Studying the effects of adsorption, recoalescence and fragmentation in a high pressure homogenizer using a dynamic simulation model

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A B S T R A C T

The emulsification in a high pressure homogenizer was studied using a dynamic simulation model based on the population balance equation. The model includes fragmentation, recoalescence and adsorption of macromolecular emulsifier and uses a simple flow model in order to link the hydrodynamics in the homogenizer to the three physical processes mentioned above.

A computer model offers an interesting opportunity to study the effect of model assumptions on the overall outcome of the process. The computer model is also an interesting complement to experiments in this case since internal measurements in the active region of homogenization are very hard to carry out, due to small scales and high forces, and information on the spatial position of the different processes is of great importance in design.

Based on a set of assumptions, mainly that the turbulent jet responsible for break-up can be described by a one dimensional model and that the macromolecular emulsifiers hindrance of recoalescence can be described by a wall like repulsion, it is shown that the active region of homogenization can be divided into two zones; a narrow zone with fast fragmentation and nearly no recoalescence in the most intense part of the region followed by a recoalescence zone as drop–drop interactions starts to dominate with decreasing turbulence intensity. The effect of operating parameters is seen to be close to the ones found from experiment.

The results are discussed in relation to a flow field obtained by a simplistic CFD and assumptions made about hydrodynamics and emulsifier behavior.

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1. Introduction

High pressure homogenization is used in food industry as a method for emulsification. A pre w/o emulsion is forced through a narrow gap under high pressure. The result is a much finer emulsion with smaller drop sizes and a narrower drop size distribution. Three simultaneous processes are thought to occur in the active region of the homogenizer; fragmentation of drops due to hydrodynamic forces, recoalescence of insufficiently protected drops and adsorption of emulsifiers at the drop interface (Walstra, 1993; Walstra & Smulders, 1998).

The exact nature of break-up forces is somewhat disputed with viscous stress (Walstra, 1993), implosion of cavitation bubbles (Kurzhals, 1977) and interactions with turbulent eddies (Walstra & Smulders, 1998) being the most predominantly found explanations. The dispute is at least partly only apparent since the mechanism probably is highly dependent on the type and especially size of the homogenizer studied. When excluding small laboratory machines

there is a consensus on turbulent inertial and viscous forces as the main source of fragmentation (Floury, Desrumaux, & Lardières, 2000; Phipps, 1985; Walstra & Smulders, 1998).

The position of the active region of homogenization, inlet gap or outlet, has also been an area of debate, but at least for large production scale machines the turbulent wall bounded planar jet created at the outlet of the gap has gained much experimental support. Detailed studies of carefully scaled models show no fragmentation at all in the gap; instead drops are elongated or unaffected until reaching a position some gap heights out from the gap exit where they are broken up by turbulent inertial and viscous forces (Budde, Schaffner, & Walzel, 2001; Innings & Trägårdh, 2005; Kolb, Wagner, & Ulrich, 2001).

The recoalescence is thermodynamically favored since it lowers the surface free energy of the system. Collisions of drops, mainly due to the highly turbulent flow, will induce coalescence unless hindered by an emulsifier.

Emulsifiers increase the efficiency of the emulsification process both by lowering the Laplace pressure and thus aiding in droplet breakup and by stabilization of newly formed droplets against recoalescence. Both processes include both static forces, due to lowering of interfacial tension, electrostatic and steric repulsive

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forces, and dynamic forces, caused by mass transport both across and along the drop interface and exemplified by the Gibbs–Marangoni effect (Bergenståhl & Claesson, 1997).

Studying the emulsification process in a high pressure homogenizer is experimentally challenged by the large velocity gradient and high static pressures in comparison to the very small geometrical scales involved. Therefore most studies take a "black-box" approach studying variations in outflow with variations in inflow and control parameters such as homogenization pressure. For example many discussions on emulsification mechanism are based on the power-law dependency of resulting Sauter mean diameter and homogenizer pressure (Floury et al., 2000; Kiefer, 1977; Phipps, 1985; Walstra & Smulders, 1998).

The drawback of this approach is that it offers only limited information on what processes are occurring inside the active region and none about the dynamics of these. This study is focused on examining the effects of fragmentation and recoalescence processes in a high pressure homogenizer with special attention to the latter. A method for measuring recoalescence rate was developed by Taisne, Walstra, and Cabane (1996) where two oils are first homogenized separately and after mixing are re-homogenized at the same pressure. The degree of mixing between the oils is measured based on difference in optical density of oil drop content. The same method has been used by Floury, Legrand, and Desrumaux (2004).

A different approach was tried by Mohan and Narsimhan (1997) and Narsimhan and Goel (2001) by measuring the change in number of drops after a negative step change in pressure in a recirculatory system. Combined with a simple population balance equation assuming a mono disperse size distribution a recoalescence rate was estimated.

