Product-Centered Processing: Manufacture of Chemical-Based Consumer Products

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A systematic framework for product-centered processing is useful particularly in developing chemical-based consumer product manufacturing processes. The objective is to provide directions and guidelines toward the development of a process for manufacturing a product with the desired performance in reduced time and effort. The product performance, represented by several quality factors, is related to product ingredients and structural attributes, as well as the process flowsheet and operating conditions. The procedure consists of five steps. First, the product functionality, form, and packaging are defined. Second, relevant quality factors are identified. Third, necessary ingredients are selected and product microstructure is determined. Fourth, the manufacturing process is designed in light of the desired product properties. Limitations on achievable product quality are also identified. Finally, the product and process are evaluated with the help of experimental data. The framework is illustrated using industrial examples, including the production of dry toner, laundry detergent, shampoo, and cosmetic lotion.

Introduction

Many of today's chemical products consist of multiple ingredients and have clearly defined size, shape, and structure. Examples include consumer and pharmaceutical products such as cosmetics, personal care products, drugs, adhesives, detergents, copier toners, and many others. The term "chemical-based consumer product" will be used throughout this article to refer to these products. As the global chemical processing industry redoubles its efforts on such high-value-added chemicals, faster and more effective development of their manufacturing process is highly desirable to shorten time-to-market and enhance competitiveness (Tanguy and Marchal, 1996; Wintermantel, 1999; Kind, 1999; Grossmann and Westerberg, 2000).

To this end, Moggridge and Cussler (2000) proposed a procedure for chemical product design, in which different products are conceptualized based on market needs and screened to identify the best candidates. The manufacturing process of these products should then be developed. Wibowo and Ng (2001a) proposed a product-oriented process synthesis and development procedure for the manufacture of creams and pastes. Product quality is the central theme and is closely linked to the manufacturing process.

Product-centered processing goes further by placing the product at the center of process synthesis and development is particularly important for the manufacture of chemical-based consumer products, which traditionally involves a considerable amount of trial-and-error. Process development can become a bottleneck, leading to delays in product launching, which in turn costs the company millions of dollars (Pisano, 1997). Another problem is the scale-up of a laboratory procedure to commercial production. Often, a product successfully developed in the laboratory fails to be produced in a large scale, although the recipe given by the chemist has been strictly followed. These problems strongly indicate that significant advantages can be gained by looking at these issues from a process systems engineering viewpoint.

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In this article, we present a systematic framework for product-centered process synthesis and development for manufacturing chemical-based consumer products. The objective is to provide directions and guidelines for developing an optimal manufacturing process in reduced time and cost. Process alternatives are systematically generated and unit operations, as well as operating conditions, are properly selected. Various related issues in each development phase, from formulation all the way to processing in the production scale, are considered. This approach calls for a high degree of integration of process systems engineering with other basic sciences and close collaboration among engineers and scientists of different backgrounds. Emphasized are the issues of how to manufacture a product with the desired qualities, rather than how to design the product to be manufactured.

Systematic Framework for Chemical-Based Consumer Product Manufacture

A chemical-based consumer product is usually a mixture of one or more key ingredients responsible for its functionality, which will be referred to as the *active ingredients*, and some *supporting ingredients* for enhancing its performance. Depending on the application, different *delivery systems* can be chosen to deliver the active ingredient. These cover the entire spectrum of product form, ranging from solid composites to aerosols. Figure 1 depicts the various product forms and delivery systems, along with examples in three major application areas. Solid products include composites, tablets and capsules, solid foam, powders, and granules. Semi-solid products can be classified into two categories: pastes (if it contains a large portion of solids) and creams (if it contains immiscible liquid phases). In practice, a cream can also contain a small amount of solid particles. Liquid products include single-phase liquids, as well as dispersions of solid in liquid (suspensions), liquid in liquid (emulsions), and gas in liquid (foam). Macromolecule solutions are solutions of large molecules such as protein, polymer, and surfactants. Finally, these products can also take the form of gas dispersions or aerosols.

Physical Form		Product form/ Delivery system	Examples		
			Cosmetics and personal care	Health care and pharmaceuticals	Household and office supplies
SOLID	SHAPED	Composites	Bar soap, lipstick	Inhalant stick	Compact disk, glue stick
		Capsules	-	Whale oil capsule	Microencapsulated carbonless paper
		Tablets	-	Aspirin tablet	Moth balls
		Solid foams	-	-	Styrofoam
	BULK	Powders and Granules	Facial powder, baby powder, diaper absorbent	Powdered herbal medicine	Powdered detergent, dry toner
SEMI-SOLID		Pastes	Toothpaste	Pain relief ointment	Silicone sealant, metal adhesive
		Creams	Cleansing cream, hair cream	Pharmaceutical cream	Multipurpose adhesive
LIQUID		Liquid foams	Shaving foam	-	-
		Macromolecular solutions	Mouthwash, shampoo	-	Dishwashing liquid
		Microemulsions	Skin cleanser, hair conditioner	Hydrocortisone, cyclosporine	-
		Dilute emulsions and suspensions	Suntan lotion, nail polish	Penicillin	Correction fluid, writing ink
		Solutions	Perfume	Eye drop, ginseng extract	Drain cleaning solution
GAS		Aerosols	Hair spray	Sore throat spray	Aerosol paint, antifreeze spray

Figure 1. Examples of chemical-based consumer products of different forms and delivery systems.

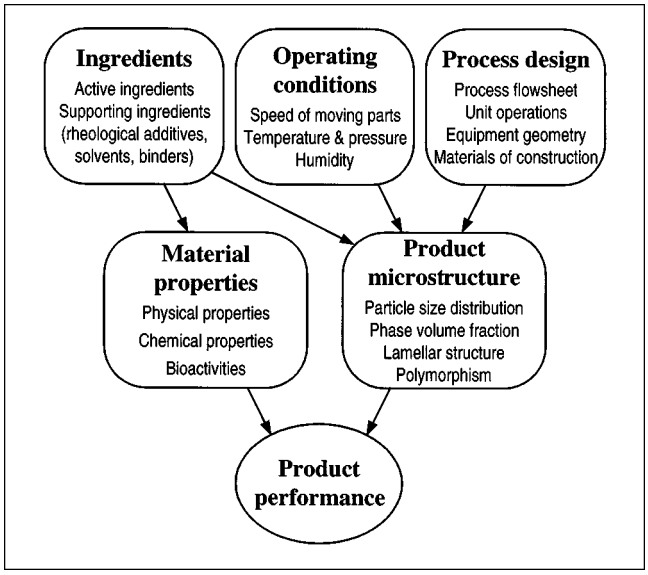

Figure 2. Factors determining product performance.

Regardless of the delivery system, the product performance, characterized by a set of attributes referred to as the *quality factors*, is determined by two factors (Figure 2). The first one is the material properties of the ingredients, such as dielectric constant, viscosity, and so on. For example, a thickener such as xanthan gum is normally used to induce strong shear-thinning behavior in cosmetic creams. Obviously, material properties are selected by appropriately choosing the ingredients. An active ingredient is typically selected according to the desired product functionality, while supporting ingredients are picked in such a way that other quality factors can be met. The second factor is the product microstructure, which describes how the constituents are assembled. It is characterized by structural attributes such as particle or droplet size distribution, phase volume fraction, and particle shape. They can be controlled by properly designing and operating the manufacturing process. For example, micron-sized particles can be obtained by selecting appropriate size reduction equipment (such as an air jet mill), and the particle size can be manipulated by adjusting the air velocity.

We propose the following five-step procedure for product-centered process synthesis and development (Table 1). First, the product is conceptualized based on consumer needs and market trends. The appropriate product form, including a suitable packaging, is selected. Second, the desired product performance is defined in terms of quality factors. Third, necessary ingredients and product microstructure are selected based on the desired quality factors. Fourth, process

Table 1. Systematic Procedure for Product-Centered Process Synthesis and Development

Step 1.	Product conceptualization
Step 2.	Identification of product quality factors
Step 3.	Selection of ingredients and product microstructure
Step 4.	Generation of process alternatives
Step 5.	Product and process evaluation

alternatives for manufacturing a product containing the selected ingredients and having the desired microstructure are identified. Equipment operating conditions are also selected. Limitations on product quality imposed by the manufacturing process are also identified. Finally, both the product and process are evaluated to ensure that a product of the desired performance is produced in an efficient manufacturing process.

Step 1: Product Conceptualization

Clearly, the very first step towards manufacturing a product is defining the product itself. In doing this, consumer needs and market trends, represented by typical issues depicted in Table 2, need to be captured. Among typical trends are the expectations that a product would last longer, cost less, be safer, and be more environmentally friendly. Consumers also tend to like a product that combines several complementary ingredients (Kirschner, 1996). For example, two-in-one shampoo and conditioner mixtures are among the leading hair care products since the 1990s (Reisch, 2000). Another example is bleach containing detergents, which account for more than 30% of the U.S. powder detergent business (McCoy, 2000).

Market trends may not present themselves so obviously. Therefore, innovation and creativity are among the key ingredients for success in product development. It is often the case that the development of a groundbreaking product begins with a creative inventor's desire to make life simpler, followed by tireless efforts to realize the idea. Market research among potential customers is also useful in conceptualizing the product and confirming the need. For example, the conception of diaper absorbents comes about because of some people's dislike of changing cloth diapers. Confirmed by research among mothers, the need for a new product, which can absorb and retain moisture without passing it back to the skin, was identified.

