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Incorporation of Heuristic Knowledge in the Optimal Design of Formulated Products: Application to a Cosmetic Emulsion

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Abstract

In particular industrial sectors, such as the cosmetic, there is a considerable amount of heuristics during the formulation stage, namely regarding qualitative function of ingredients, their incompatibilities, synergies and antagonisms, as well as their impact on sensorial attributes. In this work, the heuristic knowledge around the formulation of cosmetics emulsions has been incorporated into a systematic CAMD methodology. The methodology was tested in the creation of rinse-off hair conditioners. From an initial list of ingredients (i.e. twenty-four emollients, six thickeners and five emulsifiers) and a set of heuristics for their incorporation into cosmetic formulations, a group of optimized alternatives under specific performance and economic targets was obtained. Nine of the resulting formulations were prepared and then analyzed using instrumental methods. The rheological, textural and microstructural characteristics were similar for most of the samples, confirming the potential of this proposed methodology in designing and tailoring formulated products.

Keywords: Product Design, Optimization, Heuristics, Cosmetic Emulsion, Hair Conditioner

1. Introduction

Because of the growing competitiveness in the cosmetic sector, like in many other industrial domains dealing with chemical products, companies seek to reduce the time to market (Cooper, 2013). This is often the decisive point for successful product launch, even above the cost of production (Charpentier, 2010). Hence, chemical product design (CPD) has been proposed as a new way of thinking the chemical engineering discipline, where the product manufacture process has been the classical object of study (Cussler and Moggridge, 2011; Bernardo and Saraiva, 2015). CPD has been constructed as a systematic framework of methodologies and tools, whose aim is to provide a more efficient and faster development of products able to meet market demands (Costa et al., 2006). However, CPD has not yet developed into the foreseen third paradigm of chemical engineering (Hill, 2009), maybe because of the incomplete understanding of sensorial product attributes (Cussler et al., 2010), and also of complex interactions between materials and their impact in product performance (Picchioni and Broekhuis, 2012).

In the product engineering field, chemical products are generally classified into three categories: molecules, formulated products, and functional products and devices (Gani and Ng, 2015). Under this classification, most cosmetics would fall in any of the last two categories, as they could be seen as a mixture of one or more key ingredients responsible for the product's functionality (active ingredients) with other supporting ingredients to enhance the mixture performance (Wibowo and Ng, 2002). Cosmetics can be also classified according to their physical form or delivery system, and emulsions are probably the most commonly used due to their numerous advantages (Knowlton and Pearce, 1993). Only among the skincare and haircare segments, a considerable number of products, such as hydrating creams, body lotions, conditioners and combing creams, are formulated as emulsions (Morávková and Stern, 2011). Traditionally, emulsified cosmetic product design has been made following an experiment-based trial-and-error approach, seeking formulations that meet targeted performance (Barel et al., 2001), including product sensorial attributes that are critical for consumer acceptance (Pensé-Lhéritier, 2015). Such trial-and-error procedures are very resource-consuming, especially during early stages of product design or reformulation (Conte et al., 2011).

A more systematic search for the optimal product may be supported by computer-aided methods, known in the literature as computer-aided molecular/mixture design (CAMD) methods (Achenie et al., 2002). These are based on a set of fundamental units that may compose the desired product and on models to estimate product properties from the type and number of those units. A systematic search for the right combination of units may then be done, often using mixed-integer optimization. These methods may be very effective in the case of relatively small molecules described as a combination of molecular groups and with properties predicted using reliable group contribution methods (Gani, 2004). They have also been applied with success to relatively simple liquid formulations, once mixture properties may be reasonably estimated (Achenie et al., 2002; Conte et al., 2012, 2011; Yunus et al., 2013). For more complex formulated products, often having specific microstructural features, the lack of adequate property models hinders such systematic searches (Bernardo and Saraiva, 2015; Gani and Ng, 2015). In these more complex domains, product design then relies on less structured knowledge, such as databases of often used ingredients and heuristic rules regarding ingredients functionality and its recommended/allowed concentrations. Several product design procedures incorporating such heuristic knowledge have been proposed, most of them for specific product families, e.g., creams and pastes (Wibowo and Ng, 2002, 2001), pharmaceutical tablets and capsules (Fung and Ng, 2003), emulsions (Mattei et al., 2012; Schubert and Engel, 2004), and detergents (Martín and Martínez, 2013). It is

also worth mentioning the method proposed by Lee et al. (2014) in the scope of personal care products, which is based on case-based reasoning, i.e., reuse and revision of knowledge acquired in previous developed product formulations.

Recently, Fung et al. (2016) presented a general framework for chemical product design using rule and model-based methods, as well as tools, databases, and experiments, supported by a hand lotion case study. Also, Zhang et al. (2017) proposed a comprehensive framework applicable to several classes of formulated products, handling several sources of information and knowledge, including heuristic-based and model-based methods. For instance, when a solvent is being developed using this methodology, the product may be designed using CAMD tools incorporating the necessary property models for the main components of the liquid mixture; meanwhile the other more complex ingredients of the mixture (e.g. emulsifiers) are decided based upon heuristics. In this case, heuristics are often stated as logical conditions and thus logic-based mixed-integer programming is used (Raman and Grossmann, 1991).

In the above-mentioned methodologies, heuristic rules and property models are used as complementary sources of knowledge, but no physical prototypes are prepared to validate the design approach. In this direction, this work focused on cosmetic emulsions design, converting heuristic rules into mathematical forms that were explicitly included in the optimal design problem, side by side with property models. Then, a lab scale validation of the designed products, as obtained from the solution of the optimization algorithm, was carried out. As far as we know, this is the first attempt to fully integrate heuristic knowledge into an optimization-based CAMD tool using a specific product case, whose resulting alternatives were manufactured and evaluated using different performance indicators, proving evidence of the applicability of the methodology.

In this contribution, the design problem is formulated from an initial (long) list of available ingredients, a subset of which is to be selected. New molecular entities are thus not being equated. As a study case, we have considered the field of cosmetic emulsions, particularly an example of a rinse-off hair conditioner. The domain of cosmetic formulations has an extensive history, handles hundreds of different ingredients, and it is rich in heuristic knowledge, namely regarding qualitative function of ingredients, their incompatibilities and positive synergies, as well as their impact on sensorial attributes (Barel et al., 2001; Gilbert et al., 2013; Laba, 1993; Suzuki, 2017). It was therefore selected as a prime area of application in which the incorporation of heuristic knowledge in an optimization-based method may likely be fruitful and easy to validate at a lab scale (Arrieta-Escobar et al., 2017).

2. Overall Methodology

Although initially developed in the scope of cosmetic emulsions, the basic ideas and tools of the methodology here proposed (Figure 1) are applicable to any formulated product, whose specific functionalities result from the proper blend of ingredients and specific interactions between them.

Insert here Figure 1

The methodology starts with a list of available ingredients organized by their main function (e.g., emollients, emulsifiers, thickeners). A binary variable is associated to each ingredient, indicating whether that ingredient is selected to be part of the formulation or not. Then, available heuristics regarding choice of ingredients and their amounts are listed and modelled as algebraic restrictions. Some heuristics are first stated as logical conditions and these then translated into algebraic constraints involving binary variables, as it will be explained in section 3 (Raman and Grossmann,

1991; Williams, 2013). Heuristic-related restrictions, together with other known limits (technical and/or legal), define a reduced design space, compared to the initial design space covering all possible combinations of ingredients in all possible proportions. The search in this reduced space is then guided by available property models relating product composition to key physicochemical properties or sensorial attributes.

