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Dynamic Aroma Release from Complex Food Emulsions

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Abstract

In-vitro dynamic aroma release over oil-in-water (o/w) and water-in-oil-in-water (w/o/w) emulsions stabilised with Tween 20 or octenyl succinic anhydride (OSA) starch as a hydrophilic emulsifier and polyglycerol polyricinoleate (PGPR) as a hydrophobic emulsifier was investigated. The equal-molecular-weight hydrophilic aroma diacetyl (2,3-butanedione) or relatively-more-hydrophobic 3-pentanone was added to the emulsions prepared by high speed mixing, or membrane emulsification followed by thickened with xanthan gum removing droplet size distribution and creaming as variables affecting dynamic release. Results showed the differences of w/o/w emulsions in the dynamic release compared to o/w emulsions mainly depended on aroma hydrophobicity, emulsion type, emulsifier-aroma interactions and creaming. Xanthan led to a reduced headspace replenishment. Interfacially adsorbed OSA starch and xanthan-OSA starch interaction influenced diacetyl release over emulsions. OSA starch alone interacted with 3-pentanone. This study demonstrates the potential impact of emulsifying and thickening systems on aroma release systems and highlights that specific interactions may compromise product quality.

Keywords: dynamic aroma release; OSA starch; xanthan gum; w/o/w emulsions

Introduction

The aroma of a processed food is one of the key quality parameters for its success in the market place, and aroma release over simple oil-in-water (o/w) emulsions (for example, milk, cream, mayonnaise, salad dressing)[1] has been studied widely.[2-9] Complex water-in-oil-in-water (w/o/w) emulsions are emulsions where the oil phase of o/w emulsions is partly replaced by an inner aqueous phase. Due to the complex structure, w/o/w systems can be used for bioactive encapsulation.[10, 11] w/o/w emulsions have been shown to have advantages over o/w emulsions for fat reduction[12, 13] and salt reduction.[14, 15] Although food applications in low calorie cream or fat-reduced mayonnaise,[16] fat substitutes in meat emulsions,[17] substitutes for dairy fat in cheese[12] and so on have been reported, compared to o/w emulsions aroma release over w/o/w emulsions has obtained far less attention in the published literature.[18, 19] This might be at least in part due to the fact that w/o/w emulsions are more difficult to stabilise than o/w emulsions. For the successful application in low-fat and salt-reduced foods, an understanding of their aroma release properties is desirable.

The consumption of a food is a dynamic process as air is continuously exhaled and inhaled, rendering the acquisition of dynamic aroma release profiles more relevant to real foods, compared to static methods. If the dynamic aroma release is only affected by oil, the ability of an aroma compound to replenish a diluting headspace can be predicted by the equilibrium headspace partition coefficient (water: air-water partition coefficient K_{aw}; emulsions: air-emulsion partition coefficient K_{ae}).[20, 21] A low K_{aw} or K_{ae} value will lead to a more stable headspace concentration against headspace dilution.[20, 21] In that case, K_{ae} is calculated by Eq.1:[22]

$$K_{ae} = \frac{1}{(\frac{\Phi_o}{K_{ao}} + \frac{\Phi_w}{K_{aw}})} \quad \text{Eq.1}$$

where Φ_o and Φ_w are the oil and water volume fraction respectively, K_{ao} is the air-oil partition coefficient.

If there are other non-volatile solute-aroma interactions that limit aroma release to the headspace, the hypothesis is that there would be differences in the headspace replenishment compared to the prediction by K_{ae} above. Factors such as emulsion composition and aroma hydrophobicity (the octanol-water partition coefficient, log P or log K_{ow}) influence dynamic aroma release over o/w emulsions.[3, 4, 6-9] With regard to the impact of emulsion droplet size, dispersed volume fraction and emulsifier concentration on dynamic aroma release, published literature paints a controversial picture. On one hand side these factors are reported to have no impact,[4, 6] on the other hand side impact of droplet size, affecting emulsion viscosity, on dynamic aroma release has been reported.[3] Further, decreasing release rates with increasing fat level,[9] decreasing lipophilicity[9] and increasing gel strength[8] for lipophilic compounds have been reported. Undoubtedly, emulsifiers may interact with aroma compounds. For example, micelles of low molecular weight (LMW) surfactants forming above their critical micelle concentration in solution can solubilise hydrophobic[23, 24] or hydrophilic[25] molecules, or aroma compounds as of interest in this study, in their core. Polymeric emulsifiers such as starches are known to interact with aroma compounds[26, 27]. The suggested mechanisms is via hydrogen bonding between the hydrophilic aroma compounds and the hydroxyl groups of starch,[28] or inclusion complexes between the hydrophobic aroma compounds and amylose.[29] A consequence of these interactions is that, when used as emulsifier, the relative distribution of interfacially adsorbed to non-adsorbed starch can affect aroma distribution in emulsions and the headspace.[24, 30-32] This ratio is affected by the total surface area of the dispersed

emulsion phase, thus the droplet size characteristics for emulsions formulated at the same dispersed phase volume. Nonetheless, there is a lack of understanding of how those factors impact on dynamic release over w/o/w emulsions and their release behaviour compared to o/w emulsions.

In this study, *in-vitro* dynamic headspace analysis was carried out to evaluate the replenishment of two selected aroma compounds into the gas phase over w/o/w emulsions compared to o/w emulsions during headspace dilution. Water controls were also analysed to identify whether the emulsifier impacted dynamic aroma release. The overall aim of this study was to investigate the dynamic aroma release behaviour in fat-reduced complex food emulsions, w/o/w emulsions compared to o/w emulsions, and explore the emulsifier-aroma interaction as well as emulsion microstructure (size distribution, droplet size, specific surface area, Span and creaming) influence on dynamic release.

Materials and methods

Materials and sample composition

The oil phase in the emulsions comprised sunflower oil (density: 0.916±0.003 g/cm^3; viscosity presented in supporting information Table S1) purchased from a local supermarket. All aqueous phases were prepared with deionised water unless otherwise stated. Polyoxyethylene 20 sorbitan monolaurate (Tween 20) (HLB = 16.7), diacetyl, 3-pentanone and sodium azide, added to prevent microbial spoilage, were obtained from Sigma Aldrich (Gillingham, UK), polyglycerol polyricinoleate PGPR (PGPR 90) from Danisco (Kettering, UK), octenyl succinic anhydride (OSA) starch (N-creamer 46) from Univar (Widnes, UK) and

xanthan gum (Keltrol RD) from CP Kelco (San Diego, USA). Sodium chloride to aid microstructure stabilisation[33] was purchased from Fisher Scientific (Loughborough, UK). All concentrations are provided on a weight by weight basis, unless stated otherwise.

The composition of all liquid samples is listed in Table 1. Two hydrophilic emulsifiers including the LMW surfactant Tween 20[33, 34] and the polymeric emulsifier OSA starch[14, 15] to stabilise the external w/o/w emulsion interface were selected in this study to assess the interaction of hydrophilic emulsifier type with aroma compounds and its impact on dynamic aroma release. PGPR was chosen as the hydrophobic emulsifier due to most successfully stabilising w/o/w emulsions.[35] Simple o/w emulsions were included in the experimental design to compare with w/o/w emulsions, formulated at the same dispersed phase volume of o and w/o respectively in the emulsion system. Emulsions were initially processed with a high speed mixer. Then, emulsions were also processed via a previously reported stirred cell membrane emulsification,[34] thereby removing droplet size variation as a factor impacting aroma release. Since our initial analysis of the high speed processed emulsions suggested that droplet creaming, which was observed for all emulsions produced, might have affected aroma release, creaming was suppressed in the membrane processed emulsions by adding the viscosifying agent xanthan gum. At the same time, PGPR was added also to the oil phase of the o/w emulsions, although not required to stabilise an internalised aqueous phase, in order to retain similarity in formulation for better comparison of the aroma release results. The thickened emulsions had a comparatively lower dispersed phase volume due to the method of preparation, outlined in the following.

