

EFFECT OF HOMOGENISATION PRESSURE AND SOME HYDROCOLLOIDS ON BEVERAGE EMULSION STABILITY

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The aim of the study was to determine the effect of homogenisation parameters, arabic gum and modified starch additives on the stability of beverage emulsions. Optimal parameters for homogenisation process were determined on the basis of the characteristics of particle size of dispersed phase *vs.* homogenisation pressure and on the basis of results of emulsion stability measurement. The best among the analysed variants of homogenisation of emulsions with arabic gum appeared to be the application of the pressure range of 45–55 MPa in the first stage followed by the pressure reduction at the second stage to 1/3 of that from the first stage. The analysis of the size distribution of oil particles in the emulsions stabilized by means of arabic gum or modified starch which were homogenised under the same pressure points to the need of a proper selection of homogenisation parameters in respect of the kind of stabilisers.

INTRODUCTION

The properties of a food emulsion that contribute most to its perceived characteristics are oil particle size distribution and oil concentration [Coupland & McClements, 2001].

Emulsion instability results from physical processes, *i.e.* flocculation, coalescence, Ostwald ripening and gravitation separation. The rate of these changes can be measured by determining the size and distribution of oil droplets in the emulsion [McClements, 1999]. Stokes' law states that the velocity at which a droplet moves is proportional to the square of its radius. The stability of an emulsion to gravitation separation can therefore be enhanced by reducing the size of the droplets [Huang *et al.*, 2001].

Direct determination of these parameters (particle diameter and particle size distribution) is difficult because droplets are often too small to be observed and measured with conventional light microscopy. Electron microscopy provides adequate resolution, still sample preparation may generate artifacts [Coupland & McClements, 2001]. The most common technique used for the characterisation of particle size in beverage emulsions is laser light scattering. Nevertheless, the devices require very dilute systems ($\varphi < 0.05$ wt%) and the dilution of more concentrated emulsions may disrupt delicate aggregates [McClements & Coupland, 1996].

Beverage flavour emulsions used in the industrial production of soft drinks are oil-in-water emulsions. They are first prepared as an emulsion concentrate which is later diluted in a sugar solution in order to produce the finished beverage [Buffo & Reineccius, 2000].

The emulsions should demonstrate a high degree of stability in both the concentrated and ready-to-serve forms of beverage [Tan & Holmes, 1988]. Hydrocolloids may serve as emulsifiers and stabilisers in beverage emulsions. Arabic gum and hydrophobically modified starch are the most commonly used hydrocolloids in flavour beverage emulsions [Buffo *et al.*, 2002; Dickinson, 2003; Chanami & McClements, 2001].

Pressure homogenisation is one of the operation steps used in the preparation of beverage emulsions. Parameters of homogenisation exert a significant effect on emulsion stability [Burgaud *et al.*, 1990].

The study analyses the effect of pressures applied at the first and second stage of homogenisation on the stability of beverage emulsion. The impact of various additives of arabic gum and modified starch was also considered. The optimal parameters of homogenisation of beverage emulsions were determined on the basis of size distribution of oil particles as well as emulsion stability measurements.

MATERIAL AND METHODS

Valgum (a mixture of different species of gum acacia), Valspray A (spray dried gum acacia purified with Kordofan), and Valdamar (purified and deodorised damar gum) were obtained from the Valmar, France. Modified starch (Purity Gum 2000) was obtained from the National Starch and Chemical, Germany. Lemon oil was purchased from Pollena Aroma S.A., Poland, whereas food grade sodium benzoate and citric acid – from Orffa Food Eastern Europe, the Netherlands.

