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On the effect of the selection of suppliers on the design of formulated products

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ABSTRACT

An extended pooling problem is developed for the design of detergents, that include process and product design together with suppliers' selection. It is a multiperiod and multi-objective optimization problem since it considers the economic benefit and environmental impact as well as the contract length. This problem can be considered as a previous step to the integrated product, process and supply chain design. This type of problems is non-linear and non-convex. Two formulations are developed to tackle this problem. An MINLP and a reformulated NLP using a decision vector avoiding the use of binary variables. The NLP shows better computational performance in spite of the larger problem size. Furthermore, it is demonstrated that when considering different ingredients, formulations, pricing policies and suppliers, their selection can be adjusted until a reduction of almost 40% of CO_2 emissions is achieved without the benefit decreasing more than 1.5%.

1. Introduction

The market for consumer products is more competitive than ever as a result of globalization. For a product to be competitive, it has to meet specific consumer needs and likes. Therefore, the first stage to design any consumer product consists of identifying those needs and wishes and convert them into physicochemical properties of the product (Moggridge and Cussler, 2000; Uhlemann and Rei, 2009; Cussler et al., 2010; Bagajewicz et al., 2011; Teixeira et al., 2012; Tijskens and Schouten, 2009). To optimize this step, the new products can be designed using computer-aided tools and virtual experiments. The systematic approach for the design of products has been applied to the manufacture of polymers (Vaidyanathan et al., 1998), refrigerants (Churi and Achenie, 1997), repellents (Conte and Gani, 2011), and surfactants (Mattei et al., 2014) including social and environmental concerns lately to attract a more conscious consumer (Yue et al., 2013; Garcia and You, 2015; Mota et al., 2015). Subsequently, a process is to be put together that is capable of producing the expected product or a family of products to satisfy the consumer demand. However, the appropriate method to design a new product is to simultaneously consider the product and the production process, allowing a global analysis of the whole process from the conceptual idea of the product to its delivery to the customer (Gani, 2004; Martín and Martínez, 2013; Ng and Gani, 2018) analyzing the trade-offs between the quality of the product and the need of the manufacturing process (Taifouris et al., 2020). In this way, the technical, economic, environmental and safety analysis (Lacasa et al., al.,2016; Scruggs, 2013) are taken into account not only for the design of the product but also for its production. This allows adjusting the production costs of the products and increasing the competitiveness of the company (Zaman et al., 2018).

A particular case of products is the so-called formulated products. This type of products consists of a mixture of ingredients that altogether are capable of providing the features the consumer expects (Zhang et al., 2017). The integrated approach for the design of products is particularly important in the design of formulated products since the product composition can be modified easily affecting its production process. Therefore, the simultaneous design of the process and the product allows reducing the feasible set of formulas (Bernardo and Saraiva, 2005;Martín and Martínez, 2013, 2018) eliminating those that are not economically and environmentally viable. As a result, the physical resources can focus on the most promising products. On the one hand, the manufacture of formulated products can be approached using an extended pooling problem. In the pooling problem, a series of ingredients are mixed to obtain a product with properties that meet the customers' ex-

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Nomenclature

Parameters

Al_i	Minimum amount of raw material i necessary for the process (t)
Au_i	Maximum amount of raw material i supported by the process (t)
$Cpool_l$	Variable cost of pool l (€/kg)
$c0_{i,sup}$	Price without discount of raw material i of supplier sup(€/kg)
Loading capacity	Loading capacity (t)
$CC_{i,k}$	Composition of ingredient k in the raw material i (t_i/t_k)
$Costf_i$	Average price of the raw material i with uncertainty (€/kg)
discount	Discount parameter of policy 1
disct	Discount parameter of policy 2
$Distance_{sup}$	Distance from the supplier sup to the manufacturer(km)
$Dl_{ye,j}$	Minimum demand in the year ye of the product j (t)
$Du_{ye,j}$	Maximum demand in the year ye of the product j (t)
fixdisc	Discount parameter of policy 4
HCk_k	Equivalent CO_2 emissions of the ingredient k ($kgCO_2/kg_k$)
$Linf_{i,sup}$	Minimum amount of the raw material i by the supplier sup (t)
$Lsup_{i,sup}$	Maximum available amount of the raw material i by the supplier sup (t)
$Pg_{j,g}$	Maximum concentration of the group of ingredients g in the product j(t_g/t_j)
$Pl_{j,g}$	Minimum concentration of the group of ingredients g in the product j (t_g/t_j)
$powd_{i,sub}$	Discount parameter of policy 3
priceT	Transport price (€/km)
S_l	Maximum tank size (t)
$Priceprod_j$	Price of the product j (€/kg)

Variables

Variable	Description (Type of Variable)
$Bi_{po,i,sup}$	Binary variable which select the optimal police (Binary)
$Cakest_j$	Cake strength of the product j (kg) (Continuous)
$ccp_{ye,i,sup,po}$	Purchased amount of the raw material i from the supplier sup using policy po and in the year ye (t_i/year) (Continuous)
$costj_{ye,i,sup,po}$	Raw material i cost applying the discount of the policy po of the supplier sup the year ye (€/kg) (Continuous)
$CostP_{ye,i,sup,po}$	Combined cost of the raw material fixed by contract and with uncertainty (€/kg) (Continuous)
$Cost_{ye,i,sup}$	Raw material costs with fixed contracts(€/kg) (Continuous)
$Ctrans_{sup}$	Cost of transport for the supplier sup (€/km) (Continuous)
$CTransU_{sup}$	Unit cost of transport for the supplier sup (€/kg) (Continuous)
CTT_{sup}	Total transport cost for the supplier sup (€) (Continuous)
CTTT	Total transport cost (€) (Continuous)
$EmisionT_{ye,sup}$	Total emissions in the year ye and from the supplier sup (Kg/year) (Continuous)
$Emission_{sup}$	CO_2 emission of transport from the supplier sup to the factory ($KgCO_2$) (Continuous)
$EmissionU_{sup}$	Unit emission of CO_2 of the supplier sup ($kgCO_2$/kg) (Continuous)
HCi_{ye}	Carbon footprint of the ingredients in the year ye ($KgCO_2$/year) (Continuous)
HC_{ye}	Total carbon footprint in the year ye ($KgCO_2$/year) (Continuous)
$MassProd_{ye,j}$	Amount produced of product j per year (t/year) (Continuous)
$Particle_j$	Particle size of the product j (μm) (Continuous)
$penalty_{ye,i,sup,po}$	Penalty for supplier or policy repetition (€/kg) (Continuous)
$Performance_j$	Performance of product j (Continuous)
$PQ_{j,k}$	Composition in component k of product j (t_k/t_j) (Continuous)
Profit	Profit obtained (€) (Continuous)
$p_{ye,l,k}$	Composition in component k of pool l (t_k/t_l) (Continuous)
$x_{ye,i,l}$	Flows from raw material i to intermediate pool l (t_i/year) (Continuous)
$y_{ye,l,j}$	Flow from pool l to product j (t_i/year) (Continuous)
$z_{ye,i,j}$	Flow from raw material i to product j (t_i/year) (Continuous)

Indices

g	Group of the ingredients
i	Raw material
j	Product
k	Ingredient
l	Pool
po	Price policies
sup	Supplier
ye	Year

pectations (Audet et al., 2004). When a pooling problem is mathematically formulated, the presence of bilinear terms in the product quality, composition and the mass balances as well as the functions that model cost estimations (Audet et al., 2004), and process constraints (Martín and Martínez, 2013) makes it highly non-linear. This fact represents a challenge when addressing the integration of the pooling problem within the supply chain. Supply chain studies are typically mixed integer linear programming (MILP) problems where the process and product design have been fixed (Yue and You, 2014). Supply chains including nonlinear terms are most of the times linearized and/or decomposed to make them computationally tractable (Terrazas-Moreno et al., 2012) but this is an approximation of the original problem that for formulated products presents drawbacks. In addition, due to the mathematical complexity, pooling problems are not integrated with the supply chain, which means that it is not possible to ensure that the design of the process and the product are optimal since both are affected by the supply chain. A stage prior to the integration of the complete supply chain would be to integrate the selection of suppliers. Extensive research work on supplier selection has been carried out (Sawik, 2013; Gou and Li, 2014; Qian, 2014) studying how the supply chain is affected by these decisions. Nevertheless, the effect of these decisions on product and process design has not been considered yet. In addition, for the economic evaluation of the production process it is necessary to differentiate between two types of ingredients. Those whose price varies with the market and therefore is subjected to the uncertainty of the market and those that can be fixed by multi-period contracts of several years. To account for the variability, studies that introduce uncertainty in the optimization model have been presented (Kim et al., 2011; Martín and Martínez, 2015) while in the case of ingredients with a deterministic price, different pricing policies have been evaluated to estimate the cost of the ingredient depending on the amount of ingredient (Martín and Martínez, 2018). While both considerations have been analyzed separately, either ingredients prices with associated variability (Martín and Martínez, 2015) or ingredients whose price is fixed by multi-period contracts (Martín and Martínez, 2018), the most realistic case would be an intermediate case in which some of the prices of the ingredients are fixed by contracts and others have an associated market variability.