Table 2. Typical Market Trends to be Considered in Consumer Product Development

Consumer Wants and Needs
• The product should last longer and/or cost less
• Products performing complementary functions should be combined in one product
• The use of a personal care product should be a pleasurable exerience
• The product should be smaller in size, easy to carry when traveling
Product Safety
• The product should not contain toxic solvent or allergenic materials
• The product should not contain dangerous chemical for little children
• The product should contain more natural ingredients
Legal and Environmental Issues
• It is preferable that the product is biodegradable
• Refillable container should be used to reduce waste

Product conceptualization involves the selection of the appropriate form in which the key ingredients should be delivered, including product packaging. The packaging may greatly affect consumer perception of the product, and, therefore, should be considered carefully. Table 3 provides examples of packaging typically used for chemical-based consumer products. Innovations and new ideas on novel forms of packaging should also be considered for potential breakthroughs. Table 3 does not distinguish between suspension, emulsion, liquid foam, and macromolecular solution for two reasons. First, we cannot specify the delivery system of a liquid product at this stage, because the decision is based on whether the product contains immiscible solid, liquid, or gas ingredients, while no ingredients have been selected. Second, the choice of packag-

Table 3. Typical Packaging for Chemical-Based Consumer Products

	Product Form/Delivery System						
Type of Packaging	*Composite*	*Tablet/caspule*	*Powder/ Granule*	*Cream/ Paste*	*Viscous liquid*	*Dilute liquid*	*Aerosol*
Wrapping							
Carton box	√	√	√				
Paper/Plastic wrap	√	√					
Aluminum foil	√	√					
Bag (Paper/plastic)							
Resealable bag		√	√				
Sealed bag/sachet		√	√	√	√		
Bottle (Glass/Plastic)							
Screw cap		√	√	√	√	√	
Flip cap					√	√	
Slit orifice					√	√	
Pump top					√	√	
Tube (Metal/Plastic)							
Collapsible Tube				√	√		
Squeezable tube					√	√	
Can (Metal)							
Spray can							√

ing only depends on the overall product form, not on the phase of the individual ingredients. The choice of packaging may put additional constraints on the product. For example, the choice of using a flip-cap bottle for a viscous product, such as shampoo, leads to the requirement that the product can flow through the small hole on the cap with ease.

Step 2: Identification of Product Quality Factors

The next step towards realization of the product in question is to identify the desired performance in terms of quality factors. The desired product functionality is described in more detail. If the product is to be used in a specific device, such as a photocopier or a washing machine, it is important to understand how the device works in order to properly define the quality factors. Consumer satisfaction is not only affected by the ability of the product to perform a certain function, but also by other issues such as convenience of use, sensation, and product durability. Table 4 provides a few examples of typically expected quality factors for cosmetics, pharmaceuticals, and household supplies.

Depending on product form or delivery system, the desired quality factors can be different. For example, rheology is an important issue for emulsions, but obviously not for tablets. On the other hand, mechanical strength is a key issue for composite materials, but not relevant to solutions. Note that the delivery system for liquid products may not be obvious at this stage, since the ingredients have not been specified. Thus, additional quality factors may need to be specified in the next step, since they cannot be anticipated at the moment.

Table 4. Typical Quality Factors Expected from Chemical-Based Consumer Products

Class of Product	*Quality Factors*
Cosmetic and personal care	Protection effect Cleaning power Ease of spread Odor Shelf life
Pharmaceutical and health care	Bioactivity Dissolution or disintegration time Active ingredient release time Ease of application
Household and office supplies	Cleaning power Hiding power Mechanical strength

Since most of these quality factors are qualitative, a set of *performance indices* is used as a measure of product performance. Table 5 shows examples of representative performance indices for typical product quality factors that chemical-based consumer products are expected to possess. By nature, sensorial quality factors are perceptions that can be quantified only by using an arbitrary scale. An index is assigned to reflect the level of satisfaction in using a product. This index is then related to material properties and struc-

Table 5. Performance Indices for Typical Chemical-Based Consumer Product Quality Factors

	Product Form/Delivery System							
Quality Factor	*Composite*	*Tablet/capsule*	*Powder/ Granule*	*Cream/ Paste*	*Viscous liquid*	*Dilute liquid*	*Aerosol*	*Performance Index*
Sensorial Quality Factors								
Visual appearance: transparent, opaque, pearlescent, color	√	√	√	√	√	√	√	Arbitrary indices based on panelist evaluation
Smell: fragrant, odorless, stinky	√	√	√	√	√	√	√	
Taste: sweet, sour, bitter	√	√	√	√	√	√		
Sense upon application: smooth, oily, sticky				√	√	√		
Physicochemical Quality Factors								
Product stability (resistance against creaming)				√	√	√	√	Shelf life
Ability to change phase upon application	√	√	√	√	√			Melting point, glass transition temperature
Hygroscopicity	√	√	√	√	√	√		Moisture absorption rate
Ease of dispersion in a liquid			√					Wetting time
Ability to dissolve in a liquid	√	√	√					Dissolution time
Rate at which an active ingredient is released	√	√	√	√	√	√		Release time
Mechanical Quality Factors								
Resistance to failure	√	√	√					Tensile strength
Resistance to indentation (hardness)	√	√	√					Hardness numbers
Ease of failure by fracture (toughness)	√	√	√					Fracture energy
Elasticity	√	√	√					Young's modulus
Ease of flow			√					Flow number
Rheological Quality Factors								
Ease of spreading when rubbed onto a surface, applied by brush, or shaken				√	√			Viscosity at application shear rate
Ability to flow under gravity				√	√			Yield value
Ability to provide even coating when applied on a surface				√	√			Minimum thickness at which even coating is observed

tural attributes via psychophysical models. Some other quality factors can be satisfactorily quantified using physical properties such as tensile strength, melting point, and viscosity. Yet some others can be quantified using dimensionless numbers. For example, flow properties of a powder can be related to material properties and structural attributes by defining the flow number (Wibowo and Ng, 2001b).

Step 3: Selection of Ingredients and Product Microstructure

Having defined the desired features of the product, active and supporting ingredients that would provide such features are selected next. Ingredients are selected based on their capability of performing a certain function. In order to come up with a good choice, it is necessary to observe the physicochemical process taking place during product application or storage, and determine the necessary function. For example, cosmetic products can be kept from drying up by using a humectant such as glycerol, which has an affinity for water (Schmitt, 1992).

The selection of active ingredients often begins with a search for potential candidates, aided by techniques such as molecular design and combinatorial chemistry. The candidates are screened to identify a handful of lead compounds, which are further investigated to verify their capability and to select the best one. Although previous experiences may help to narrow down the options to only several candidates prior to screening, it is often unavoidable to perform a large number of screening tests. High throughput screening (HTS) techniques can be used to expedite such a search. Examples of HTS techniques in aiding product-oriented process development are presented in Table 6. In the search process for active and supporting ingredients, the samples are tested for a particular response. For example, the bioactivity of an active pharmaceutical ingredient (API) is reflected by its capability to bind to a target such as the active site of an enzyme. Fluorescence technology can be used to identify whether or not such a binding occurs (Borman, 2000). Other potential applications of HTS include identification of a certain structural attributes of the sample and determination of an optimum set of operating conditions.

The development of multifunctional products is often a bigger challenge compared to products containing a single active ingredient, because of the need to combine incompatible ingredients in one delivery system. Molecular modification of an active ingredient is often the key to create such a product. For example, the alkyl chain length of a surfactant molecule can be modified to give the correct hydrophilic-lipophilic balance (HLB) value, such that it possesses the desired ability to remove fats and oils, as well as to dissolve in water (Willey et al., 1995).

Supporting ingredients can be chosen in a similar way, but such an elaborate screening process is usually not necessary unless there is a specific need for a new substance in place of a typical one. For example, beeswax and other waxes have traditionally been the preferred choice as the cream base for cosmetic products (Mitsui, 1997). It is much simpler to select among these typical materials, rather than using a new substance which, due to its use as a personal care product component, may have to be approved by the regulatory authorities. Obtaining such an approval can lengthen the development time considerably.

As discussed previously, the product delivery system of liquid products can only be defined after all ingredients have been selected. Therefore, additional quality factors related to specific delivery systems need to be defined at this point. For example, if solid ingredients are suspended in a liquid product, it is desirable to retard sedimentation or flocculation in the product.

At the same time, the correct product microstructure should be chosen such that the desired function may perform. For example, the color of an emulsion is a result of light absorption, scattering, reflection, and refraction (Block, 1996). A transparent emulsion can be obtained by dispersing the inner phase as very small droplets ($< 0.05\ \mu$m), since they do not scatter nor reflect light.

