplet area into droplet diameter as mentioned previously and also separate different droplet sizes into their size ranges, second re-calculate previous absolute frequency into relative frequency in order to normalize them into comparable data sets. Prior to running the code, there are a few things needed to be checked;

1. Path; the excel files have to be located in the same folder as MATLAB.
2. The file name must be identical.
3. Size distribution is in the B column of the excel file.

The main structures of the first part are re-calculating the size of spherical droplets and then arranging those droplets into the right bins (range of droplet size) as following code;

```

- Bottom Position
- 1st
filename = 'Bottom.xlsx';
B1 = xlsread(filename, 'B:B'); % read column B
DB1 = sqrt(B1*4/pi());
DB1min = min(DB1);
DB1max = max(DB1);
bbinB1 = linspace(0, 15, 30);
hist(DB1, bbinB1);
hold on;

```

This code accounted for one position on the micrograph, which can be simply duplicated by matching the new variables related to the analyzing samples, this is depending on the user, such as;

```

- Middle Position
- 1st
filename = 'Mid.xlsx';
M1 = xlsread(filename, 'B:B'); % read column B
DM1 = sqrt(M1*4/pi());

```

```

DM1min = min(DM1);
DM1max = max(DM1);
bbinM1 = linspace(0,15,30);
hist(DM1,bbinM1);
%2nd
filename = 'Mid2.xlsx';
M2 = xlsread(filename,'B:B'); %read column B
DM2 = sqrt(M2*4/pi());
DM2min = min(DM2);
DM2max = max(DM2);
bbinM2 = linspace(0,15,30);
hist(DM2,bbinM2);

```

or

```

%Right Position Histogram
%1st
filename = 'Right.xlsx';
R1 = xlsread(filename,'B:B'); %read column B
DR1 = sqrt(R1*4/pi());
DR1min = min(DR1);
DR1max = max(DR1);
bbinR1 = linspace(0,15,30);
hist(DR1,bbinR1);
%2nd
filename = 'Right2.xlsx';
R2 = xlsread(filename,'B:B'); %read column B
DR2 = sqrt(R2*4/pi());
DR2min = min(DR2);
DR2max = max(DR2);
bbinR2 = linspace(0,15,30);
hist(DR2,bbinR2);

```

In our study, the codes are duplicated as much as the samples were taken. Our format code contains five different positions and each of them also consists of another five replicates. However, the code of missing samples can be directly “umcomment” in order to neglect that analysis and continue analyzing the rest.

Once we obtain the absolute frequency of droplet size, we recall previous code as named “DSD_multiple_histogram.m” for further re-calculation. After running this code, the droplet size fractions in each range of droplet size are obtained and we can directly copy these data and make the DSD as well as further calculation for volume-based mean diameter. As mentioned in previous paragraph, the code of missing samples can be directly “umcomment”. The code showed below is a part of the full-code used in our research;

```

DSD_multiple_histogram;

nelements1 = hist(DB1,bbinB1); %Bottom
nelements2 = hist(DB2,bbinB2); %Bottom2
nelements6 = hist(DL1,bbinL1); %left
nelements7 = hist(DL2,bbinL2); %left2
nelements11 = hist(DM1,bbinM1); %Mid
nelements12 = hist(DM2,bbinM2); %Mid2
nelements16 = hist(DR1,bbinR1); %Right

```

```

nelements17 = hist(DR2,bbinR2); %Right2

Bot1 = nelements1/sum(nelements1); %Bottom
Bot2 = nelements2/sum(nelements2); %Bottom2
Left1 = nelements6/sum(nelements6); %left
Left2 = nelements7/sum(nelements7); %left2
Mid1 = nelements11/sum(nelements11); %Mid
Mid2 = nelements12/sum(nelements12); %Mid2
Right1 = nelements16/sum(nelements16); %Right
Right2 = nelements17/sum(nelements17); %Right2

```

Those code generate following DSD results as shown in Table D1 and the average results for DSD at different conditions are in Table D2.