Preparation of emulsions by high shear mixing

w/o/w emulsions

A two-step emulsification method with a batch high speed overhead mixer (L5M fitted with emulsor screen, Silverson, Chesham, UK) was used to produce the w/o/w emulsions. Initially, the internal w_1/o emulsion was prepared by slowly adding w_1 into oil while mixing at 7000 rpm for 4 min and cooling the process beaker (4-6 °C). Batch size was kept constant at 100 g with a ratio of w_1:o of 2:3. This primary w/o emulsion was then added to w_2 during mixing at 6700 rpm for 4 min while cooling (4-6 °C). Batch size was also 100 g with a ratio of w_1/o:w_2 of 3:7. Finally, 1 mL of aqueous sodium azide solution was added to the w/o/w emulsions to obtain a final sodium azide concentration of 0.02% and the emulsion was stored at room temperature (21 ± 5 °C) until further use.

o/w emulsions and water controls

o/w emulsions manufactured by high speed mixing were prepared by adding the oil to the water. The same high speed overhead mixer as for preparation of the w/o/w emulsions was used, operated at 6700 rpm for 4 min while cooling (4-6 °C). The mixing ratio of oil to water was 3:7 and batches of 100 g were processed. The water controls contained Tween 20 or OSA starch as the hydrophilic emulsifier at the same concentration as the external water phase of w/o/w emulsions.

Preparation of xanthan gum thickened emulsions with stirred cell membrane emulsification

w/o/w emulsions

w/o/w emulsions were manufactured in two steps followed by the addition of xanthan gum. First, w/o emulsions were produced by slowly adding w_1 into o under high shear mixing (Ultra Turrax, model T25, IKA Works, Staufen, Germany) at 24000 rpm for 5 min while cooling the process beaker (4-6°C). Batch size was kept constant at 100 g with a ratio of w_1:o of 2:3. The w/o/w emulsions were then manufactured using stirred cell membrane emulsification. w/o emulsions were injected through a microporous membrane surface into the external aqueous phase stirred by a paddle stirrer. Maximum shear stress at the membrane surface was controlled by the rotational speed. The experimental conditions were a maximum shear stress of 14 and 36 Pa for the continuous aqueous phase containing Tween 20 and OSA starch respectively, and a constant w/o emulsion injection speed of 1 mL min^{-1} corresponding to a transmembrane flux of 70 L h^{-1} m^{-2}. The experiments were run until the dispersed phase volume fraction reached 30 vol.% as determined by reading from the syringe scale. Batches of 100 g were prepared, transferred into a glass beaker followed by the addition of 1 mL of aqueous sodium azide solution to obtain a final sodium azide concentration of 0.02% and stored at room temperature (21 ± 5 °C) until further use.

o/w emulsions

o/w emulsions manufactured by stirred cell membrane emulsification were prepared following the actual membrane emulsification step of preparing the w/o/w emulsions, with the difference that the dispersed phase corresponded to a single oil phase. In order to obtain a droplet size similar to that of the w/o/w emulsions, the process parameters were tested in preliminary experiments. These were a maximum shear stress at the membrane surface of 10

Pa and 36 Pa respectively for Tween 20 and OSA starch as emulsifier, and an oil phase injection speed of 1 mL min^{-1}.

Xanthan gum solution preparation and addition

A 1% xanthan gum solution was prepared and added to the membrane processed w/o/w and o/w emulsions as follows. Initially, the appropriate amount of xanthan gum was dispersed into 0.1 M NaCl and 0.02% sodium azide solution pre-heated to 80 °C while stirring at 1500 rpm with an overhead mixer (RW20 fitted with a Propeller 4-bladed stirrer, IKA, Staufen, Germany). Temperature was maintained at 80°C during 1 h of mixing after which the solution was allowed to cool down at room temperature and left overnight for complete hydration before use. 70 g of xanthan gum solution was then added to 100 g of membrane processed emulsion sample contained in a 600 mL glass beaker followed by mixing at 600 rpm on a magnetic stirrer for 30 min. The resulting xanthan gum concentration in the external aqueous phase of the w/o/w and o/w emulsions was 0.5%.

To prepare the xanthan gum thickened water controls, 100 g of the xanthan gum solution was mixed with 100 g of w_2 at 600 rpm to also obtain a final xanthan gum concentration of 0.5%.

Emulsion characterisation

Emulsions were analysed immediately after manufacturing and then regularly during 6-day storage at room temperature (21 ± 5 °C).

173 Microscopy

174 The microstructure of the w/o/w and o/w emulsions was visualised using bright field
175 microscopy (EVOS FL, Life Technologies, USA). Slides were prepared by placing a small drop
176 of emulsion diluted with water onto a glass slide and placed onto the optical stage without
177 adding cover slips. Objective lenses x4, x10 and x20 were fitted and at least three randomly
178 selected areas of each slide were imaged with each objective. Three slides were prepared for
179 each emulsion.

180

181 Droplet size measurement

182 Droplet size distributions were acquired with a laser diffraction particle size analyser
183 (Beckman-Coulter LS 13 320, Meritics Ltd, Dunstable, UK) fitted with a dispersion cell
184 containing deionized water. Measurement set up and analysis was controlled by the
185 instrument's software package. Once the emulsion was dispersed in the water, three
186 measurements were taken and the raw data was averaged before analysis based on the input
187 of the refractive indices of the dispersion medium (water; 1.33) and the dispersed phase (oil;
188 1.47). The absorption value of the dispersed phase was set to 0. Samples were prepared in
189 triplicates. The results are reported as the averaged droplet size distributions on a volume
190 basis, the mean droplet size on a volume basis ($d_{4,3}$), the specific surface area (SSA) and the
191 span of the monomodal size distributions.

192

193 *In-vitro* dynamic headspace analysis

194 A volume (95 mL) of w/o/w emulsion or o/w emulsion or water control were placed into a
195 134 mL total volume glass bottle with a 25 x 6 mm magnetic stirrer bar at the bottom and
196 stored at room temperature. Diacetyl or 3-pentanone was added to the liquid samples after,
197 rather than prior to, emulsion preparation, including addition of xanthan gum to the
198 membrane processed emulsions, in order to reduce aroma loss during processing due to
199 exposure to open air. These two aroma compounds were selected as they vary in log P (the
200 hydrophilic aroma, diacetyl: -1.34; the relatively more hydrophobic aroma, 3-pentanone: 0.75
201 estimated from EPI SUITE (EPA's and Syracuse Research Corp., USA) at 20 °C) whilst being
202 equal in molecular weight (diacetyl: 86.09 g/mol; 3-pentanone: 86.13 g/mol) to eliminate the
203 effect of molecular mass on aroma release. 400 µL L^{-1} of aroma standard solution containing
204 0.1 M NaCl was prepared in a 100 mL volumetric flask. 5 mL of the aroma standard solution
205 was added into each bottle to obtain a final aroma concentration of 20 µL L^{-1} in the liquid
206 sample and a headspace volume of 34 mL. The bottles were immediately sealed and stirred
207 at 200 rpm for 1 min to ensure rapid distribution of the aroma compounds before the dynamic
208 headspace analysis. Samples were then allowed to equilibrate for at least 4 h at room
209 temperature (21 ± 5 °C) to equilibrate aroma distribution between liquid and headspace. 4 h
210 was chosen because it was the minimum time required for the aromas to reach equilibrium,
211 as determined in preliminary tests. Samples were prepared in triplicate.

212 To dilute the headspace, nitrogen gas (N_2) was introduced into the bottle at a flow rate of 70
213 mL min^{-1} measured using an electronic flow meter (vary-flow 500, Agilent Technologies,
214 Berkshire, UK). 5 mL min^{-1} of the gas phase was sampled into the APCI-MS (Ultima Micromass,
215 Manchester, UK) over 10 min. The transfer line to the mass spectrometer was heated (140 °C)
216 and the source was operated in positive ionisation mode (4kV corona discharge). The
217 compounds were measured in selected ion mode at 87 mz^{-1} (molecular weight +1) with a

dwell time of 0.1 s. Raw data was exported to Excel (Microsoft Corporation) and graphs were plotted as the average headspace intensity (%). The first peak of average headspace intensity was set to 100%. The points measured after the first peak were divided by the first peak of average headspace intensity.

