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Effect of surface characteristics on cleaning performance for CIP system in food processing

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Abstract

In food processing, insufficient cleaning can result in reduced efficiency, contamination in final product, and energy losses. To optimise widely implemented clean-in-place (CIP) systems, it is critical to understand the influence of the interactions between surfaces, foulant, and chemical agents on the efficiency of the cleaning process. The present work investigates the effect of wall temperature and surface roughness on the surface free energy of stainless steel 316L coupons. Equilibrium contact angles (ECA) of four commonly used liquids, namely ethylene glycol, 1-bromonaphathalene, water, and diiodomethane were measured on the surfaces of interest. Finally, ECAs of liquids were used to quantify surface free energy (SFE) of the solid substrate. Our results show that surface energy is proportional to the roughness and well-prediction of liquids wettability as a function of roughness and temperature. It demonstrates the importance of surface characteristics in determining interfacial energy, and consequently the efficiency of CIP for food engineering.

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1. Introduction

In the food industry, due to the physicochemical properties of the processed products, foulant adheres to industrial surfaces forming films that are difficult to remove during cleaning operations. Some of the most important fouling problems generated are the consequence of thermal processing that is often used to inhibit the growth of microorganisms. Temperature affects both fouling generation and its composition [1]. Hence, the use of aggressive treatment, such as strong chemical agents and excessive amount of energy can be needed to effectively remove foulant from surfaces in contact with food. If the optimisation of cleaning parameters is not achieved, clean-in-place (CIP) systems could deliver an inefficient cleaning performance.

The equipment involved in food processing is almost entirely made of stainless steel. However, depending on the design parameters, physical characteristics of metal surfaces such as surface finish or surface treatment/composition can be different. Stainless steel 304 and 316 are the most commonly used materials for food contact surfaces due to their intrinsic properties such as neutrality, cleanliness, and durability [2]. Despite the ease of cleaning stainless steel, cleaning procedures need to be followed carefully to prevent fouling and bio-fouling.

Understanding how the micro and nano-topography of stainless steel and its wettability can affect fouling generation and its removal could help to develop new food-processing and cleaning techniques for industrial applications, and minimise energy and product losses. To determine how surface properties can affect cleaning performance, a study of the surface free energy (SFE) of stainless steel coupons (SS) as a function of both temperature and roughness was carried out. For that purpose, firstly, the equilibrium contact angle (ECA) of four different liquids, including two polar solvents: ethylene glycol (EG) and distilled water (W), and two non-polar liquids: 1-brononaphthalene (BN) and diiodomethane (DM) was measured. After identifying ECA variation, two ECA models as a function of temperature and roughness were applied. Finally, SFE was characterised for the substrate of interest.

Nomenclature			
SFE	Surface free energy	BN	1-Bromonaphthalene
SS	Stainless steel	DM	Diiodomethane
ECA	Equilibrium contact angle	EG	Ethylene glycol
Ra	Arithmetic average of the roughness profile	W	Distilled water
SK	Sharp-Kink approximation	DTm	Decreasing Trend model
$\Delta\rho$	Difference of densities liquid-air	I	Van der Waals integral
γ_{lv}	Surface tension liquid-air	γ_{sv}	Surface tension solid-air
γ_D	Disperse component of SFE	γ_P	Polar component of SFE

2. Materials & Methods

2.1. Characterisation of surface morphology

Three types of samples, stainless steel 316L with different levels of surface finish – Mirror (Ra $0.0295 \pm 0.0045\mu m$), satin ($0.3090 \pm 0.0095\mu m$), and brush ($0.8250 \pm 0.1276\mu m$) were used to understand how substrate roughness affects surface free energy on a real food contact environment. Squares test surfaces of 2.54 x 2.54 cm were prepared by an abrasive polishing process using different sandpapers grit (600, 240, and 180). The polishing process offers unidirectional oriented surfaces within the standard roughness limit defined for dairy industries (Ra < 0.8 µm) [3]. White Light Interferometry, a non-contact optical method, was used to characterise metal surfaces.