Emulsion concentrates were prepared according to the following formula: essential oil – 10% (w/w), weighing agent

(Valdamar) – 8% (w/w), arabic gum – 8% (w/w) or modified starch – 12% (w/w), sodium benzoate – 0.1% (w/w), citric acid – 0.3% (w/w), and distilled water – up to 100% (w/w). The emulsifier was dispersed for half an hour with an RW 20 DZW mixer by Janke & Kunkle, Germany, in water at 20°C (modified starch) or 40°C (arabic gum), in which the sodium benzoate had been previously dissolved. Next, citric acid was added. The water phase with arabic gum was stored for 24 h to hydrate the emulsifier. Pre-emulsion was prepared by adding together the water and oil phases (*i.e.* the hydrocolloid solution and the essential oil with damar gum) and stirring with the mixer RW 20 DZM for 10 min with the velocity of 1700 rpm. A fine emulsion was achieved by subjecting the premixes to a two-stage homogenization with an APV-1000 homogenizer by APV, Denmark. Two variants of the relations between pressure values at the first and second stage of homogenization were analysed in the paper. Namely, it was assumed that in the second stage the pressure reaches 1/3 or 2/3 of the pressure value achieved in the first stage, respectively.

Mean particle size and particle size distribution of the dispersed phase of beverage emulsions were determined with static light scattering using a Malvern Mastersizer (Malvern Instruments Ltd., Malvern, UK) on the next day after preparation. The emulsions were diluted with distilled water (1:200).

The average droplet size was characterised by mean diameters related to the volume $D_{[4,3]}$ and surface $D_{[3,2]}$, defined respectively as:

$$D_{[4,3]} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3},$$

and

$$D_{[3,2]} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2},$$

where n_i is the number of droplets with diameter d_i .

Turbidity evaluation of emulsion stability [Kaufman, 1984] consisted in the measurement of the absorbance of emulsion samples diluted at 1:1000 ratio. The absorbance was read at 400 and 800 nm, using a Helios β spectrophotometer (Unicam, UK). The particle size index (R) was determined from the ratio of the absorbance at 800 and 400 nm.

In order to determine the emulsion stability end-point (time to breakage), the emulsions were diluted in a 5% sugar solution and stored in 1-L plastic bottles (PET) at a temperature of $20 \pm 1^\circ\text{C}$ and daylight. The absorbance was read at 500 nm, using a Helios β spectrophotometer (Unicam, UK). A 5% sugar solution was used as a blank sample for absorbance measurements. Samples were consistently taken from a point at 4 cm from the bottom of the bottle. Daily readings were performed until a week from the first reading. The first-order logarithmic model has been used to the mathematical description of the absorbance *vs.* time relation.

The first-order model is characterised by the following equation:

$$\ln A = \ln A_0 - k_1 t,$$

where t is time, A absorbance at time = t , A_0 absorbance at time = t_0 , k_1 the first-order rate constant.

Emulsion stability (time to breakage) was computed from the above fitting equation at $A=0.1 A_0$ [Buffo *et al.*, 2002].

The statistical analysis was carried out with use of the computer program *Statgraphics Plus* produced by Statistical Graphics Corporation, using the one-way analysis of variance, at a confidence level of 5%.

RESULTS AND DISCUSSION

The limitation of the destabilisation processes in beverage emulsions can be achieved among others by obtaining the proper dispersion degree [Horne & Hermar 1998]. The emulsion stability can be expected to be higher when the droplet size is smaller. An emulsion containing weighing agents and an acceptable emulsifying constituent will typically not separate if the average particle size of the emulsion is below $1 \mu\text{m}$ [Buffo & Reineccius, 2000].

In our investigations, the pressure applied at the first stage of homogenization ranged from 35 to 65 MPa. At the second stage, the pressure was reduced to 2/3 and 1/3 of the pressure from the first stage. Figure 1 shows the size distribution of particles in emulsions which were stabilised with a mixture of arabic gum preparations (8%). The course of the curves (Figure 1a) obtained for volume fractions of particles with the given size indicates that the emulsions homogenised under the pressure of 35/12 and 35/23 MPa contained a significant fraction of particles having the diameter larger than $10 \mu\text{m}$ (the second significant pick was observed for diameter range of 10–100 μm). The fraction of coarse particles was considerably smaller upon applying the pressure variant of 35/12 MPa, as compared to the 35/23 MPa variant. Figure 1b shows more significant differences in particle size distribution. Homogenisation under the pressure of 45/15 MPa enabled obtaining emulsion samples containing oil droplets with diameter range of 0.1–1.68 μm , whereas pressure treatment at 45/30 MPa resulted in the formation of oil droplets with diameter range of 0.05–76 μm . An analysis of results shown in Figures 1c and 1d confirmed that the reduction of pressure at the second stage of homogenisation to 2/3 of that from the first stage results in the widening of particle size distribution and in the appearance of oil droplets with diameters larger than $10 \mu\text{m}$.