Let y be the vector of binary variables associated with the choice of ingredients and x the vector of corresponding mass fractions. Let p be the vector of product performance metrics, including well defined physico-chemical properties (e.g., rheological profile of a cream-like product) and also metrics related to more subjective sensorial attributes (e.g., greasiness of a cream-like product measured in a scale derived by sensorial tests). Product quality is often evaluated in terms of the deviation of p from target values p^* (product performance specifications). Property models, also known as the property function, are any relationship between metrics p and product composition, here represented by the set of equations $h(x, y, p) = 0$ (Bernardo and Saraiva, 2015). Heuristic rules represent additional knowledge that is incorporated in the problem formulation as the set of constraints $g_1(x, y, p) \leq 0$. Finally, let f be a global objective function to be maximized, accounting for both product quality and cost. The problem of optimal product formulation may then be stated as the following optimization problem:

$$\begin{aligned}
 & \min_{x,y} f(x, y, p, p^*) \text{ [product performance]} \\
 & \text{s. t. } h(x, y, p) = 0 \text{ [property function]} \\
 & \quad g_1(x, y, p) \leq 0 \text{ [heuristic-related restrictions]} \\
 & \quad g_2(x, y, p) \leq 0 \text{ [other restrictions]}
 \end{aligned} \tag{P1}$$

Problem (P1) does not incorporate the role of the product manufacturing process. Let u and v be continuous and binary design variables regarding the manufacturing process (including its scale-up). Then, the final product state s (e.g., microstructural attributes, homogeneity of active ingredients) is a function of x, y, u and v . This is known as the process function, which often includes mass, energy and momentum balances, and other models describing materials transformation during processing, and is here represented by the set of equations here represented by the set of equations $h_2(u, v, x, y, s) = 0$. In this extended design domain, the property function should now include product state variables s , which clearly have a role in defining product properties. The property function is then written as: $h_1(x, y, p, s) = 0$. Heuristics relating the choice of ingredients (x, y) with the design of the manufacturing process (u, v) should also be considered. Problem (P1) may then be extended to the following optimization formulation integrating both product and process design decisions:

$$\begin{aligned}
 & \min_{x,y,u,v} f(u, v, x, y, p, p^*) \text{ [product/process performance]} \\
 & \text{s. t. } h_1(x, y, p, s) = 0 \text{ [property function]} \\
 & \quad h_2(u, v, x, y, s) = 0 \text{ [process function]} \\
 & \quad g_1(x, y, u, v) \leq 0 \text{ [heuristic-related restrictions]} \\
 & \quad g_2(x, y, u, v) \leq 0 \text{ [other restrictions]}
 \end{aligned} \tag{P2}$$

More than a single optimal solution, which due to model uncertainties may only be called optimal in a strictly mathematical sense, one is interested in a small set of promising solutions to be subjected to experimental tests. A set of solutions with different combinations of ingredients may be generated through successive solutions of problems (P1) or (P2), adding integer cuts that prohibit previous integer solutions (Tsai et al., 2008). More precisely, in order to generate S solutions, one first solves the original problem obtaining $y^{(1)}$. Then, one solves the problem again but with the binary cut $y \neq y^{(1)}$, thus obtaining a new formulation $y^{(2)}$. Next, we solve the problem one

more time, now with two cuts: $y \neq y^{(1)}$ and $y \neq y^{(2)}$. And so on, until obtaining $y^{(s)}$. The binary cut $y \neq y^{(k)}$ is imposed through the constraint

$$\sum_i |y_i - y_i^{(k)}| \geq 1,$$

which may be simplified to the differentiable form:

$$\sum_{i:y_i^{(k)}=0} y_i - \sum_{i:y_i^{(k)}=1} (1 - y_i) \geq 1.$$

When generating the s -th solution, one must prohibit all $(s - 1)$ previous solutions and thus the restriction above is written for $k = 1, \dots, s - 1$. It should be noted that if all solutions are obtained to global optimality, then they are a well ranked list of alternatives according to the objective function f .

The list of solutions thus obtained constitutes a plausible set of alternative product formulations to be produced, tested in the laboratory and assessed by customers. In principle, directly or indirectly, all performance metrics p should be evaluated. The methods used are naturally case-dependent and thus are not here discussed. In the example of section 4, tests of alternative formulations for a hair conditioner include rheological and textural measurements.

Finally, as sketched in Figure 1 above, computer-generated alternatives and their experimental testing should evolve in successive cycles where results from experimental tests are fed back to problem formulation (P1) and (P2), in the form of updated models and heuristics. Successive cycles should desirably result in a decreasing number of alternatives under study, until all product specifications are met.

Remarks

In the practical case of section 4, the process function is not studied and thus only a problem of type (P1) is formulated and solved. The incorporation of processing aspects, including scale-up and useful associated heuristics (e.g., mixing intensity, processing temperatures and heating/cooling rates depending on selected ingredients) will be the subject of coming research.

Product design problems are certainly multiobjective, with the typical conflicting pair being product performance vs production cost. In formulations (P1) and (P2) above, a global objective f is considered, which may be an effective approach if for instance deviations from a target quality are modelled using quality loss functions in a monetary basis (Bernardo and Saraiva, 2015, 2005). If however one wants disaggregated results, for instance in the form of a Pareto curve, then multiobjective optimization tools should be used, such as the ε -constraint method (this will be illustrated in section 4.6.6 with a Pareto graph of a product sensorial index vs cost of raw-materials).

Most heuristic rules have a linear formulation, as will be explained in the next section. In general, however, property and process functions are likely to be non-linear and thus problems (P1) and (P2) will be MINLP problems. Global optimization methods are thus needed, moreover to guarantee a correct rank of product alternatives. Nevertheless, in the case study of section 4, problem (P1) is formulated as a MILP problem and then, global optimality is guaranteed using standard optimization solvers.

3. Modelling of Heuristic Rules

In order to incorporate available heuristic knowledge into an overall optimal product design formulation, we propose that heuristic should be first modelled using binary variables and propositional logic. The modelling techniques we will describe below have roots on classical operations research problems (Williams, 2013) and have been widely used in process synthesis (e.g., Raman and Grossman, 1991; Grossmann et al., 1999). A related topic is disjunctive programming (Balas, 1985; Raman and Grossmann, 1994) which has been recently applied to optimal product formulation (Jonuzaj et al., 2016), but its application to our modelling task will not be here discussed.

The simplest rules are often recommended (or regulatory) limits for the quantity of some ingredients. Let y be the vector of binary variables associated with the choice of ingredients and x the vector of corresponding mass fractions. Then, recommended limits for ingredient i are easily modelled through the linear constraints $Ly_i \leq x_i \leq Uy_i$. If ingredient i is chosen ($y_i = 1$), then the desired limits L and U are imposed. If, otherwise, ingredient i is not chosen ($y_i = 0$), the above restrictions result in $x_i = 0$. If no heuristic limits are known, one simply writes $0 \leq x_i \leq y_i$.

Other type of simple rules are limits on the total number of ingredients or on the number of ingredients belonging to a certain class. These are easily modelled adding up corresponding binary variables. For instance, if the formulation should have between M and N ingredients of the subset $\{k\}$, one writes $M \leq \sum_k y_k x_i \leq N$.

More sophisticated heuristics are often initially stated as logical expressions, which in the language of propositional logic are denominated as sentences. These are composed of unit propositions (here designated by capital letters P, Q, R, \dots) linked by logical operators: “or”, “and”, “not”, “implies”, “if and only if”, “exclusive or” (with respective symbols $\vee, \wedge, \sim, \Rightarrow, \Leftrightarrow, \dot{\vee}$). Sentences may be simple (e.g., $P \Rightarrow Q$) or compound [e.g., $(P \wedge \sim Q) \Leftrightarrow R$].

In general, each unit proposition P may be associated with the satisfaction of a general constraint $g(x, y) \leq 0$, involving both continuous and binary variables, x and y , respectively. One then writes: $P \leftrightarrow g(x, y) \leq 0$. Here, we will describe two particular cases of this general relationship and illustrate its usefulness.