2.2. Cleaning of metal surfaces

Following a previous study [4], to achieve a proper cleaning of the metal surfaces after polishing process, coupons were cleaned using 2.0% (wt./wt.) NaOH aqueous solution at 80°C under agitation for 1h, then cooling then to room temperature in a water bath. Surfaces were subsequently removed and rinsed by 1.0% (vol./vol.) aqueous solution of

HCl. They were then soaked in hexane for 5 min and acetone for another 5 min. After being removed from acetone, samples were dried by a compressed air stream. In addition, to ensure complete removal of the liquid droplets in contact angle measurements, coupons were rinsed three times using distilled water at room temperature, rinsed with acetone and dried by an air stream. The cleaning with acetone allows reliable results to be obtained within the degree of expected accuracy on 316L stainless steel surfaces [5]. All solvents were HPLC grade.

2.3. Equilibrium contact angle

There is a wide variety of methods established to measure contact angles [6,7], the sessile drop method is selected in this work. Since a sessile droplet has a time-dependent contact angle due to droplet evaporation, contact angle is measured when the equilibrium balance of the forces acting on the liquid–vapour interface in contact with solid surface is reached. Therefore, the evaluation of the equilibrium contact angle (ECA) was carried out on a stage where the influence of convective motion on the value of contact angle is negligible. ECA was used to compare the behaviour of four different liquids as a function of temperature from 25 to 80°C under ambient pressure.

The device used to measure the ECA is composed of (i) a heating stage connected to a thermal bath (ii) coupons placed on the stage to ensure controlled wall temperature. A high-speed camera (1000 fps; FastCam Photrom SA3®) was placed to capture images that were processed using an image processing program (ImageJ®). Finally, a pipette is used to place droplets (10 µL) on the substrate of interest.

2.4. Modelling of ECA as a function of temperature

As shown in previous studies [8,9], it is possible to describe temperature dependence of the contact angle of liquids on several substrates. In this work, modelling of liquids contact angle was done as a function of both temperature and surface finished for stainless steel coupons. The two models used are:

- The sharp-kink approximation [8], which predicts the contact angle from the liquid-gas surface tension, the difference in density between the liquid and vapour and the van der Waals potential describing the net preference of the adsorbate water for wetting the substrate instead of forming a droplet. SK equation (1) shows that the temperature-dependence of cos (ECA) is the temperature-dependence of $\Delta\rho/\gamma_{lv}$.

$$\cos(ECA) = -1 + \Delta\rho \cdot I / \gamma_{lv} \qquad (1)$$

- The decreasing Trend Model (DTm), which was proposed by Villa and colleagues [9] to study the variation of the ECA as a function of both fluid and wall temperatures for all surfaces. Based on the Young–Laplace equation and assuming that surface tension decreases linearly with temperature for most liquids, the model has two formulations depending on the type of liquid used, non-polar (2) or polar (3). The surface tension of the solid can be extrapolated from ambient conditions.

$$\cos(ECA) = -1 + 2 \cdot \sqrt{\gamma_{sv}}/\sqrt{\gamma_{lv}} \qquad (2)$$

$$\cos(ECA) = -1 + \frac{2}{\sqrt{\gamma_{lv}}} \cdot \sqrt{\gamma_{sv}{}^D \cdot \frac{\gamma_{lv}{}^D}{\gamma_{lv}} + \gamma_{sv}{}^P \cdot \frac{\gamma_{lv}{}^P}{\gamma_{lv}}} \qquad (3)$$

2.5. Surface free energy

Surface free energy of metal surfaces was determined using three different polished surfaces at temperatures up to 80°C and under atmospheric pressure. Liquids with high boiling point were used to avoid evaporation. In this work, 1- bromonaphthalene, ethylene glycol and diiodomethane were the liquids selected to characterise solid SFE with polar and disperse components. It is well known that interfacial water plays a central role in many systems. Hence, the study of water contact angle in contact with hydrophilic surfaces could clarify the behaviour of aqueous-systems

at different temperatures. The two methods used to calculate and compare SFE are the Owens & Wendt method and the Wu method. The former [10] is commonly used to calculate the solid surface energy from the contact angle of liquids, in which SFE is divided in polar and disperse part. According to Young's equation and building on the Fowkes' method, the interfacial tension solid-liquid can be calculated based on both surface tensions, solid and liquid, and the similar interactions between the phases (using geometric mean approach). The Wu method [11,12], similar to that proposed by Owens & Wendt, allows calculation of the surface free energy of a solid , dividing it into polar and disperse parts. However, the Wu harmonic mean model often provides more reliable values between both parts for low surface free energies systems.