To be more quantitative, it is desirable to express the performance indices (PI) as functions of material properties (MP) and structural attributes (SA)

$$PI_i = PI_i(MP_1, \ldots, MP_m, SA_1, \ldots, SA_n), \quad i = 1, 2, \ldots, k \tag{1}$$

This expression can be used to map out the target values of material properties and structural attributes that would give the desired product performance. An ingredient (or a mixture of ingredients) with suitable material properties is then selected to meet the target. Examples of material properties

Table 6. Potential Applications of HTS in Product-Oriented Process Synthesis and Development

Screen for	Example	Detection Techniques	Ref.
Active and Supporting Ingredients	Bioactivity	Fluorescence	Borman (2000)
	Superconductivity	Resistance measurement	Jandeleit et al. (1999)
	Catalyst activity	Infrared thermography	Jandeleit et al. (1999)
	Glass transition temperature	Differential scanning calorimetry (DSC)	Brocchini et al. (1997)
	Polymer molecular weight	Gel permeation chromatography (GPC)	Brocchini et al. (1997)
Structural Attributes	Crystal structure	X-Ray diffraction (XRD)	Akporlaye et al. (1998)
Operating Conditions	Reaction temperature, pressure, and feed composition	High performance liquid chromatography (HPLC)	Rouhi (2000)
	Protein crystallization conditions	Microscope observation	Bastin et al. (2000)

Table 7. Dependence of Performance Indices on Material Properties and Structural Attributes

Performance Index	*Material Properties*	*Structural Attributes*	*Relationship*
Tables			
Tensile strength, σ_t	Hamaker constant, A	Grain particle size, d_p Porosity, ϵ	Rumpf's order-of-magnitude model assuming equal-sized particles (Pietsch, 1997) $\sigma_t = \frac{9}{8} \cdot \frac{1-\epsilon}{\epsilon} \cdot \frac{F_{adh}}{d_p^2}$ (2) $F_{adh} \approx F_{vdW} = \frac{Ad_p}{24z^2}$ (3)
Disintegration time, t_{di}	Diffusivity, $\mathfrak{D}$	Tablet size, H Grain particle size, d_p Porosity, ϵ	Order-of-magnitude model derived from Fick's law and Darcy's law $t_{di} = \frac{2m^2}{\pi^2 \rho_s^2 H^4 \mathfrak{D}\epsilon(1-\epsilon)^2}$ (4)
Powders			
Flow number, N_{Fw}	Hamaker constant, A Density, ρ_S	Particle size, d_p	Order-of-magnitude analysis from comparison of gravity and adhesion forces $N_{Fw} = \frac{W}{F_{vdW}} = \frac{2\pi\rho_S d_p^2 g z_0^2}{A\eta}$ (5)
Creams and Pastes			
Viscosity, μ_e (at shear rate $\dot{\gamma}$)	Continuous phase viscosity, μ_c Interfacial tension, σ	Droplet size, d_p Phase volume fraction, ϕ	Correlation for concentrated emulsions ($\phi >$ 0.83) (Princen and Kiss, 1989) $\mu_e = \frac{\tau_0}{\dot{\gamma}} + 32(\phi - 0.73)\left(\frac{2\mu_c\sigma}{d_p\dot{\gamma}}\right)^{1/2}$ (6) $\tau_0 = \frac{2\sigma}{d_p}\phi^{1/3}[-0.08 - 0.1140\log(1-\phi)]$ (7)

and structural attributes determining the performance indices of several product forms are presented in Table 7, along with expressions of their relationships.

Expressions relating *PI* to *MP* and *SA* can be obtained in three different ways (Table 8). When the underlying physics behind the relationship is perfectly understood, rigorous modeling can be used to derive theoretical expressions based on detailed analysis of the physical phenomena. Such an approach has been successfully applied to problems in transport phenomena. Models obtained this way are predictive, and experimental data are only needed for verification purposes.

Unfortunately, complete scientific elucidation of underlying physical phenomena behind the technology of chemical-based consumer product manufacture is still a long way off (Wintermantel, 1999). Therefore, it is generally not possible to derive Eq. 1 from rigorous modeling. Order-of-magnitude analyses, which are still based on the physical phenomena but include simplifying assumptions, can be considered instead. Although such analyses are not very predictive, they can be expected to give the correct dependence on the variables, thus tremendously cutting down the required amount of experimental data. Comparison of causal and opposing effects in solids handling (Wibowo and Ng, 2001b) is an example of such an approach.

In many cases, especially those involving solids, the physical phenomenon is poorly understood and any effort to do detailed modeling is futile with the time constraint. Under these circumstances, there is no choice but to consider the process as a black box. There are two common approaches for obtaining a model for the process. First, the relationship between input and output is expressed as a correlation, and parameters in the model are determined from experimental data through regression analysis. Second, one can use neural networks, which identifies correlative patterns by mimicking

Table 8. Approaches for Relating Product Performance to Material Properties and Microstructure

Approach	*Rigorous Modeling*	*Order-of-magnitude Analysis*	*Black Box Analysis*
Technique	Detailed analysis of the phenomena	Simplified analysis of the phenomena	Data fitting, neural networks
Understanding of physical phenomena	Completely understood	Partially understood	Poorly understood
Range of validity	Relatively wide	Limited to the assumed conditions	Limited to the range of available data
Predictability of parameters	Relatively accurate	Order of Magnitude estimates	Inaccurate or impossible
Experimental efforts	None or for verification only	Minimal, directed by theory	Parallel, combinatorial

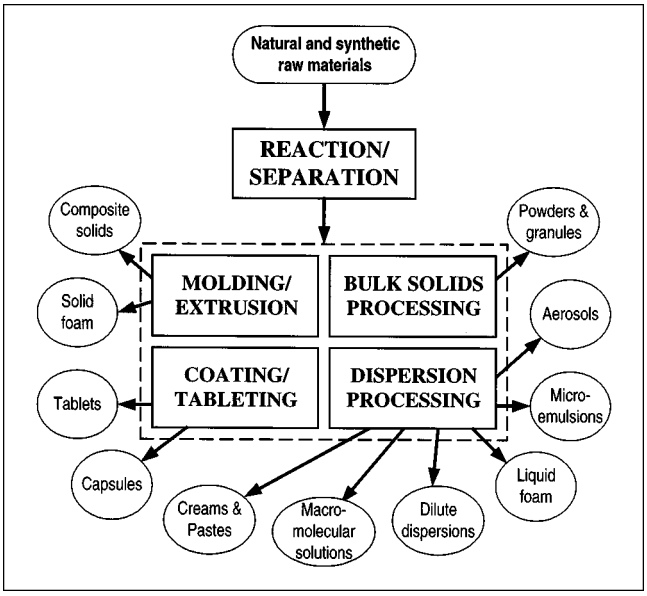

Figure 3. Unit operations in chemical-based consumer product manufacture.

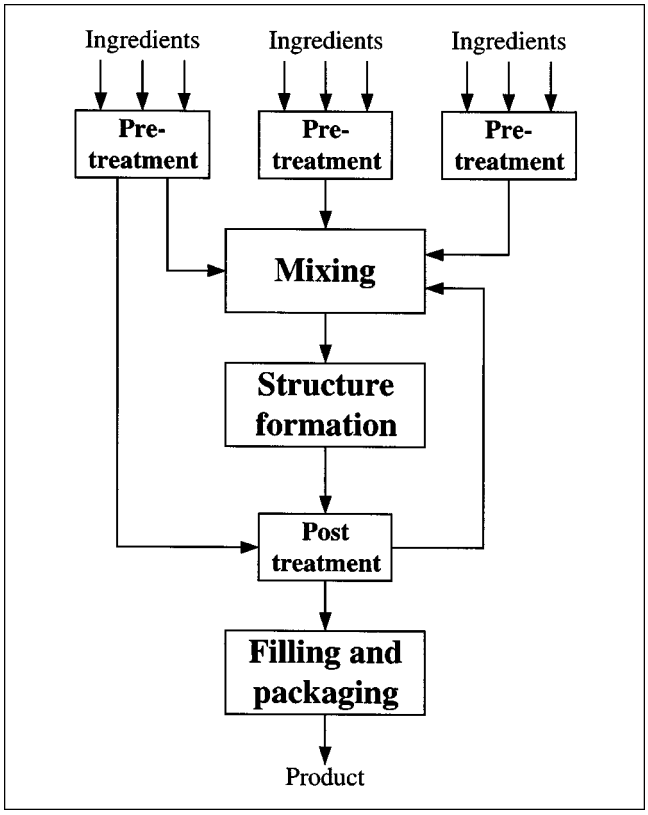

Figure 4. Generic flowsheet of chemical-based consumer product manufacturing processes.

human learning process (Bhagat, 1990). Once trained using a set of input and output data, the network can be used to predict the output for a given input without providing an explicit functional model. The accuracy of the prediction depends only on the amount of data fed to the network during training. Clearly, the applicability of black box models obtained using either approach is limited to the range of the collected data.

Step 4: Generation of Process Alternatives

Depending on the product composition and delivery system, the process for manufacturing chemical-based consumer products may be a sequence of processing steps (Figure 3). The process typically involves production and isolation of the active ingredients, as well as product formulation. Products containing natural ingredients, such as spices and antioxidants, may be obtained by direct recovery from natural resources. APIs are often produced via chemical reactions or bioprocesses followed by separation to isolate them. Active and supporting ingredients produced via any of these sequences can also be mixed together in further process steps to make more complex products. Powders and granules are produced in bulk solids processing steps. Composite solids are normally manufactured through a molding or extrusion process, while tablets and capsules typically go through a bulk solids processing step followed by tableting and coating. Structured liquid or semi-solid products such as emulsions, suspensions, and surfactant solutions are produced through dispersion processing. The liquid components may come directly from a recovery or separation step, while the solid components may go through bulk solids processing steps first.

The general structure of chemical-based consumer product manufacturing process is depicted in Figure 4. There are basically five major processing steps: pre-treatment, mixing, structure formation, post-treatment, and packaging. The objective of the pre-treatment step is to condition the ingredients before entering the mixing step. Liquid ingredients may need to be heated or cooled, while solid ingredients may require drying, humidification, washing, dissolution, surface modification, or particle-size change. Solid ingredients with low melting temperature may be melted to assist subsequent mixing. Compatible ingredients can be pre-mixed and processed together, while those requiring different treatments have to be processed separately. In the mixing process, various ingredients, with possibly very different properties, are brought together to form a mixture. Therefore, it is crucial to determine which ingredients must be pre-mixed prior to entering this processing step.