The studies find an expected increase in recoalescence rates for higher volume fraction of oil and lower concentrations of emulsifier per volume of oil. Further it is found that the recoalescence increases with an increase in homogenizer pressure. Still information on the spatial position, needed in for example constructing and optimization of homogenizer valves, of recoalescence is scarce. Some authors (Karbstein & Schubert, 1995; Phipps, 1974; Taisne et al., 1996) have theoretically discussed a two step process with fragmentation in the most hydrodynamically fierce part of the active region followed by a recoalescence zone.

A dynamic simulation model incorporating simultaneous fragmentation, recoalescence and adsorption of macromolecular emulsifier was developed and tested by Håkansson, Trägårdh, and Bergenståhl (submitted for publication). It was found to give a representative description of the emulsification process in a high pressure homogenizer and could be used to study the spatial fragmentation and recoalescence in the active region of homogenization. This model assumes a constant surface tension and that the probability that a collision should lead to recoalescence is proportional to the complement of the surface coverage. The model

is obviously quite simplistic, although it can be assumed to describe certain macromolecular emulsifiers, for example hydrophobically modified starch displaying a comparable low interfacial pressure (Nilsson & Bergenståhl, 2006b), thus decreasing the importance of dynamics in surface tension and surface mobility such as Gibbs–Marangoni effects well known to be of great importance for other, especially micelle forming low molecular, emulsifiers (Walstra, 2005).

This study is focused on using the proposed computer model in order to examine what the consequences are of treating the three processes fragmentation, adsorption and recoalescence simultaneously under stated models and assumptions, and further what they imply on the droplet formation process during high pressure homogenization. The trends are compared to data obtained in various experimental studies in order to discuss how well the models describe the true process.

Of outmost importance is the spatial division between fragmentation and recoalescence, having a more profound understanding of this can improve homogenizer design. Therefore the implications from the proposed model on this factor are given special attention. Special attention is also put on the recoalescence since controlling this process is of particular interest both theoretically and for practical emulsification applications.

Since all model results are dependent on the model assumptions, the influences on the results from these should also be discussed in order to investigate the generality of the conclusions.

2. Numerical methods

The dynamic simulation model uses a Population Balance Equation (PBE) approach (Ramkrishna, 2000) to describe the development of oil drop size distribution over time as the emulsion passes through the active region of homogenization. All three processes are simultaneously included in the final model; fragmentation due to collisions and shearing with turbulent eddies, recoalescence of insufficiently covered drops and adsorption of macromolecular emulsifier at the drop interface due to collisions. Fragmentation and recoalescence enter the model directly as terms in the PBE while the adsorption acts implicitly by modulating surface excess and thereby the recoalescence efficiency. The equations used in the model are given in Table 1. A more thorough discussion including derivations of new additions can be found in Håkansson et al. (submitted for publication).

In summary the fragmentation can be said to be based on the turbulent fragmentation model of Martínez-Bazán, Montañés, and Lasheras (1999) using the difference between disruptive turbulent pressure and stabilizing Laplace pressure as defined by Walstra and Smulders (1998) as a driving force. This original model was extended with a term taking into effect the limited life time of turbulent eddies in comparison to the time it takes for deformation

Table 1
Model description of dynamic simulation model presented by Håkansson et al. (submitted for publication).

Phenomena	Sub type and description	Determining factor	Model
Fragmentation, $g = g_{TI} + g_{TV}$	Turbulent Inertial (TI) breakup	$\Delta\sigma_{TI} = \sigma_{turb,TI} - We_{cr} \cdot \sigma_{Laplace}$	$g_{TI} \propto \sqrt{\Delta\sigma_{TI}/d} \cdot T_{eddy/def}^{TI}$
	Turbulent Viscous (TV) breakup	$\Delta\sigma_{TV} = \sigma_{turb,TV} - Ca_{cr} \cdot \sigma_{Laplace}$	$g_{TV} \propto \sqrt{\Delta\sigma_{TV}/d} \cdot T_{eddy/def}^{TV}$
Recoalescence	Flocculation: orthokinetic (turbulence induced) and perikinetic (Brownian motion induced)	$\theta_x = 1 - (\Gamma(x)/\Gamma_{max})$	$\beta(v,u) \propto (N_{orthok}^{dd}(v,u) + N_{perik}^{dd}(v,u)) \cdot \theta_u \cdot \theta_v$
Adsorption of macromolecular emulsifier	Emulsifier adsorbing as a particle through orthokinetic (turbulence induced) and perikinetic (Brownian motion induced) collision events	$\theta_x = 1 - (\Gamma(x)/\Gamma_{max})$	$\partial\Gamma(v)/\partial t \propto (N_{orthok}^{ed}(v,u) + N_{perik}^{ed}(v,u)) \cdot \theta_v$