Statistics

The mean values and their standard deviations were calculated using the spreadsheet software Microsoft Excel. Statistical analysis of the dynamic headspace intensity by MANOVA statistical analysis with least significant difference (LSD) post hoc test ($p < 0.05$) using the SPSS software (IBM Statistics 21, USA) at 2, 5 and 9 min, as early, mid and late stage of dynamic headspace analysis was carried out to explore significant differences in data sets.

Results and discussion

Emulsion characteristics

The o/w and w/o/w emulsions, stabilised with Tween 20 or OSA starch and processed by high speed or membrane emulsification, were viewed under a bright field microscope and it was confirmed that the expected emulsion structure had formed. The oil continuous droplet phase of the w/o/w emulsions showed their previously noted characteristic dark appearance (micrographs shown in supporting information Figure S1).[36] The volume based droplet size distributions of all of the prepared o/w and w/o/w emulsions are presented in Figure 1.

The droplet size distribution of each type of the high speed mixed emulsions (Figure 1A) was not affected by the choice of emulsifier. This indicates that the outcome of the high speed

process was controlled by the processing parameters rather than the emulsifier type and its concentration. The droplet size distributions were broad showing a shoulder at smaller droplet diameters, which was more pronounced for the o/w emulsions and shifted slightly to larger droplet diameters for the w/o/w emulsions. With around 20 μm, the main distribution peak of the w/o/w emulsions was also slightly larger compared to 10 μm for the o/w emulsions. Since the same processing conditions were used for emulsifying the oil and the w/o into their respective external emulsion phase, it can only be concluded that the increased viscosity of the o/w emulsion compared to the oil (see supporting information Table 1), and the additional presence of PGPR in the oil phase of the w/o/w emulsion led to this result. As a consequence of these differences in droplet size distribution between the o/w and w/o/w emulsions, the specific surface area of the oil droplets was larger in the case of the o/w emulsions and thus the proportion of adsorbed emulsifier rendering the interpretation of aroma release data in terms of aroma-emulsifier interactions challenging.

The droplet size distributions of the xanthan gum thickened membrane processed emulsions (Figure 1B) were monomodal and the volume based mean diameter, $d_{4,3}$, of all of these emulsions was approximately 60-70 μm resulting in the specific surface area of around 0.1 m^2 mL^{-1}, independent of the type of emulsion. Both types of Tween 20 stabilised emulsions had a span of around 0.6, whereas both types of OSA starch stabilised emulsions had slightly larger span of approximately 0.7.

All emulsions were tested in terms of microstructure stability by checking droplet size distribution over a storage period of 6 days, during which the aroma release experiments were conducted. There were no changes for any of the emulsions (data not shown for the sake of brevity).

263

264 Dynamic headspace analysis

265 The theoretical equilibrium headspace partition coefficients (K_{ae}) calculated by Eq.1 are
266 reported in Table 2. According to Table 2, it is expected that if there were only oil-aroma
267 interactions, diacetyl would most easily replenish the diluting headspace over water controls,
268 then w/o/w and finally o/w emulsions. This would be the opposite for 3-pentanone. If the
269 headspace replenishment did not meet that predicted by K_{ae}, this would suggest emulsifier-
270 aroma interactions and an impact of emulsion microstructure on dynamic release.

271 The first peak in the dynamic headspace analysis was effectively representative of the
272 undiluted headspace and therefore regarded as the equilibrium headspace intensity, which
273 was set to 100%. Afterwards the equilibrium was disturbed during headspace dilution, so the
274 headspace intensity decreased over the course of the measurement. The values shown in the
275 following were normalised by the first peak headspace intensity (signal = 100%).

276

277 High speed mixed emulsions

278 *Diacetyl*

279 Figures 2A and B show the changes of dynamic headspace intensity of diacetyl over water,
280 the water controls and the emulsions for Tween 20 and OSA starch as emulsifier respectively.
281 Across all samples, the diacetyl headspace intensity decreased by 20 to 40% during headspace
282 dilution. Over water and water containing emulsifier (water controls), the diacetyl headspace
283 intensity decreased initially but then stabilised at approximately 80%. According to the
284 statistics reported in Table 3, the headspace concentration of all emulsions was significantly

lower than that over water at 9 min ($p < 0.05$). This behaviour was expected because emulsions had higher air-emulsion partition coefficients than water as reported in Table 2.

Diacetyl initially showed less replenishment into the headspace over the o/w and w/o/w emulsions than water controls. Then the intensity of diacetyl progressively decreased more than over the water controls, without asymptotically reaching an equilibrium value. In Table 3, at 2 min and for Tween 20 as surfactant, the diacetyl concentration over the o/w emulsion was higher than that over the w/o/w emulsion ($p < 0.05$). Thus, the fat-reduced w/o/w emulsion system showed an inhibition of the dynamic diacetyl release compared to the o/w emulsion.

Aroma release under dynamic condition is mainly affected by the air-liquid interface, as this interface replenishes the headspace with volatile compounds as the headspace is diluted. All of the high speed mixed emulsions creamed; a cream phase on top and a serum phase at bottom was observed visually. Hence, underneath the layer of emulsifier molecules at the air-emulsion interface there was a layer of creamed oil droplets representing an additional barrier affecting aroma release. Due to the broad droplet size distribution (Figure 1), the creamed layer of oil droplets would have contained larger droplets towards its top and smaller droplet towards its bottom. So the higher diacetyl release over the o/w emulsion contrary to expectation was probably due to the cream layer acting as a barrier for diacetyl movement from the continuous water phase underneath the creamed oil droplets. The thickness of the cream layer was different between the emulsions due to the difference in the droplet size, size distribution and density in addition to the viscosity of the continuous phase. The w/o/w emulsions had a thicker cream layer due to their larger main distribution peak compared to the o/w emulsions (Figure 1), leading to the poorer headspace

replenishment of diacetyl over the w/o/w emulsions. Another reason could be the presence of PGPR in the oil phase of the w/o/w emulsions, which was absent in the o/w emulsions. PGPR could have trapped diacetyl molecules, partitioned into the oil phase, in the hydrophilic core of their micelles thereby slowing transfer into the aqueous phase as a result of equilibrium disturbance and ultimately aroma release.

However, the release of diacetyl over the o/w emulsion and the w/o/w emulsion was not different for the OSA starch as emulsifier (Table 3). Hence, the w/o/w emulsion had a similar ability to maintain the headspace concentration of diacetyl as the o/w emulsion. This could be because diacetyl interacted with the interfacially adsorbed starch at the oil-water interface. There was a higher amount of the starch adsorbed at the creamed oil droplet interface of o/w emulsions than that of the w/o/w emulsions due to its smaller main distribution peak (Figure 1) resulting in a larger SSA of o/w emulsions, which led to no significant difference in the diacetyl release over OSA starch stabilised o/w and w/o/w emulsions.

In summary, the dynamic release behaviour of diacetyl over high speed mixed emulsions was mainly driven by emulsion type, creaming resulting from the broad droplet size distribution and SSA of the emulsion characteristics and diacetyl-OSA starch interactions.

3-pentanone

Figures 2C and D show the changes of dynamic headspace intensity of 3-pentanone over emulsions and water controls. The headspace intensity decreased by 20% to 60 % for 3-pentanone during headspace dilution for all samples. This was more than for diacetyl (Figures 2A and B), the lower headspace replenishment would be caused by 3-pentanone's higher K_{aw}

compared to diacetyl (Table 2). The water control and the emulsifier alone showed an initial major decrease in headspace intensity, which stabilised at about 40%. As expected in Table 2, they had the lowest headspace 3-pentanone intensity over time, which suggests the weakest headspace replenishment among all samples. As reported in Table 4, OSA starch alone led to a significant decrease in the dynamic headspace intensity compared to the water control at 2, 5 and 9 min ($p < 0.05$), which suggests an interaction of starch with 3-pentanone possibly through hydrophobic interaction or a starch barrier effect at the air-water interface reducing volatile movement.