Case 1. Each unit proposition P_i is associated with a single binary variable y_i : $P \leftrightarrow y_i$. Simple sentences composed of unit propositions $\{P_i\}$ are easily translated into linear constraints in the binary variables $\{y_i\}$. For instance, regarding the choice of ingredients 1 and 2, $P_1 \vee P_2$ is represented by $y_1 + y_2 \geq 1$, $P_1 \wedge P_2$ by the two restrictions $y_1 \geq 1$ and $y_2 \geq 1$, and $P_1 \Rightarrow P_2$ is logically equivalent to $\sim P_1 \vee P_2$, which is in turn represented by $1 - y_1 + y_2 \geq 1$ (see Raman and Grossmann, 1991, for a complete list of equivalences). In the case of compound sentences, there is also a systematic approach. First, one converts the sentence into the conjunctive normal form using basic properties of logical operations (e.g., distributive property, De Morgan’s laws). The conjunctive normal form is a conjunction of sentences, each one being a disjunction of unit propositions P_i or $\sim P_i$. This normal form is then easily translated to a set of linear constraints in the binary variables $\{y_i\}$. This procedure is better understood with an example.

Example 1. Rule to be modeled: if ingredients 1 or 2 are chosen then ingredients 3 and 4 must be chosen. In proposition logic, one has the sentence:

$$(P_1 \vee P_2) \Rightarrow (P_3 \wedge P_4).$$

Using the definition of implication, this is equivalent to:

$$\sim(P_1 \vee P_2) \vee (P_3 \wedge P_4).$$

Then moving the negation inwards, one obtains:

$$(\sim P_1 \wedge \sim P_2) \vee (P_3 \wedge P_4).$$

Recursively distributing “ \vee ” over “ \wedge ” results in:

$$\begin{aligned} & [\sim P_1 \vee (P_3 \wedge P_4)] \wedge [\sim P_2 \vee (P_3 \wedge P_4)] \\ \Leftrightarrow & (\sim P_1 \vee P_3) \wedge (\sim P_1 \vee P_4) \wedge (\sim P_2 \vee P_3) \wedge (\sim P_2 \vee P_4), \end{aligned}$$

Finally, the translation to linear constraints is:

$$\begin{aligned} 1 - y_1 + y_3 &\geq 1, \\ 1 - y_1 + y_4 &\geq 1, \\ 1 - y_2 + y_3 &\geq 1, \\ 1 - y_2 + y_4 &\geq 1. \end{aligned}$$

Case 2. The proposition P is associated with the satisfaction of the constraint $g(x) \leq 0$: $P \Leftrightarrow g(x) \leq 0$.

In this case, an extra binary variable z is associated with the satisfaction of the constraint: $P \Leftrightarrow z \Leftrightarrow g(x) \leq 0$. Different $g - z$ logical associations may then be useful, such as $z = 1 \Rightarrow g(x) \leq 0$, $g(x) \leq 0 \Rightarrow z = 1$, or both the implications. These implication sentences may be modelled using the so-called big-M technique (Raman and Grossmann, 1991).

Case 2.1. The implication $z = 1 \Rightarrow g(x) \leq 0$ is modelled by the constraint $g(x) \leq U_g(1 - z)$, where U_g is an upper bound for $g(x)$ such that $g(x) \leq U_g$ is certainly non-active. If $z = 1$, then the constraint $g(x) \leq 0$ is “activated”. If otherwise $z = 0$, then $g(x) \leq U_g(1 - z)$ results in the non-active constraint $g(x) \leq U_g$.

Case 2.2. The reciprocal implication $g(x) \leq 0 \Rightarrow z = 1$, translated by the constraint $g(x) \geq L_g z + \varepsilon$, where L_g is a lower bound for $g(x)$ and ε a small positive tolerance to guarantee that, when $z = 1$, $g(x)$ is strictly positive.

Case 2.3 The equivalence $z = 1 \Leftrightarrow g(x) \leq 0$ may be written as the two implications in cases 2.1 and 2.2 and thus it is represented by the two constraints $L_g z + \varepsilon \leq g(x) \leq U_g(1 - z)$.

Example 2. Here we consider heuristic 3 of Table 5 that will be used in the case study of section 3. The heuristic is first stated as follows: “When no thickening polymer is used, the concentration of fatty alcohols is at least twice the cationic surfactants’ in a molar base”. The rule involves three different subsets of ingredients: thickening polymers – set $\{n\}$, fatty alcohols – set $\{m\}$, and cationic surfactants – set $\{r\}$. The heuristic is thus written as the implication:

$$y_n = 0, \forall n \Rightarrow g(x) \leq 0, \text{ with } g(x) = 2 \sum_r \frac{x_r}{M_r} - \sum_m \frac{x_m}{M_m}, \quad (\text{S1})$$

where M designates molar mass (g/mol). Next, this implication is decomposed into two simpler logical sentences, using an auxiliary binary variable z :

$$y_n = 0, \forall n \Leftrightarrow z = 1 \quad (\text{S2})$$

$$z = 1 \Rightarrow g(x) \leq 0 \quad (\text{S3})$$

Sentence (S2) may be modelled using the approach of case 1 above. There are three possible polymer thickeners belonging to set $\{n\}$. One then writes: $(\sim P_1 \wedge \sim P_2 \wedge \sim P_3) \Leftrightarrow Z$, with P_n being the unit proposition “thickener n is chosen” and Z the proposition “ $z = 1$ ”. Unfolding the equivalent into two implications, one has:

$$[(\sim P_1 \wedge \sim P_2 \wedge \sim P_3) \Rightarrow Z] \wedge [Z \Rightarrow (\sim P_1 \wedge \sim P_2 \wedge \sim P_3)].$$

Converting this sentence to the conjunctive normal normal, one obtains:

$$(P_1 \vee P_2 \vee P_3 \vee Z) \wedge (\sim P \vee \sim Z) \wedge (\sim P_2 \vee \sim Z) \wedge (\sim P_3 \vee \sim Z).$$

This is easily translated into the following set of linear restrictions:

$$\begin{aligned} z &\geq 1 - (y_1 + y_2 + y_3), \\ z &\leq 1 - y_1, \\ z &\leq 1 - y_2, \\ z &\leq 1 - y_3. \end{aligned}$$

Sentence (S3) corresponds to case 2.1 above and thus is represented by $g(x) \leq U_g(1 - z)$, with $g(x)$ given by the expression in (S1) with the upper bound $U_g = 2$.

4. Hair Conditioner Case Study

A rinse-off conditioner is a cream-like product applied to wet, freshly washed hair, and rinsed out after a couple of minutes. It improves hair combing and several hair sensorial attributes, mainly through adsorption of cationic surfactants to the hair surface (Idson, 1967). Typically, it is an O/W emulsion containing 10 to 25 % oil phase, stabilized with a combination of emulsifiers (cationic surfactants) and thickeners (Barel et al., 2001). The oil phase is rich in emollients that improve the spread of the product. These three main groups of ingredients – emulsifiers, thickeners and emollients – will be considered in this case study and a suitable combination to be used within each group selected.

4.1. Emulsifiers

Hair conditioning emulsifiers are usually cationic surfactants that define to a great extent sensorial properties, such as consistency and feel of use (Barel et al., 2001). Table 1 shows the list of cationic surfactants considered as possible components of the product formulation, together with some heuristic rules to define the effect of surfactants on the desired “feel of use” attribute of the final product. Most consumers classify products in three alternative categories (moist and lubricating, moist and soft, or soft and moist), and some proportions of surfactants are known to provide a certain classification. For instance, a product perceived as “moist and soft” typically has a molar fraction ratio $x_{r3} : x_{r2}$ going from 1:2 to 1:4 and does not have surfactant $r1$ (Iwata and Shimada, 2013).

4.2. Thickeners

Thickeners used in hair conditioners are often water-soluble polymers and/or fatty alcohols (Table 2). They increase the viscosity of the product and thus influence how it is felt to the touch. Skin creams and conditioners have a similar consistency and thus data regarding skin creams will be here used.