$\sigma_{turb,TI}$ = fragmentation pressure in régime TI [Pa], $\sigma_{turb,TV}$ = fragmentation pressure in régime TV [Pa], $\sigma_{Laplace}$ = Laplace pressure [Pa], We_{cr}/Ca_{cr} = Critical Weber/Capillary number [–], g_{TI}/g_{TV} = break-up frequency in régime TI/TV [Hz], $g = g_{TI} + g_{TV}$ = total break-up frequency [Hz], d = Drop diameter [m], $T_{eddy/def}^{TI}/T_{eddy/def}^{TV}$ = deformation time scale in régime TI/TV [–], β = recoalescence frequency [Hz], N_{orthok}^{dd} = frequency of orthokinetic drop–drop collisions [Hz], N_{perik}^{dd} = frequency of perikinetic drop–drop collisions [Hz], v/u = drop volumes [m³], Γ = adsorbed amount of emulsifier per surface area [kg/m²], Γ_{max} = Γ corresponding to complete surface coverage [kg/m²], N_{orthok}^{ed} = Frequency of orthokinetic emulsifier-drop collisions [Hz], N_{perik}^{ed} = frequency of perikinetic emulsifier-drop collisions [Hz].

of a viscous drop of oil, this factor is closely linked to the viscosities of continuous and disperse phase, factors that are theoretically (Walstra & Smulders, 1998) as well as experimentally (Pandolfe, 1981) proven to be of importance for homogenization results.

The recoalescence frequency is modeled as a drop–drop collision frequency including turbulent (Delichatsios & Probstein, 1977; Saffman & Turner, 1956) and Brownian collisions (Smoluchowski, 1916) multiplied with an efficiency factor based on the amount of drop surface uncovered by emulsifier assuming that the emulsifier generates a wall like repulsion and that it is immobilized at the interface. This is far from a mechanistic theory of the recoalescence event, but should rather be considered as a descriptive model.

Adsorption is modeled assuming that the macromolecular emulsifier can be described as particles and that the adsorption process is controlled by the collision frequency between the bare o/w interface and the emulsifier particles. A much similar model has been used by Nilsson and Bergenståhl (2006a). It is further assumed that the macromolecular emulsifier studied has a negligible effect on the surface energy of the oil–water system. This is modeled by a constant surface tension of 19 mN/m.

A simple one dimensional flow model to describe the turbulence intensity in form of the dissipation rate of turbulent kinetic energy (henceforth; turbulent dissipation rate, ε) is used, i.e. we assume that the spread of the turbulent wall jet is comparatively small, see Fig. 6b. The turbulent dissipation rate as a function of position in the active region of emulsification was derived based on the scale model velocity measurements of Innings and Trägårdh (2007), energy conservation derivations and an assumption of local equilibrium between production and dissipation of turbulent kinetic energy as shown by Håkansson et al. (submitted for publication). The scaling of the profile is given by an integral relation including a comparison to a theoretical expression for the total energy dissipation in a region from the gap outlet to twenty gap heights into the flow derived by Innings and Trägårdh (2007).

The gap height is an important parameter in describing the emulsification process, but it is only set implicitly in practical experiments to obtain the target homogenization pressure. The actual gap height evades measurements and instead the model of Phipps (1985) is used in this study to relate flow and pressure to gap height.

The obtained population balance equation was discretized by the fixed pivot technique (Kumar & Ramkrishna, 1996) yielding a system of ordinary differential equations and solved using MATLAB r2007a (Mathworks, Nantucket, USA).

The Sauter mean diameter, d_{32}, defined in Eq. (1) is used as a one dimensional measure of the drop size distribution.

$$d_{32} = \frac{\sum_{i=1}^{M} d_i^3 N_i}{\sum_{i=1}^{M} d_i^2 N_i} \tag{1}$$

In Eq. (1) d_i is the diameter and N_i is the number density of drops in size class i.

In order to interpret the result in relation to the flow geometry, a simplistic two dimensional stationary Computational Fluid Dynamic (CFD) model was set up over the outlet region in openFOAM (OpenCFD, Reading, UK) and solved for a qualitative representation of the flow field. A standard k–ε turbulence model (Jones & Launder, 1972) was used with a grid resolution of between 1/4 and 1/6 of a gap height. The k–ε turbulence model also assumes local equilibrium between the production and dissipation of turbulent kinetic energy. In the CFD model a one phase flow of water in the entire domain is assumed.

3. Results and discussion

This section is divided in five subsections. The first three sections present and discuss the results; in Section 3.1 the position

of fragmentation and recoalescence is examined, in Section 3.2 the effect on fragmentation and recoalescence strength from variations in operating conditions and in Section 3.3 the results are discussed in relation to a calculated velocity flow field. In the last two subsections the assumptions made in obtaining the models are discussed in relation to how they are likely to affect the generality of the results presented in the previous sections.