According to Figures 2C and D and Table 4, 3-pentanone had the strongest headspace replenishment ($p < 0.05$) over the o/w emulsions over 10 min without asymptotically reaching an equilibrium value, then w/o/w emulsions and last water. It met the expectation as K_{ae} predicts in Table 2. It has been reported previously that an o/w emulsion system stabilised the hydrophobic aroma headspace concentration during headspace dilution relative to the water system[37, 38] as a direct result of the emulsion decreasing the air-liquid partition coefficient. There was no significant difference among o/w or w/o/w emulsions (Table 4). This is probably due to 3-pentanone favouring oil so the oil phase played a major role in 3-pentanone release and the hydrophilic emulsifier type could not limit the headspace intensity. The cream layer of the emulsions could facilitate the replenishment of 3-pentanone into the gas phase during headspace dilution.

Thus, the dynamic release behaviour of 3-pentanone over high speed mixed emulsions was mainly driven by emulsion type and creaming.

353 Membrane processed and xanthan gum thickened emulsions

354 *Diacetyl*

355 Figures 3A and B reveal the dynamic headspace release of diacetyl over xanthan gum-
356 thickened samples. The headspace intensity decreased by approximately 40% for diacetyl
357 during dilution for all samples. All samples showed a progressive decrease in the headspace
358 intensity without asymptotically reaching an equilibrium value. The xanthan gum thickened
359 water had a lower headspace intensity at mid and late stage compared to water in the
360 absence of xanthan gum (Figures 2A and B). This was probably caused by the xanthan gum
361 increasing the viscosity of the water (supporting information Table S1) such that the xanthan
362 gum network at the air-water interface delayed the release of diacetyl. It has been reported
363 that significant binding of all tested compounds (diacetyl, 1-octen-3-ol, diallyl sulfide, diallyl
364 disulfide) occurred at 0.1% xanthan under equilibrium headspace analysis and hydrogen
365 bonding was found in 1-octen-3-ol-xanthan interactions by exclusion chromatography.[39] It
366 can be speculated that hydrogen bonding between diacetyl and xanthan gum may also have
367 occurred.

368 For Tween 20 (Table 5), diacetyl showed the most stable headspace intensity over water and
369 Tween 20 alone, then w/o/w and last o/w emulsions. This is as expected on the basis of the
370 K_{ae} values. For the membrane emulsification processed and xanthan gum thickened
371 emulsions, creaming was reduced due to the increased viscosity of the continuous aqueous
372 phase (supporting information Table S1). The impact of emulsion microstructure on dynamic
373 release was also minimised because all the emulsions had a similar size distribution (Figure
374 1), droplet size, SSA and a low Span. The emulsion droplets were homogenously dispersed in

375 the continuous water phase. Hence, oil was the only factor influencing on the diacetyl release
376 over water and emulsions in the presence of Tween 20.

377 For OSA starch (Table 5), the OSA starch and xanthan gum water control showed a
378 significantly lower headspace concentration than the xanthan gum alone only at 2 min ($p <$
379 0.05), which indicates an interaction of diacetyl with OSA starch or with OSA starch and
380 xanthan gum. It was reported above that there was no interaction of diacetyl with OSA starch
381 under dynamic headspace conditions in the absence of xanthan gum. Therefore, this
382 interaction of diacetyl was associated with xanthan gum and OSA starch. Furthermore, the
383 viscosity of these water controls and emulsions was measured revealing an interaction of
384 xanthan gum with OSA starch as its addition lowered the viscosity of the xanthan gum
385 (supporting information Table S1). Thus, a xanthan gum-OSA starch interaction influenced the
386 dynamic release of diacetyl. However, there was no significant difference among o/w or
387 w/o/w emulsions. Hence, interaction of diacetyl with xanthan gum and OSA starch appeared
388 to be absent in o/w and w/o/w emulsions (Table 5). It is worth noting thought that in the
389 presence of xanthan gum the viscosity of the OSA starch stabilised emulsions was lower
390 compared to those stabilised with Tween 20 (supporting information Table S1). Consequently,
391 while xanthan gum-OSA starch interactions are evident, these did not impact on the dynamic
392 release of diacetyl in the emulsion systems whereas they did in the control system. Further
393 detailed analysis of this system is required to understand why the fact that a proportion of
394 the OSA starch molecules adsorbed at the oil droplet interface, therefore not available to
395 interact with xanthan gum, might be the reason for the dynamic release of diacetyl
396 observation.

Hence, the dynamic release behaviour of diacetyl over membrane processed and xanthan gum thickened emulsions was mainly driven by emulsion type and interactions between diacetyl and xanthan-OSA starch association.

3-pentanone

Figures 3C and D show the changes of dynamic headspace of 3-pentanone over xanthan gum thickened samples. The headspace intensity decreased by approximately 60% for 3-pentanone during dilution for all samples. All samples also showed a progressive decrease in the headspace intensity without asymptotically reaching an equilibrium value. The xanthan gum thickened emulsions had no difference in dynamic headspace intensity with the xanthan gum solution (Table 6). They also showed a much weaker resistance to dilution compared with the high speed mixed emulsions (Figure 2C and D). This may have been due to diffusion barriers that limited headspace replenishment,[8] or increased viscosity[40] that decreased droplet mobility, or, abundance of droplets at the air-emulsion interface. The droplets in high speed mixed emulsions on the other hand were more mobile as these emulsions were not thickened and 3-pentanone continually released into the headspace. There was no significant factor influencing the dynamic release behaviour of 3-pentanone over membrane processed and xanthan gum thickened emulsions.

Conclusions

The conclusions that could be drawn based on the experimental data acquired in this study are summarised in Table 7. Xanthan gum led to a reduced aroma headspace replenishment

mainly due to the effect of increased viscosity. OSA starch alone interacted with 3-pentanone possibly through hydrophobic interaction or a starch barrier effect. Dynamic diacetyl release was affected by the OSA starch adsorbed at the oil-water interface and xanthan gum-OSA starch interaction. This study demonstrates the potential impact of emulsifying and thickening systems on aroma release systems and highlights that specific interactions may compromise product quality.

Acknowledgement and Declaration

Pu acknowledges a scholarship from China Scholarship Council (CSC).

Supporting Information

Micrographs of high speed mixed or membrane processed and xanthan thickened w/o/w and o/w emulsions, see Figure S1.

Viscosity results of oil and external water phase of w/o/w emulsions and xanthan gum thickened w/o/w emulsions, see Table S1.

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547 List of figure captions

548 Figure 1 Averaged droplet size distributions on a volume basis of A) high speed mixed or B)
549 membrane processed and xanthan thickened o/w (ow) and w/o/w (wow) emulsions stabilised
550 with Tween 20 (T) or OSA starch (S): □ Day of making; ▩ Day 6.

551

552 Figure 2 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan
553 gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,
554 C) Tween 20 (T) or B, D) OSA starch (S). Values are based on 3 replicates.

555

556 Figure 3 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan
557 gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,
558 C) Tween 20 (T) or B, D) OSA starch (S) in the absence or presence of xanthan gum (XG). Values
559 are based on 3 replicates.