Table 1 compiles results of measurements of the mean sizes of oil particles *vs.* homogenisation parameters. The mean size of oil droplets obtained ($D_{[4,3]}$) was lower when the pressure at the second stage reached 1/3 of the pressure value applied at the first stage, compared with the mean size of droplets obtained when the pressure at the second stage was reduced to 2/3 of that at the first stage. Emulsions obtained upon homogenisation under the pressure set of 55/35 MPa and 55/18 MPa contained oil droplets with diameters $D_{[4,3]}$ equal to 2.66 μm and 0.89 μm , respectively. Thus, applying the pressure variants of 55/18 MPa as well as 45/15 MPa, the condition of high stability of beverage emulsions (average particle size below $1 \mu\text{m}$) postulated by Buffo and Reineccius [2000] was met. Taking into account the dispersion degree of beverage emulsions, it can be stated that

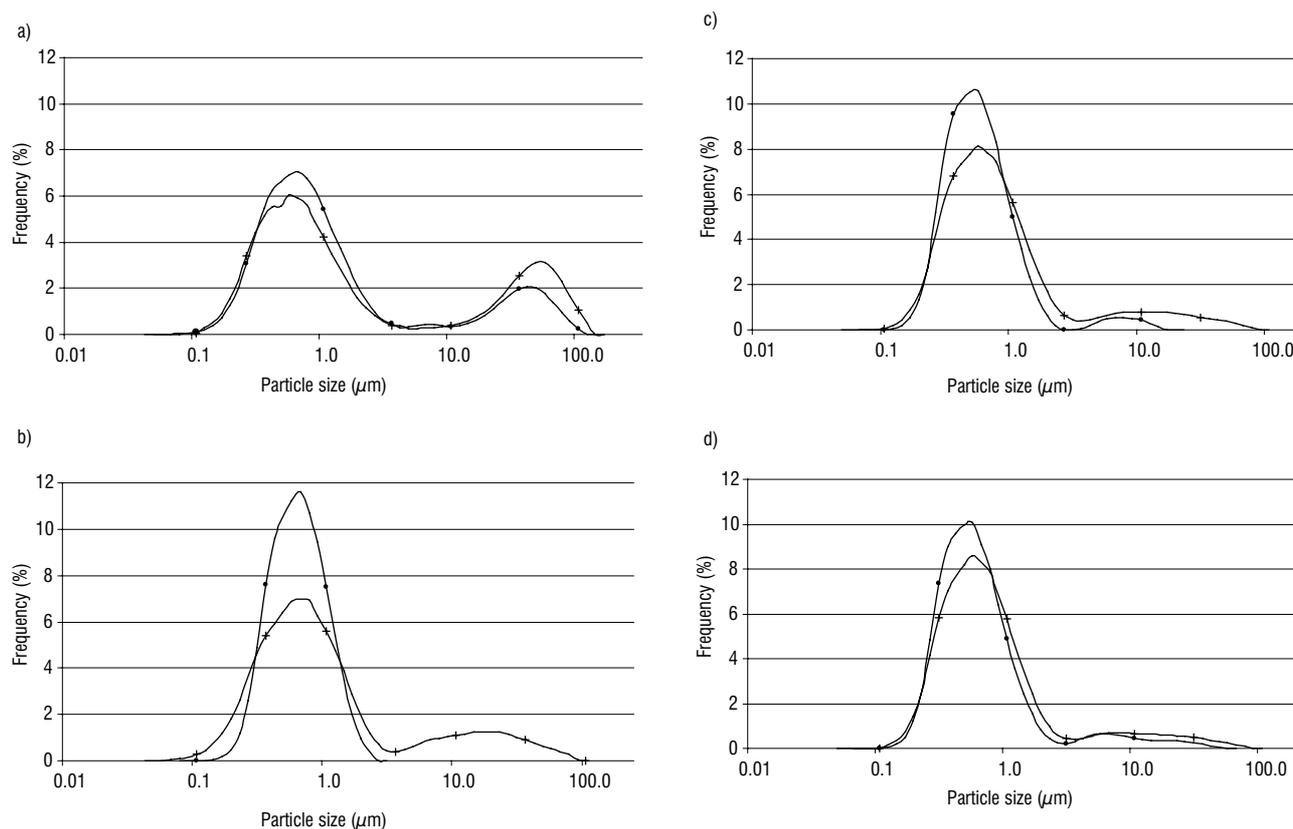


FIGURE 1. The size distribution of the dispersed phase particles in beverage emulsions with preparations of arabic gum:

a) homogenisation pressure: ●—● 35/12 MPa; +—+ 35/23 MPa, b) homogenisation pressure: ●—● 45/15 MPa; +—+ 45/30 MPa, c) homogenisation pressure: ●—● 55/18 MPa; +—+ 55/35 MPa, d) homogenisation pressure: ●—● 65/22 MPa; +—+ 65/42 MPa.

the reduction of pressure at the second stage to 1/3 than to 2/3 of the pressure from the first stage is a more profitable solution. It is also clearly indicated by the analysis of the emulsion stability, including particle size index and time to breakage; the lower the particle size index, the higher the emulsion stability [Kaufman, 1984].