The output of the mixing unit may not possess the desired microstructure. For example, immiscible liquid phases are mixed to form a pre-emulsion, which is subject to further processing to get the desired droplet size. In the structure formation process, the mixture is further processed to yield a product with the desired microstructure. Processing-sensitive ingredients, which may decompose if subjected to the harsh processing conditions at the mixing and structure formation steps, can be added at the post-treatment step. Sterilization, which is necessary in the production of pharmaceuticals prepared for oral administration, is also an example of post-treatment. Finally, the product is packaged in appropriate containers for sale.

Equipment units are selected next. For the mixing step, they must be chosen based on the ingredients to be mixed, but agitated vessels are the most common. For structure for-

Table 9. Selected Unit Operations for Mixing and Structure Formation Steps in Chemical-Based Consumer Product Manufacturing Processes

Processing Step/Criterion	*Unit Operation*	*Examples of Equipment*
Mixing		
Ingredients to be Mixed		
Soluble liquids	Mixing	Agitated vessel, in-line mixer
Liquid and soluble solids	Dissolution	Agitated vessel
Liquid and insoluble solid	Dispersion	Agitated vessel, planetary mixer, mixer-kneader
Two immiscible liquids	Emulsification	Agitated vessel
Two solid phases	Melt mixing Solids Powder coating	Agitated vessel, high-speed mixer V-shaped mixer, ribbon blender Coating machine
Structure Formation		
Product delivery system		
Composite	Molding	Extruder
Tablets	Tableting	Tableting machine
Capsules	Filling	Encapsulation machine
Powders/granules	Size enlargement Size reduction Spray drying	Pan granulator, roller compactor Jaw crusher, roller crusher, cutter, fluid jet mill fluid jet mill Spray drier
Creams, emulsions	Homogenization	Pressure homogenizer, ultrasonic homogenizer
Pastes, suspensions	Wet milling	Ball mill, roller mill, pebble mill

mation, the choice is dictated by the selected product delivery system. Examples of unit operations involved in mixing and structure formation steps are given in Table 9. It may be necessary to use several unit operations in series. For example, size reduction can be used after molding to produce powder from a slab of composite material. Similarly, different equipment units can be installed one after the other to accomplish the task in a single unit operation. For example, a jaw crusher followed by an air jet mill can be used to produce fine powder from relatively big pieces of material (Wibowo and Ng, 1999). Table 10 summarizes some heuristics for selecting appropriate equipment units from the available options.

Table 10. Heuristics for Selecting Unit Operations

Heuristics for Selecting Mixing Unit
• Choose melt mixing if one of the solids to be mixed has a relatively low melting or glass transition temperature (50–80°C)
• Choose solids blending to mix particulate solids with comparable sizes
• Choose powder coating if it is desired to put very small particles on the surface of larger particles
• Choose an equipment unit operating under vacuum and/or at low agitation rate, if the mixture contains a high concentration of surfactant
Heuristics for Selecting Structure Formation Unit
• Choose size enlargement (size reduction) if the desired product particle size is larger (smaller) than the particle size at the output of the mixing step
• Choose size reduction followed by tableting (capsule filling) to produce tablets (capsules) with constituent particles smaller than the output of the mixing step
• Choose spray drying (followed by size enlargement) if the desired product form is powder (granular) and the output of the mixing step is a liquid

The next task is to determine the suitable operating conditions in each unit, in such a way that the desired product microstructure can be obtained. Again, to be quantitative, we would like to relate structural attributes with operating variables (OV)

$$SA_i = SA_i(OV_1, \ldots, OV_p), \qquad i = 1, 2, \ldots, n \qquad (8)$$

The objective is now to identify a set of OV which would give the desired SA. This relationship can also be obtained using the three approaches described previously (Table 8). Some examples of such relationships are given in Table 11. The use of order-of-magnitude analysis, curve fitting, and neural networks are more common compared to rigorous analysis, due to the complexity of the typical processes involved. For example, the determination of the droplet-size distribution of an emulsion formed in an agitated vessel would include detailed modeling of the flow in the vessel (such as using computational fluid dynamics/CFD), as well as droplet breakage and agglomeration processes. A simpler, order-of-magnitude analysis yields a shortcut model (Eqs. 12–13), which is capable of giving a reasonable first estimate.

At this stage, in case the target value of performance index is not achievable because the required values of OV fall outside the range of equipment operability, it may be necessary to modify the ingredients and product structure, or to redesign the process such that the target can be met.

Step 5: Product and Process Evaluation

The procedure results in a base-case product and preliminary design of the process. These mostly theoretical results need to be evaluated and tested using bench-scale equip-

Table 11. Examples of Dependence of Structural Attributes on Operating Variables

Structural Attributes	*Operating Variables*	*Relationship*
Tablets		
Grain particle size, d_p	Air velocity, u_f (fluid jet mill)	Breakage equations (Hill and Ng, 1995, 1996), along with correlation to relate the parameters to operating variables $p_i = p_i(u_f)$ (9)
Porosity, ϵ	Applied pressure, σ_c (tableting machine)	Combination of Leuenberger's correlation and Rumpf's order-of-magnitude equation for tablet tensile strength (Wibowo and Ng, 2001b) $k_c \sigma_c(1-\epsilon) = \ln\left(\frac{\sigma_{t,m} - \frac{1-\epsilon}{\epsilon}\cdot\frac{F_{adh}}{d_p^2}}{\sigma_{t,m} - \frac{1-\epsilon_0}{\epsilon_0}\cdot\frac{F_{adh}}{d_p^2}}\right)$ (10)
Powders		
Particle size, d_p	Rotation speed, N, and angle of inclination, θ (pan granulator)	Correlation determined from experimental data $d_p = d_p(N,\theta)$ (11)
Creams and Pastes		
Droplet size, d_p	Applied pressure (homogenizer)	Order of magnitude estimate: comparison of breakup and collision times (Walstra, 1993) $d_p = \left(\frac{150\Gamma\mu_c^{1/2}\phi}{m_s \rho_c^{1/2}\epsilon^{1/2}}\right)^{3/5}$ (12)
		Order of magnitude estimate: comparison of potential and kinetic energies (Dickinson, 1994) $\epsilon_{av} = \frac{k_e p^{3/2}}{h\rho_e^{1/2}}$ (13)

ment. Any deviation from the target quality factors specified in Step 2 are identified, and the necessary modifications to meet the objectives are determined. Using the models relating *PI* to *OV* (Eqs. 1 and 8), necessary changes in operating conditions and/or equipment design are identified. For example, Eqs. 12–13 indicate that increasing pressure in a homogenizer leads to smaller droplet size, while Eq. 6 predicts that the viscosity of a cream increases as droplet size decreases. Therefore, if it is found that a cream product is not sufficiently viscous, a possible solution is to increase the pressure in the homogenizer. All these make the development process essentially an iteration scheme. A more detailed discussion on this topic, especially in the context of creams and pastes, is available elsewhere (Wibowo and Ng, 2001a). A similar discussion in the context of pharmaceutical suspension is available in Floyd and Jain (1996).

Since the procedure often results in multiple alternatives rather than yielding a single, superior process, the alternatives need to be compared using various criteria, such as economics, safety, environmental impact, and so on. The details of such comparisons are beyond the scope of this article. At this point, optimization techniques can supplement the procedure as a tool to screen the alternatives and determine the optimum process.

Scale-up issues also need to be considered in this step. With the fundamental approach taken in the previous steps, better understanding of the process, and therefore more reliable scale-up, is expected. However, since the complexity of the underlying physics does not allow accurate estimations solely based on theory, pilot-plant tests are almost always necessary. Unforeseen problems may be revealed during such tests, and the design may need to be modified accordingly before building the full-scale plant. For some equipment units, it may be necessary to perform full-scale tests using vendor's equipment. The procedure is now illustrated using four examples, highlighting the key steps to be taken when synthesizing a manufacturing process.

Example 1: Manufacture of Dry Toner

This example illustrates the development of a process for manufacturing a new toner for use in copying machines. The basic component of the machine is the photoreceptor, covered with ions of appropriate charge (Gruber and Julien, 1991; Borsenberger and Weiss, 1998). During copying, an image of the document is formed on the photoreceptor by an optical system. Light from white parts of the document causes neutralization of charge on corresponding spots on the photoreceptor, thus creating a latent image. Toner particles of the opposite charge are then brought into contact with this image, causing bonding of individual particles to the photoreceptor by electrostatic forces. These particles are finally transferred to a piece of paper, and forced to fuse into the paper using heat or pressure. Any remaining toner particles must then be removed from the photoreceptor prior to the next copying cycle.

Step 1. The development begins with a research on market trends to identify consumer expectations of an improved product. Potential consumer needs include a toner material with lower price (Table 2), giving a sharper image and fusing rapidly into the paper. It is also desirable to reduce the environmental impact caused by minimizing the use of hazardous chemicals. While the toner itself is not hazardous, it often creates a waste problem for customers. A potential solution to this problem is to launch a recycling program, in which post-consumer toner is returned to the manufacturing pro-

cess and resold as "remanufactured" (Mandel, 2000). Therefore, it is desirable to design the manufacturing process in anticipation of this recycling possibility. The appropriate product form is powder, which melts and diffuses into the paper when heated. The product packaging suggested in Table 3 is not suitable since the container must be a part of the copying machine. Therefore, a special packaging (a cartridge) is chosen instead.