In this work, we integrate the selection of suppliers into the integrated process and product design problem for a specific case of formulated products, powder detergents. Therefore, it is a step towards the integration of product design, process and supply chain in formulated consumer products. Two objectives will be taken into account, the economic benefit and the environmental impact. This type of problem is complex and requires an analysis to address it in order to consider the impact of the environmental impact on the benefit, the optimal formulation of the product, the selection of suppliers and the selection of pricing policies. The optimization model developed, which is multi-objective and multi-period, seeks to analyze the trade-off between the economic benefit as the environmental impact limit is reduced and the effect on a wide variety of decision variables such as the amount and type of purchased raw material, suppliers and price policies. The rest of the paper is organized as follows. In Section 2, the mathematical optimization model is developed including the formulation of the process, the ingredients considered and the price estimation method, whether fixed by contracts or subject to market variability, the estimation of the environmental impact index and the main objective function.The two formulations considered are presented. In Section 3.The model is applied for a case study in Europe. In Section 4, the results are shown and in Section 5, the conclusions and future work are discussed.

2. Mathematical model

2.1. Problem description

We address the sustainable production of three types of powder detergents with different performances and prices, from economic and environmental points of view. In addition, to integrate the process and product design with the supply of the ingredients, we seek to analyze the effect of the selection of different suppliers on both objectives. Several suppliers are considered for each type of ingredient, with different distances between the suppliers and the factory and different prices related to those distances. The environmental impact associated with the transport is also considered. The detergent performance is introduced as a constraint with minimum and maximum values for each type of detergent. In an attempt to get closer to reality, 7 groups of ingredients are considered. These groups include the most used ingredients in industry (European Ecolabel, 2011). 17 ingredients with different environmental impacts and prices are evaluated, see Table 1. In addition, the price of some ingredients can be arranged through multi-period contracts (3 years) and others have an associated market variability. For those whose price is fixed throughout the year, the best pricing policy is to be selected based on the amount used. The final product is obtained by mixing the ingredients as long as processing and performance constraints are met including particle size and cake strength. Both types of constraints are modelled as a function of the concentration of the ingredients as in previous works but updated to account for the use of different ingredients within the same group.

Over the years, tighter environmental regulations have been passed. To evaluate the effect of the ever-decreasing emission limits, the environmental impact of the production of the final products is computed. By using the ε-constraint method, the trade-off between the profit and the environmental impact due to the ingredients and their transportation is evaluated. Therefore, a mathematical model is developed that takes into account the mass balances of the detergent production process, the limitations associated with this process, the calculation of the performance of the final product, the environmental impact of the ingredients and their transport, the ingredient pricing policies, purchased through contracts and the price of ingredients with associated uncertainty. For the sake of the length of the work, we refer the reader to previous works for details on the modelling of the process constraints (Martín and Martínez, 2013, 2018).

2.2. Model development

In this section, two different formulations of the problem are described. The original one is an extension of the work of Martín and Martínez (2015, 2018) based on a mixed integer nonlinear programming (MINLP) formulation. However, the complexity of the problem and the expected extension to address the entire supply chain suggest a different solution approach. Therefore, an alternative formulation is also developed.

2.2.1. Production process

The mathematical formulation for the design of detergents used in this work is based on the model presented by Martín and Martínez (2013). The ingredients follow five stages: The mixture of the ingredients where a series of physico-chemical reactions is favored, the atomization of the slurry to avoid possible jams, a drying process in a spray drier, a cooling process and a finishing stage where a series of additives is added to adjust the properties. We refer the reader to previous work of Martín and Martínez (2013) for the complete process. In this work, the formulation is updated to account for various ingredients within the same group and several suppliers per ingredient.

2.2.1.1. Mass balances and process constraints. In order to follow the mass balances and the rest of the sections presented below, it is necessary to explain the difference between the 'i' index, which represents the types of raw materials that are fed to the plant and previously purchased from the suppliers; and the 'k' index that represents the pure ingredients. In this work, it has been considered that the raw materials only contain a single ingredient, so that the flow $i = 1$ only contains the component $k = 1$ (same for the rest). However, formulating the model in this way allows the raw material to be composed of different ingredients (in previous work, some of these flows of raw materials had several ingredients because they were residues of other processes).

The purchased amount of the raw material is related to the inflows to the factory, given by Eq. (1).

$$\sum_{sup} ccp_{ye,i,sup} = \sum_{l} x_{ye,i,l} + \sum_{j} z_{ye,i,j} \forall ye,\ i \tag{1}$$

Where $ccp_{ye,i,sup}$ is the amount purchased in the year "ye" of the raw material "i" from the supplier "sup". It is not necessary to use binary variables for the selection of suppliers because the variable $ccp_{ye,i,sup}$ will select to buy the optimal amount of raw material 'i' from the best supplier, considering the availability, the distance, the prices and the rest of variables that influence it. In this way, if the necessary amount of raw material 'i' can be purchased from

Table 1
Ingredients considered.

Group	Ingredient	Abbreviation
Surfactant	Linear alkyl aryl sulfonates	LAS
	Alcohol ethoxylates and Alkyl amides	AE
	Esterified mono-alkyl	MTEA
Builder	Polyphosphates	STPP
	Zeolite	ZE
Bleach	Sodium perborate tetrahydrate	S. PERBO
	Sodium percarbonate.	S. PERCA
Fillers	Sodium sulfate	S.SU
	Xylene sulphonate	X.SU
Antifoaming agents	–	ANTI
Enzymes	Protease	PRO
	Lipase	LIP
	Cellulose	CELL
Polymers (Antiredeposition agents)	Carboxymethyl cellulose	CMC
	Sodium polyacrylate	S. POLY
	Polyethylene glycol	POLYGLY

a single supplier, only one will be selected (the optimal one), because centralizing purchases will reduce the prices of the raw material by economies of scale (see Eqs. (30)-(33)). But if a single supplier cannot supply the needs of a raw material, the model will proceed to buy first to the optimum and then to the second best.

It is necessary to differentiate between the limits imposed by each of the suppliers according to their own capacity:

$Lsup_{i,sup}$ and $Linf_{i,sup}$

And the inherent limits to the process:

Au_i and Al_i

Nevertheless, by default we consider that there is no maximum or minimum production limit. However, in this work these limits will be fixed by the maximum and minimum amount of raw material available. The differentiation between the limits is maintained for the model to be generic. In this way, if it is necessary to set a production capacity limit, the model will not need important changes. Therefore, we include Eqs. (2) and (3) in the model.

$$\sum_{sup} Lsup_{i,sup} = Au_i \ \forall i \tag{2}$$

$$\sum_{sup} Linf_{i,sup} = Al_i \forall i \tag{3}$$

The sum of the flows of raw materials that go to the intermediate tanks and those that go to the final product tank must be between the upper and lower limit of the process (Eq. (4)).

$$Al_i \leq \sum_l x_{ye,i,l} + \sum_j z_{ye,i,j} \leq Au_i \ \forall ye, i \tag{4}$$

As it can be seen, all these limits are not per unit of time because the same limits are assumed every year. The total amount sent to the intermediate tanks must be less than or equal to the maximum capacity of the intermediate tank (Eq. (5)).

$$\sum_i x_{ye,i,l} \leq S_l \ \forall \ ye, l \tag{5}$$

The amount of detergent produced must be between the maximum and minimum limit of the detergent demand (Eq. (6)).

$$Dl_{ye,j} \leq \sum_l y_{ye,l,j} + \sum_i z_{ye,i,j} \leq Du_{ye,j} \ \forall ye, j \tag{6}$$

The demand depends on the period since the demand for the first year may be different from the demand in second year depending on the result of the market study in the region of study.