560

Table 1 Composition of w/o/w and o/w emulsions and water control. w_1: the internal water phase. w_2: the external water phase. T20: Tween 20. S: OSA starch. XG: xanthan gum. For each emulsion, the dispersed phase mass fraction of the xanthan gum thickened membrane processed emulsions lowered compared to that of high shear mixed emulsions due to the experiment design.

sample ID	w_1 (wt.%)	composition of w_1	oil (wt.%)	composition of oil	w_2 (wt.%)	composition of w_2
wT	-	-	-	-	100	2% T20, 0.1 M NaCl
wS	-	-	-	-	100	4% S, 0.1 M NaCl
owT	-	-	30	-	70	2% T20
owS	-	-	30	-	70	4% S
wowT	12	0.1 M NaCl	18	4% PGPR	70	2% T20, 0.1 M NaCl
wowS	12	0.1 M NaCl	18	4% PGPR	70	4% S, 0.1 M NaCl
XG	-	-	-	-	100	0.5 % XG
wT+XG	-	-	-	-	100	2% T20, 0.1 M NaCl, 0.5 % XG
wS+XG	-	-	-	-	100	4% S, 0.1 M NaCl, 0.5 % XG
owT+XG	-	-	18	4% PGPR	82	1% T20, 0.1 M NaCl, 0.5 % XG
owS+XG	-	-	18	4% PGPR	82	2% S, 0.1 M NaCl, 0.5 % XG
wowT+XG	7	0.1 M NaCl	11	4% PGPR	82	1% T20, 0.1 M NaCl, 0.5 % XG
wowS+XG	7	0.1 M NaCl	11	4% PGPR	82	2% S, 0.1 M NaCl, 0.5 % XG

Table 2 Theoretical equilibrium headspace partition coefficients (K_{ae}) of two aroma compounds, diacetyl and 3-pentanone, calculated by Eq.1 at 20 °C under dynamic headspace analysis conditions: water: air-water partition coefficient (K_{aw}) estimated from EPI SUITE (EPA's and Syracuse Research Corp., USA) at 20 °C.; emulsions: air-emulsion partition coefficient. XG: xanthan gum.

XG addition	aroma type	water	o/w emulsion	w/o/w emulsion
No XG	diacetyl	$5.4x10^{-4}$	$7.6x10^{-4}$	$6.6x10^{-4}$
	3-pentanone	$3.6x10^{-3}$	$1.5x10^{-3}$	$2x10^{-3}$
+XG	diacetyl	$5.4x10^{-4}$	$6.5x10^{-4}$	$6.1x10^{-4}$
	3-pentanone	$3.6x10^{-3}$	$2x10^{-3}$	$2.4x10^{-3}$

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562

Table 3 Dynamic headspace intensity (%) of diacetyl above water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
water	83.9±1.0^{a*}	80.4±1.9^{a}	80.4±1.9^{a}
wT	82.8±1.4^{ab}	80.6±3.1^{a}	81.0±3.9^{a}
wS	81.1±2.5^{ab}	76.8±1.2^{ab}	79.9±7.8^{a}
owT	85.0±3.4^{a}	77.9±3.5^{ab}	70.3±3.9^{b}
owS	84.7±1.9^{a}	75.0±3.7^{ab}	67.8±4.1^{b}
wowT	78.9±3.1^{b}	73.0±6.2^{b}	66.0±5.9^{b}
wowS	83.0±0.7^{a}	75.9±2.4^{ab}	68.5±1.7^{b}

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

* Within a column, different letters indicate statistically significant values ($p < 0.05$).

Table 4 Dynamic headspace intensity (%) of 3-pentanone above water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
water	58.0±1.7^{a*}	48.6±1.7^{a}	45.0±1.7^{b}
wT	52.6±2.5^{ab}	44.7±3.5^{ab}	42.0±4.7^{b}
wS	50.9±1.4^{b}	40.2±0.2^{b}	35.3±0.4^{a}
owT	87.4±0.8^{d}	78.6±1.5^{d}	70.6±1.3^{d}
owS	89.4±7.9^{d}	77.1±7.4^{d}	67.3±6.5^{d}
wowT	73.1±0.2^{c}	62.1±2.7^{c}	53.0±3.7^{c}
wowS	72.1±2.2^{c}	59.7±2.6^{c}	51.1±2.4^{bc}

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

* Within a column, different letters indicate statistically significant values ($p < 0.05$).

Table 5 Dynamic headspace intensity (%) of diacetyl above xanthan thickened (+XG) water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
w+XG	89.0±1.0^{ab*}	79.5±1.2^{a}	70.2±2.5^{ab}
wT+XG	90.0±1.4^{a}	79.8±3.4^{a}	72.4±4.1^{a}
wS+XG	79.5±1.9^{cd}	73.8±3.8^{ab}	68.2±6.5^{ab}
owT+XG	80.1±4.2^{cd}	69.4±5.2^{b}	63.6±4.0^{ab}
owS+XG	75.7±2.2^{d}	68.4±3.3^{b}	63.2±4.3^{b}
wowT+XG	83.7±4.0^{bc}	74.4±4.7^{ab}	67.7±6.6^{ab}
wowS+XG	79.4±5.7^{cd}	73.5±4.0^{ab}	68.5±6.0^{ab}

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

* Within a column, different letters indicate statistically significant values ($p < 0.05$).

Table 6 Dynamic headspace intensity (%) of 3-pentanone above xanthan thickened (+XG) water (w), o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S) at 2, 5 and 9 min during headspace dilution. The headspace intensity at the first time point was set to 100%.

Samples	2 min	5 min	9 min
w+XG	64.1±2.0^{ab*}	49.7±2.0^{ab}	39.1±1.0^{ab}
wT+XG	60.6±4.9^{ab}	49.9±2.6^{ab}	38.8±1.3^{ab}
wS+XG	61.4±6.0^{ab}	47.7±2.9^{a}	34.9±2.1^{a}
owT+XG	67.1±4.1^{a}	51.6±4.8^{ab}	39.8±4.0^{ab}
owS+XG	56.6±6.0^{b}	44.8±6.3^{a}	35.8±4.7^{a}
wowT+XG	69.0±6.3^{a}	56.4±5.2^{b}	44.5±2.8^{b}
wowS+XG	60.0±6.9^{ab}	44.9±3.3^{a}	38.7±5.0^{ab}

Values for relative headspace intensity are the mean of 3 replicates ± the standard deviation.

* Within a column, different letters indicate statistically significant values ($p < 0.05$).

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Table 7 Results summary of the inhibition, enhancement or similar ability of w/o/w emulsions in the dynamic headspace release of diacetyl or 3-pentanone compared to o/w emulsions and the main factors driving the phenomenon. A) High speed mixed or B) membrane processed and xanthan gum thickened emulsions stabilised with Tween 20 or OSA starch as the hydrophilic emulsifier.

Preparation method	Aroma compounds	Tween 20	OSA starch	Main factors
A)	Diacetyl	Inhibition	Similar	Emulsion type, creaming and diacetyl-OSA starch interactions
	3-pentanone	Inhibition	Inhibition	Emulsion type and creaming
B)	Diacetyl	Enhancement	Similar	Emulsion type and diacetyl-xanthan gum-OSA starch interactions
	3-pentanone	Similar	Similar	None

Figure 1 Page 1

A)