Step 2. Product quality factors are considered next. The toner material needs to be chargeable, so that it can stick to the photoreceptor. However, the charge also has to be easily neutralized to allow easy removal of remaining particles from the photoreceptor after image transfer. As a powder, it must flow well to assure constant supply from the cartridge during use (Table 5). The toner must also melt and flow into the pores of the paper.

Step 3. Based on the desired product quality factors, ingredients and microstructure are selected. The active ingredient is carbon black, which makes up the image of the reproduced document. If it were desirable to manufacture color toner, other pigments could be used. Table 12 is a summary of the chosen supporting ingredients. Most important is the binding agent, which carries the pigment and causes adhesion to the paper.

The binding agent must be a solid at room temperature, but melts at the fusing temperature. A good choice is a polymer resin such as polypropylene, whose glass transition temperature is below the fusing temperature. Often, a mixture of polymers is used to obtain the desirable glass transition temperature of 50–60°C (Gruber and Julien, 1991). Another important consideration is the rate of toner penetration into the paper. According to the capillary model of Lee (Williams, 1984), the depth of penetration for cylindrical paper pores is

$$z = \left(\frac{\sigma w t}{3\mu} \right)^{0.5} \tag{14}$$

where w is the pore diameter, t is penetration time, σ is interfacial tension, and μ is viscosity. Taking typical values of $z = 10\ \mu$m, $\sigma = 0.025\ \text{N}\cdot\text{m}^{-1}$, $w = 20\ \mu$m, and $t = 30$ ms, Eq. 14 predicts that the suitable viscosity of the suspension (melted toner particle) is around 500 Pa·s at the fusing temperature (about 130°C). According to the Krieger-Dougherty equation (McClements, 1999), this viscosity is related to the polymer viscosity,

$$\mu_s = \mu_c \left[1 - \left(\frac{\phi}{\phi_m} \right) \right]^{-[\mu]\phi_m} \tag{15}$$

where μ_c is the continuous phase (polymer) viscosity, ϕ is the volume fraction of solids, ϕ_m is the volume fraction at the maximum packing condition, and $[\mu]$ is intrinsic viscosity. Assuming monodisperse spherical particles ($\phi_m = 0.632$ and $[\mu] = 3.28$), it is estimated that for the typical pigment concentration ($\phi = 0.1$), the suspension viscosity is about 1.43 times the polymer viscosity. Therefore, it is desirable to use a polymer mixture with a viscosity of about 350 Pa·s at 130°C.

Other supporting ingredients are also selected. For example, charge control additives are chosen based on how fast it can induce charging and discharging of the toner particles. Surface additives are added to assure good flow of the toner particles from the container. It is important that all selected ingredients are compatible, that is, they do not react with or reduce the effect of each other.

Because of the requirement of high-resolution copies, the particle size of the toner beads should be as small as possible. A typical figure is about 10–20 μm, since significantly larger particles usually produce ragged dots and lines (Gruber and Julien, 1991). The size of the pigment particles inside the toner beads must be even smaller. It is taken to be 1.5 μm for illustration purposes.

Step 4. Next, the manufacturing process is synthesized. Based on the general structure (Figure 4), we can construct the process flowsheet shown in Figure 5. The key unit operation is mixing, because the various ingredients have to be combined. An agitated vessel is an appropriate choice for mixing solid pigment particles and melted polymer (Table 9). Pigments (carbon black) may need grinding, if not available in micron size. The polymer needs to be melted before mixing. A dispersion of pigment in liquid polymer is formed in the melt mixing step (heuristic in Table 10). If necessary, the suspension is passed through a rubber mill. The mixture is then cooled and molded into slabs using an extruder. To obtain the desired bead size of 10–20 μm, the slabs are crushed in two steps, using units such as a roller crusher first then an attrition mill (Wibowo and Ng, 1999). Screening is used to separate undersized particles. Finally, a post-treatment unit (coating) is added to introduce surface additives.

The flowsheet in Figure 5 agrees with the conventional dry toner manufacturing process described in the literature (Gruber and Julien, 1991; Tomiyama et al., 1995). In practice, other equipment units are often used instead of those shown in the flowsheet. For example, a hammer mill can be used instead of a roller crusher to perform the first grinding step (Diamond and Floersheim, 1981). Alternatively, cryogrinding techniques are used to produce 100–300 μm particles, which are then jet-milled. Other process alternatives have also been followed in industrial practice. For example, dry blending of the pigment with polymer beads followed by

Table 12. Supporting Ingredients for Toner Beads (Example 1)

Desired Function	*Ingredient Chosen*	*Examples*
Delivering the pigment and causing binding	Polymer	Polypropylene, polyethylene
Providing adequate level or rate of charging	Charge control additives	Quaternary ammonium salts
Flow properties	Surface additives	Fumed silica
Enabling transport of toner through the developer	Magnetic additives	Magnetite
Preventing adhesion to fusing roll	Release agent	Silicone oil

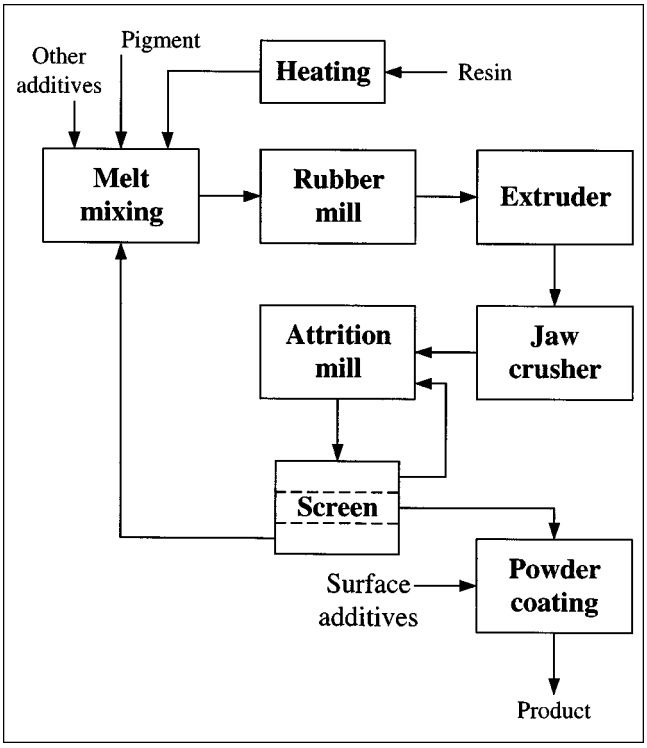

Figure 5. Flowsheet for the dry toner manufacturing process (Example 1).

hot extrusion is a common alternative to melt mixing. Another alternative is the suspension polymerization process, where toner particles of the desired size are generated by controlling the degree of polymerization (Kato et al., 2001).

Operating conditions are then considered. Let us first consider the dispersion process. We can use an order-of-magnitude model proposed by Hansen et al. (1998), which was derived from the comparison between viscous shear strength and the tensile strength of the aggregates formed in a suspension. It involves the fragmentation number, defined as

$$N_{Fa} = \frac{3\pi\mu_c \dot{\gamma} d_p^3}{4A} \tag{16}$$

whose value has to be larger than a critical value for aggregate breakup to occur. Here, d_p is the aggregate size and A is the material's Hamaker constant. Equation 16 can be used to predict the required shear rate $\dot{\gamma}$, which would produce a dispersion with a certain aggregate size. Although the model is expected to be physically correct, no estimate is available for the actual critical value of the fragmentation number. For illustration, let us assume $N_{Fa,crit} = 3 \cdot 10^5$, as suggested by the experimental results of Sonntag and Russell (1986).

The shear rate can be further related to equipment operating conditions. For example, the shear rate in an agitated vessel can be estimated as follows (Miner, 1993)

$$\dot{\gamma} = \frac{4\pi N}{1 - \left(\frac{D}{T}\right)^2} \tag{17}$$

where N is the agitation speed (s^{-1}), and D and T are the impeller and vessel diameter, respectively. Equations 16 and 17 can be used to estimate the operating conditions required to produce a suspension containing pigment particles of the desired size (1.5 μm). The calculation results are depicted in Figure 6, in which the required agitation speed is plotted as a function of D/T for two different polymers, both of which have a viscosity of approximately 350 Pa·s at low shear rates (10^{-3} s^{-1}). If we assume that the practical range of N is between 50 and 500 rpm and D/T is between 0.4 and 0.8 (shaded region in Figure 6), we can conclude that using polymer II, an agitated vessel is sufficient to obtain the desired suspension. However, if polymer I is used, an agitated vessel can be used alone only if D/T is around 0.8.

Let us now consider another example of equipment-imposed constraint. Suppose there is a change in product specification, such that the required particle size is 1 μm instead of 1.5 μm. Taking $D/T = 0.8$, Eqs. 16–17 predict that N has to be around 2,100 rpm for polymer I and 880 rpm for polymer II. Since such values are unachievable for the existing equipment, we conclude that by using either polymer, it is not possible to produce a suspension containing 1 μm particles using an agitated vessel alone. Another polymer with lower viscosity or another mixing unit capable of imposing higher shear rate, such as a rubber mill, should be used instead.

For the crusher and attrition mill, a simulation using population balance equations can be used to predict the outcome (Hill and Ng, 1995, 1996). Since it is impossible to predict the breakage parameters in the equation, correlations must be developed using experimental data. The breakage parameters are then related to operating conditions such as gap width and roller speed (for roller crusher) and air velocity (for attrition mill). In a roller crusher, roller speed determines the residence time, while gap width dictates the pressure applied to the particles. Table 13 summarizes the assumed data as well as the equations used for simulation. The simulation is useful for assuring that equipment constraints are met. Let us assume that the mean particle size of the crusher outlet must be between 800–1000 μm for the attrition mill to work properly. Also, there is a product constraint that the fraction of particles larger than 20 μm in the product stream of the attrition mill should not exceed 15%. It is desirable to minimize the amount of particles rejected by the screen, because these undersized particles need rework, thus reducing process throughput.