Table D1 Relative frequency of droplet size from some samples

bbin (μm)	Bot1 (130)	Left1 (68)	Left2 (81)	Mid1 (815)	AVG	SD
0.517241	0	0	0	0	0.103448	0.231317
1.034483	0.123077	0.117647	0.074074	0.509202	0.371697	0.410221
1.551724	0.153846	0.176471	0.197531	0.195092	0.454933	0.613376
2.068966	0.169231	0.25	0.185185	0.11411	0.557498	0.846323
2.586207	0.153846	0.073529	0.17284	0.067485	0.610781	1.105294
3.103448	0.061538	0.058824	0.061728	0.039264	0.66496	1.363188
3.620690	0.061538	0.044118	0.08642	0.017178	0.765989	1.596026
4.137931	0.038462	0.014706	0.037037	0.014724	0.848572	1.838844
4.655172	0.061538	0	0.012346	0.011043	0.94802	2.072497
5.172414	0.007692	0.029412	0.012346	0.009816	1.046336	2.306564
5.689655	0.030769	0.029412	0.061728	0.003681	1.163049	2.530533
6.206897	0.030769	0.058824	0.012346	0.004908	1.262749	2.763941
6.724138	0.015385	0.058824	0.012346	0.002454	1.362629	2.997253
7.241379	0.015385	0.014706	0.012346	0.003681	1.457499	3.233291
7.758621	0.023077	0.014706	0.012346	0	1.56175	3.464166
8.275862	0	0.014706	0.012346	0.002454	1.661074	3.697785
8.793103	0.030769	0	0.012346	0.001227	1.767489	3.927457
9.310345	0.007692	0.014706	0.024691	0.001227	1.871732	4.15832
9.827586	0	0	0	0	1.965517	4.39503
10.34483	0	0.014706	0	0	2.071907	4.624708
10.86207	0.015385	0.014706	0	0.001227	2.178677	4.854169
11.37931	0	0	0	0.001227	2.276107	5.088845
11.89655	0	0	0	0	2.37931	5.3203
12.41379	0	0	0	0	2.482759	5.551617
12.93103	0	0	0	0	2.586207	5.782934
13.44828	0	0	0	0	2.689655	6.014252

bbin (μm)	Bot1 (130)	Left1 (68)	Left2 (81)	Mid1 (815)	AVG	SD
13.96552	0	0	0	0	2.793103	6.245569
14.48276	0	0	0	0	2.896552	6.476887
15	0	0	0	0	3	6.708204

Table D2 Average DSD of oil-in-water emulsion with OF 10 vol% and 50 vol%

Range (μm)	OF 10 vol%				OF 50 vol%			
	t=0 hr		t=48 hr		t=0 hr		t=48 hr	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD
0.5172414	0	0	0	0	0	0	0	0
1.0344828	0.4074	0.0683	0.3146	0.0419	0.3058	0.0417	0.2949	0.0531
1.5517241	0.2398	0.0321	0.2340	0.0257	0.1975	0.0302	0.2031	0.0375
2.0689655	0.1356	0.0219	0.1670	0.0166	0.1605	0.0201	0.1663	0.0282
2.5862069	0.0943	0.0201	0.1024	0.0167	0.1196	0.0162	0.1208	0.0196
3.1034483	0.0434	0.0025	0.0618	0.0174	0.0651	0.0140	0.0704	0.0241
3.6206897	0.0289	0.0143	0.0345	0.0125	0.0462	0.0165	0.0447	0.0167
4.1379310	0.0132	0.0068	0.0199	0.0076	0.0236	0.0074	0.0266	0.0133
4.6551724	0.0086	0.0055	0.0157	0.0088	0.0193	0.0081	0.0200	0.0110
5.1724138	0.0058	0.0049	0.0099	0.0054	0.0155	0.0079	0.0126	0.0062
5.6896552	0.0032	0.0025	0.0062	0.0024	0.0108	0.0050	0.0096	0.0068
6.2068966	0.0037	0.0021	0.0067	0.0062	0.0085	0.0063	0.0057	0.0054
6.7241379	0.0026	0.0028	0.0069	0.0031	0.0072	0.0064	0.0073	0.0074
7.2413793	0.0024	0.0028	0.0044	0.0036	0.0054	0.0055	0.0034	0.0035
7.7586207	0.0014	0.0021	0.0015	0.0013	0.0040	0.0026	0.0035	0.0041
8.2758621	0.0019	0.0020	0.0035	0.0034	0.0028	0.0025	0.0017	0.0025
8.7931034	0.0012	0.0013	0.0017	0.0026	0.0016	0.0017	0.0027	0.0030
9.3103448	0.0017	0.0018	0.0016	0.0016	0.0009	0.0009	0.0010	0.0018
9.8275862	0.0014	0.0014	0.0010	0.0014	0.0017	0.0018	0.0013	0.0017
10.3448276	0.0008	0.0014	0.0013	0.0020	0.0014	0.0017	0.0013	0.0022
10.8620690	0.0002	0.0005	0.0014	0.0014	0.0006	0.0012	0.0005	0.0009
11.3793103	0.0006	0.0008	0.0004	0.0007	0.0005	0.0008	0.0004	0.0008
11.8965517	0.0002	0.0004	0.0004	0.0010	0.0004	0.0009	0.0003	0.0009
12.4137931	0.0003	0.0007	0.0005	0.0010	0.0004	0.0009	0.0003	0.0007
12.9310345	0.0000	0.0000	0.0002	0.0005	0.0003	0.0006	0.0005	0.0011
13.4482759	0.0003	0.0007	0.0002	0.0007	0.0001	0.0003	0.0004	0.0011
13.9655172	0.0005	0.0008	0.0002	0.0007	0.0000	0.0000	0.0002	0.0005
14.4827586	0.0000	0.0000	0.0005	0.0009	0.0001	0.0002	0.0001	0.0003
15.0000000	0.0005	0.0008	0.0016	0.0021	0.0001	0.0004	0.0003	0.0009