For skin creams, the consumer evaluation of skin feeling has a strong correlation with the product rheological profile (Brummer and Godersky, 1999). More precisely, the primary feeling is correlated to the high viscosity η_1 , perceived on the onset of flow of the product, under low applied stress, while the secondary feeling corresponds to a much lower final viscosity η_2 , when the product is being applied under higher stress (the cream has a strong shear-thinning behavior). Sensorial tests indicate that the ideal cream should have an “initial” viscosity η_1 between 1350 and 3500 Pa.s and a “final” viscosity η_2 between 0.023 and 0.500 Pa.s. Also, the “final” viscosity is perceived at a

typical shear rate of $\sim 500 \text{ s}^{-1}$, corresponding to the cream application over small areas (Brummer and Godersky, 1999).

Composition-viscosity data for polymer thickened aqueous solutions are available for several polymers (Prospector®, 2017). These data, together with a reliable theoretical model to predict the effect of the dispersed phase (Pal, 2001), were used to construct equations of the type $\log(\eta) = a + bx_n + c\phi$ (average relative errors 22%), for each polymer n in Table 2 and for both η_1 and η_2 (ϕ is the mass fraction of oil phase). Since usually only one polymer is used, mixing rules are not needed. Also, often no polymers are used at all and only fatty alcohols are enough to attain a good product's consistency. In that case, fatty alcohols should be present in a concentration at least twice of cationic surfactants', in a molar base (Nakarapanich et al., 2001). This and other heuristic rules will be modelled as algebraic restrictions and included in the design problem formulation, as explained further below.

4.3. Emollients

Emollients are required in the oil phase to improve the spreadability of the product. A proper combination of three or more emollients of high, medium and low spreading types provides the complete profile for a well performing product (Ansmann et al., 2005). Table 3 presents the list of emollients of three different types initially considered as possible ingredients of the formulation.

Emollients are also responsible for the remaining sensorial characteristics (greasiness) after other materials have evaporated (Barel et al., 2001). The greasiness value (γ) of a mixture of emollients can be estimated as a weighted average from individual values available for a wide range of ingredients (Mentel et al., 2014). A typical product specification is a greasiness value γ in the middle of the scale: between 2.0 and 2.4 (Bagajewicz et al., 2011).

4.4. Formulation of the optimal design problem

Product design variables, performance metrics and corresponding desired specifications for the present case study are shown in Table 4. Cationic surfactants, thickeners (polymers or fatty alcohols) and emollients will be selected from an initial list with a total of 35 ingredients, organized as in the above Tables 1 to 3. Vectors y and x of decision variables thus both have dimension 35. The formulation also includes Water, Glycerol and three additional minor ingredients (Disodium EDTA, Propylparaben and Perfume). These five ingredients are mandatory and thus their selection will not be equated. The mass percentage of the last four is also fixed (details are given in section 4.5.2, where the manufacturing procedure is described).

The desired product performance is specified as follows: (i) "feel of use" attribute is set to "moist and soft"; (ii) a cream-like consistency and corresponding feel to the touch is aimed (viscosities η_1 and η_2 within the known ideal ranges for a cream); and (iii) greasiness value γ between 2.0 and 2.4. Specification (i), according to heuristics in Table 1, implies that cationic surfactants r_2 and r_3 must be chosen and in amounts such that x_{r_2} is 2 to 4 times x_{r_3} , and that cationic surfactant r_1 is not chosen. Regarding specification (ii), one has the above-mentioned property models of the type $\log(\eta) = a + bx_n + c\phi$, for both η_1 and η_2 . If no thickeners n are chosen, then heuristic 3 (below described) is activated. Specification (iii) is easily imposed through a linear mixing rule to estimate γ from known individual values for each emollient. The feasible design space is further reduced through other heuristic rules, a sample of which is given in Table 5, together with the corresponding mathematical formulation. The modelling of heuristic 3 is described in detail in example 2 of section 3.

The chosen objective function is the total cost of the formulation in USD/kg, only considering the unit cost of each ingredient and excluding fixed ingredients. The problem of finding the best formulation may then be stated as: “find vectors y and x that minimize cost, subject to property models (for $\log(\eta_1)$, $\log(\eta_2)$ and γ), product specifications ($2x_{r3} \leq x_{r2} \leq 4x_{r3}$, desired intervals for $\log(\eta_1)$, $\log(\eta_2)$ and γ) and a list of heuristic-related restrictions. This is a MILP problem with 87 variables (33 of which binary) and 112 restrictions, which is solved in less than 1 s using GAMS/CPLEX. The problem is solved several times, successively adding binary cuts prohibiting previous solutions y . Since global optimality is guaranteed, a correct rank of solutions with increasing cost is generated, all corresponding to products with similar performance (according to the models and heuristics adopted).

4.5. Experimental tests

4.5.1. Materials

The emulsifiers used for the preparation of samples were Behentrimonium Chloride (BTAC) 85% (Incroquat® Behenyl TMC-85, Croda, USA) and Cetrimonium Chloride (CTAC) 30% (Quartamin® 60, Kao, Mexico). Samples differed in seven components of the oil phase: *Paraffinum Liquidum* (Mineral Oil USP, DISAN, Colombia), Glyceryl Stearate (Cithrol® GMS 40-PA, Croda, Brazil), Octyldodecanol (Eutanol® G, BASF, Mexico), Cyclopentasiloxane (Xiameter® PMX-245, Dow Corning, China), Dimethicone (Xiameter® PMX-200 Fluid, Dow Corning, China) Stearyl Alcohol (ThaiOl 1898, TFA, Thailand) and Cetyl Alcohol (EcoRol 16/98P, PT Ecogreen Oleochemicals, Indonesia). Ingredients common to all samples (Glycerol, Disodium EDTA, Propylparaben and Perfume) were provided by local producers.

4.5.2. Emulsion processing

All sample emulsions were prepared for a total weight of 500 g. Initially, 1 g Disodium EDTA was added to 150 g distilled water (Phase A) and heated to 80°C. In the meantime, the corresponding oily ingredients of each sample were mixed (Phase B) and then heated to 80°C under manual stirring. When both phases reached the desired temperature, Phase B was added to Phase A under continuous agitation using a high-performance dispersing mixer Ultraturrax, (IKA, Germany) at minimum speed (around 2300 rpm) for 10 min. If the sample contained Dimethicone, it was added after the second minute of this step. After completing the homogenization, the emulsion was cooled down by adding the remaining water with 15 g Glycerol (Phase C), and by locating the mixing vessel within an ice-cold water bath. At this point, the emulsion was stirred with a propeller (Heidolph, Kelheim, Germany) at 1000 rpm for 10 minutes. Finally, Cyclopentasiloxane (if selected), Propylparaben and Perfume (Phase D) were added to the mixture when the temperature of the emulsion was below 40°C and then kept under stirring for an additional period of 15 min (at 200 rpm). When needed, the pH value was adjusted to 3.7 ± 0.5 using a Lactic Acid Solution (85%), as the isoelectric point of hair shaft is 3.67 (Gavazzoni Dias et al., 2014). All the samples were stored in polyethylene containers under dry and dark conditions.

4.5.3. Microscopy

Homogeneity and stability of each sample emulsion were verified by optical microscopy (Motic B3-223 Professional Series, Hong Kong, China) using a 400X magnification. The droplet size was measured using Motic Images plus 2.0 software. A small amount of each sample was put on a glass slide, covered with a coverslip and pressed to make

it as thin as possible. All samples were examined 1 month after preparation to assure long term stability.

4.5.4. Rheological measurements

Steady-flow properties were measured on a rotational rheometer Bohlin CVOR 200 (Malvern Instruments, Southborough, USA) with a cone-and-plate geometry. The cone diameter was 40 mm and the gap angle between the cone and plate was 4° . The shear rates were measured from 0.001 to around 2000 s^{-1} , with a logarithmically increasing scale (30 points). All samples were tested 1 week after preparation to assure that the emulsions were stable. The cone-and-plate gap was carefully filled with a defined amount of product, and any extra sample was wiped with a metal spatula. All measurements were conducted at least in duplicate. The measuring temperature was $20 \pm 0.1^\circ\text{C}$.