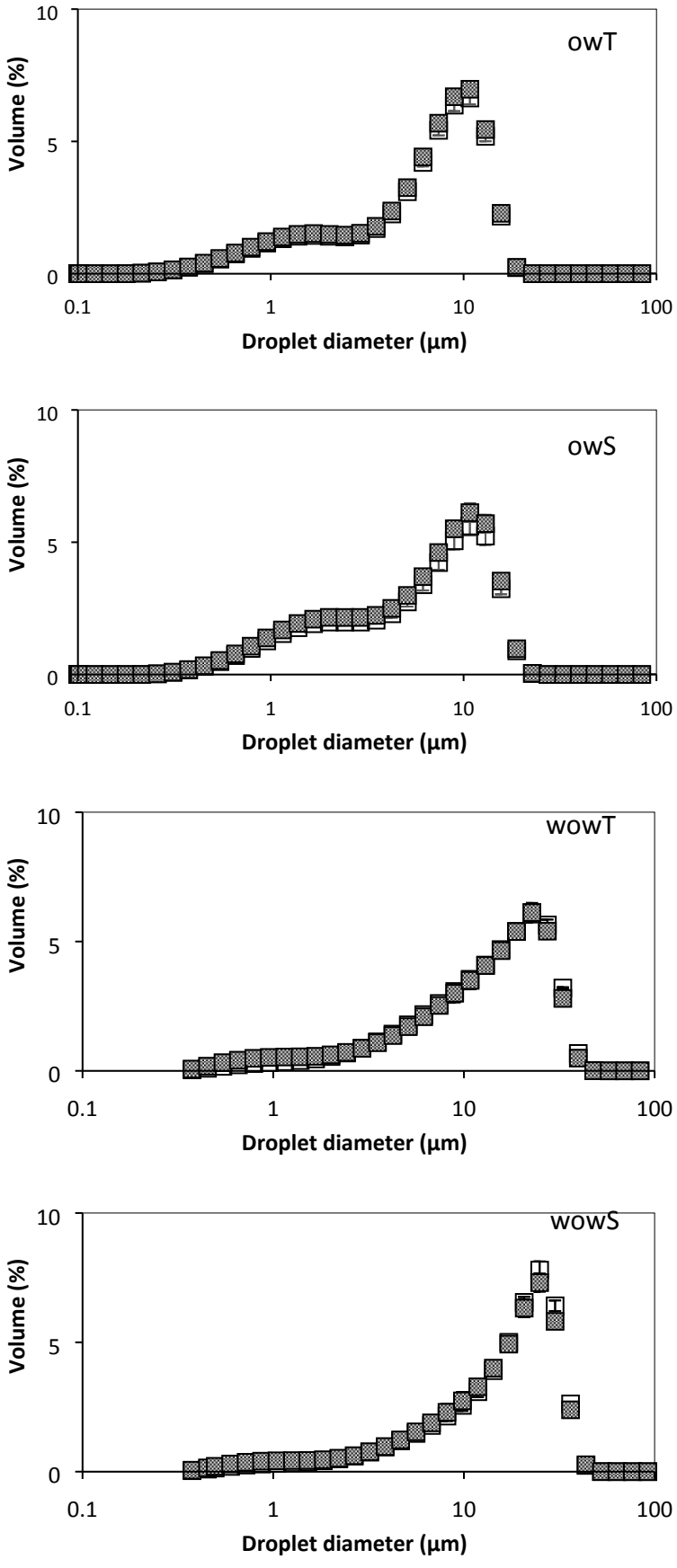

Figure 1 Page 2

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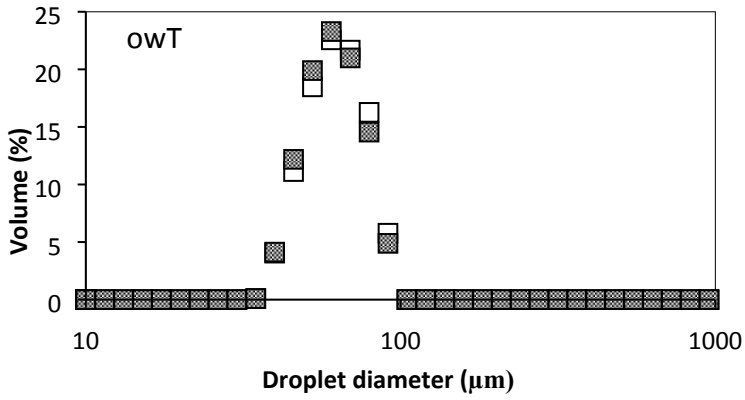

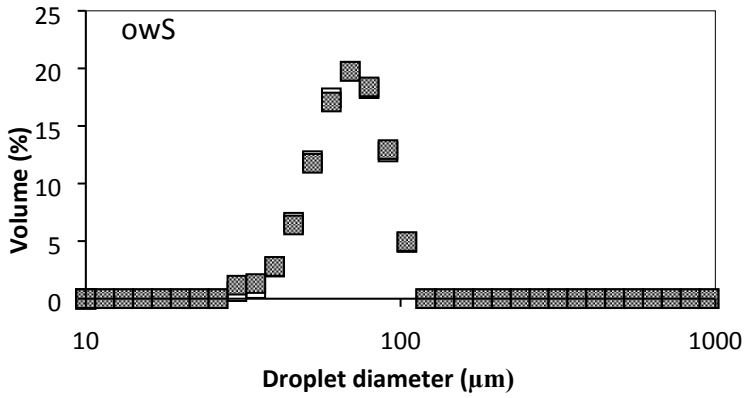

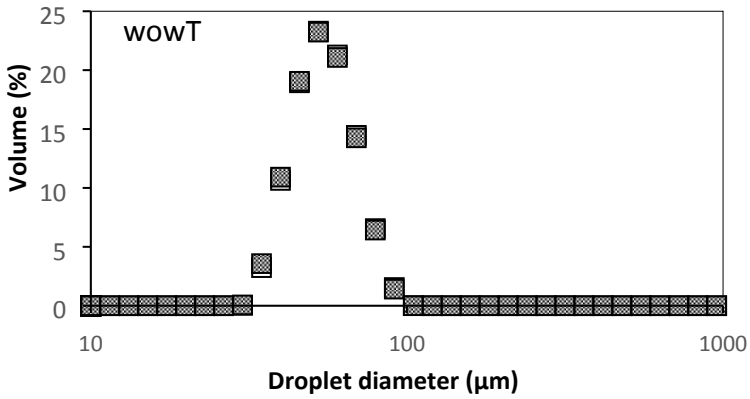

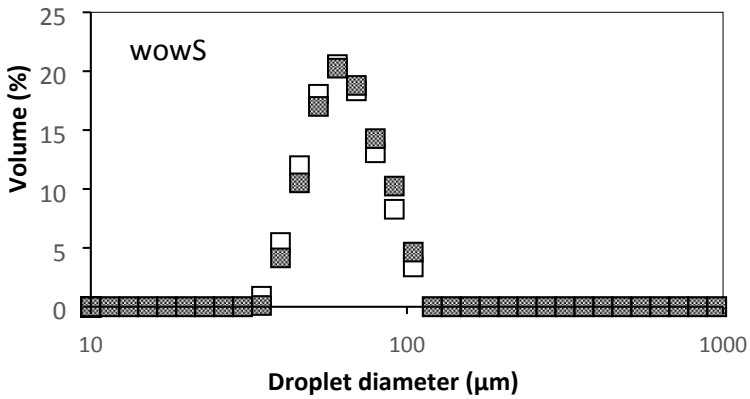

Figure 1 Page 3

Figure 1 Averaged droplet size distributions on a volume basis of A) high speed mixed or B) membrane processed and xanthan thickened o/w (ow) and w/o/w (wow) emulsions stabilised with Tween 20 (T) or OSA starch (S): □ Day of making; ▩ Day 6.

Figure 2 Page 1

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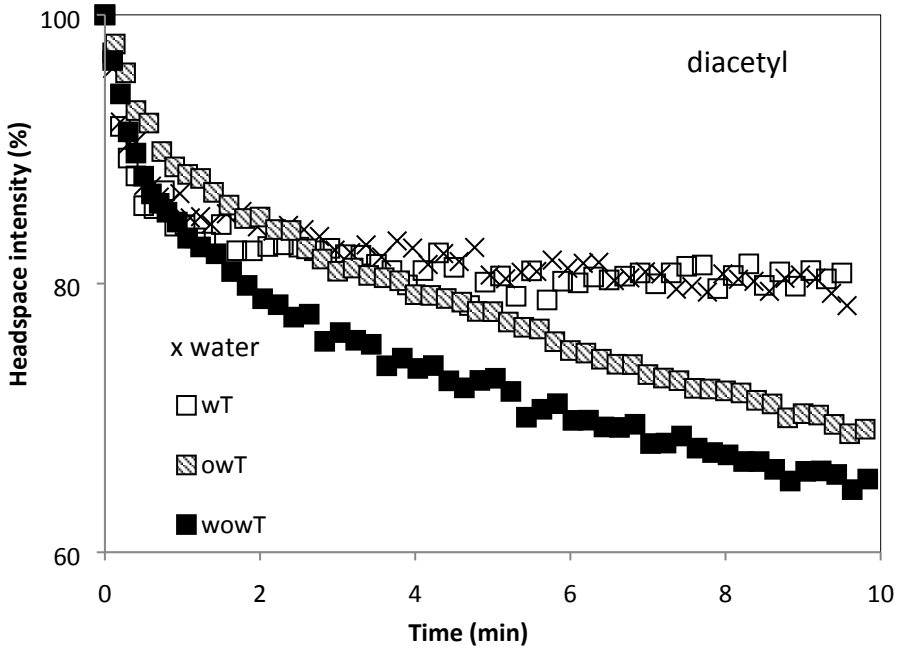