Eq. (7) shows the mass balances to intermediate tanks.

$$\sum_i^{17} x_{ye,i,l} = \sum_j^{3} y_{ye,l,j} \forall ye, l \tag{7}$$

The mass balances to the different ingredients between the input streams and the intermediate tanks are shown by Eq. (8).

$$\sum_i^{17} CC_{i,k} * x_{ye,i,l} = \sum_j^{3} p_{ye,l,k} * y_{ye,l,j} \forall \ \text{ye, l, k} \tag{8}$$

Where $CC_{i,\,k}$ is the initial concentration of component 'k' of the raw material streams 'i' and $p_{ye,l,k}$ is the concentration of component 'k' in tank 'l' in year 'ye'. It is considered that the initial concentration of the raw material streams will be the same every year. It does not depend on the time period or the chosen supplier.

To establish the limits of the composition of each ingredient 'k' in the final product, a new dimension is defined since the limits, both lower and upper, will be set taking into account the group to which it belongs and not the particular ingredient. In this way, there are common limits to different chemical substances depending on whether they are surfactants, builders, bleaches or the rest of groups. Thus, within each group, the mathematical model can choose a different amount of each ingredient of the same group (in order to meet the expected properties) with respect to the limits of the group. For example, in the case of the group 'surfactants', there will be an upper and a lower limit for the sum of the three different surfactants, but not for LAS, AE or MTDI individually. Thus, the composition can be properly adjusted. Therefore, a new dimension is defined, corresponding to the group 'g', and upper and lower limits are established for each group. The equivalences between the minimum and maximum compositions of each group and the sum of the different ingredients are shown by Eqs. (9)-(16).

$$Pl_{j,1} \leq \left(PQ_{j,1} + PQ_{j,2} + PQ_{j,3}\right) \ \leq Pg_{j,1} \ \forall j \tag{9}$$

$$Pl_{j,2} \leq \left(PQ_{j,4} + PQ_{j,5}\right) \ \leq \ Pg_{j,2} \ \forall j \tag{10}$$

$$Pl_{j,3} \leq \left(PQ_{j,6} + PQ_{j,7}\right) \leq Pg_{j,3} \ \forall j \tag{11}$$

$$Pl_{j,4} \leq \left(PQ_{j,8} + PQ_{j,9}\right) \ \leq Pg_{j,4} \ \forall j \tag{12}$$

$$Pl_{j,5} \leq PQ_{j,10} \ \leq \ Pg_{j,5} \ \forall j \tag{13}$$

$$Pl_{j,6} \leq \left(PQ_{j,11} + PQ_{j,12} + PQ_{j,13}\right) \ \leq \ Pg_{j,6} \ \forall j \tag{14}$$

$$Pl_{j,7} \leq \left(PQ_{j,14} + PQ_{j,15} + PQ_{j,16}\right) \leq \ Pg_{j,7} \ \forall j \tag{15}$$

$$Pl_{j,8} \leq \left(PQ_{j,17}\right) \leq \ Pg_{j,8} \ \forall j \tag{16}$$

These limits are considered to be constant over the periods of time, just like the optimal formulation of the final product. The global balance of ingredients is given by Eq. (17).

$$PQ_{j,k} * \left(\sum_{l} y_{ye,l,j} + \sum_{i} z_{ye,i,j} \right) = \sum_{i} CC_{i,k} * z_{ye,i,j} + \sum_{l} p_{ye,l,k} * y_{ye,l,j} \ \forall ye, j, k \quad (17)$$

The limits of each stream are given by Eqs. (18)-(20).

$$0 \le x_{ye,i,l} \le min \left\{ A_i^U, S_l, \sum_j D_{ye,j}^U \right\} \ \forall ye, i, l \quad (18)$$

$$0 \le y_{ye,l,j} \le min \left\{ S_l, D_{ye,j}^U, \sum_i A_i^U \right\} \ \forall ye, l, j \quad (19)$$

$$0 \le z_{ye,i,j} \le min \left\{ D_{ye,j}^U, A_i^U \right\} \ \forall ye, i, j \quad (20)$$

In addition, it is necessary to include the surrogates that predict the product performance, the environmental impact and the process constraints.

2.2.1.2. Calculation of the product performance. To determine the effect of the concentration of ingredients in the final product on the performance, a design of experiments (DOE) was formulated using open literature data to evaluate which ingredients were the ones that were most likely to affect the cleanliness of the clothes. Using those data, a correlation was obtained and used in the mathematical model. For more details on how the correlations were developed, see the work of Martín and Martínez. (2013). Assuming that the different types of surfactants, enzymes, builders, polymers and bleaches have the same effect on the performance, the original formulation of the work of Martín and Martínez (2013) was modified and Eq. (21) is obtained.

$$\begin{aligned} Performance_j = & (107 * \left(PQ_{j,surf1} + PQ_{j,surf2} + PQ_{j,surf3} \right) \\ & + 1872 * \left(PQ_{j,enz1} + PQ_{j,enz2} + PQ_{j,enz3} \right) \\ & + 53.9 * \left(PQ_{j,bu1} + PQ_{j,bu2} \right) \\ & + 134 * \left(PQ_{j,pol1} + PQ_{j,pol2} + PQ_{j,pol3} \right) \\ & + 119 * \left(PQ_{j,bl1} + PQ_{j,bl2} \right) \ \forall j \end{aligned} \quad (21)$$

The quality of the detergent is directly related to the value of the performance. To identify three detergents, three different performances are established:

Detergent A (High quality and high price) ≥ **0.95**
Detergent B (Average quality and average price) ≥ **0.80**
Detergent C (Sufficient quality and lower price) ≥**0.70**

Note that a more detailed correlation can be developed to evaluate the effect of each ingredient but, due to confidentiality issues and the difficulty in making up a reasonable correlation, we used this correlation for the model formulation.

2.2.1.3. Process constraints. The detergent production process has a series of constraints related to the processing of the mixture and the final product. To estimate a correlation that relates the concentration of the ingredients in the final product to the particle size and cake strength, the same procedure was followed as in the case of the performance. On the one hand, the particle size can neither be larger than 500 μm nor smaller than 400 μm (Bayly et al., 2006). This size determines the correct dissolution of the detergent in water within the washing machine. To estimate the particle size (μm) as a function of the composition, Eq. (22) is used.

$$\begin{aligned} Particle_j = & 224.5 + 1509.78 * PQ_{j,water} \\ & + 1000 * \left(PQ_{j,filler1} + PQ_{j,filler2} \right) \\ & - 31 * PQ_{j,water} * \left(PQ_{j,filler1} + PQ_{j,filler2} \right) \ \forall j \end{aligned} \quad (22)$$

On the other hand, for the detergent to be functional, the cake strength should be below 1 kg (Ebihara and Watano, 2003). To determine the cake strength(kg), Eq. (23) is used.

$$\begin{aligned} Cakest_j = & 2.98 * PQ_{j,water} + 2.69 * \left(PQ_{j,poly1} + PQ_{j,poly2} + PQ_{j,poly3} \right) \\ & + 0.08 * PQ_{j,water} * \left(PQ_{j,poly1} + PQ_{j,poly2} + PQ_{j,poly3} \right) \ \forall j \end{aligned} \quad (23)$$

2.2.2. Implementation of environmental impact

The location of the suppliers of raw materials does not only affect the production cost, but also the environmental impact associated with the production of the final product.

The environmental impact of a chemical can be evaluated with different indexes depending on the focus of the analysis. On the one hand, there are exhaustive studies where all the possible impacts of a chemical are analyzed throughout its life cycle, that is, from the order of the raw materials, their transportation, the production process, the packaging, its distribution and use. These studies are called Life Cycle Assessment (Saouter and Van Hoof, 2002). On the other hand, the Ecolabel (The European Parliament and the Council of the European Union, 2009) evaluates the pollution that a chemical can cause to the aquatic environment. It is evaluated as the critical dilution volume, which represents the amount of water necessary for the impact of that substance to be negligible in the medium to which it is released. Therefore, this index evaluates the impact that the detergent may generate as a result of its manufacture and use, and when it is released to the sewage. In other to analyze the environmental impact in the atmosphere in the form of emissions of greenhouse gases, the carbon footprint (United Nations Industrial Development Organization, 2017) is typically used (Gong and You, 2014; Peng et al., 2019; Ai et al., 2020). Each ingredient used to produce a detergent has a carbon footprint associated with its own production process and the sum of all these results in the carbon footprint of the production of the detergent. The emissions generated by the transport of the raw material from suppliers to the factory are the second contribution to the footprint. In this work, only the carbon footprint will be used.