4.5.5. Texture analysis

The characterization of textural properties was performed to assure that the obtained products were suitable as hair conditioning emulsions, considering the reported properties of such products. The textural properties were measured with Texture Analyzer TA.XT Plus (Stable Micro Systems Ltd., Godalming, U.K.) using a suitable method specified by the equipment manufacturer. An A/BE Back Extrusion Rig was used, which included: Locating Base Plate, Sample Containers (50mm internal diameter) and Compression Discs (35mm diameter). To accurately determine the textural properties of the hair conditioner, samples were put in the Sample Containers (75% full) and kept at a specific temperature of $20 \pm 0.2^\circ\text{C}$. The disc penetrated 25 mm deep inside the sample at a rate of 2.0 mm/s, and the force exerted (up and down) was automatically measured. The following parameters were calculated: firmness, consistency (related to hardness), cohesiveness and index of viscosity (related to adhesiveness). Each sample was analyzed in duplicate and average values were calculated for all parameters (expressed as positive values).

4.6. Results

4.6.1. Optimal formulations

Table 6 shows a rank of nine formulations with increasing cost generated using binary cuts and then all have a different combination of ingredients. As observed, all alternatives contain the same quantity of CTAC and BTAC as emulsifiers, but different contents of emollients and thickeners in phases B and D, and water in Phase C. It is to underline that none of these formulations contain thickening polymers, as the option of using fatty alcohols in a sufficient amount (heuristic 3) turned out to be cheaper. All nine alternatives were prepared and tested as described in section 4.5 above.

4.6.2. Visual inspection and stability

Most of the sample products exhibited the expected creamy consistency, characteristic of this type of personal care products. The exceptions were Formulations 5 and 9, which both had a rather runny appearance. All samples were stable (no phase separation) after being centrifuged at 10000 rpm for 10 min.

4.6.3. Microscopy

Representative optical microphotographs (400X) of the nine sample emulsions are presented in Figure 2, evidencing that all hair conditioners exhibited a similar

microstructure, with droplet sizes ranging from 0.5 to 5 μm . It should be noted that all samples were prepared following the exact same procedure. This could explain the similarities in droplet size, which is known to be a strong function of processing conditions. The understanding of the impacts of the processing conditions in the product structure and in its performance is out the scope of this work and will be explored in a further study.

Insert here Figure 2

4.6.4. Rheological measurements

The viscosity of the nine samples at different exerted shear rates is presented in Figure 3. The plot is divided in two sections to facilitate the analysis: Figure 3(a) for the low shear rate section (below 10 s^{-1}) and Figure 3(b) for high shear rate section (above 10 s^{-1}). All samples 1 to 8 all have a viscosity profile within specifications: an initial viscosity η_1 between 1350 and 3500 Pa.s (Figure 4a, point just before the strong shear-thinning region, $\sim 0.003 \text{ s}^{-1}$) and a final viscosity η_2 between 0.023 and 0.5 Pa.s (see Figure 4b, η_2 at about 500 s^{-1}). All these formulations do not contain thickening polymers but instead a significant amount of fatty alcohols, according to heuristic 3 (Table 5). These results then show that the assumed heuristic 3 is in fact correct. Only Formulation 9 exhibited a different behavior from the rest of the formulations, consistently showing a lower viscosity, moreover at low shear rates. Though the microscopic image of this sample is very similar with the others, it is common to observe differences in the viscosity of some emulsions using fatty alcohols, due to the formation of aggregates (Suzuki, 2017) and the different content of Dimethicone, which seem to have an antagonism together.

Insert here Figure 3

4.6.5. Texture analysis

The parameters obtained from the textural analysis in all prepared sample emulsions are presented in Figure 4 as box and whisker plots, where whiskers extend to 5th and 95th percentile. Except for Formulation 7, all samples are within this range and for all parameters. Although no sensorial tests were performed on these formulations, it has been reported that the textural parameters here evaluated do correlate well with the sensorial attributes of the product. In particular, firmness is related to the texture as perceived by the user, and consistency, cohesiveness and index of viscosity all directly correlate with slipperiness (Lukic et al., 2012). As these textural parameters for all obtained formulations were found to be similar, this indicates that main sensorial attributes are similar as well. However, there remains a need for conducting a sensory evaluation, namely regarding “feel of use” and greasiness, which were the key sensorial attributes initially specified (Table 4).

Insert here Figure 4

4.7. Discussion

For illustrative purposes, Table 7 shows how sensible the optimal solution is (first solution without any binary cuts) to variations in the cost of two ingredients, Cyclopentasiloxane and Dimethicone, with a total of 9 scenarios. In the scenarios of the first two rows of Table 7, the optimal product formulation remains the same (the one in column #1 of Table 6) and the minimum cost varies in the expected proportion. Conversely, in the scenarios of the third row (40% increase in the cost of Cyclopentasiloxane), the same combination of ingredients is selected but the level of

Cyclopentasiloxane decreases to its lower bound of 1% and the amount of other emollients increases in order to comply with a total of 6% in the set of emollients.

To illustrate how multiple objectives may be handled, we now consider product greasiness vs cost. The original problem was formulated with the specification of greasiness value γ between 2.0 and 2.4 and all optimal solutions of Table 7 converged to the upper limit of 2.4 (heavier emollients perceived as more greasiness are cheaper). A Pareto curve showing the greasiness/cost trade-off may thus be constructed solving the problem with the constraint $\varepsilon - 0.4 \leq \gamma \leq \varepsilon$ for decreasing values of ε . Such a curve is shown in Figure 5 with values of ε between 1.38 and 3.2. All points in the figure correspond to optimal solutions that have converged to $\gamma = \varepsilon$. These results may be read as the additional cost one has to pay for a product with a lower greasiness value, more adequate for greasy hair. For example, taking a greasiness value of 2.4 as a base, if we set this value to 1.4, the minimal cost for a formulation would increase from 0.60 to 1.51 USD/kg. Indeed, a formulation with lower values of greasiness requires less greasy emollients, which are in general more expensive than more greasy emollients.

Insert here Figure 5

In a scenario with an increasing number of ingredients, it will be expected a much greater number of equally performing feasible alternatives, along with a higher level of uncertainty due to the synergies and antagonisms of the new ingredients. The first issue could be partially addressed by better understanding the critical performance parameters and incorporating them in a multi-objective optimization function with a multicriteria decision-making tool that allow the designer to choose the solution that better suits the required performance goals. This approach will be further explored in a future contribution. Besides, to cope with a higher level of uncertainty, in the practice, designers use a chassis formulation as a base, on which they perform small changes using experimental design (Claeys-Bruno et al., 2009; Ochoa et al., 2017), in order to adjust the optimal level of a new ingredient.

5. Conclusions

We have proposed an optimization-based methodology for the design of formulated products, which explicitly incorporates available heuristic rules. These may be initially stated as logical constraints that are easily translated into algebraic restrictions using binary variables and propositional logic. The methodology was applied to a cosmetic emulsion example, being generated a rank of alternative solutions that fulfill expected properties with minimum ingredient costs. These computer-generated solutions were then manufactured and tested. The rheological, textural and microstructural properties of the alternative formulations show that most of them are similar, and so any of them could serve as a starting point for inexperienced designers. It was thus demonstrated that is possible to reduce the time and resources spent in cosmetic emulsions design comparing with the traditional trial-and-error methods.