The simulation results are depicted in Figure 7. In Figure 7a, the shaded area indicates the window of operation, that is, the combination of gap width and rotational speed which leads to crusher outlet particle size between 800–1000 μm. The dotted lines indicate the practical limits of gap width and rotational speed. Figure 7b shows the effect of air velocity in the attrition mill on the amount of undersized particles (expressed as the ratio of screen undersize to the attrition mill feed) and on the amount of particles larger than 20 μm in the product stream. It turns out that the minimum air velocity, below which the amount of oversized particles is unacceptable, is about 153 m/s. At that speed, the fraction of screen undersize is only about 4%.

Step 5. The last step is product and process evaluation. The product is evaluated using various available methods,

Table 13. Equations and Assumed Parameter Values Used for PBE Simulations in Example 1

Equations	
Discretized mass-based breakage equation (Hill and Ng, 1995)	$\frac{d\omega_i}{dt} = \frac{\omega_{f,i} - \omega_i}{\tau} = \sum_{j=i+1}^{n} \beta_j b_{M,ij} S_j \omega_j - \delta_i S_i \omega_i$
Specific rate of breakage	$S_i = S_0 i^q$
Mass-based breakage function	$b_{M,ij} = \frac{v_i}{v_j} b_{ij}$
Number-based breakage function	$b_{ij} = \frac{12(k-2)v_i(v_j - v_i) + (6-2k)v_j^2}{v_j^3}$
Birth term correction factor	$\beta_i = \frac{1}{2 - \frac{1}{v_i}\sum_{j=1}^{i-1} v_j b_{ji}}$
Death term correction factor	$\delta_i = \frac{\frac{1}{v_i}\sum_{j=1}^{i-1} v_j b_{ji}}{2 - \frac{1}{v_i}\sum_{j=1}^{i-1} v_j b_{ji}}$
Particle volume and size	$v_i = \frac{\pi d_i^3}{6} = v_1 i^r$
Probability of passing a screen (Wibowo and Ng, 1999)	$P(d_i) = 1 - \left[1 - \left(\frac{b - d_i}{b + c}\right)^2\right]^n$
Parameter Values	
Size interval parameters	$v_1 = 1\ \mu\text{m}^3$
Roller crusher parameters	$r = 2.154$
	$S_0 = \frac{2.5 \cdot 10^{-18}}{y^{0.8}}\text{s}^{-1}$; y in mm
	$\tau = \frac{3{,}000}{N}\text{s}$; N in rpm
	$q = 3$
	$k = 2$
Fluid jet mill parameters	$S_0 = \frac{u_f}{2500}\text{s}^{-1}$; u_f in m/s
	$\tau = 0.3$ s
	$q = 1.5$
	$k = 3$
Screen parameters	$n = 80$
	$c/b = 1.3$
Upper deck screen opening	$b_1 = 30\ \mu\text{m}$
Lower deck screen opening	$b_2 = 10\ \mu\text{m}$

such as particle-size counters, rheometers, charge spectrographs, and so on. When there is a deviation from the desired quality, the models and correlations developed previously are used to determine ways to fix the problem. Table 14 lists some examples of potential problems and the appropriate corrective actions. It is also important to evaluate the process. In particular, we need to check the applicability of the selected equipment and operating conditions to handle remanufactured material, which may have different physical properties compared to fresh feed.

Example 2: Powdered Detergent

A leading detergent manufacturer would like to produce a new brand of detergent to capture recent market trends, which indicate a shift from low-density to compact powdered laundry detergent. This is because compact products are easier to carry and require less space to store. In addition, the product should perform well in new washing machines, which are expected to operate with less water and at lower temperatures. It is also desirable that the manufacturing process be as economical as possible.

Step 1. As mentioned, a need for a more compact detergent product was identified. Market trend analysis also shows that a detergent product containing bleach is more attractive to consumers, in agreement with Table 2. Therefore, it is desirable to develop a product which combines detergent with bleach, and has a bulk density of about 700–800 kg/m^3 (Showell, 1998). Due to previous experience and company competence, it is decided to produce powdered detergent. Carton boxes are chosen as the preferred packaging, among the typical ones listed in Table 3.

Step 2. Product quality factors are identified next. As a cleaning product, the detergent is expected to possess the capability of removing water-insoluble grease and soils. It is also

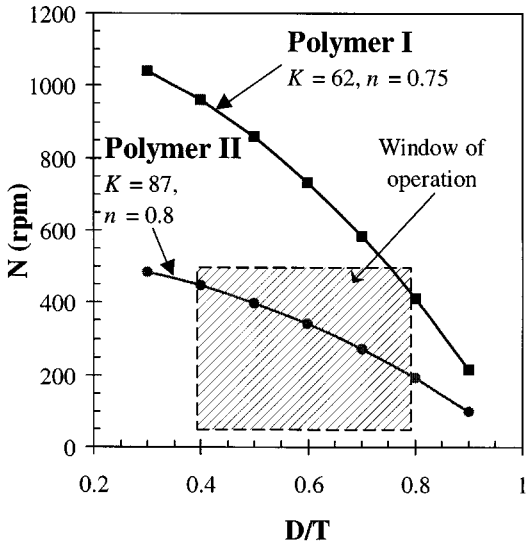

Figure 6. Required rotational speed as a function of D/T for producing a suspension using two different polymers.

K and n are the constants in the viscosity expression: $\mu = K\dot{\gamma}^{n-1}$.

desirable that the product is more readily soluble in cold water, such that it would be suitable for use in washing machines operating at 40°C. Less water consumption, about only 25% of the volume of water conventionally used, leads to the need for lower foaming and stronger soil suspension capability (Showell, 1998). The powder should also flow well and does not agglomerate due to moisture absorption during storage (Table 5).

Step 3. The requirement of a water-soluble product that is capable of removing hydrophobic materials leads to the use of a surfactant as an active ingredient. The choice of surfactant depends on its washing power. Biodegradable materials are preferred due to their minimum environmental impact. Since the surfactant level in the washing solution must be kept above its critical micelle concentration (CMC) to perform effectively, it is desirable to have a low CMC, such that the surfactant requirement is lower. The Krafft point, the temperature below which the surfactant exist as solid crystals, must be lower than the washing temperature, otherwise the surfactant will not dissolve. The need of introducing a bleaching agent adds a complication to the problem, since the bleach is not compatible with the detergent molecule due to its oxidative power. Moreover, since it must be effective in cold water, conventional bleaches such as peroxygen compounds cannot be used. A possible solution to this problem is to use inactivated bleach such as sodium perborate, which transforms into the active peracid bleach once it dissolves in the wash water.

Based on the quality requirements, the supporting ingredients summarized in Table 15 are chosen. To activate the bleach once it enters the wash solution, an activator must be present in the product. The peracid bleach, formed as a reaction product between the perborate and the activator, must have the correct HLB value such that it dissolves in water, but can remove oily stains. Procter & Gamble has patented

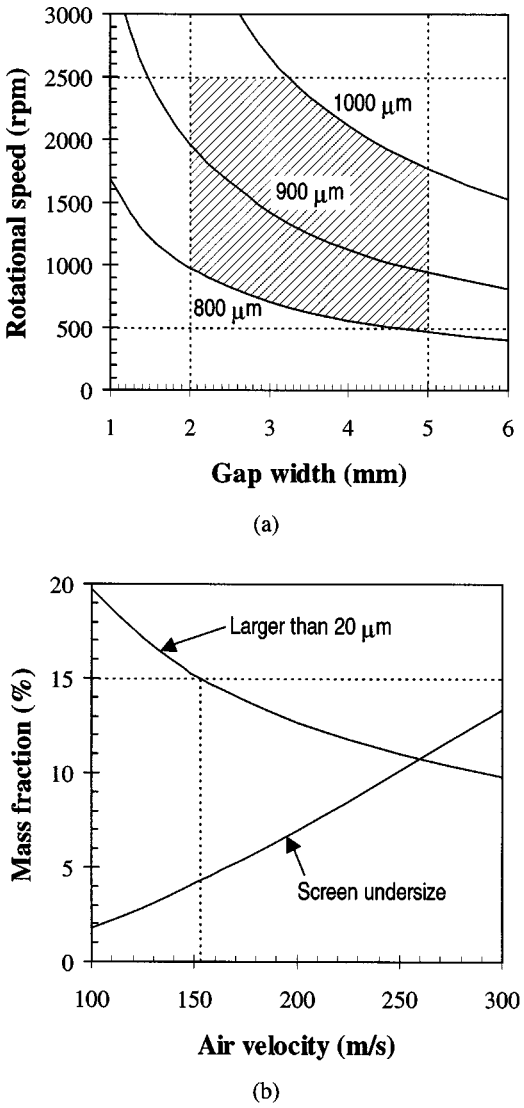

Figure 7. Simulation results for Example 1.

(a) Mean particle size of the roller crusher output as a function of rotational speed and gap width; (b) fraction of screen undersize and oversized product as a function of air velocity in the fluid-jet mill.