Volume-based mean diameter

The volume-based mean diameter can be calculated from DSD with Equation D1;

$$\tilde{d} = \frac{\sum_{i=1}^n (N_i \cdot d_i^3) \cdot d_i}{\sum_{i=1}^n N_i \cdot d_i^3} \quad (\text{D1})$$

where

\tilde{d} is volume-based mean diameter

N_i is quantity of droplet in certain range

d_i is droplet size

As we know the absolute frequency of droplet in each range, volume-based mean diameter can be directly calculate as following example shown in Table D3. And the results of average volume-based mean diameter for different condition showed in Table D4.

Table D3 Volume-based mean diameter spreadsheet for the bottom position containing 130 droplets

bbin (d_i)	Bot1 (130)	N_i	$\sum_{i=1}^n (N_i \cdot d_i^3) \cdot d_i$	$\sum_{i=1}^n N_i \cdot d_i^3$
0.517241379	0	0	0	0
1.034482759	0.12307692	16	18.3236931	17.7129034
1.551724138	0.15384615	20	115.954621	74.726311
2.068965517	0.16923077	22	403.121249	194.841937
2.586206897	0.15384615	20	894.711579	345.955144
3.103448276	0.06153846	8	742.109572	239.124195
3.620689655	0.06153846	8	1374.8496	379.720366
4.137931034	0.03846154	5	1465.89545	354.258067
4.655172414	0.06153846	8	3756.92971	807.044159
5.172413793	0.00769231	1	715.769263	138.382057
5.689655172	0.03076923	4	4191.83111	736.746074
6.206896552	0.03076923	4	5936.87657	956.496781
6.724137931	0.01538462	2	4088.61718	608.050761
7.241379310	0.01538462	2	5499.3984	759.440731
7.758620690	0.02307692	3	10870.7457	1401.11833

Table D3 Volume-based mean diameter spread sheet for the bottom position containing 130 droplets (cont'd)

bbin (d_i)	Bot1 (130)	N_i	$\sum_{i=1}^n (N_i \cdot d_i^3) \cdot d_i$	$\sum_{i=1}^n N_i \cdot d_i^3$
8.275862069	0	0	0	0
8.793103448	0.03076923	4	23912.7058	2719.48419
9.310344828	0.00769231	1	7513.85941	807.044159
9.827586207	0	0	0	0
10.34482759	0	0	0	0
10.86206897	0.01538462	2	27840.7044	2563.11247
11.37931034	0	0	0	0
11.89655172	0	0	0	0
12.41379310	0	0	0	0
12.93103448	0	0	0	0
13.44827586	0	0	0	0
13.96551724	0	0	0	0
14.48275862	0	0	0	0
15	0	0	0	0
Summation	1	130	99342.4033	13103.2586
Volume-based mean diameter	7.58150366			

Table D4 Average volume-based mean diameter of oil-in-water emulsion with OF 10 vol% and 50 vol%

OF (vol%)	t=0 hr		t=48 hr	
	AVG	SD	AVG	SD
10%	7.90691278	1.84764591	7.88439097	1.67894563
50%	6.40377491	1.02140227	6.21998415	1.70716459

Appendix E Wax Deposition Growth Data and Wax Content Analysis

Wax deposition experiments consist of two main parts; first is to pre-coat the cold finger with n-C₂₈ waxy solution and then conduct the wax deposition experiments with pre-coated cold finger in waxy oil-in-water emulsion. The wax content is then characterized using gas chromatography (GC). The results from GC will be further calculated regarding the carbon number distribution as shown in Table E1.