2.6. Statistical analysis: ANOVA

Analysis of variance (ANOVA) is a parametric statistical technique to analyse the differences among group means in a sample [13]. It provides a statistical test of whether the population means of several groups are equal, and therefore generalises the t-test to more than two groups.

3. Results & discussion

3.1. ECA as a function of both surface temperature and roughness

Experiments were conducted to measure the ECA in an environment with three components (solid, liquid and air) at ambient pressure (1atm) up to 80°C. Temperature influences directly the properties of any liquid, and as expected, in accordance with the literature [14], contact angle decreases with the increase of surface temperature (Fig.1) influenced by the variations of liquid surface tension.

At room temperature, water showed the highest contact angle, decreasing the values of liquids ECA as a function of liquid surface tension: W(72.0 mN/m)[15]; DM(50.0 mN/m)[16]; EG(47.5 mN/m)[17]; BN(44.6 mN/m) [18]. However, at 80°C, the surface tension of diiodomethane is smallest, showing the greatest reduction of surface tension [16]. Despite this change, the contact angle follows the same trend as that found at room temperature with respect to the other liquids. Therefore, some anomalies on the contact angle of the DM with respect to temperature-dependence were found.

Although the ECA of liquids tend to decrease as a function of increased temperature, water contact angle increases above 60°C (Fig.1). As described by Garcia et al. [8], such increase is likely related to the evaporation of water. The stability of the water droplet used in the contact angle study is affected when temperature exceeds 60°C by a slow single-phase evaporation (without boiling). It was observed that liquid spreads and oscillates due to temperature differences on the interface immediately after placing the drop on the metal surface, until equilibrium is reached – at which point the ECA is constant and is measured. Then, the drop decreases in thickness until is fully evaporated [19]. The increase of water ECA shows a relationship between temperature and roughness, which shows an increase in ECA is produced at lower temperatures for higher roughness values. This suggests that the roughness influences directly on the evaporation of water, increasing the total time of droplet evaporation with the decrease of channel thickness [20]. Liquids showed small variations between their ECA measurements except for water, which showed the highest standard deviation. It is known that the presence of air and the lack of saturation condition in the gas phase (vapour and air) can induce inaccuracy on the measurements of equilibrium contact angle [21].

In all cases, assuming that the droplet completely wets the rough surface according to Wenzel [22] for hydrophilic surfaces, ECA of tested liquids decreases when the roughness of metal surfaces increased. Although surface roughness affects ECA values in the studied range (Ra<0.83μm), for some of the liquids used, no significant statistical differences can be found between values.

On the other hand, the highest decrease in contact angle was presented by EG (between 20 and 28% depending on surface tested), followed closely for BN (~23%). Both liquids showed a statistically significant reduction of ECA with regards to temperature. However, no significant differences between ECA values can be found with regards to type of roughness - influenced by the spreading effect. Although both water and diiodomethane show more sensitivity of the surface tension to temperature (decrease of 13 and 15%, respectively), their spreading effect is small. Their ECA

has a slight reduction – it might be possible to see more differences as a function of surface roughness by the ANOVA test.