3.1. The occurrence of fragmentation and recoalescence zones

Both recoalescence and adsorption of macromolecular emulsifier are assumed to be induced by collision, for relevant temperatures ($\sim$60 °C) and drop sizes ($\sim$1 μm) turbulent collisions will dominate over the Brownian ones (Levich, 1962). Fragmentation is in turn assumed to be completely controlled by turbulent forces. Therefore the turbulent dissipation rate profile is important in interpreting the simulation results. The turbulent dissipation rate profile obtained from the one dimensional flow model is shown in Fig. 1 as a function of a flow coordinate, x, in the turbulent wall jet at the outlet of the gap made dimensionless by normalization with gap height, h. The results are shown for three different pressures. The maximum turbulent dissipation rate is obtained at the starting point of the developed turbulent jet. Based on the measurements of Innings and Trägårdh (2007) the starting point is assumed to be at 5h from the gap exit. From that point the rate decreases since the energy available in the flow decreases with distance from the gap, as inferred from experiments (Innings & Trägårdh, 2007). Homogenization pressure scales the profile without affecting its shape. The result in this study should naturally be seen in view of the assumption in this one dimensional ε-model.

In Fig. 2 a typical profile is compared to the development of Sauter mean diameter, d_{32} (defined in Eq. (1)), in the active region obtained from the simulation model (see Table 1). When the flow enters the turbulent region it instantly starts to fragment the disperse phase drops which are rapidly fragmented resulting in much smaller drops. Although also some recoalescence may occur in the zone, the total outcome of the processing is fragmentation. After approximately ten gap heights the fragmentation rate slows down, becomes equal to the particle growth and particle size reaches a minimum at a distance of 15 gap heights. From that point the second zone characterized by dominating recoalescence starts. The recoalescence will ultimately stop as the drops have reached a size distribution with complete surface coverage, but the simulations
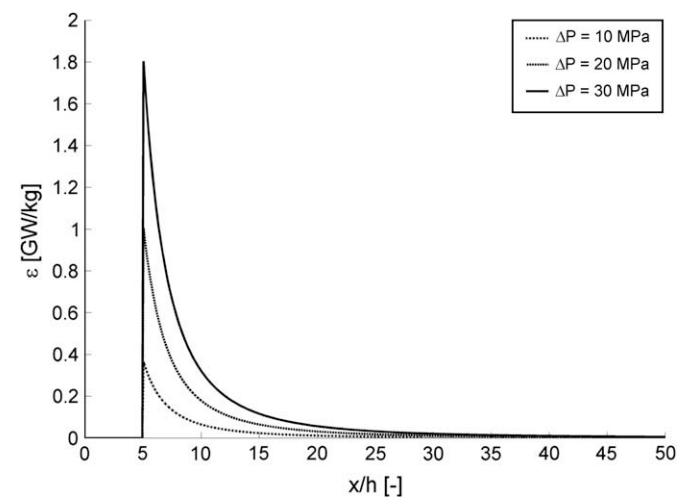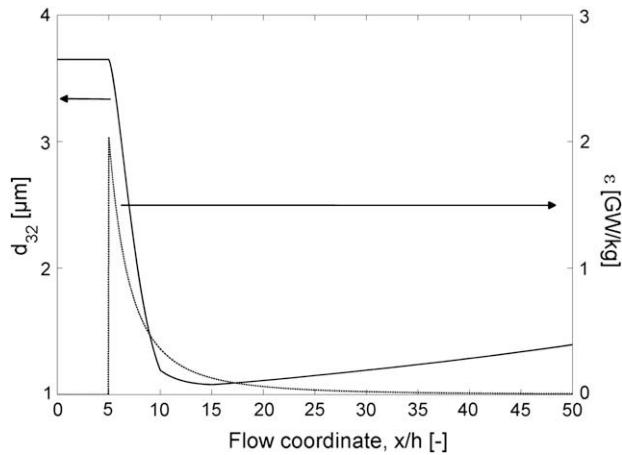

Fig. 1. Turbulent dissipation rate of kinetic energy, ε, as a function of flow coordinate, x normalized by gap height, h, in the turbulent jet at the outlet of the gap. Here shown for three different homogenization pressures.

Fig. 2. Comparison between simulated development of Sauter mean diameter, d_{32} (left), and turbulent dissipation rate, ε (right), as functions of normalized flow coordinate in the jet, x/h. Homogenization pressure, $\Delta P = 30$ MPa, volume fraction of oil, $\varphi_D = 10\%$ (v/v) and amount of emulsifier, $\varphi_E = 2\%$ (w/v of oil).

reveal that this will not happen until after several hundred gap heights from the gap outlet.

3.2. Influence of operating conditions on fragmentation and recoalescence zones

Of most practical interest for describing the effects of fragmentation and recoalescence on an emulsification event are the changes in the actual size distribution. Here we focus on the development of Sauter mean diameter, d_{32}, as seen in Fig. 2 as a description of the process.

In describing recoalescence one sometimes finds qualitative measures of recoalescence rate (Mohan & Narsimhan, 1997; Narsimhan & Goel, 2001). These could certainly be useful in cross-comparisons between different approaches but there is a difficulty in this kind of integral estimations since the recoalescence varies both in space, in the active region due to changes in turbulent dissipation rate, and with the size of the recoalescing drops. For a true system or for a dynamic model incorporating multiple droplet sizes as used in this study, obtaining a representative recoalescence rate is therefore not uncomplicated.