To evaluate the carbon footprint**,** the distance between suppliers and the factory must be considered.The emissions are estimated to be approximately 0.5 $kgCO_2$ / km (European Commission,2018). Therefore, the emissions due to goods shipping will be calculated as indicated in Eq. (24)

$$Emission_{sub} = distance_{sup} * 0.5 kgCO_2/km \ \forall sup \quad (24)$$

The unit emission associated with transport is calculated as indicated in Eqs. (25) and (26).

$$EmissionU_{sup} = \frac{Emision_{sup}}{\text{Loading capacity}} \forall sup \quad (25)$$

$$Emision\ T_{ye,sup} = EmisionU_{sup} * \sum_i ccp_{ye,i,sup} \ \forall ye, sup \quad (26)$$

The loading capacity value is set to 7 t, while the carbon footprint associated with the different ingredients can be calculated from the composition of the final product (Eq. (27)):

$$\mathrm{HCi}_{\mathrm{ye}} = \sum_{j,k} MassProd_{ye,j} * PQ_{j,k} * HCK_k \ \forall ye \quad (27)$$

Where $MassProd_{ye,j}$ is defined by Eq. (28).

$$MassProd_{ye,j} = \sum_l y_{ye,l,j} + \sum_i z_{ye,i,j}\ \forall ye, j \tag{28}$$

and HCK_k is the carbon footprint associated with the ingredients. This value can be found in the supplementary material. To determine this value, the manufacturing process of each ingredient is evaluated, focusing on the energy consumed to produce them and how that energy is provided, that is, if either natural gas, coal, oil or steam is used. Based on these two parameters, the carbon footprint associated with the manufacturing process is computed. It also evaluates whether CO_2 or other greenhouse gases are released in the process due to the chemical reactions involved. In this way, this index assesses the impact on the atmospheric environment produced by the gases released in the production process.

The total carbon footprint will be computed using Eq. (29):

$$HC_{ye} = HCi_{ye} + \sum_{sup} Emision\ T_{ye,sup}\ \forall ye \tag{29}$$

2.2.3. Calculation of raw material and transportation cost

For a more realistic estimation of the price of the raw material, two cases are considered. On the one hand, the price of certain ingredients can be fixed through contracts with the suppliers, using pricing policies with discounts that will depend on the amount purchased. A wide variety of pricing policies associated with raw materials sales contracts have been presented in the literature. Some studies have evaluated the selection of the types of contracts for each situation (Tsay et al., 1999; Park et al., 2006;Bansal et al., 2007; Höhn, 2010; Khalilpour and Karimi, 2011). Other authors have studied them from the point of view of the supply chain (Park et al., 2006;Calfa and Grossmann, 2015). In this model, four different discount policies are considered for each supplier according to the amount of raw material used. However, there will be ingredients whose price is more variable throughout the year and cannot be fixed in the long term. In this case, it will be necessary to assume that there exists a market variability associated with the price. In addition, the price of the raw material of each supplier will depend on the distance so that those suppliers that are further away have a lower ingredient price than the nearest ones. Ingredient prices also depend on the environmental impact associated with the ingredient contained in the raw material of the supplier. The more polluting the ingredient is, the cheaper it will be.

2.2.3.4. Assessment of market price variability. In this study, only exogenous uncertainty is considered, which is the uncertainty imposed by external factors such as the market (supply and demand (Govindan and Fattahi, 2017)) on the sale prices of the product or the prices of the ingredients (Martín and Martínez, 2015). However, in the literature, you can find different authors (Sahinidis, 2004) that implement uncertainty within their models through the use of scenarios. The probability of each uncertain value is computed from the probability distribution function of each one. With that, it is possible to compute the probability of each scenario and the price/demand associated with it. However, the number of possible scenarios to represent the probability distribution is typically extremely large, so scenario reduction techniques are used. Some examples of these techniques have been proposed by Karuppiah et al. (2010) and Liz and Floudas (2014). These techniques were applied to product design in previous work (Martín and Martínez, 2015). For this work, even using the scenario reduction techniques, as it is necessary to evaluate each of the variables of the model for each of the scenarios, the model becomes computationally unsolvable. The large and complex problem when suppliers are considered lead to the use of an average price for those ingredients that present market variability using the probability. This approach follows from the findings in Martín and Martínez (2015) where the optimization using the average price and that using the scenarios showed similar results. It will be considered that the prices with market variability are the surfactants, antifoams and polymers. Three levels of prices are used for each ingredient, high, medium or low. The average price is computed using their associated probabilities.

2.2.3.5. Selection of the pricing policies. The equations necessary to calculate the discount in each of the price policies considered are given by Eqs. (30)-(33). These expressions were obtained from previous works (Martín and Martínez, 2018) and modified to adapt them to the current formulation.

P1 Linear discount: The discount applied to the original price follows a linear profile based on the amount of raw material purchased.

$$cost\,j_{ye,i,sup,1} = c0_{i,sup} - \left(\frac{c0_{i,sup} * discount}{Lsup_{i,sup} - Linf_{i,sup}}\right) \cdot \left(ccp_{ye,i,sup} - Linf_{i,sup}\right) \forall ye, i, sup \tag{30}$$

$c0_{i,\,sup}$ is the initial price of the raw material 'i' from the supplier 'sup', $Lsup_{\,i,\,sup}$ and $Linf_{\,i,\,sup}$ are the maximum and minimum amount of raw material 'i' that can be purchased from the supplier 'sup'. "discount "is a parameter of the policy that must be negotiated with the company and that will set the maximum discount. Note that discount policies only apply to raw materials that can be set by contracts. The $costj_{ye,I,sup,po}$ value for the ingredients subject to variability will be equal to 0.

P2 Logarithmic discount: The discount is the maximum once the amount purchased reaches a certain level, but the decrease is also fast depending on the maximum amount available, $Lsup_{\,i,\,sup}$:

$$cost\,j_{ye,i,sup,2} = c0_{po,i,sup} * \left(\left(\frac{1}{1+disct}\right) + \left(\frac{\left(\exp\left(-\left(\left(\frac{1}{Lsup_{i,sup}}\right) + \left(\frac{10}{Lsup_{i,sup}}\right) * ccp_{ye,i,sup}\right)\right)\right)}{\left(disct + \exp\left(-\left(\left(\frac{1}{Lsup_{i,sup}}\right) + \left(\frac{10}{Lsup_{i,sup}}\right) * ccp_{ye,i,sup}\right)\right)\right)}\right)\right) \forall ye, i, sup \tag{31}$$

'disct' is a parameter that sets the applied discount.

P3 Constant elasticity: The applied discount is exponential depending on the amount used of the raw material. 'powd' is a model parameter that can be different for each raw material and for each supplier.

$$cost\,j_{ye,i,sup,3} = c0_{po,i,sup} * \left(ccp_{ye,i,sup}\right)^{\left(-powd_{i,sup}\right)}\ \forall ye, i, sup \tag{32}$$

P4 Fixed discount: In this case, the discount is independent of the amount of the raw material 'i' used. This type of discount is very appropriate when the amount you are going to buy a raw material is small.

$$cost\,j_{ye,i,sup,4} = c0_{po,i,sup} * (1 - fixdisc)\ \forall ye, i, sup \tag{33}$$

'fixdisc' is the discount parameter of this policy.

The selection of a particular policy depends on the amount purchased and the maximum and minimum amount available for each raw material. In order to reduce the unit cost, the policy that provides the largest discount on the original price will be selected. To select a single reduction policy, it is necessary to introduce Eq. (34) and change $c0_{i,sup}$ for $c_{po,i,sup}$ in Eqs. (30)- (33).

$$c_{po,i,sup} - c0_{i,sup} * bi_{po,i,sup} = 0\ \forall po, i, \mathrm{sup} \tag{34}$$

Eq. (34) assigns $c_{po,i,sup}$ the value of $c0_{i,sup}$ if the policy is selected and the value of 0 if that policy is not taken into account in the final price of the raw material.

In addition, only one pricing policy per raw material and per supplier will be selected (Eq. (35)).

$$\sum_{po} bi_{po,i,sup} = 1 \ \forall i, sup \tag{35}$$

Since at most one must be different from 0 (Eq. (35)), the one that assigns the lowest final cost for raw material 'i' as a function of the amount purchased will be selected. If the variability in the price of some of the ingredients is such that it can no longer be fixed by contract, in the formulation this ingredient is assigned to the group of those who have uncertainty without requiring a significant change in the model formulation.