Table 14. Deviations from Desired Product Performance and Possible Remedies (Example 1)

Problem	*Possible Remedy*
Printed image has ragged dots and lines	Decrease toner particle size
Supply of toner from cartridge is not continuous	Increase toner particle size Use a better surface or magnetic additive
Penetration into paper is too deep	Increase binder viscosity by using polymer with higher molecular weight and glass transition temperature
Not enough penetration into paper	Decrease binder viscosity by using polymer with lower molecular weight and glass transition temperature
Too much residue left in photoreceptor	Use a better charge control agent Use a better release agent

Table 15. Powdered Detergent Supporting Ingredients (Example 2)

Desired Function	*Ingredient Chosen*	*Examples*
Bleach activation	Bleach activator	Alkanoyloxybenzene sulfonate, N-acyl caprolactam
pH control	Buffer	Sodium carbonate
Enhancement of washed fabric appearance	Whitening agent	Bistriazinyl derivatives of diaminostilbene disulfonic acid
Removal of unpleasant odors	Fragrance	Perfumes
Removal of protein, carbohydrate, carbohydrate, and fat stains	Enzyme	Proteases, amylases, lipases, cellulases
Control of water hardness Providing alkalinity Preventing redeposition Preventing corrosion Improving powder flow	Builder	Zeolite A, soda ash (Na_2CO_3), sodium polycarboxylate, δ-disilicate
Filling	Filler	Sodium sulfate

the use of nonanoyloxybenzene sulfonate (NOBS), which reacts with peroxide in the wash solution (Willey et al., 1995). Since there may be a side reaction between NOBS and the activator, the pH of the wash solution needs to be controlled at about 10 using a buffer. Other cleaning agents such as enzymes are added to remove various kinds of stain from fabric. The choice should be based on their capability to remove the stain without destroying the cloth. It is desirable to choose a multifunctional material for the builder. Zeolite A is the popular choice at present, but more environmentally friendly silicates, such as δ-disilicate, are expected to gain market share in the future (Rieck, 1998).

Product microstructure requirement includes high bulk density and sufficiently small primary particle size (300–900 μm) to be dissolved quickly. Bulk density is determined by both particle-size distribution (PSD) and individual particle porosity. The desired bulk density of 700–800 kg/m^3 is achieved when particle porosity is about 5% (Appel et al., 1992). A wide PSD leads to higher bulk density, but is not desirable because small particles can cause dusting, while large particles dissolve more slowly. Therefore, the best way to achieve the high bulk density is to minimize the individual particle porosity.

To predict the required particle size for good flow properties, we can analyze the competing forces (Molerus, 1982; Wibowo and Ng, 2001b). Comparison of gravity and cohesion forces yields the criterion

$$\frac{W}{F_{vdW}} = \frac{2\pi\rho_s d_p^2 g z_0^2}{A\eta} > 1 \tag{14}$$

for the powder to flow easily. Using an estimate of $A = 10^{-20}$ J, $\eta = 0.01$, and $z_0 = 4 \cdot 10^{-10}$ m, we obtain that the minimum particle size, below which flow problems due to particle cohesion may occur, is about 100 μm. This indicates no potential problem with the desired particle size of 300–900 μm.

Step 4. The manufacturing process is depicted in Figure 8. Some ingredients are solid, but some are liquid. Therefore, an agitated vessel is used to form a slurry (Table 9). The slurry is then transformed into powder, which is the desired product form. Spray drying is chosen for powder production, because the facilities are already in place. Because the sprayed product has a low bulk density, it is sent to a high-shear mixer, where high shear is applied to fracture the porous particles to form smaller, but less porous, particles. To achieve the desired size, the small particles are then agglomerated with the aid of a liquid binder. The final product may require post-treatment step such as drying to remove excess liquid. The flowsheet is similar to the one found in the literature (Appel et al., 1992; Capeci and Welch, 1998).

The particle size of the spray-dried product depends on processing variables such as air/liquid flow ratio (M_G/M_L), relative air velocity at the nozzle (v_r), and liquid viscosity. The following correlation has been proposed for droplet size from the two-fluid nozzle atomizer (Masters, 1991)

$$d_d = \frac{C_1(\mu_L, \rho_L, \sigma, A_G)}{(\rho_G v_r^2)^{\alpha}} + \frac{C_2(\mu_L, \rho_L, \sigma, v_r)}{(M_G/M_L)^{\beta}} \tag{15}$$

The values of the constants can be determined experimentally. The value of M_G/M_L typically ranges from 0.1 to 10. The solid particle size can be obtained from droplet size using

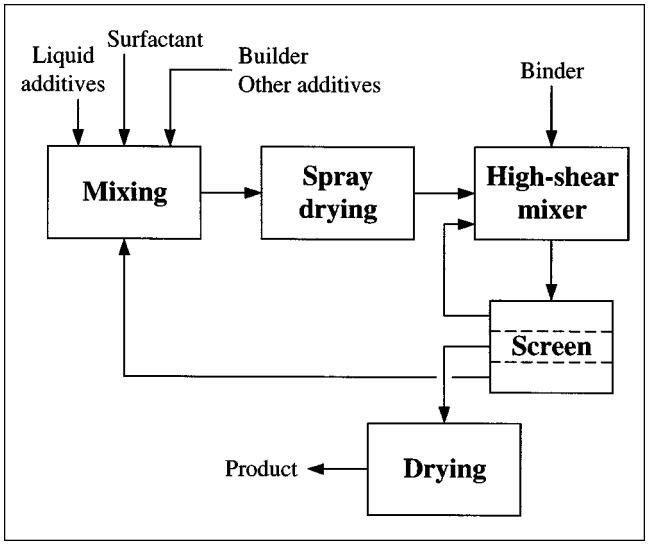

Figure 8. Manufacturing powdered detergent (Example 2).

$$d_p = \left[\frac{\rho_d (1 - w_{L,S})}{\rho_S (1 - w_{L,F} - \epsilon_p)} \right]^{1/3} d_d \qquad (16)$$

where $w_{L,S}$ and $w_{L,F}$ are the liquid content of the slurry and of the final product, respectively, and ϵ_p is the particle porosity (about 0.4 for conventional detergent powder). Equations 15 and 16 relate droplet size to the operating conditions, as well as the product composition. If the functional form of C_1 and C_2 is known, we can predict the required operating conditions and achievable droplet size. In the absence of such a functional form, the effect of operating conditions on droplet size must be determined experimentally before a simulation can be performed. Neural network models seem to be a good choice for this application. Based on such a simulation, a set of operating conditions which would yield an optimum droplet size can be predicted.

Step 5. As in Example 1, the product can be evaluated to identify necessary modifications. Process alternatives are also considered. For example, it may be desirable to use "non-tower routes," which requires less energy and yields even better product compared to spray drying. A common process is dry neutralization, where the surfactant is synthesized in a low water activity environment, resulting in a thick paste. Additional ingredients are blended in, and the paste is then agglomerated to form powder with fairly high density (above 650 kg/m^3) (Capeci and Welch, 1998). This alternative can be compared to the spray drying process based on product quality as well as economics.

Example 3: Shampoo and Conditioner in One Product

This example illustrates the development of a conditioning shampoo and the corresponding manufacturing process. It is loosely based on real case histories documented in various patents (Bergmann, 1995; Snyder et al., 2001; among others).

Step 1. Many shampoo products provide acceptable cleaning, but leave the hair difficult to comb or brush. Consequently, a separate styling product is needed to condition the freshly shampooed hair. Among typical market trends is the tendency towards a product that combines complementary ingredients, and makes hair maintenance more pleasurable (Table 2). Therefore, it is decided to make a product that functions both as an anti-dandruff shampoo and a hair conditioner. The product should be a liquid to allow easy application to the hair. This means it can be a macromolecular solution, emulsion, liquid foam, suspension, or combination thereof (Figure 1). Among the appropriate product packaging found in Table 3, a plastic bottle with flip cap is chosen.

Step 2. The primary product functionality is clearly to clean the hair as well as to give it desirable combing or brushing properties. If any ingredient is deposited to the hair to achieve the desirable function, it must be washable in subsequent shampoo treatment to prevent buildup. Rheological quality factors must also be considered for this liquid product (Table 5). It is desired that the product has a high viscosity (about 500 Pa·s) at low shear rates to prevent it from splashing, and a low viscosity (about 2 Pa·s) upon application on the hair at high shear (10,000 s^{-1}) (Lochhead, 1993). The shampoo should also be stable while in storage.

Step 3. The active ingredients are selected next. Anionic synthetic surfactants, such as alkyl and alkyl ether sulfates, are chosen since they are highly effective in cleaning (Snyder et al., 2001). Mild surfactants are preferred to prevent the hair and scalp from becoming dry. Cationic surfactants and cationic polymers are known to be suitable hair conditioners (Bergmann, 1995). However, the anionic and cationic substances cannot be used in combination because of the formation of an insoluble salt. To resolve this problem, a search for other classes of materials capable of performing the conditioning function is conducted, utilizing techniques such as molecular design and combinatorial chemistry. It is found that water-insoluble nonionic compounds such as polydimethylsiloxane, which produces a thin film on the hair after application, can give superior hair softness. Because of the presence of this ingredient, it is necessary to design the product in such a way that phase separation does not occur during distribution and storage. On the other hand, the material has to be released and deposited on the hair upon application. This can be achieved by making a product with an apparent yield stress of 10 Pa, such that gravitational phase separation is retarded (Lochhead, 1993). The requirement that the shampoo has shear-thinning properties as defined in Step 2 also helps to impede flocculation during storage, but allows the suspension to be broken during use. To treat dandruff, which is caused by coagulation of dead cells stripped off from the scalp, it is desirable to incorporate ingredients that can alleviate the exfoliation process. Among such ingredients are quaternary ammonium compounds, salicylic acid, and vitamin B12 (Levere et al., 2000).