For most of emulsion samples homogenised under the pressure reduced to 1/3 at the second stage of homogenisation, the particle size index was lower and the time to breakage was longer, compared to respective samples homogenised under the pressure reduced at the second stage to 2/3 of the pressure from the first stage (Table 1). An opposite tendency was observed for emulsion samples homogenised at the first stage under 35 MPa, namely the time to breakage appeared to be longer for the sample

homogenised under the pressure reduced to 2/3 at the second stage of homogenisation. It is worth emphasizing that both the samples homogenised at the first stage under 35 MPa were found to be the least stable of all samples analysed. It was likely that their stability was strongly affected by the presence of oil droplets with diameters larger than 10 μm . The $D_{[V\ 0.9]}$ value reached *ca.* 28 μm and 52 μm for the samples homogenised under the pressure of 35/12 and 35/23 MPa, respectively (Table 1).

The highest values of mean size of particles in oil phase ($D_{[4,3]}=14.6\ \mu\text{m}$) were noted in samples homogenised under the pressure of 35/12 MPa. In these emulsions, 90% of particles had their diameters shorter than 28.28 μm . The presence of such large particles of the dispersed phase can accelerate negative processes leading to destabilisation of

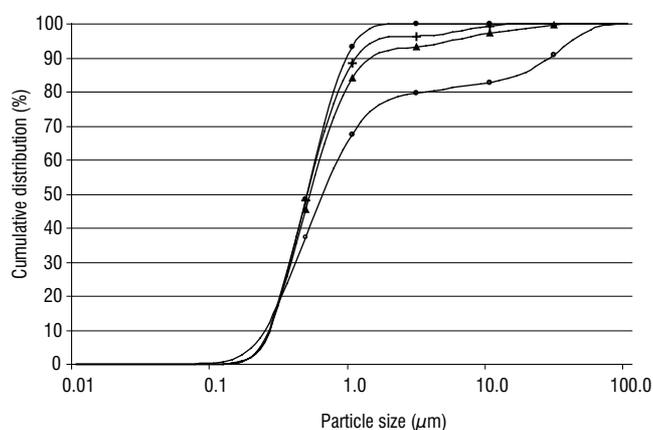
TABLE 1. The particle size of the dispersed phase in emulsions with arabic gum vs. homogenisation pressure.