The unit cost will be given by Eq. (36).

$$Cost_{ye,i,sup} = \sum_{po} Cost\,j_{ye,i,sup,po} \quad \forall ye, i, sup \tag{36}$$

The problem is **multiperiod.** Not only one production year is considered, but several years with different demands from the customers. This means that the price discount will be calculated each year, but the contracts will be made for several years. Therefore, if a particular policy is chosen for the first year, the next one will have to use the same policy. As the binary variable does not depend on the year, once a policy is selected, it will be maintained every year, although the evaluation of the cost of the prices is per year.

2.2.3.6. Calculation of the unit price of the raw material ingredients. The total raw material cost is computed adding the cost of the ones fixed by contracts and those subjected to the market as given by Eq. (37). In this case, the $\mathrm{Costf_i}$ represents the average price of the ingredients with uncertainty, being 0 for the ingredients whose price is set by contract. Thus, by adding $\mathrm{Cost_{ye,i,sup}}$ and $\mathrm{Costf_i}$, the resulting price vector, $\mathrm{CostP_{ye,i,sup}}$, contains the price of all ingredients.

$$CostP_{ye,i,sup} = Cost_{ye,i,sup} + Cost\,f_i \ \forall ye, i, sup \tag{37}$$

2.2.3.7. Transportation cost. Transportation is expected to have a considerable impact on annual production costs. The transportation cost for each supplier is calculated by Eq. (38).

$$Ctrans_{sup} = distance_{sup} * priceT \ \forall sup \tag{38}$$

priceT is determined considering a consumption of 25 L / 100 km and a cost of diesel of € 1 / L, to become 0.25 € / km. The distance will depend on the location of the supplier. The unit cost of transport will be given by Eq. (39).

$$CTransU_{sup} = \frac{Ctrans_{sup}}{Loading\ capacity} \ \forall sup \tag{39}$$

And the total transport cost per supplier will be defined by Eq. (40).

$$CTT_{sup} = CtransU_{sup} * \sum_{i,ye} ccp_{ye,i,sup} \ \forall sup \tag{40}$$

The total cost of transport on the objective function will be given by Eq. (41):

$$CTTT = \sum_{sup} CTT_{sup} \tag{41}$$

2.2.4. Main objective function

The model developed to represent the production of a powder detergent is optimized using a simplified profit (Eq. (42)) as the main objective function.

$$Profit = \sum_{ye,l} priceprod_j * \left(\sum_{l} y_{ye,l,j} + \sum_{i} z_{ye,i,j} \right) - \sum_{ye,i,sup} CostP_{ye,i,sup} * ccp_{ye,i,sup} - CTTT - \sum_{l} c\_pool_l * \sum_{ye,l,j} y_{ye,l,j} \tag{42}$$

Note that only the variable cost of the intermediate tanks will be considered and not the fixed cost, unlike the objective function in Martín and Martínez, 2013. Analyzing the work of these authors, intermediate pools were not chosen in any of the cases studied, so it is assumed that in the cases considered in this study, they will not be selected either. However, for the sake of maintaining a general formulation, the possibility remains that these can be chosen but only considering variable cost. In this way, if the tanks are not selected considering the variable cost, it is demonstrated that neither would be considering also the fixed cost. In the case that any of the intermediate tanks is chosen, it would be necessary to reformulate the model to include the fixed costs. The reason for this simplification is to avoid including binary variables associated with the fixed cost, which complicates the problem computationally.

In addition, the ε-constraint method is used to include the environmental objective given as the carbon footprint allowed per year in the overall process. Thus, for each value of carbon footprint, a maximum profit will be obtained, being able to draw the Pareto curve that allows evaluating the problem as a multi-objective one. Note that a third objective is given by the detergent performance that must be achieved so that it is accepted by the consumer.

2.2.5. Alternative formulation

The large problem due to the number of ingredients, including suppliers and the price reduction policies results in a computational challenge. For a representative case of study, the previous formulation could not find a solution after days of computation. An alternative formulation is developed to make it tractable by eliminating the binary variables, using only continuous variables. The variable corresponding to the raw material flow ($\mathrm{ccp_{ye,i,sup}}$) is reformulated to include an additional dimension to account for the discount policy ($\mathrm{ccp_{ye,i,sup,po}}$).

In this way, the binaries that were used to select the best policy for each case can be removed at the expense of a larger number of equations. In the reformulation, this variable will be responsible for selecting and indicating which is the best policy through its indexes, similarly as it was formulated for the suppliers. For each year and for each raw material, the variable $\mathrm{ccp_{ye,i,sup,po}}$ will select the supplier or suppliers, as well as the policy, through the amount purchased of raw material 'i' from each supplier and using each policy. The information provided by $\mathrm{ccp_{ye,i,sup,po}}$ will be the amount purchased of raw material 'i' in the year 'ye' and from supplier 'sup' using policy 'po'. In short, its value corresponds to the amount purchased and its subscripts to the optimal suppliers and policies . This variable is schematically explained in Fig. 1.

The introduction of a new dimension of $\mathrm{ccp_{ye,i,sup,po}}$ modifies the model formulation. Eqs. (1), (26), (30), (31), (32), (40), (42) change in the new formulation. The new equations would be (1B), (26B), (30B), (31B), (32B), (40B), (42B) as follows:

$$\sum_{ye,po} ccp_{ye,i,sup,po} = \sum_{l} x_{ye,i,l} + \sum_{j} z_{ye,i,j} \ \forall \mathrm{ye,\ i} \tag{1B}$$

$$Emision\ T_{ye,sup} = EmisionU_{sup} * \sum_{i,po} ccp_{ye,i,sup,po} \ \forall \mathrm{ye, sup} \tag{26B}$$

$$cost\,j_{ye,i,sup,1} = c0_{i,prov} - \left(\frac{c0_{i,sup} * discount}{Lsup_{i,sup} - Linf_{i,sup}} \right) \cdot \left(ccp_{ye,i,sup,1} - Linf_{i,sup} \right) \forall \mathrm{ye, i, sup} \tag{30B}$$

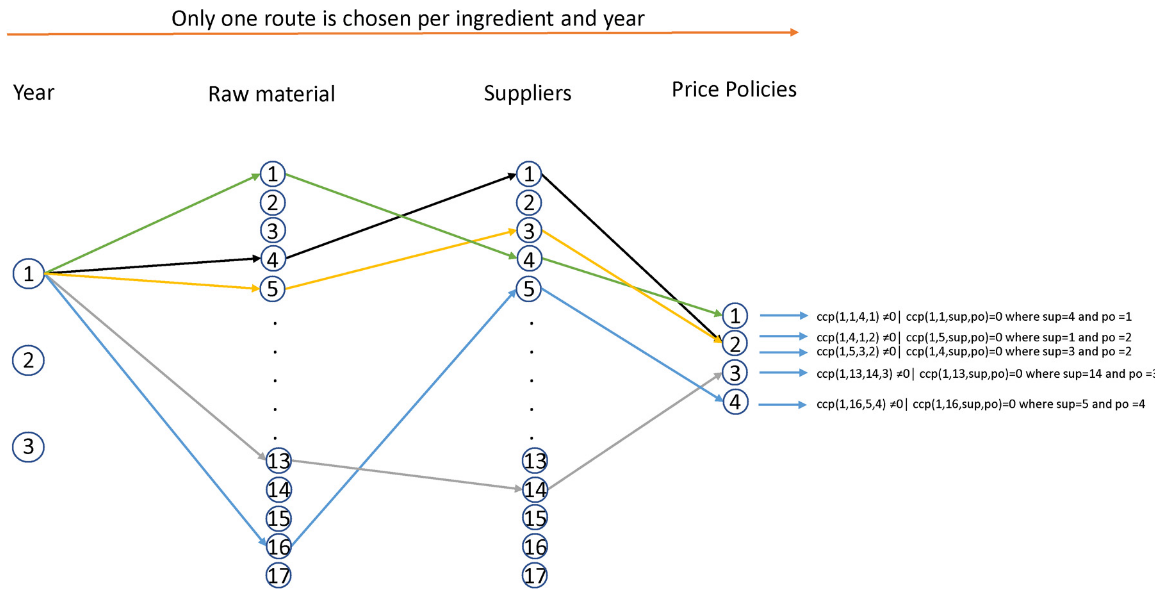

Fig. 1. Example of the optimal selection of raw material, suppliers and price policies using $\mathrm{ccp}_{(ye,i,sup,po)}$.