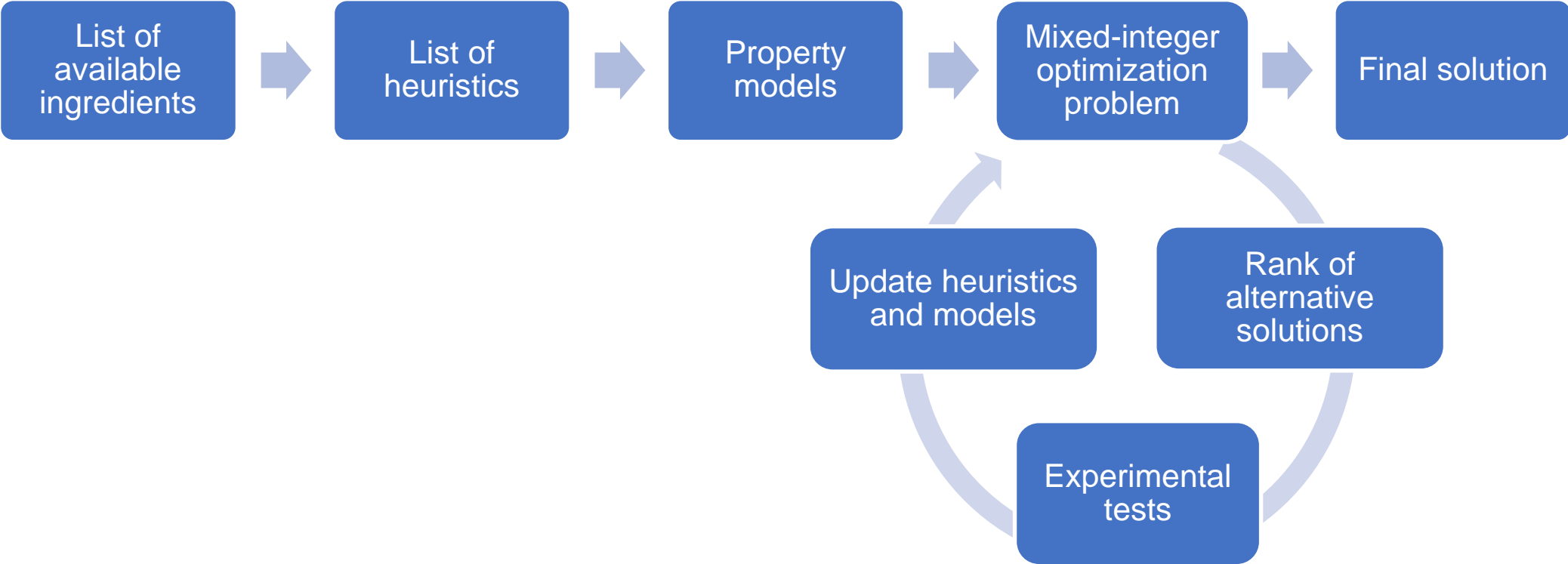
Acknowledgments

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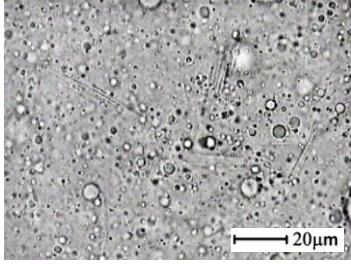
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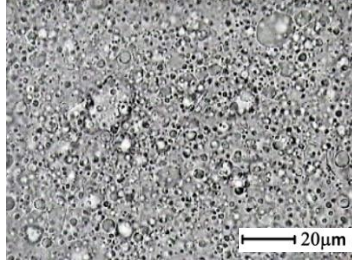
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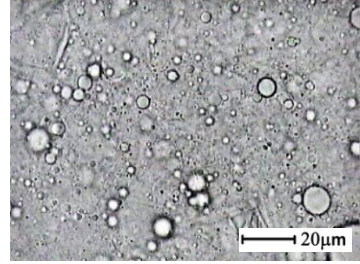
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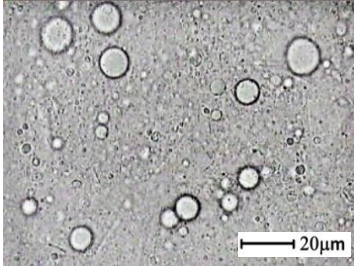
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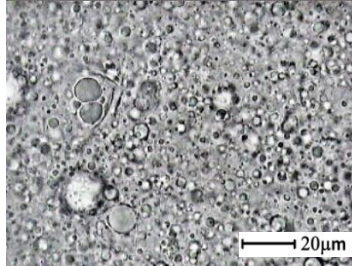
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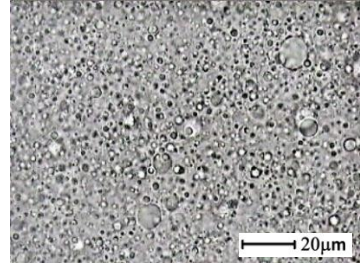
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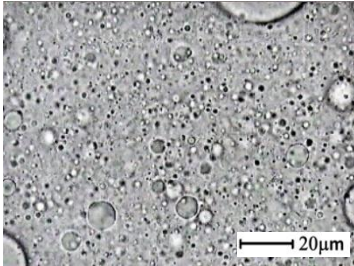
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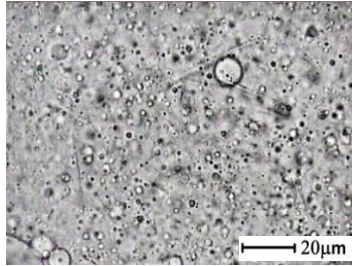
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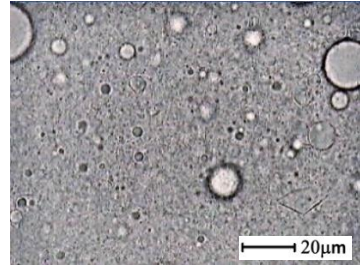
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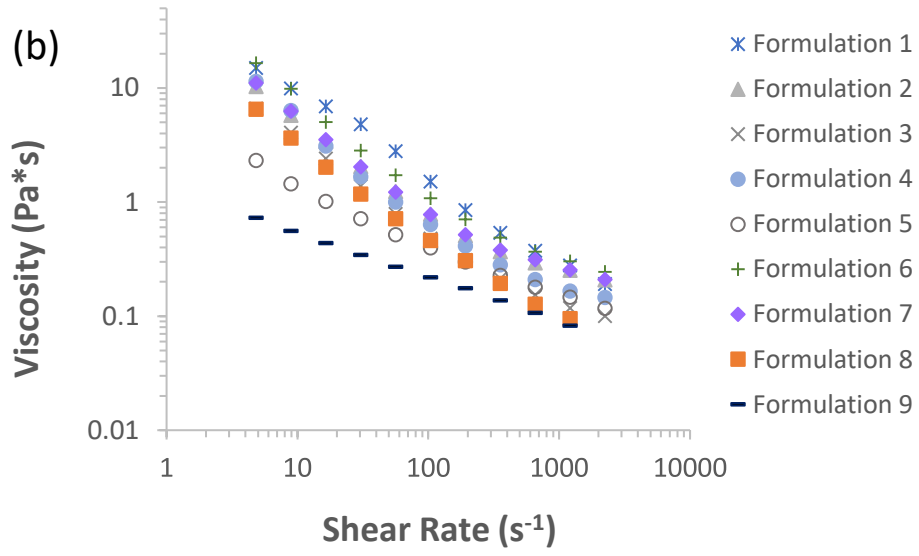
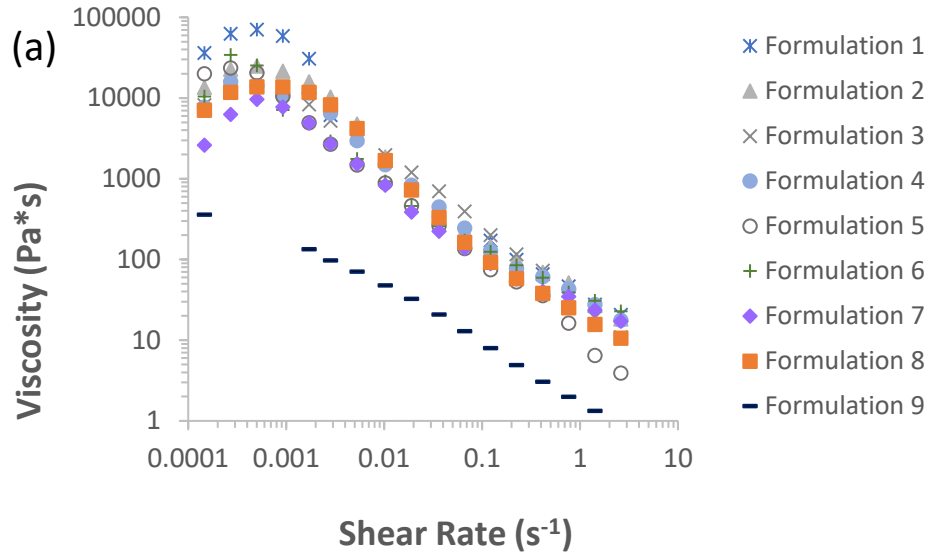