Homogenisation pressure (MPa)	Droplet diameter (μm)				Emulsion stability	
	$D_{[4,3]}$	$D_{[3,2]}$	$D_{(V\ 0.5)}$	$D_{(V\ 0.9)}$	Particle size index R	Time to breakage (days)
35/12	14.60	0.67	0.65	28.28	0.46 ^{ab}	282 ^a
35/23	13.56	0.65	0.83	51.76	0.42 ^a	343 ^b
45/15	0.89	0.45	0.49	1.14	0.41 ^a	458 ^c
45/30	1.54	0.47	0.71	13.41	0.43 ^{ab}	395 ^d
55/18	0.82	0.46	0.51	1.13	0.39 ^a	411 ^d
55/35	2.66	0.53	0.62	5.56	0.79 ^c	386 ^c
65/22	1.36	0.48	0.53	1.44	0.45 ^{ab}	391 ^d
65/42	2.33	0.52	0.61	3.51	0.53 ^b	364 ^c

a–e – mean values denoted by different superscripts in the same column differ significantly from each other ($\alpha=0.05$)

an emulsion, *i.e.* gravitation separation and/or flocculation [McClements, 1999]. The mean sizes of oil droplets ($D_{[4,3]}$) in emulsions homogenised under the pressures of 45/15 MPa and 55/18 MPa were many times lower and did not exceed even $1 \mu\text{m}$, in addition 90% of the dispersed phase particles were characterised by diameters smaller than $1 \mu\text{m}$. A pressure rise up to 65 MPa resulted in increasing the mean particle size of oil phase in the emulsion (Table 1).

The measurements of emulsion stability confirmed a significant influence of homogenisation pressure on the dispersion degree of beverage emulsion. The analysis of the time of emulsion breakage showed that the application of the pressure of 45/15 MPa enabled obtaining emulsion stability twice as long as that achieved at the pressure variant of 35/12 MPa. It seems, therefore, that the results of emulsion stability determination shown in Table 1 indicate that the pressure set of 45/15 and 55/18 MPa enables obtaining the emulsion with extended stability, compared to the samples obtained at other variants of pressure considered.



○—○ pressure 35/12 MPa; ●—● pressure 45/15 MPa; +—+ pressure 55/18 MPa; ▲—▲ pressure 65/22 MPa

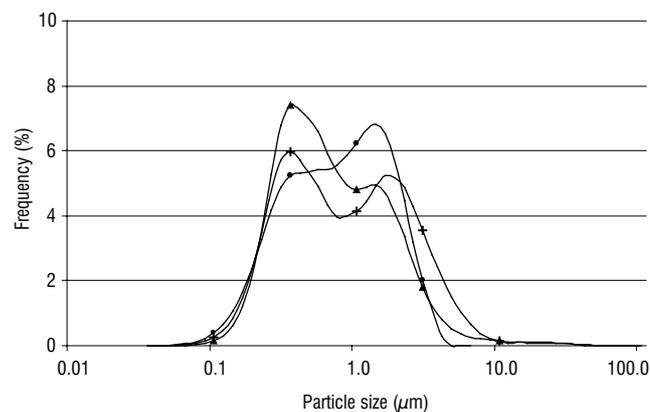
FIGURE 2. The cumulative distribution of the dispersed phase particles in beverage emulsions with arabic gum.

Figure 2 presents cumulative distribution of particles in the emulsion stabilised with a mixture of arabic gums. Considering the effect of pressure obtained at the first stage on the distribution of particle size, it was pointed out that over 90% of particles with diameters lower than $1 \mu\text{m}$ occurred in the emulsion sample homogenised under the pressure of 45/15 MPa. The application of the higher as well as lower pressures (65/22 and 35/12 MPa) resulted in decreasing the particle fraction with diameters lower than $1 \mu\text{m}$ to 83% and 70%, respectively.

This proves that the best variant of homogenisation pressure is the one where the pressure at the second stage

reaches 1/3 of the pressure value from the first homogenisation stage (ranging from 45 to 55 MPa).