$$cost\,j_{ye,i,sup,2} = c0_{i,sup} * \left(\left(\frac{1}{1+disct} \right) + \left(\frac{\left(\exp\left(-\left(\left(\frac{1}{Lsup_{i,sup}} \right) + \left(\frac{10}{Lsup_{i,sup}} \right) * ccp_{ye,i,sup,2} \right) \right) \right)}{\left(\mathrm{disct} + \exp\left(-\left(\left(\frac{1}{Lsup_{i,sup}} \right) + \left(\frac{10}{Lsup_{i,sup}} \right) * ccp_{ye,i,sup,2} \right) \right) \right)} \right) \right) \quad \forall \mathrm{ye, i, sup} \tag{31B}$$

$$Cost\,j_{ye,i,sup,3} = c0_{i,sup} * \left(ccp_{ye,i,sup,3} \right)^{\left(-powd_{i,sup} \right)} \forall \mathrm{ye, i, sup} \tag{32B}$$

$$CTT_{sup} = CtransU_{sup} * \sum_{i,po,ye} ccp_{ye,i,sup,po} \forall \mathrm{sup} \tag{40B}$$

$$Profit = \sum_{ye,l,j} priceprod_j * y_{ye,l,j} + \sum_{ye,i,j} priceprod_j * z_{ye,i,j} - \sum_{ye,i,sup,po} CostP_{ye,i,sup,po} * ccp_{ye,i,sup,po} - CTTT - \sum_{l} c\_pool(l) * \sum_{ye,l,j} y(ye,l,j) \tag{42B}$$

However, as discussed above, the problem is a multiperiod one, that is, not only one production period, one year, will be considered, but several years with different demands from the customers. This means that the price discount will be calculated each year, but the contracts will be made for several years. Therefore, if the first year a specific policy is chosen, the next one will have to use the same policy. Because binaries are not used, it will be necessary to introduce a penalty for configurations that do not choose the same policy every year. The same applies to suppliers, so that the same supplier is chosen every year. Thus, a penalty will also have to be introduced. Both the penalty for different policies and that for different suppliers can be calculated together introducing into the model the variable $\mathrm{penalty}_{\mathrm{ye,i,sup,po}}$. It is defined for each of the 3 years, Eqs. (43)-(45).

Year 1:

$$\mathrm{penalty}_{1,i,sup,po} = \sum_{po} \sum_{sup} ccp_{1,i,sup,po} - \mathrm{ccp}_{1,\mathrm{i,sup,po}} \quad \forall \mathrm{i, sup, po} \tag{43}$$

Year 2:

$$\mathrm{penalty}_{2,i,sup,po} = \sum_{po} \sum_{sup} ccp_{1,i,sup,po} + \sum_{po} \sum_{sup} ccp_{2,i,sup,po} - \mathrm{ccp}_{1,\mathrm{i,sup,po}} - \mathrm{ccp}_{2,\mathrm{i,sup,po}} \quad \forall \mathrm{i, sup, po} \tag{44}$$

Year 3:

$$\mathrm{penalty}_{3,i,sup,po} = \sum_{po} \sum_{sup} ccp_{1,i,sup,po} + \sum_{po} \sum_{sup} ccp_{2,i,sup,po} + \sum_{po} \sum_{sup} ccp_{3,i,sup,po} - \mathrm{ccp}_{1,\mathrm{i,sup,po}} - \mathrm{ccp}_{2,\mathrm{i,sup,po}} - \mathrm{ccp}_{3,\mathrm{i,sup,po}} \forall \mathrm{i, sup, po} \tag{45}$$

With this formulation, for the cases in which the same supplier and the same policy are chosen over the 3 years (that is, the three-year contract with the same supplier is fulfilled) this penalty will be 0. This formulation also allows changing supplier and policy year after year if that is the management will. Therefore, Eqs. (34) and (37) are also affected giving rise to Eqs. (34B) and (37B).

$$Cost_{ye,i,sup,po} = Cost\,j_{ye,i,sup,po} + penalty_{ye,i,sup,po} \forall \mathrm{ye, i, sup, po} \tag{34B}$$

$$CostP_{ye,i,sup,po} = cost_{ye,i,sup,po} + Cost\,jf + penalty_{ye,i,sup,po} \forall \mathrm{ye, i, sup, po} \tag{37B}$$

3. Case of study

To show the use of the formulation for the design of formulated products, a case study in Europe is considered. A number of suppliers per ingredient is taking into account. The facility that produces the three types of detergents is already installed and in operation. It is assumed that bulk chemicals are subjected to market variability, such as surfactants, polymers and antifoam, and three price levels, low, medium and high, are used, while specialty chemicals price is fixed by contracts, for instance enzymes. The data used to apply the formulation to this case study can be found in Tables SI.1-SI.14 in the supplementary information. We divide this section to present the features commented on these lines starting with the definition of the suppliers.

Fig. 2. Location of the suppliers.

3.1. Suppliers

Suppliers will be grouped by the type of chemical they supply:

Inorganic Suppliers (from 1 to 3): They will be responsible for supplying fillers, builders and bleaches. Three suppliers will be considered with the same availability of raw materials and different prices depending on their proximity. The more expensive is the one that is closer to the manufacturing site and the cheapest is the one that is further away from it. This is so, because it would not make sense from the economic point of view to select a supplier that is more expensive and, at the same time, is further away since it is negative for both objectives (economic and environmental) and would never be selected.

Organic suppliers (from 4 to 6): They will be responsible for supplying surfactants, polymers and antifoams. Three suppliers will be considered.

Enzyme suppliers (From 7 to 12): They will be in charge of supplying the different enzymes used to eliminate specific stains. Six suppliers will be considered (two for each type of enzyme).

The optimal selection of suppliers is paramount since the distance affects both the price of the products and the environmental impact. It is interesting to consider different combinations of suppliers and analyze the effect on the formulation of the final product.

The main plants from three of the larger chemicals producers in Europe have been selected to be the suppliers on our detergent plant, which has been located in Frankfurt (Germany). In Fig. 2, the relative location of the suppliers with respect to the plant is presented. The distances between the plant and suppliers will be included in the supplementary information.

3.2. Prices of the raw material

3.2.1. Prices fixed with contracts

The prices without applying the discounts, base prices, are indicated in the supplementary information. The discount policy selected will be applied to reduce the base prices based on the amount purchased, the discount parameters and the supplier. We set the discount parameters of the different policies to take the following values:

$$\text{discount} = \mathbf{0.5}$$
$$\text{disct} = \mathbf{1}$$
$$\text{fixdisc} = \mathbf{0.15}$$

In this case, the parameters have been adjusted randomly, while in a real problem, these parameters can be negotiated with the different suppliers. It is considered that the maximum discount will be **50%**.

3.2.2. Prices with variability

It has been considered that the ingredients most susceptible to changes in their price throughout the year are surfactants, antifoams and polymers. Three different prices have been established for each ingredient, low, medium and high. The values are included in the supplementary information. This information is used to calculate the average price (see Section 2.2.3).

3.3. Additional considerations

The aim of this work is to develop a mathematical formulation for the design of formulated products. It is a multi-objective and multiperiod problem that yields the composition of the final product as a function of the environmental impact. The economic benefit decreases when more environmentally friendly products are designed. A trade-off between both objectives is computed. To do this, in order to facilitate the location of this point, the maximum and minimum demand of the 3 years contract is assumed to be the same. Because if this is not the case, the model could spread the environmental impact among the different years, increasing the number of variables with which the program can work and making it difficult to analyze the results.

4. Results

The problem of the design of three different powder detergents is formulated as a multi-objective, multiperiod and multiscale one.

Table 2
Results without environmental constraint.