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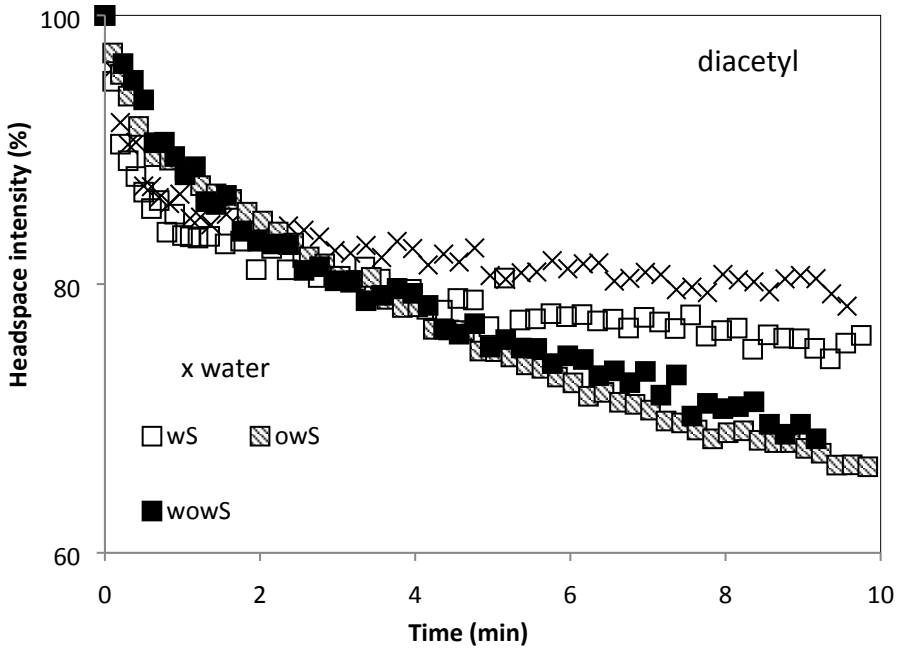

Figure 2 Page 2

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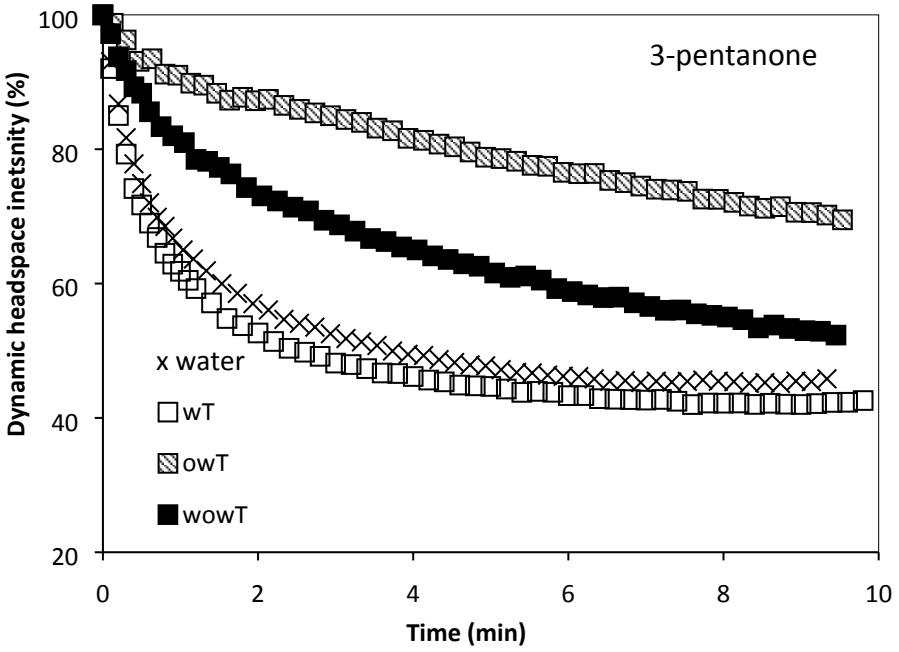

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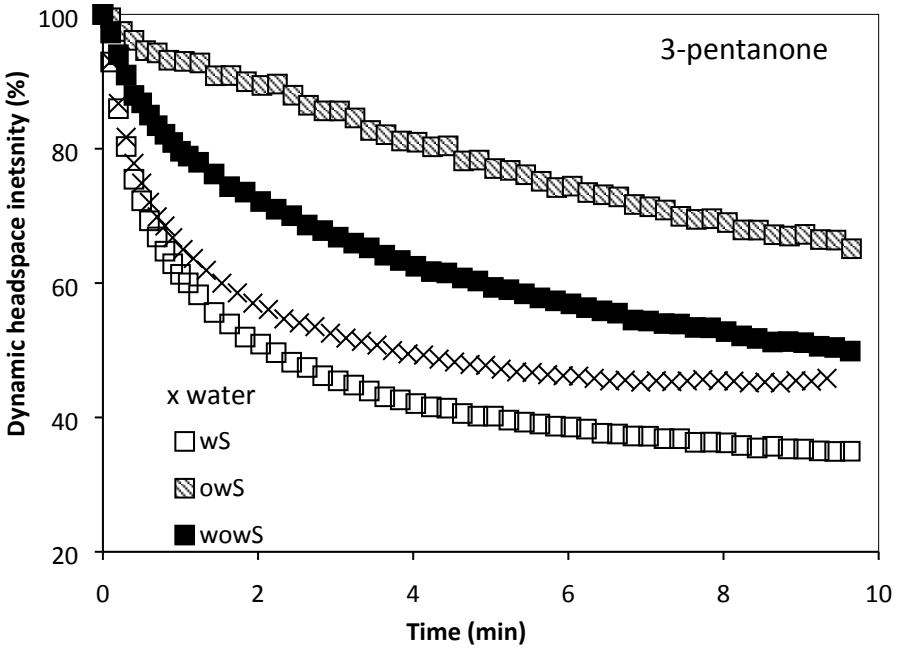
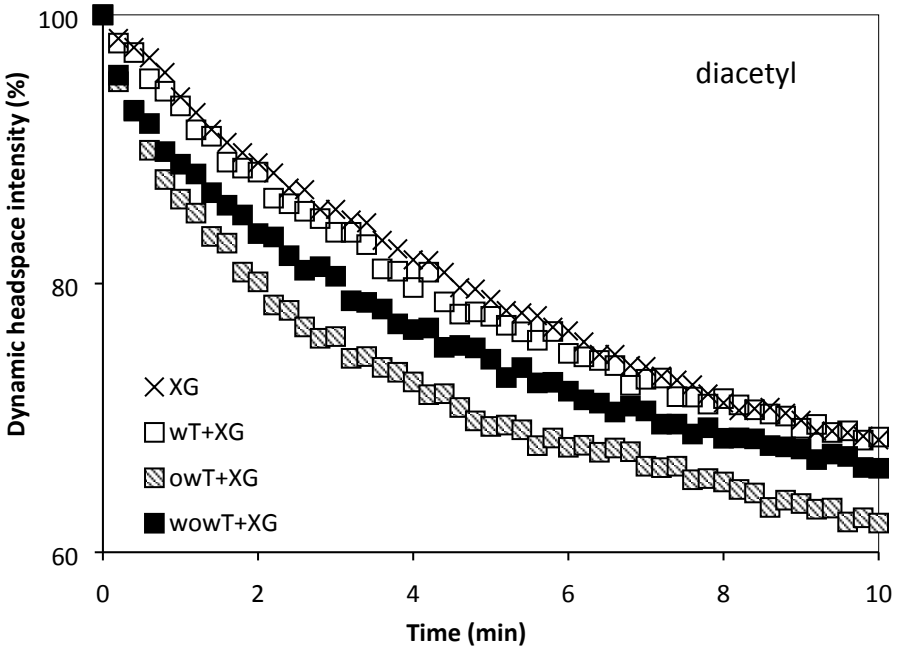


Figure 2 Dynamic headspace intensity of A, B) diacetyl or C, D)3-pentanone above xanthan gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,C) Tween 20 (T) or B, D) OSA starch (S). Values are based on 3 replicates.