The results demonstrate that surface parameters play an important role for contact angle measurement and liquid wettability. The liquids tested showed hydrophilic behaviour on the SS surface, and the metal wettability is improved for small differences between surface tension of liquid/solid and temperature increasing. Therefore, the findings suggest that a good surface finishing could result in better repellence property to liquids such as water. From an industrial point of view, for aqueous based food products such as milk, mirror surface could be considered as the best candidate in terms of cleanliness, assuming that it could be the least affected by foulant deposition.
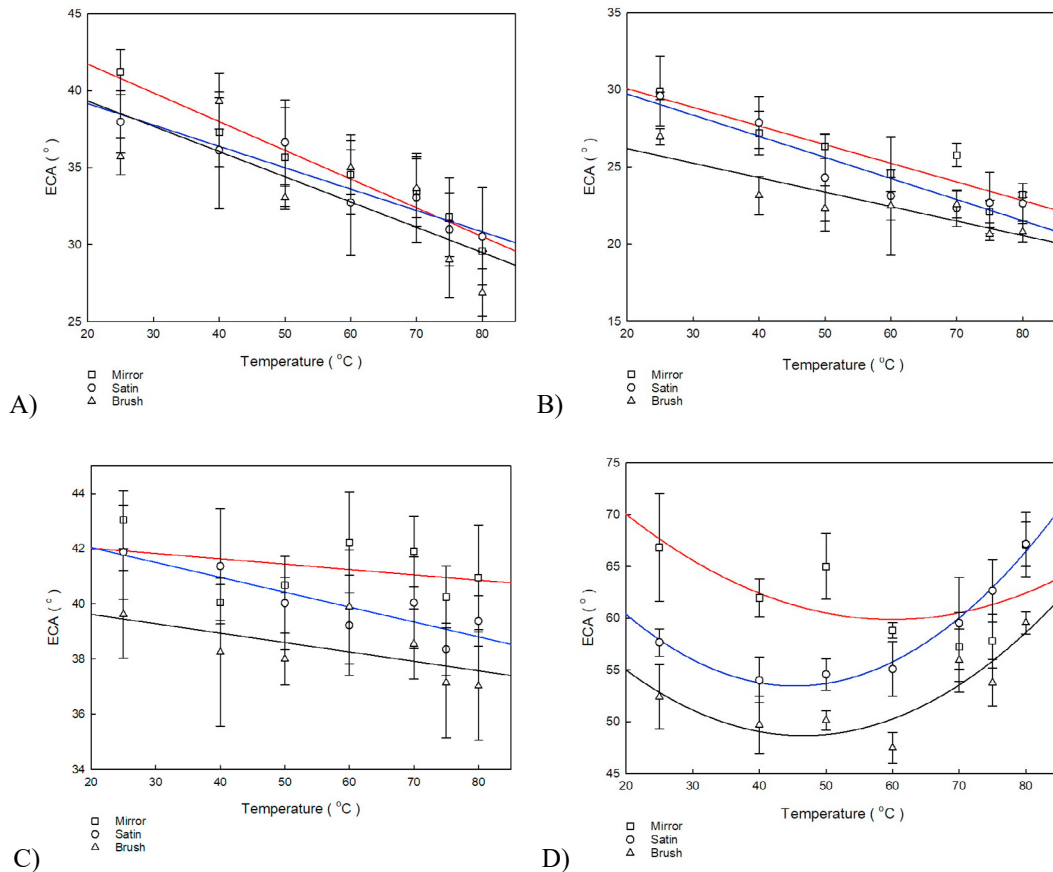

Figure 1. Equilibrium contact angle of liquids as a function of temperature over three different types of polished surfaces. Liquids tested: ethylene glycol (A); 1-bromonaphthalene (B); diiodomethane (C); distilled water (D). Error bars represent the standard error. Lines are "guide to the eye": mirror (red), satin (blue) and brush (black).

3.2. ECA modelling as a function of temperature

For clear data visualisation, averaged ECA of liquids on three different surfaces tested was selected to illustrate contact angle modelling as a function of temperature. In addition, to show the good approach of two models regarding roughness parameters, the ECA of water is presented as an example in this section.

The SK approximation, which uses only van der Waals type forces, could successfully predict the temperature-dependence of contact angle for three out of four liquids, except DM. According to equation detailed in section 2.4, the contact angle decreases monotonically with the temperature. Consistent with the SK approximation, DTm predicts the ECA of water, ethylene glycol and 1-bromonaphthalene as a function of temperature on stainless steel, with exception of DM. Although the DM contact angle at room temperature is well predicted by both models, as

temperature increases, the deviation between observed contact angle and predicted contact angle increases showing an unpredictable behaviour. Even so, the ECA of DM shows a similar decrease to that reported by Zhao et al. [14] regarding temperature for stainless steel 304. In addition, because of water evaporation (see section 3.1), models only predict the ECA of water up to 60°C. Figures 2C and D illustrate the modelling of water ECA as a function of wall temperature and surface roughness. According to literature [23], both models predict the decrease of contact angle when surface roughness increase into small roughness limits. Therefore, wettability of liquids could be well predicted within the small roughness range that are standard for dairy applications [3].