Ingredients	Supplier	Amount(t/yr)	Optimal formulation (t_{ingr}/t_{prod})			Policy	HC (tCO_2e/yr)	Profit(M€)
			A	B	C			
LAS	4	120.00	15%	15%	15%	–	1404	7.95
ZEO	3	427.00	56%	50%	60%	2		
S.PERBO	1	95.50	5%	19%	5%	2		
S.SO	3	80.00	10%	10%	10%	3		
ANTI	4	0.80	0%	0%	0%	–		
CELL	12	12.67	3%	1%	1%	2		
CMC	4	0.80	0%	0%	0%	–		
WATER	13	63.37	12%	5%	8%	–		

The solution to this problem should yield the selection of the supplier, the amount produced, and the ingredients selected subject to process and availability constraints. The main objective is the optimization of the profit for an allowed level of CO_2 emissions. Two formulations are developed. The first one consists of an MINLP of 5195 equations and 4320 variables (780 binary variables). The second one uses only continuous variables (NLP) with 11971 equations and 14083 variables. Although the MINLP model is much smaller in terms of equations and variables, the presence of integer variables makes it much more difficult to solve, so that a solution is not found in 20 h. Therefore, we evaluate the performance of the NLP model giving feasible results in the 20 h established as a limit with a tolerance lower than 6%. A commercial solver BARON is used for in an Intel Core i7–7700 computer with 3.6 GHz of speed and 32 Gb of RAM. Note the other global solvers such as GlOMIQO or ANTIGONE can also be used.

4.1. Optimal selection of supplier, ingredients and pricing policies

4.1.1. Optimal economic solution

The first result to be presented is the optimal economic product design. To compute it, the environmental impact will not be considered. Table 2 shows the selection of suppliers and the ingredients purchased. The cheapest and most polluting ingredients have been selected. However, note that in some cases the farthest supplier has been selected (as in the case of ingredient S.PERBO and CELL) while in other cases the solution selects the closest one (such as the cases of LAS, ZEO, S.SO, ANTI and CMC). The reason behind is the fact the transportation cost of these ingredients is significant compared to the ingredient cost. Although the environmental impact is not being evaluated, it may not be profitable in some cases to buy ingredients from nearby suppliers because their cost is higher than the sum of their cost and that of transportation. Note that the suppliers selected are either the nearest or the most distant ones, but not the intermediate cases. This is the trade-off between ingredient and transportation cost. Extreme cases occur since the intermediate is not the best trade-off for that ingredient. In the case of water, its cost has not been considered as it is necessary and irreplaceable by another. Supplier 13 has a distance 0 (and therefore cost 0) because it is understood water is taken at the manufacturing site, unless, in the place where the plant is built, it will simply be necessary to connect it to the water network.

4.1.2. Environmentally friendly product design

The ε-constraint method will be used to include the second objective into the formulation. The selection of ingredients and suppliers will be evaluated aiming at maintaining the maximum profit. In this way, the ability of the system to adapt to more restrictive environmental policies is evaluated and, for an equivalent CO_2 value, how it is possible to modify the product composition to maintain the profit without significant variation. This study starts with a carbon footprint value of 1404 tCO_2 per year. Representing the Pareto curve of the profit versus the carbon footprint, Fig. 3 is obtained. It can be seen that the system has a high capacity to reduce the carbon footprint before a significant reduction of the profit occurs. By means of different configurations of ingredients / suppliers it is possible to reduce the CO_2 equivalent emitted to the atmosphere from 1404 tCO_2e/year down to 850 tCO_2e/year, representing a 40% reduction and, even though, the profit only decreases by 1.29%. As environmental impact decreases further along the Pareto-optimality curve, the profit decreases sharply. There are no feasible solutions which show an environmental impact below 775 tCO_2e/year, since demands cannot be satisfied at that level of emissions. Part of the reason is that the environmental impact is an extensive variable that also increases with the volume of product. From 850 tCO_2e/year and 950 tCO_2e/year it can be seen a rapid decrease of the profit and therefore this is the region for the optimal solution as it will be presented below.

The results of the selection of suppliers and the ingredients purchased as well as the composition of the different products are shown in Tables 3 and 4. If the case of 950 tCO_2e/year is compared with the case with no environmental constraints, it can be observed that the model is forced to choose less polluting ingredients, changing LAS by AE, ZEO by STPP and S.SO by X.SU. In all cases, these ingredients are less polluting but more expensive. With this composition, the facility can still maintain a benefit close to the maximum. This is achieved with an adjustment of the detergent composition. However, if a 785 tCO_2e/year limit is established, the profit decreases considerably, reducing the profit by 3.9% when the carbon footprint decreases by 7.6% (from 850 tCO_2e/year to 785tCO_2e/year) while between 1404 tCO_2e/year and 850 tCO_2e/year (40% reduction) the profit only falls by 1.3%. In this way, it is shown that the system loses the ability to compensate for the environmental impact when the carbon footprint value allowed is quite low. If the case of the carbon footprint of 850 tCO_2e/year is compared with that of 950, 900 and 825 tCO_2e/year, the following changes can be observed:

- Comparing the cases of 950 tCO_2e/year and 900 tCO_2e/year, it can be seen that the amount of builder decreases (less amount of STPP) and the amount of bleaches increases (larger amount of S. PERBO). Since bleaches are more expensive than builders, the cost of the raw materials increases. These changes in the composition of the final product are due to the fact that the bleaches have less associated carbon footprint than the builders and therefore, when the CO_2 emissions allowed are lower, the composition is to be altered to simultaneously meet the performance and the environmental constraints. If the comparison is made between the emission values of 900 tCO_2e/year and 850 tCO_2e/year, something similar occurs. In this case, the purchase of STPP is further reduced, since the environmental limit is tighter, and the amount of X.SU is increased, which is more expensive. However, the most important change occurs in the

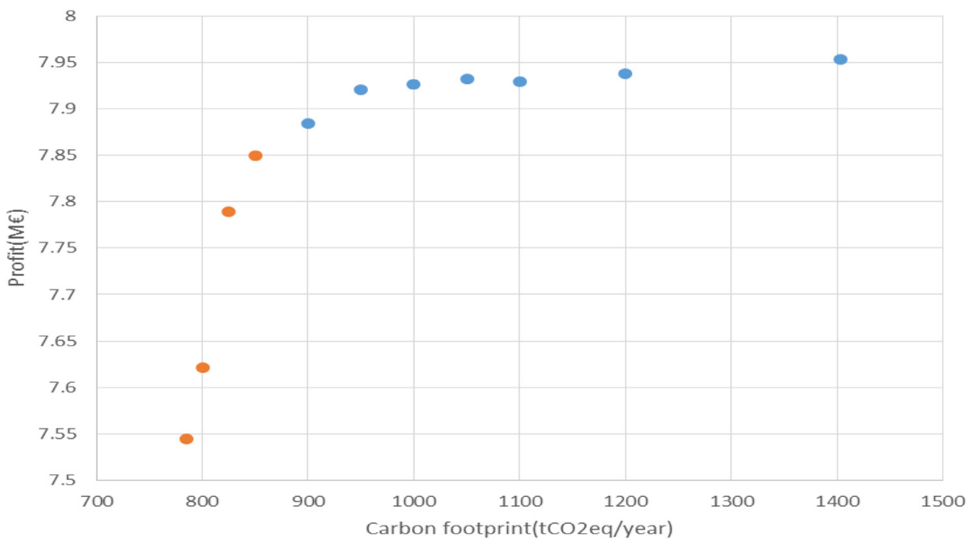

Fig. 3. Pareto curve for the design of formulated powder detergents.

Table 3
Results with environmental impact constraints HC: 950, 900, 850 and 825 tCO2e/year.

HC (tCO2e/yr)	Ingredient	Amount(t/yr)	Supplier	Price policy	Profit(M€)
950	AE	120.00	4		7.92
	STPP	358.80	3	2	
	S.PERCA	134.25	1	2	
	X.SU	80.00	3	2	
	ANTI	0.80	4	–	
	CELL	12.18	12	2	
	CMC	0.80	4	–	
	WATER	93.18	13		
900	AE	120.00	4		7.88
	STPP	295.40	3	2	
	S.PERBO	200.00	2	2	
	X.SU	79.27	1	1	
	ANTI	0.80	5	–	
	PRO	9.82	12	2	
	POLI	0.80	4	–	
	WATER	93.18	13		
850	AE	120.00	4	–	7.85
	STPP	240.68	3	1	
	S.PERBO	200.00	2	2	
	X.SU	200.00	3	2	
	ANTI	0.80	4	–	
	PRO	10.41	12	2	
	POLI	14.52	4	–	
	WATER	13.58		–	
825	AE	119.89	4	–	7.79
	STPP	216.00	3	3	
	S.PERBO	199.77	2	1	
	X.SU	200.00	3	1	
	ANTI	0.80	4	–	
	CELL	9.29	12	2	
	POLI	40.00	4	–	
	WATER	13.41	13	–	

group of polymers. The amount of polymers purchased goes from 0.8 t to 14.52 t per year to meet the performance constraint. Polymers are the most expensive substances after enzymes, so the change is significant. Finally, when comparing the cases of 850tCO_2e/year and 825tCO_2e/year, it is observed that the amount of polymers necessary to reach the expected yields is doubled again, going up to 40 t per year. This is because the amount purchased of STPP and enzymes is reduced and therefore, raw materials cost rises again. Below 825tCO_2e/year, the maximum demand cannot be met because combinations of ingredients that simultaneously meet the requirements of carbon footprint and performance cannot be found, so that by lowering the amount sold, the profit obtained falls.