Fig. 3 shows the recoalescence behavior for three different homogenization pressures, shown as d_{32} development. Two clear
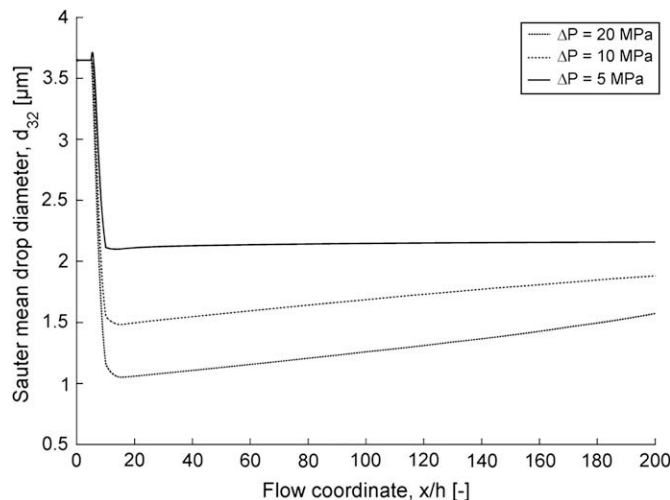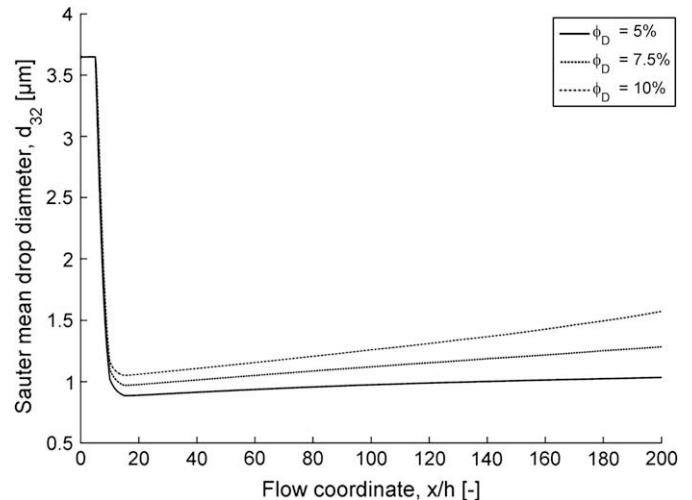
trends can be seen in the figure. First, an increase in pressure substantially lowers the minimal drop in size from approximately 2.1 μm to 1 μm when going from 5 to 20 MPa; however, the position of the minimum remains close to 15 gap heights from the exit of the gap. This is a reasonable result since the minimum drop size should be highly dependent on the amount of energy available for the emulsification and pressure level only scales the turbulent dissipation rate profile as could be seen in Fig. 1. Secondly the recoalescence contribution becomes more pronounced with higher pressures. This is in agreement with the experimental results (Floury et al., 2004; Mohan & Narsimhan, 1997; Narsimhan & Goel, 2001). Due to the smaller droplets obtained at high pressures, the orthokinetic collision rate is higher at higher pressures.

An interesting effect seen in the results is that the increase of recoalescence rate with pressure is most notable in the latter part of the flow, it can be seen that the slope of d_{32} is larger at $x = 200h$ than at $x = 40h$ and that this effect is most notable for the highest pressure. This effect can be explained from the turbulent dissipation rate profiles in Fig. 1. For higher pressure it will take longer for the turbulence intensity to shrink low enough to be totally dominated by the recoalescence as modeled here. For higher pressure, even if the fragmentation region stops at approximately the same position, fragmentation of recently coalesced droplets will continue to compete with the recoalescence for a longer period of time than at a lower pressure.

In Fig. 4 the effect of volume fraction of disperse phase can be seen. The recoalescence rate increases with volume fraction of oil as has also been shown by experiments on high pressure homogenizers (Floury et al., 2004; Mohan & Narsimhan, 1997; Narsimhan & Goel, 2001; Taisne et al., 1996). What cannot be seen in experiments is the increase also in the minimum drop size at the end of the recoalescence zone. When doubling the amount of oil from 5% to 10%, keeping the amount of emulsifier per volume of oil constant, the minimum drop size increases with almost 20%. Looking at the underlying model used in obtaining the simulations this could be interpreted as an effect of recoalescence in the fragmentation zone since the fragmentation rate is independent of volume fraction of oil while the orthokinetic recoalescence rate is proportional to the volume fraction. However, a higher volume of oil does also imply more drops of oil to be fragmented by the same amount of turbulent energy, for constant pressure, meaning that even if fragmentation rate in "number of collisions per time" is unaffected by the volume of oil, the proportion of drops being fragmented decrease with increasing amount of oil. Not captured in this model is the

Fig. 3. Development of Sauter drop diameter as a function of flow coordinate for different homogenization pressures ($\varphi_D = 10\%$ (v/v), $\varphi_E = 2\%$ (w/v of oil)).