Figure 3 shows the size distribution of particles in emulsions which were stabilised with modified starch added in the amount of 12%. The influence of pressure variants was not as explicit as in the case of emulsions stabilised with arabic gum. Nevertheless, also in this case the pressure set 45/15 MPa seems to be more profitable in comparison with pressure variants 55/18 and 65/22 MPa. So adjusted homogenisation pressures (45/15 MPa) enabled obtaining oil droplets with diameters ranging from 0.05 to *ca.* $6 \mu\text{m}$. In the emulsion samples, the increased homogenisation pressure caused the appearance of particles with diameters longer than $30 \mu\text{m}$. On the basis of the results shown in Table 2, it was concluded that the mean particle size in the samples homogenised under the pressure of 45/15 MPa was considerably smaller than that of the particles obtained under the pressure of 55/18 MPa. The breakage time of the emulsions homogenised under 45/15 MPa was also longer than of those homogenised under 55/18 MPa or 65/22 MPa. For the samples homogenised under the pressure of 55/18 MPa, the value of $D_{[3,2]}$ was higher than that for the samples homogenised under 65/22 MPa, which suggests their higher stability. The measurement of the breakage time did not confirm this dependency. It is likely to be due to the great influence of particle size distribution on the stability of beverage emulsion (narrow distribution desired). The analysis of mean size of oil particles and emulsion stability with the addition of modified starch (Table 2) also indicated considerably smaller differences between the samples homogenised under various pressures, compared to the samples with the addition of arabic gum. A substantial impact of



●—● pressure 45/15 MPa; +—+ pressure 55/18 MPa; ▲—▲ pressure 65/22 MPa

FIGURE 3. The size distribution of the dispersed phase particles in beverage emulsions with modified starch.

TABLE 2. The particle size of the dispersed phase in emulsions with modified starch vs. homogenisation pressure.

Homogenisation pressure (MPa)	Droplet diameter (μm)				Emulsion stability	
	$D_{[4,3]}$	$D_{[3,2]}$	$D_{(V,0.5)}$	$D_{(V,0.9)}$	Particle size index R	Time to breakage (days)
45/15	0.89	0.49	0.65	1.82	0.42 ^a	399 ^c
55/18	1.39	0.53	0.79	3.02	0.48 ^b	386 ^b
65/22	1.09	0.49	0.60	2.14	0.43 ^a	368 ^a

a–e – mean values denoted by different superscripts in the same column differ significantly from each other ($\alpha=0.05$)

homogenisation parameters as well as the kind of a stabiliser on the size of particles of the oil phase and their distribution suggest that the pressure variants should be adjusted for each emulsion separately with the addition of various emulsifiers.

CONCLUSIONS

1. The analysis of the stability of beverage emulsion homogenised under various pressure sets shows that more favourable results are obtained when at the second stage of homogenisation the pressure reaches 1/3 of the pressure value applied at the first stage. Worse results are obtained when at the second stage the pressure reaches 2/3 of the value from the first stage.

2. More stable emulsions were obtained with arabic gum additive by applying the pressure sets of 45/15 and 55/18 MPa in comparison with the emulsions homogenised under other pressures considered in the paper. In the case of emulsions with modified starch additive, greater stability was reached under the pressure set of 45/15 MPa.

3. The determination of the size distribution of the oil particles in emulsions homogenised under the same pressure with the addition of various stabilisers points to the need of a proper selection of homogenisation parameters depending on the kind of stabilisers applied.

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WPLYW CIŚNIENIA HOMOGENIZACJI ORAZ WYBRANYCH HYDROKOLOIDÓW NA STABILNOŚĆ EMULSJI NAPOJOWYCH

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Celem pracy było określenie wpływu parametrów homogenizacji oraz dodatku gumy arabskiej i skrobi modyfikowanej jako emulgatorów na stabilności emulsji napojowych. Na podstawie charakterystyki wielkości cząstek fazy zdyspergowanej w zależności od ciśnienia homogenizacji oraz wyników pomiaru stabilności emulsji podjęto próbę ustalenia optymalnych parametrów procesu homogenizacji. Najlepszym spośród analizowanych wariantów homogenizacji emulsji z dodatkiem gumy arabskiej okazał się wariant, w którym w I stopniu homogenizacji zastosowano ciśnienie rzędu 45 – 55 MPa, a w II stopniu – ciśnienie zredukowano do 1/3 ciśnienia zastosowanego w stopniu I (tab. 1, rys. 1 i 2). Analiza rozkładu wielkości cząstek emulsji stabilizowanych gumą arabską lub skrobią modyfikowaną, które poddano homogenizacji przy tych samych ciśnieniach, wskazuje na konieczność doboru parametrów homogenizacji z uwzględnieniem rodzaju stosowanego stabilizatora.