- Regarding transportation, among the four cases considered (950, 900, 850 and 825 tCO_2e/year) the suppliers selected are usually the same. In most cases, the supplier is the one closer to the factory, except in the case of bleaches (S. PERBO and S. PERCA). For this type of ingredient, the supplier changes from supplier 1 (the farthest from the factory) in the case of 950tCO_2e/year to supplier 2 (intermediate supplier) in the case of 825 tCO_2e/year. Similarly, for X.SU the supplier changes from 3 to 1 and back to 2.

Table 4
Optimal formulation with environmental impact constraints HC: 950, 900, 850 and 825 tCO2e/year.

	Optimal formulation(t_{ingr}/t_{prod})							
HC	950 tCO2e/yr							
Ingredients/Products	AE	STPP	S.PERCA	X.SU	ANTI	CELL	CMC	WATER
A	15.00%	55.59%	5.00%	10.00%	0.10%	2.56%	0.10%	11.65%
B	15.00%	37.87%	24.28%	10.00%	0.10%	1.00%	0.10%	11.65%
C	15.00%	40.53%	22.13%	10.00%	0.10%	0.50%	0.10%	11.65%
HC	900 tCO2e/yr							
Ingredients/Products	AE	STPP	S.PERBO	X.SU	ANTI	PRO	POLI	WATER
A	15.00%	36.31%	25.00%	10.00%	0.10%	1.84%	0.10%	11.65%
B	15.00%	37.18%	25.00%	10.00%	0.10%	0.97%	0.10%	11.65%
C	15.00%	37.76%	25.00%	9.68%	0.10%	0.40%	0.10%	11.65%
HC	850 tCO2e/yr							
Ingredients/Products	AE	STPP	S.PERBO	X.SU	ANTI	PRO	POLI	WATER
A	15.00%	31.07%	25.00%	25.10%	0.10%	1.99%	0.10%	1.63%
B	15.00%	28.72%	25.00%	24.94%	0.10%	0.97%	3.53%	1.74%
C	15.00%	32.58%	25.00%	24.92%	0.10%	0.54%	0.10%	1.75%
HC	825 tCO2e/yr							
Ingredients/Products	AE	STPP	S.PERBO	X.SU	ANTI	CELL	POLI	WATER
A	15.00%	26.42%	25.00%	25.03%	0.10%	1.78%	5.00%	1.68%
B	15.00%	27.28%	25.00%	25.03%	0.10%	0.91%	5.00%	1.68%
C	15.00%	27.86%	25.00%	25.03%	0.10%	0.33%	5.00%	1.68%

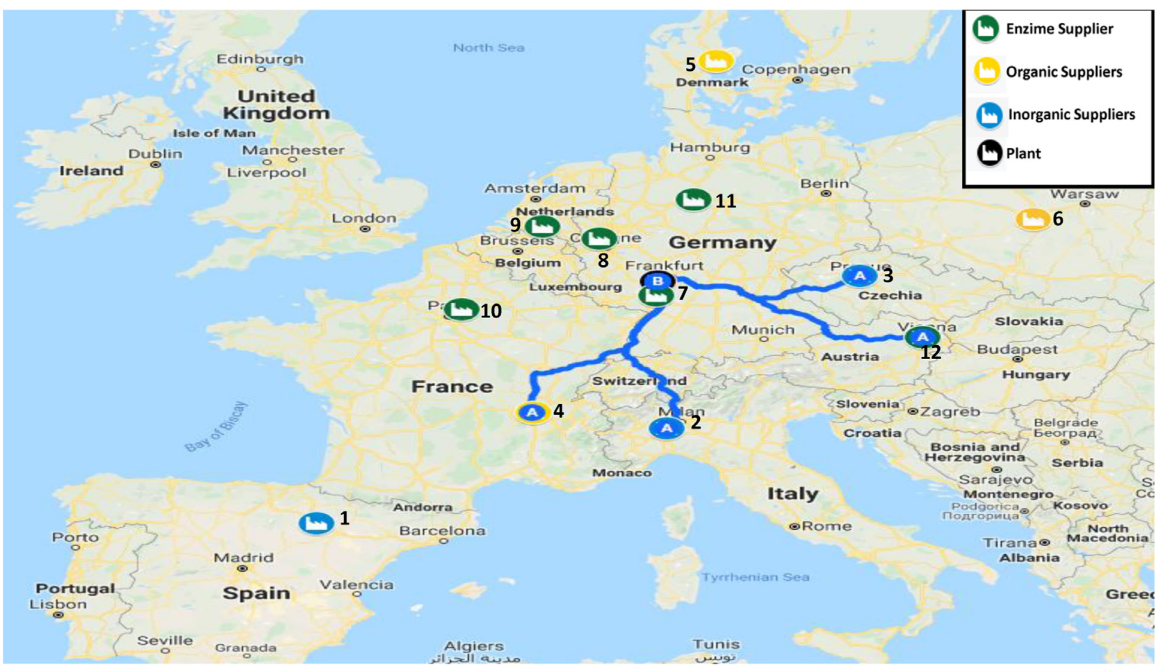

Fig. 4. Selected suppliers to the optimal case.

- The detergent composition is shown in Table 4. As the CO_2 emissions are to be smaller, the surfactant compositions decrease while the bleaches, the fillets and polymers increase. Typically, to improve the performance, a higher concentration of enzyme is used.

Therefore, the limit value of carbon footprint that best balances both objectives (economic and environmental) is the value of 850 t CO_2e/ year since, below this value, the benefit begins to decrease abruptly with small variations in the limit of environmental impact and above that value, the benefit does not increase that much. For this limit value of carbon footprint, the map of the suppliers is showed in Fig. 4. Most of the ingredients that are purchased through contracts are abundant and policies 1, 2, 3 are used, see Table 3. It is important to indicate that the upper limit of enzyme supplies is 20 tons per year, therefore, if the amount purchased is close to half of the available amount of enzyme, then policy 4 is not suggested. Therefore, in none of the cases raised, policy 4 is chosen. The selection of price reduction policies is complex from the computational point of view since the discount is very similar in all (except for 4). This fact is found in this work, but it can be different if the parameters of discounts change, which are established by negotiation with the different suppliers. For this reason, it is convenient not to discard any of it in the mathematical formulation.

5. Conclusion and future work

In this work, we have developed a mathematical formulation for the optimal design of formulated products selecting the supplier and the ingredients to obtain three different types of detergents. This framework can be applied to any formulated product in the food, pharmaceutical and cosmetics industries among others. The results show that the proper selection of ingredients and suppliers allows a substantial reduction of the environmental impact, more than 40%, without significantly affecting the benefit. The simultaneous selection of suppliers, ingredients and discount policies provides the ability to adapt to different environmental limits. This work shows that the integrated product and process design and suppliers selection allows finding a trade-off between the benefit and significant reductions in environmental impact. However, there is a limit value beyond which the profit decreases sharply since it is no longer possible to compensate for the environmental impact without reducing the production or having to use more expensive ingredients which reduce the benefit.

Future work will seek to integrate this model within a supply chain, so as to also take into account different possible locations of the plant depending on the suppliers and also the customers. It is also possible to introduce different types of uncertainties (in customer demand for example) or other types of metrics, such as customer acceptance. This integrated problem will require additional analysis and solution procedures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Manuel Taifouris: Data curation, Investigation, Methodology, Validation, Software, Visualization, Writing - original draft, Writing - review & editing. **Mariano Martín:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Visualization, Writing - original draft, Writing - review & editing. **Alberto Martínez:** Conceptualization, Resources, Project administration, Supervision, Writing - review & editing. **Nats Esquejo:** Conceptualization, Resources, Project administration, Supervision, Writing - review & editing.

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Supplementary materials

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