Fig. 4. Development of Sauter drop diameter as a function of flow coordinate for different volume fractions of oil ($\Delta P = 20$ MPa, $\varphi_E = 2\%$ (w/v of oil)).

likely turbulence depression by increasing volume fractions of oil, this effect will most likely be of even larger importance for technical high pressure homogenizers (Walstra, 2005).

The effect from changes in the amount of emulsifier (expressed per volume of oil) was also studied with simulation results shown in Fig. 5. The emulsifier will decrease recoalescence rates which can be seen both in the simulation results in Fig. 5 and in experimental results (Floury et al., 2004; Mohan & Narsimhan, 1997; Narsimhan & Goel, 2001; Taisne et al., 1996). Even these relatively small variations in emulsifier concentration reduce the recoalescence rate considerably. In the fragmentation zone the emulsifier concentration seems to be quite unimportant. Since recoalescence is linearly dependent on surface coverage of emulsifier in our model, the relative unimportance of emulsifier concentration in this region implies low importance of recoalescence in the fragmentation zone.

3.3. The location of the active region in the homogenizer

Fig. 6 is drawing of the outlet of a high pressure homogenizer with some information on what is presently known about the flow field in the region. In Fig. 6a the schematic outline of the homogenizer can be seen, with forcer, seat and impact ring marked. (Note that the figure is not to scale and highly schematic.) Fig. 6b shows the resulting flow field, coloring by magnitude of local velocity, in the detail of the homogenizer known to contain the active region of homogenization, marked in Fig. 6a by a bold line rectangle. Light regions depict high speed and dark are low speed. As was reported by Innings and Trägårdh (2007) the flow exits the gap as a planar turbulent jet clinging to the forcer. A flow coordinate shown as a dark line ending with an arrow has also been included in the image to show the major flow direction, this should be interpreted as the *x*-axis shown in Figs. 1–5. Only the qualitative image is shown as more detailed information on the flow requires a substantially finer grid and more advanced modelling. The image shown in Fig. 6b is, however, highly consistent with the measurements from Innings and Trägårdh (2007) on a scale model.

The results discussed above can now be used to give a tentative description of the spatial division of the three processes; fragmentation, recoalescence and adsorption of a macromolecular emulsifier, based on the discussed model assumptions.

The emulsion droplets will be elongated in the high velocity gradients at the inlet of the gap but relax somewhat as they travel through the gap (Innings & Trägårdh, 2005). Upon exiting the gap

Fig. 5. Development of Sauter drop diameter as a function of flow coordinate for different amounts of emulsifier ($\Delta P = 20$ MPa, $\varphi_D = 10\%$ (v/v)).

they will first be transported for approximately 5*h* before the turbulence is developed. Between 5 and 15 gap heights out the fragmentation zone can be found. Here the drops are fragmented very fast to a minimum drop size mainly controlled by the homogenization pressure and the amount of energy thus supplied seen in relation to the amount of oil that needs to be fragmented. The simulation model indicates that recoalescence is not found to a significant amount in this zone. When compared to the break-up experiments of Innings and Trägårdh (2005) the fragmentation zone tends to be situated further away in the jet than seen in the simulations (Fig. 2). This discrepancy is probably due to the equilibrium condition on production and dissipation of turbulent kinetic energy of the turbulence model as discussed in Section 2.

After 15*h* the recoalescence grows strong enough to balance the fragmentation; creating the recoalescence region. Here the importance of the fragmentation processes is much smaller but as could be seen in Fig. 2, at high pressure the fragmentation delays the steepest recoalescence somewhat. As was seen in Figs. 3 and 4 the recoalescence rate in this region is controlled by the amount of emulsifier and volume fraction of oil. Increasing the homogenization pressure will also give a higher recoalescence rate.

An important factor that has been left out of the discussion above is the effect of boundaries such as walls on the flow and the models based on the flow. The graphs in Figs. 3–5 stop at 200*h* in the flow coordinate meaning that the flow continues without wall effects for 200 gap heights. Eventually the flow will reach the outlet piping. This distance as seen in Fig. 4 is approximately 60*h* but will differ with homogenizer model. In the model considered by Kleinig and Middelberg (1997) it is close to 70*h*.

3.4. Discussion on flow and fragmentation model improvement

As has been noted earlier, the results and specially the spatiality are highly dependent on the flow model used.

Two separate flow models are discussed in the study for various needs. First a simple one dimensional model based on empirical findings from particle velocimetry imaging measurements of Innings and Trägårdh (2007). This model is used in the emulsification simulations presented above. The model is a rough estimation of the true hydrodynamics of the system. Ideally the motion of individual eddies and pressure fluctuations of the chaotic turbulence at small scales should be used. The assumption of local equilibrium has been noted in Section 3.3 with the conclusion that it would probably move the point of maximal turbulent dissipation somewhat downstream.