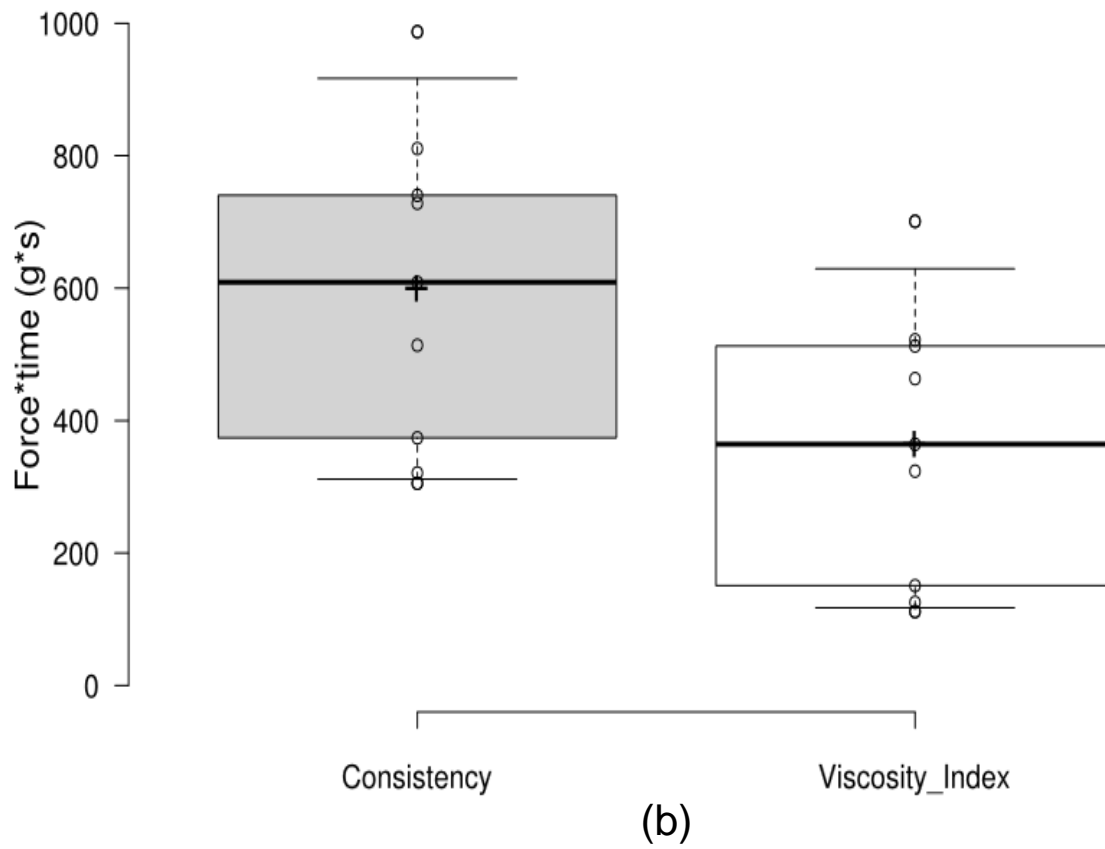
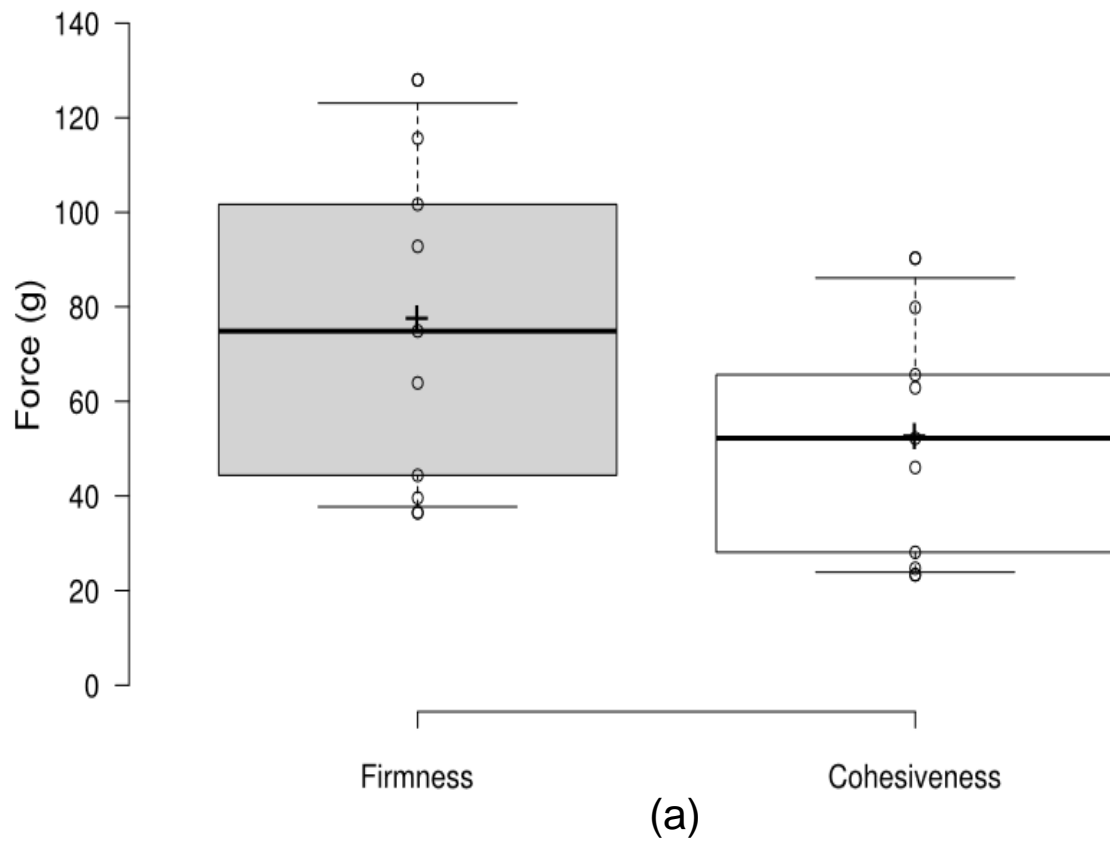
Formulation #8