The modelling of liquid wettability, as a function of the roughness and temperature of the process, could help to simulate the wettability of typical aqueous solutions used in the food industry, achieving a better understanding of the fouling generation and its elimination. Both of the two models used in this work predict the ECA variation as a function of surface roughness and temperature satisfactorily, but the DTm model shows a better fit with the experimental data.
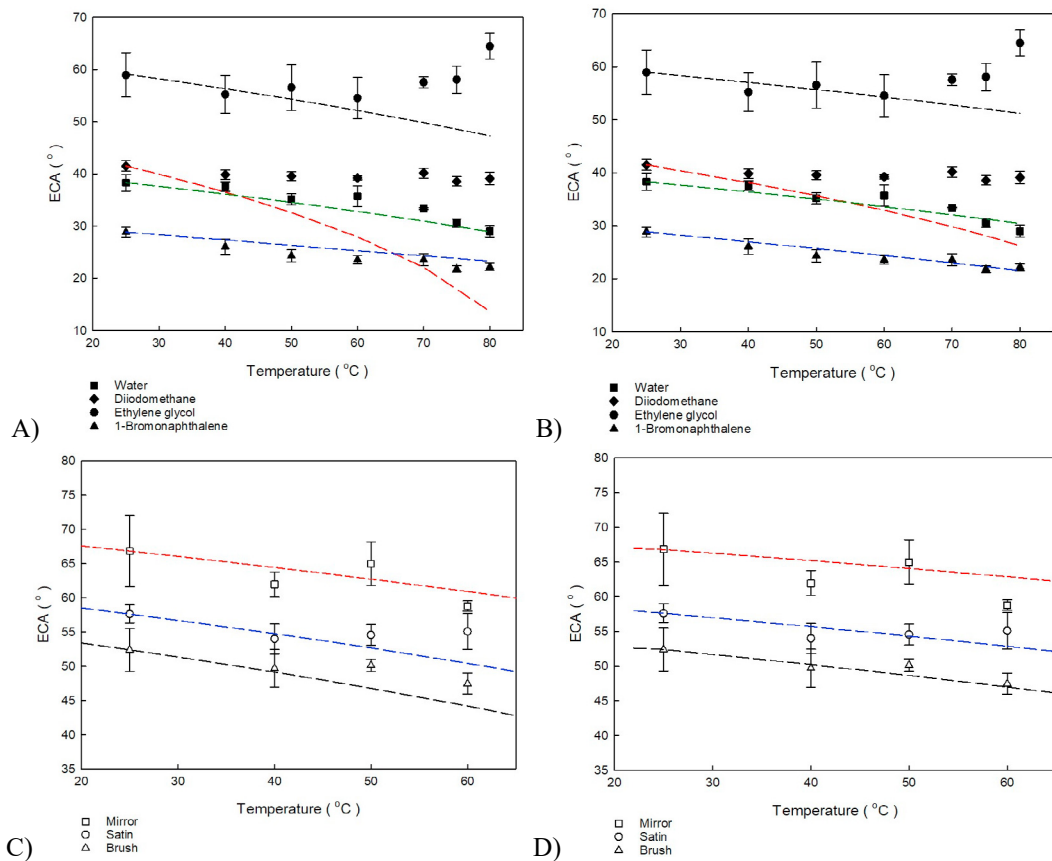

Figure 2. A & B) Modelling of ECA average as a function of wall temperature for real food-contact surface (Ra < 0.8µm). Liquids tested: water; diiodomethane; 1-bromonaphthalene and ethylene glycol. **C & D)** Modelling of water ECA as a function of both wall temperature and surface roughness. Models: SK approximation (A and C) and DT model (B and D). Error bars represent the standard error. Colours represent: ECA of liquids in figures A & B (W (black), DM (red), EG (green), BN (blue)); ECA of water regarding surface finish in figures C & D (mirror (red), satin (blue), brush (black)).

3.3. Determination of stainless steel SFE

The inconsistent behaviour of the DM contact angle as a function of surface tension (section 3.1) and the unpredictable modelling, and the evaporation of the water droplets, suggests that the system formed by ethylene glycol and 1-bromonaphthalene is the most appropriate to calculate the surface free energy of solid as a function of temperature.