The results on recoalescence being focused at a region far downstream of the fragmentation are dependent on the outlet jet being sufficiently focused in order to make the one dimensionality a reasonable simplification. If a substantial amount of drops were to escape into the surrounding liquid where the turbulent dissipation rate is much lower, the division would not be as sharp as in the simulation results. Therefore the CFD was used to examine the flow field in the relevant region as shown in Fig. 6b. Inspection of the flow velocity vectors shows a highly focused flow indicated by the flow coordinate in Fig. 6b. This was also measured by dividing each velocity vector on the line in two components, one parallel to it and one perpendicular to it. The length of the parallel component to the total length was used to measure its degree of focus. The average ratio is 99.4% with a standard deviation of 1.27%. The focus is close to 100% except where the jet moves towards the right wall at approximately $x = 15h$ where it decreases to ~95% and towards the end of the region (the focus has decreases to 93% at 60*h*). It should be stated that this analysis will overestimate the focus slightly since it only includes two dimensions, also the turbulence model used in this CFD is based on averaging, the true turbulent structures contain random fluctuations that will lead to a somewhat broader
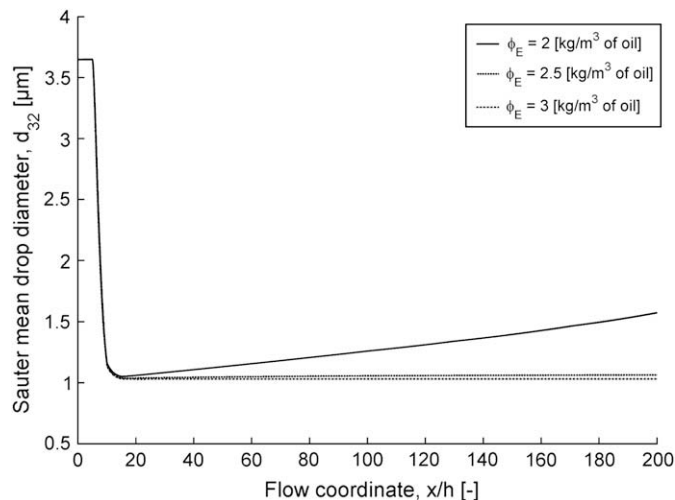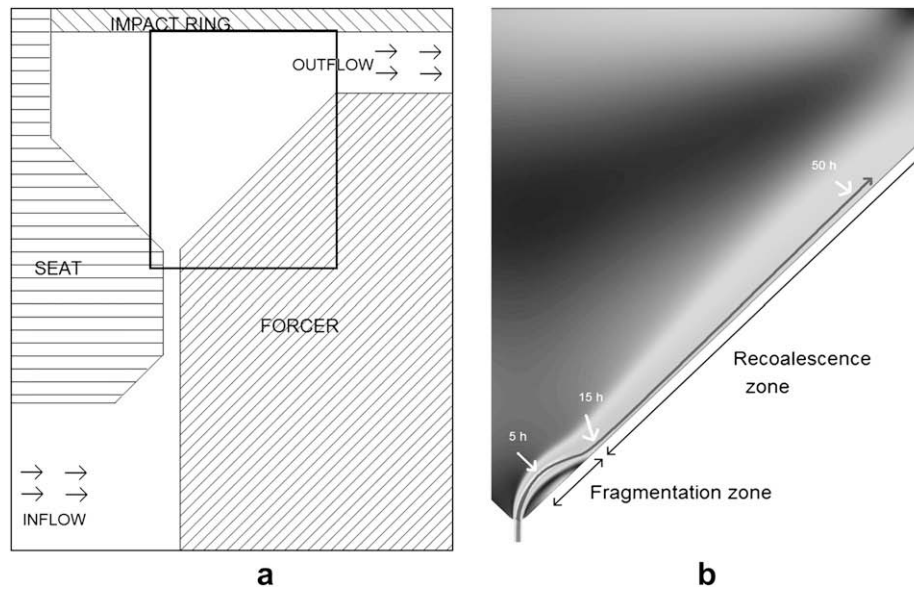
Fig. 6. To the left (a) is a schematic not to scale image of the gap region of a high pressure homogenizer showing a cross-section of the geometry with the lower line as axis of symmetry. To the right (b) is a flow field image showing the outline of the flow in the outlet obtained from a simplistic CFD, the corresponding part of the drawing in (a) has been marked with a bold box. The light regions in (b) are regions with high velocity. A black line (ending with an arrow) has been drawn to indicate the flow coordinate axis, x. Three positions $x = 5h$, $15h$ and $50h$ has been marked on the axis.

flow. Still the flow shows a high degree of flow direction focus, supporting the one dimensional representation used.

The relative convergence in fragmentation theories makes the uncertainties in this model smaller than for the recoalescence and adsorption (see Section 3.5). Still the models used only consider an average turbulent dissipation which is clearly a simplified way of looking at turbulence. For fragmentation treated in detail, including simulation of individual eddies interacting with the bubble interface, an extremely high resolution flow field is needed which lies outside of the scope of this study.