Formulation #9







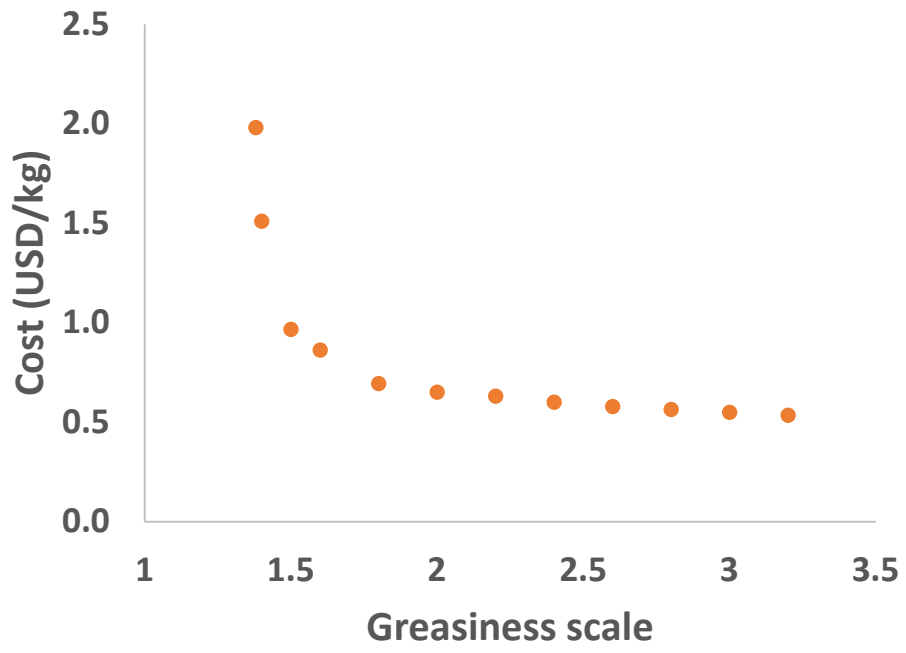


Table 1. List of available cationic surfactants and heuristics for feel of use attribute

	Cationic surfactant (<i>r</i>)	Moist and lubricating	Moist and soft	Soft and moist
1	Steartrimonium Chloride (STAC)	1 to 4 parts	-	2 to 4 parts
2	Cetrimonium Chloride (CTAC)	1 to 4 parts	2 to 4 parts	-
3	Behentrimonium Chloride (BTAC)	-	1 part	1 part
4	Stearamidopropyl Dimethylamine	-	-	-
5	Behenamidopropyl Dimethylamine	-	-	-

Table 2. List of available thickeners

	Thickening polymer (<i>n</i>)	Fatty alcohol (<i>m</i>)
1	Hydroxypropyl Starch Phosphate	Stearyl alcohol
2	Hydroxyethyl Cellulose	Cetyl alcohol
3	Hydroxypropyl Guar	Cetearyl alcohol

Table 3. List of available emollients

	High spreading (i)	Medium spreading (j)	Low spreading (k)
1	Cyclopentasiloxane	C12-C15 Alkyl benzoate	Oleyl erucate
2	Isoamyl cocoate	Glyceryl stearate	<i>Persea gratissima</i> oil
3	Diethylhexyl carbonate	Cetyl ethylhexanoate	PPG-15 stearyl ether
4	Isopropyl Myristate	Cetearyl Isononanoate	Cetyl Dimethicone NP**
5	Isopropyl palmitate	Cetyl Dimethicone MP*	PPG-14 butyl ether
6	Decyl cocoate	PPG-3 Myristyl ether	Triisostearin
7	Ethylhexyl palmitate	<i>Paraffinum Liquidum</i>	Dimethicone
8	Phenoxyethyl caprylate	Octyldodecanol	
9	Caprylic/Capric triglyceride		

*MP = Medium polarity; **NP=Nonpolar

Table 4. Product design variables, performance metrics and specifications

Design variables: choice of ingredients y and mass percentages x
cationic surfactants: y_r, x_r
thickening polymers: y_n, x_n
fatty alcohols: y_m, x_m
high spreading emollients: y_i, x_i
medium spreading emollients: y_j, x_j
low spreading emollients: y_k, x_k
Performance metrics
1. Feel of use = $f(x_r)$ (see Table 1)
2. Consistency/feel to the touch: related to viscosities η_1 and η_2 (both function of x_n, x_m and ϕ) or of fatty alcohols content
3. Greasiness $\gamma = f(x_i, x_j, x_k)$
Specifications
1. "Moist and soft"
2. $\eta_1 \in [1350, 3500]$ (Pa.s) and $\eta_2 \in [0.023, 0.500]$ (Pa.s), or satisfy heuristic 3 (see Table 5)
3. $2.0 \leq \gamma \leq 2.4$

Table 5. Sample of heuristics used in the problem formulation

Heuristic	Mathematical formulation
1. There should be at least two but no more than three cationic surfactants.	$2 \leq \sum_r y_r \leq 3$
2. Cationic surfactants at about 20% of the oil phase should stabilize the emulsion.	$0.16\phi \leq \sum_r x_r \leq 0.24\phi$
3. When no thickening polymer is used, the concentration of fatty alcohol is at least twice the cationic polymers' in a molar base.	Let $z \in \{0,1\}$: $y_n = 0, \forall n \Leftrightarrow z = 1$ $z = 1 \Rightarrow \sum_m \frac{x_m}{M_m} \geq 2 \sum_r \frac{x_r}{M_r}$
4. If heuristic 3 holds, then product viscosity profile is expected to be satisfactory.	$z = 1 \Rightarrow \eta_1$ and η_2 are within specifications
5. At least one emollient of each type should be used: high, medium and low spreading.	$\sum_i y_i \geq 1; \sum_j y_j \geq 1; \sum_k y_k \geq 1$

Table 6. Nine alternative formulations with increasing cost

Phase	Ingredient	Cost \$/kg	Formulation								
			#1	#2	#3	#4	#5	#6	#7	#8	#9
A	Water		60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%
	Disodium EDTA		0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%
B	Cetyl Alcohol (<i>m2</i>)	2.4	4.1%	4.1%	-	4.1%	-	4.1%	4.1%	4.1%	-
	Stearyl Alcohol (<i>m1</i>)	2.4	-	-	4.5%	-	4.5%	-	-	-	4.5%
	CTAC (30%) (<i>r2</i>)	2.6	6.7%	6.7%	6.7%	6.7%	6.7%	6.7%	6.7%	6.7%	6.7%
	BTAC (85%) (<i>r3</i>)	10.0	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%
	Glyceryl stearate (<i>j2</i>)	6.0	1.0%	-	1.0%	1.0%	-	1.0%	-	-	1.0%
	<i>Paraffinum Liquidum</i> (<i>j7</i>)	1.3	1.1%	1.1%	1.1%	-	1.1%	1.4%	-	1.0%	-
	Octyldodecanol (<i>j8</i>)	7.0	-	1.0%	-	-	1.0%	1.0%	1.0%	-	-
	Dimethicone (<i>k7</i>)	3.1	1.0%	1.0%	1.0%	2.6%	1.0%	1.0%	2.6%	1.0%	2.6%
C	Water		18.1%	18.1%	17.7%	18.1%	17.7%	18.1%	18.1%	16.6%	17.7%
	Glycerol		3.0%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%
D	Cyclopentasiloxane (<i>i1</i>)	3.5	2.9%	2.9%	2.9%	2.4%	2.9%	1.6%	2.4%	5.5%	2.4%
	Propylparaben		0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%
	Perfume		0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
			100%	100%	100%	100%	100%	100%	100%	100%	100%
Cost	(USD/kg)		0.60	0.61	0.61	0.62	0.62	0.63	0.63	0.63	0.63

Table 7. Optimal product cost increase with variations in the costs of Dimethicone and Cyclopentasiloxane.

		Dimethicone cost increase		
		0%	20%	40%
Cyclopentasiloxane cost increase	0%	0.0%	1.0%	2.1%
	20%	3.4%	4.4%	5.4%
	40%	6.1%	7.2%	8.2%

Figure 1. Proposed methodology for optimal design of formulated products

Figure 2. Photomicrographs of investigated samples (400X)

Figure 3. Rheological profiles of tested formulations at low (a) and high (b) shear rates.

Figure 4. Results of texture analysis: (a) firmness and cohesiveness; (b) consistency and viscosity index

Figure 5. Pareto curve of product greasiness vs cost