Table E1 Wax content calculation spread sheet

Retention time	Carbon Number	Integration Area	MW	Mass	Mass Fraction
14.00799	22	26.57845879	310.59	8255.003514	0.05125
14.57161	23	51.05791092	324.61	16573.90846	0.10289
15.11284	24	72.80310822	338.64	24654.04457	0.15306
15.63350	25	76.38295746	352.666	26937.67208	0.16723
16.13623	26	76.47518921	366.692	28042.84008	0.17410
16.62071	27	59.04565811	380.718	22479.74486	0.13956
17.08848	28	47.40761566	394.744	18713.87184	0.11618
17.54070	29	33.30252075	408.77	13613.07141	0.08451
17.97832	30	23.51532936	422.796	9942.187192	0.06172
18.4020	31	15.43789577	436.822	6743.612508	0.04187
18.81425	32	10.20826244	450.848	4602.374706	0.02857
19.21326	33	5.270668983	463.866	2444.884139	0.01518
19.60019	34	3.177389145	476.884	1515.246045	0.00941
19.98053	35	1.832027435	489.902	897.5139046	0.00557
20.38312	36	0.975098789	502.92	490.3966828	0.00304
			Total	161077.46	1.00000

The pre-coated cold finger undergoes the same characterization in order to measure the mass of pre-coated and also the wax produced by pre-coating procedure as shown in Table E2.

Table E2 Mass of n-C₂₈ pre-coated element

No. of Replicates	Pre-coated Mass (g)	Wax Content
1	0.4854	10.916%
2	0.4676	12.951%
3	0.4957	14.967%
4	0.4980	16.323%
5	0.4717	15.357%
6	0.4239	16.689%
7	0.4941	15.532%
8	0.4704	16.410%
9	0.5024	14.228%
10	0.5048	14.440%
AVG	0.4814	14.781%
SD	0.0243987	0.017737

Prior to performing wax deposition experiment with waxy oil-in-water emulsion, the preference wax was first characterized in place of getting its carbon number distribution indicated in Table E3.

Table E3 Carbon number distribution of studied wax

Carbon Number	Mass fraction			
	1 st replicate	2 nd replicate	AVG	SD
22	0.02785	0.02539	0.02662	0.00174
23	0.06107	0.05488	0.05798	0.00438
24	0.09676	0.08704	0.09190	0.00687
25	0.11752	0.10821	0.11286	0.00658
26	0.12350	0.11553	0.11951	0.00564
27	0.11529	0.11099	0.11314	0.00304
28	0.09841	0.09873	0.09857	0.00022
29	0.08558	0.08892	0.08725	0.00236
30	0.06799	0.07201	0.07000	0.00284
31	0.05813	0.06329	0.06071	0.00365
32	0.04593	0.05154	0.04873	0.00397
33	0.03520	0.04079	0.03800	0.00395
34	0.02371	0.02797	0.02584	0.00301
35	0.01819	0.02217	0.02018	0.00282
36	0.01329	0.01718	0.01524	0.00275

Table E3 Carbon number distribution of studied wax (cont'd)

Carbon Number	Mass fraction			
	1 st replicate	2 nd replicate	AVG	SD
37	0.01159	0.01536	0.01348	0.00266

The wax deposition experiments were then performed with two different oil fractions, OF 5 vol% and 50 vol%, under various operating time in order to obtain the wax deposition growth rate as well as wax content with increasing operating time. Those results for OF 5 vol% and 50 vol% were shown in Table E4 and E5, respectively.

Table E4 Wax deposit mass as a function of operating time with OF 5 vol%

Operating time (min)	AVG $m_{\text{new deposit}}$	SD $m_{\text{new deposit}}$	AVG w_{exp}	SD w_{exp}
0.1667	0.57241	0.35501375	0.11566	0.00535360
0.5	0.58004	0.31386543	0.13160	0.01285019
2	0.48104	0.42945193	12.436%	0.03171134
15	0.77704	0.43321989	12.394%	0.01903038
30	0.60358	0.08709319	10.981%	0.01057468
120	0.48438	0.25982083	12.010%	0.02380358
720	0.95585	0.25441412	12.103%	0.00194338
1440	0.75730	0.16027771	12.008%	0.00623402

Table E5 Wax deposit mass as a function of operating time with OF 50 vol%

Operating time (min)	AVG $m_{\text{new deposit}}$	SD $m_{\text{new deposit}}$	AVG w_{exp}	SD w_{exp}
0.1667	0.19514	0.14016	15.304%	0.00431
0.5	0.34707	0.18415	11.375%	0.00415
2	0.56682	0.26680	11.355%	0.00219
15	0.51528	0.20204	11.837%	0.00825
30	0.67908	0.34493	11.566%	0.00153
120	0.92414	0.48613	11.817%	0.01078
720	1.90858	0.32286	10.433%	0.00793
1440	2.32838	0.56660	9.983%	0.00551

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