3.5. Discussion on recoalescence and adsorption model improvement

The model uses the percentage of free surface to control the recoalescence and adsorption efficiency, implying a wall like repulsion as the mechanism for drop stabilization by macromolecular emulsifiers. The basis of this simplistic approach is the unknown nature of the interactions between partially covered emulsion droplets under extreme hydrodynamic interactions and short time scale of the collision event.

A great number of mechanisms have been suggested for recoalescence hindering. Strong electrostatic forces would give a wall like repulsion. The importance of this mechanism can, however, be disputed. Walstra (2003) for example states that electrostatic forces can never be sufficiently strong for hindering drop coalescence since the stabilizing force due to the presence of emulsifier is in the order of 100 times weaker than the aggregating pressure under turbulent conditions in a high pressure homogenizer. This argument is based on the assumption of strong hydrodynamic forces in the region where recoalescence takes place, i.e. the holdup time in this intense region is sufficiently long to enable significant recoalescence and that the recoalescence is sufficiently fast in comparison to fragmentation. Given the turbulent dissipation profile as modeled here, the simulations show that recoalescence is scarce in this region. Instead the recoalescence is found in the latter part of the process, where the aggregation is so weak that it could be hindered by electrostatic repulsions. At 15 gap heights into the jet where recoalescence can be noticed in Fig. 2, the

dissipation rate is only about 6% of the maximal value, and at 50 gap heights it is down to 0.3%, levels for which even electrostatic interactions may have enough energy for stabilization against recoalescence.

A possible approach to describe the consequences on strong repulsive interactions of surface gradients is the Gibbs–Marangoni effect, explaining recoalescence hindering by a decrease in drop–drop film drainage for approaching drops due to interfacial gradients. Theoretical as well as experimental observations show a significant effect of this mechanism especially when micelle forming low molecular surfactants are used as emulsifiers (Walstra, 2005). Including these effects for the recoalescence efficiency will probably give rise to a stronger dependency on surface coverage than the proposed proportionality in Table 1. However, adding this stabilization mechanism will not alter the conclusion about separate fragmentation and recoalescence zones since it will most likely increase the stability in the high intensity zone. Adding a Gibbs–Marangoni model could lower the quite severe recoalescence seen in Figs. 3–5, to more modest levels, but since the trends in the study qualitatively agree well with experimental studies we do not expect them to alter the general trends in the results. No simple models for incorporating surface gradient mechanisms such as the Gibbs–Marangoni effects for dynamic modelling can be found in the literature, however, even the surface gradient based models may to some extent be approximated by the models used in this study. A surface with low surface coverage will give a less active surface rheology than a higher surface excess as can be seen by comparing Marangoni numbers (Walstra, 2005). The exact formulation could be disputed but the form in Table 1 should be able to give a first approximation even to these kinds of mechanisms.

The effect of various operating parameters studied in Section 3.2 shows that the models behave similarly to an experimental high pressure emulsification process, indicating it as a possible description given the hydrodynamics.

Adsorption of emulsifier at an oil-in-water interface will give rise to a decrease in surface tension and for many surfactants the effect is quite large. As described in Section 2 the results are therefore only valid for species where this effect is low, typically macromolecular emulsifiers such as a hydrophobically modified

starch. For species with a higher surface pressure, such as small surfactants, surface tension will decrease as adsorption proceeds, lowering the Laplace pressure and thus increase fragmentation. Compared to the constant value used in this study, including a dynamic surface tension will probably increase the break-up somewhat in the recoalescence zone. Including a relationship between surface excess increase and surface tension would be an interesting extension in order to model influence of emulsifier parameters.

In summary it is not unlikely that adsorbant mobility and dynamics due to adsorption, which is not included in the present model, have an effect on the emulsification process studied, though the extent is probably low when describing macromolecular emulsifiers which have a low interfacial pressure.

An important limitation in the present model is our inability to follow the final recoalescence level. A natural next step in improving the model and comparing the recoalescence to experiments is therefore to modify the PBE and its discretization to enable managing and tracking the simultaneous emulsification of two different types of oil drops and thereby being able to integrate a recoalescence rate that should be directly proportional to the experimentally measured rate by the technique of Taisne et al. (1996).

4. Conclusions

As has been shown, the simulation model presents a possibility to investigate, in a relatively direct way, the effects of adding together models for fragmentation, recoalescence and adsorption of macromolecular emulsifier on a simulated high pressure homogenization event.

The results are based on the assumptions used in the study like the simplified turbulent dissipation model, assumptions that the recoalescence is hindered mainly by a wall like repulsions for this type of emulsifiers, the collision induced adsorption and the effect of partial coverage. This leads to a very clear division between a fragmentation zone in the first part of the active region and a recoalescence zone further downstream. The fragmentation was seen to be controlled by the extent of homogenization pressure in relation to the amount of oil present and the recoalescence is affected by pressure, volume fraction of oil and amount of emulsifier.

It was further found that the general dependencies shown closely resemble the ones found in experimental studies, indicating that the proposed models can give valuable qualitative information on the emulsification process in a high pressure homogenizer.

Acknowledgements

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