Figure 3 Page 1

A)



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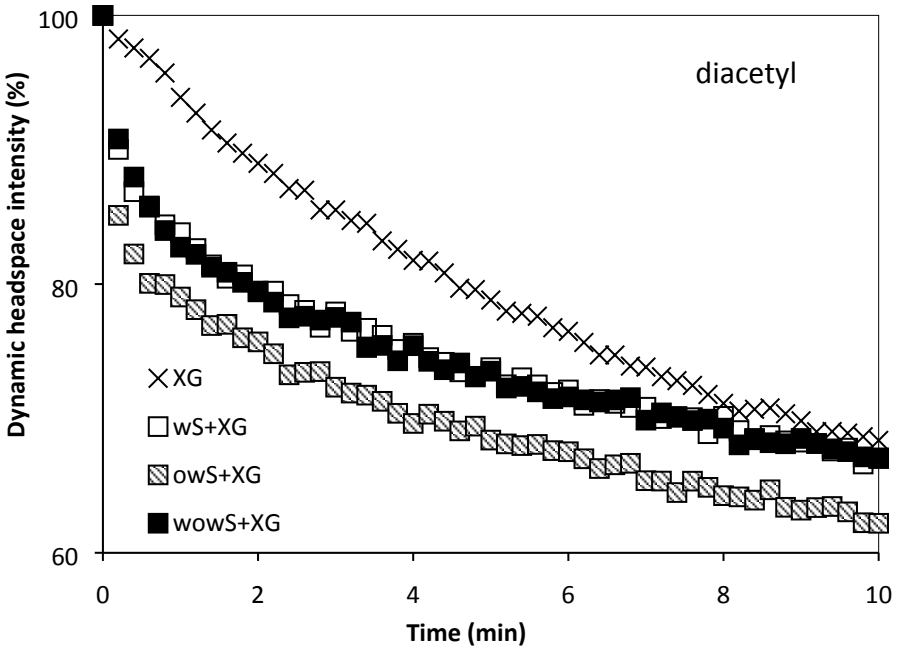

Figure 3 Page 3

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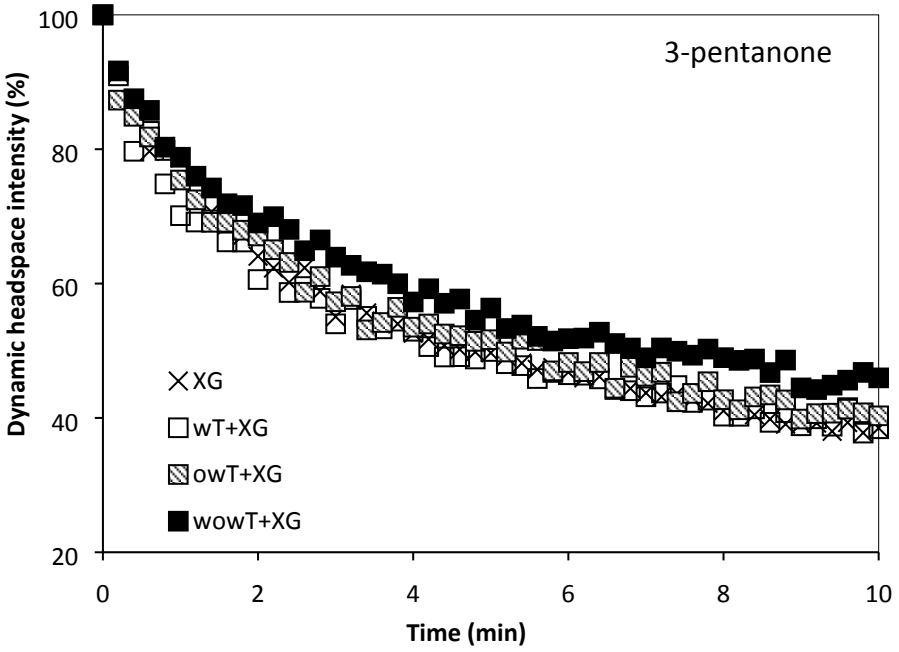


D)

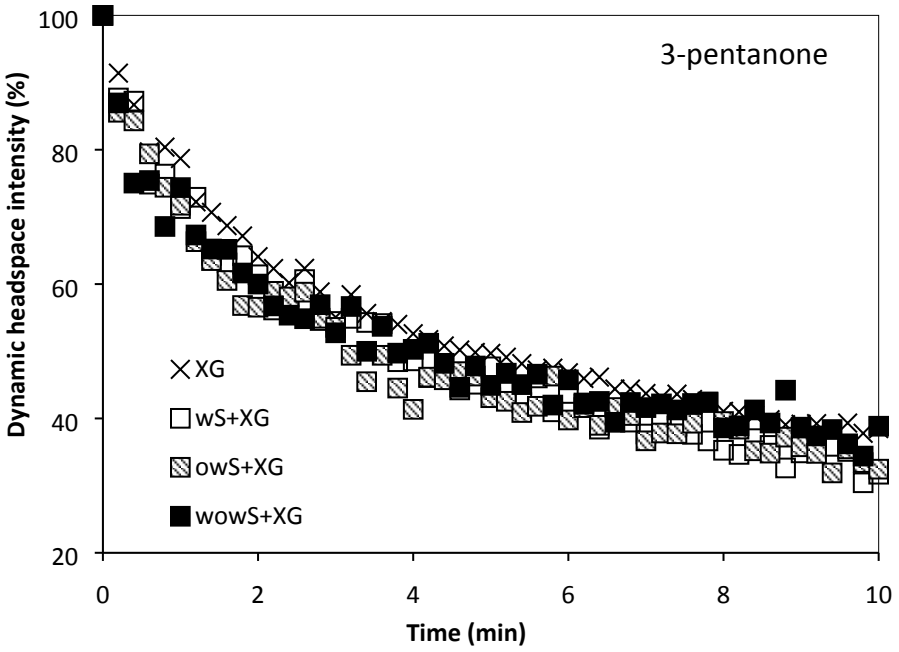
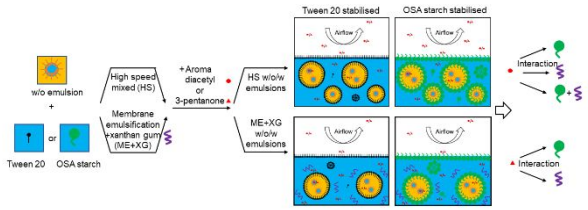


Figure 3 Dynamic headspace intensity of A, B) diacetyl or C, D) 3-pentanone above xanthan gum thickened water (w), o/w (ow) emulsions and w/o/w (wow) emulsions stabilised with A,

Figure 3 Page 3

C) Tween 20 (T) or B, D) OSA starch (S) in the absence or presence of xanthan gum (XG). Values are based on 3 replicates.

TOC graphic


Tween 20 stabilised
OSA starch stabilised
w/o emulsion
+
Tween 20
or
OSA starch
High speed mixed (HS)
Membrane emulsification + xanthan gum (ME+XG)
+Aroma
diacetyl
or
3-pentanone
HS w/o/w emulsions
ME+XG w/o/w emulsions
Airflow
Interaction
Interaction