The analysis of the surface free energy of the stainless steel coupons by different methods (section 2.4) indicates that the surface free energy of SS coupons remains constant with temperature (Fig.3A). ANOVA analysis does not show significant differences of the polar part regarding roughness and temperature. However, disperse part shows variations as a function of substrate roughness. The greater the surface roughness, the higher the value of disperse part - as this forms the majority of the free energy, there is some roughness-dependence of the metal surface free energy. As surface free energy is in terms of force per unit of area, results are consistent in showing an increase of the force with contact area increasing, i.e. with greater roughness values.
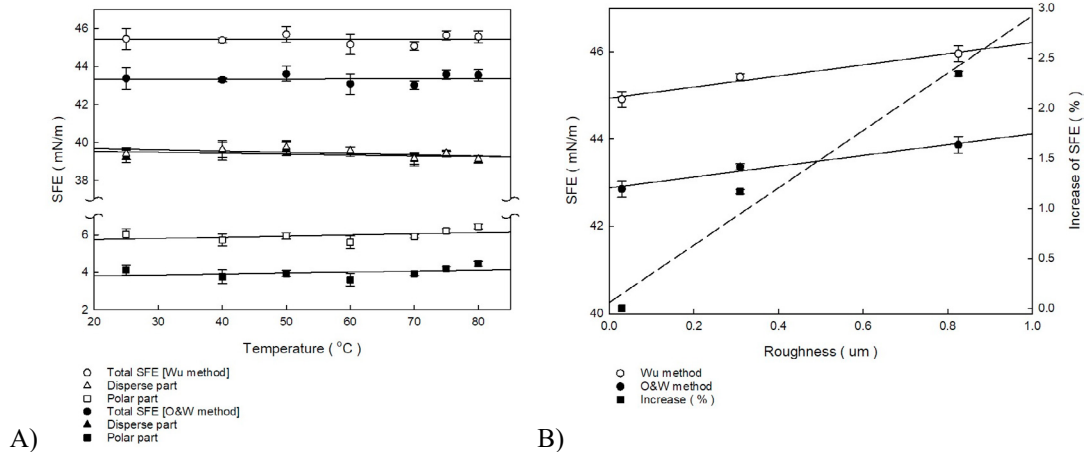

Figure 3. A) Averaged values of solid surface free energy as a function of temperature on three different types of polished surfaces. Methods: Owens & Wendt and Wu method. **B)** Surface free energy increasing (%) of SS316L as a function of surface roughness. Averaged values of both methods: Owens & Wendt and Wu method. Liquids tested: Ethylene glycol and 1-Bromonaphthalene. Error bars represent the standard error.

Despite the results being dependent on the methods used as well as the liquids employed [14], these two methods had consistent values showing similar trend. The values of SFE calculated by the geometric mean method and the harmonic mean method are similar, between 43 and 45 mN/m, showing proportional values of disperse and polar components.

Results indicate that SFE of stainless steel 316L remains constant over the temperature range commonly used for pasteurization processes [24]. Accordingly, the attractive interactions with which the metal could influence the food flowing through the production lines is the same with as temperature increases up to 80°C. In addition, other parameters such as the surface roughness seem to affect that force significantly. Further analysis of SFE versus roughness (Fig.3B) shows a linear relation, showing that the increase in SFE is proportional to the topographical length scales of the surface. Therefore, the greater the surface roughness, the higher the SFE in the system, as well as the greater adhesion of liquids over the same projected area.

4. Conclusions

Experiments show that, as suggested in the literature, the contact angle of liquids decreases with increasing wall temperature on hydrophilic surfaces like stainless steel. The highest contact angle was found for the smoothest surface, decreasing as a function of the surface roughness increasing. Generally, it can be supposed that the impact of small roughness variations on the contact angle is insignificant. However, for liquids with high surface tension as water, ECA changes considerably affecting wettability. Therefore, wettability is favoured by the increase of both temperature and roughness for all of the liquids tested.

Successful approaches regarding wall temperature and surface roughness parameters were achieved. The modelling of liquid contact angle as a function of the roughness and process temperature could help to simulate the wettability of typical aqueous systems used in the food industry, achieving a better understanding of both fouling generation and its removal.

Analysis of the surface free energy for stainless steel coupon by different methods suggests that surface free energy remains constant as a function of temperature within the range examined in the present study. No significant differences were observed between the polar parts at studied conditions. However, disperse part shows variations as a function of substrate roughness, indicating a roughness-dependence of the metal surface free energy.

For mild pasteurisation processes, the attractive interactions which metal surface could attract the food flowing through the production lines is independent of temperature - up to 80°C. However, other parameters such as the surface roughness seem to affect significantly those interactions. The linear relationship between the SFE and the topographical characteristics suggests that the greater the surface roughness, the higher the SFE of the system, as well as the greater adhesion force of liquids for the same projected area.

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