Table 16 summarizes the shampoo ingredients, including the supporting ingredients. To blend the immiscible phases, an emulsifier is used. Cationic deposition agents are used to aid the deposition of the conditioning agent on the hair. An

Table 16. Shampoo and Conditioner Supporting Ingredients (Example 3)

Desired Function	*Ingredient Chosen*	*Examples*
Aiding the deposition of conditioning agent	Deposition polymer	Quaternary ammonium polymers
Improving spreadability of conditioning agent	Spreading agent	Quaternary ammonium compounds
Dissolving the conditioning agent	Organic solvent	Silicone oil
Shampoo base	Aqueous solvent	Water
Viscosity control	Thickening agent	Carboxyvinyl polymers, cellulose ethers, guar gum, starch
pH control	Acid or base	Sodium hydroxide, citric acid
Improving product appearance	Pearlescent agent	Ethylene glycol distearate
Enhance attractiveness	Perfume, pigment	Essential oils

organic solvent such as silicone oil is used to dissolve the conditioning agent and form a liquid phase, which is then dispersed into the aqueous base in the form of small droplets. To increase the pleasurable feel of wet hair, special polymers can be used to control the texture of the foam produced when shampooing (Reisch, 2000). Since it is desirable that a shampoo is neither too acidic or basic, pH controlling agents are used to keep the pH around 4 to 7. To obtain the desired appearance, pearlescing agents such as ethylene glycol distearate (EDGS) are added to the product. Perfumes and preservatives can also be added to improve product performance.

The product microstructure must be selected in such a way that the product has the desired viscosity, appearance, and stability. The viscosity is mainly controlled by the phase volume fraction and size of the silicone oil droplets in the mixture (Bergmann, 1995). Viscosity models (Eqs. 6–7) can be used to predict the microstructure that gives the desired rheological properties. The emulsion droplet size also affects product appearance. As mentioned, if we want the shampoo to be transparent, the droplets should typically be smaller than 0.05 μm. It is also important to control the particle size of EDGS crystals, since it determines the smoothness of the product, as well as the pearlescent appearance.

Step 4. The manufacturing process is depicted in Figure 9. The water-soluble anionic surfactant is mixed with water, while the conditioning agent is dissolved in silicone oil. The emulsifier and other hydrophilic ingredients are then mixed into the organic phase. The pearlescing agent is introduced as a liquid since it has a low melting point (Table 10). To form the desired oil-in-water emulsion, an agitated vessel is used in the mixing step (Table 9). A homogenizer is used next to achieve the desired droplet size. Due to the high concentration of surfactant, it is important to perform the homogenization under vacuum to minimize incorporation of air into the product (Table 10). The product is then cooled to room temperature.

An important operational issue to be considered is the effect of mixing and homogenization operating variables on droplet size. Interested readers are referred to Wibowo and Ng (2001a) for a more detailed discussion on this topic. Another issue is the particle size of the pearlescing agent, which crystallizes during the cooling process and forms a crystalline network in the product (Baravetto et al., 2001). The cooling profile and heat exchanger design must be adjusted to balance the nucleation and growth of the crystals, so that the desired particle-size distribution can be obtained (Diepen et al., 1997; Wibowo et al., 2001).

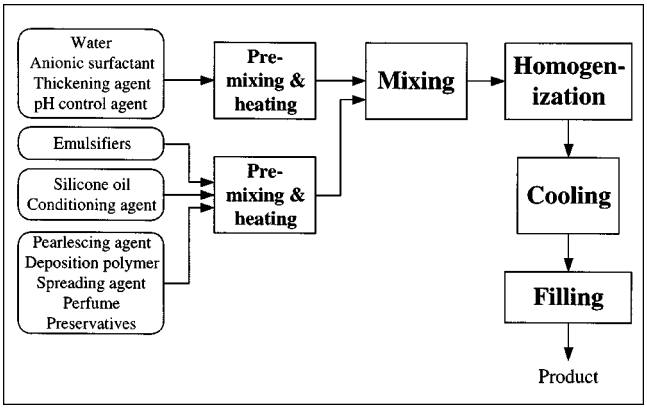

Figure 9. Manufacturing powdered detergent (Example 3).

Step 5. The product needs to be tested to make sure that it is acceptable to customers. This includes evaluation of properties such as ease of application, foaming speed, ease of combing, fragrance, and ability to cause irritation. The evaluation is usually performed by trained panelists using standard methods such as salon test (Bergmann, 1995). If necessary, the composition and microstructure are changed to give a more satisfactory product, and the manufacturing process is modified accordingly.

Example 4: Preservative-free Cosmetics

In recent years, natural and preservative-free cosmetic products have attracted interest, mostly due to the fact that currently available antimicrobial preservatives may cause irritation or allergic reactions in some individuals (Kabara and Orth, 1997). In response to this market trend, a cosmetic company would like to manufacture a preservative-free hand lotion based on an existing product which has been successful in these past few years. This example illustrates the application of the procedure in modifying an existing product and process. Only Steps 1 to 4 will be discussed, since the product and process evaluation (Step 5) is similar to the previous examples.

Step 1. While conventional lotion contains preservatives to deactivate any microorganism contaminating the product during use, preservative-free products must be specially packaged to prevent microbial contamination. The original lotion was contained in plastic tubes with open screw cap. In accordance with study results on contamination of unpreserved skin lotions (Brannan and Dille, 1990), the pump-top bottle is selected among the possible packaging listed in Table 3. Another factor to consider is the presence of microbes in the air entering the container when the lotion is dispensed. A possible solution is to install a hydrophobic filter to sterilize the entering air (Clements and Killinger, 1991).

Step 2. The product functionality remains the same, that is, to keep the skin moisturized and to provide a good feel when applied to the skin. Rheological quality factors are considered (Table 5). The viscosity of the lotion should be low enough during pumping (shear rate around 10 s^{-1}), but not so low that it flows uncontrollably. Let us assume that after several tests using the pump-top container, it is found that the convenient viscosity at this shear rate is between 0.1–0.5 Pa·s. At high shear (500 s^{-1}), the viscosity should be around 0.025 Pa·s for good consumer perception (Brummer and Godersky, 1999). The existing product is found to have a viscosity of 2 Pa·s at 10 s^{-1}, which is too high. Therefore, there is a need for a less shear-thinning product.

Step 3. The active ingredient remains the same. For the lotion to have the desired moisturizing capability, emollients such as stearic acid, cetyl alcohol, and petrolatum are typically used. In selecting supporting ingredients and product microstructure, we need to look at skin morphology, as well as microorganism survival strategies. Table 17 provides a list of selected ingredients. To reduce water availability for a mi-

Table 17. Preservative-Free Lotion Supporting Ingredients (Example 4)

Desired Function	*Ingredient Chosen*	*Examples*
Control of lotion humidity	Humectant	Glycerol
Emulsion stabilization	Surfactant	Glyceryl monostearate, quaternary ammonium salts
Increasing viscosity and obtaining shear-thinning behavior	Thickener	Carbomer, propylene glycol
Providing additional attractiveness	Aroma chemicals	Essential oils
Reducing water activity	Salts	Aluminum chlorohydrate, cationic surfactants
pH control	Organic acid	Citric acid
Preventing deterioration of fragrance and color	Chelating agent	EDTA, citric acid

croorganism to live, we choose ingredients that can reduce water activity a_w (defined as the ratio of the vapor pressure of the solution to that of the solvent), such as humectants and inorganic salts. Typically, microbial growth is prevented at acidic condition (pH < 4.5) or low water activity ($a_w < 0.8$) (Kabara and Orth, 1997). Ingredients with natural antibacterial capacity, such as fatty acids and esters, are preferred. To bind metal ions, which may cause deterioration or are cofactors for enzymes required for bacterial metabolism, chelating agents are used. It is also preferable to use high surfactant concentration to create an undesirable condition for bacterial growth. Other ingredients such as fragrances and pigments are added to make the product more attractive.

Because the product must be suitable for the new container, the viscosity requirement is different compared to the existing product. Also, the phase volume fraction may change due to the alteration of product composition. Since microstructure is not expected to have a significant effect on viscosity, the product viscosity is controlled mainly by the addition of thickening agent. Therefore, the main issue is to obtain the desired rheological properties by selecting the right type and concentration of the thickening agent.

Step 4. The next step is to construct a flowsheet for the manufacturing process. The flowsheet turns out to be the same as the existing one. Compatible ingredients are premixed before being fed into an agitated vessel to form an emulsion (Table 9). Then, a colloid mill is used to reduce the droplet size to several microns.

We also consider operating conditions and equipment limitations. Due to the thickener modification, the new lotion is expected to be less viscous at the typical shear rate inside an agitated vessel (about 15 s^{-1}). Therefore, the blending time, as well as the power consumption, would be less compared to the original lotion. To avoid incorporation of air into the product, it may be necessary to lower the agitation speed. Prolonged stirring, which can cause irreversible change in product viscosity, should also be avoided by minimizing the processing time in the agitated vessel. Therefore, the lotion should not be stirred longer than it needs to completely mix the ingredients.

At the shear rate of the colloid mill (about 10,000 s^{-1}), the new product is expected to be more viscous, since it has the same viscosity as the existing product at 500 s^{-1} (application shear rate), but is less shear-thinning. The droplet size of the colloid mill output can be estimated using the Weber number

$$N_{We} = \frac{\dot{\gamma}\mu_c d_p}{2\sigma}, \tag{17}$$

whose value must exceed a critical value for breakup to occur (Walstra, 1993). If the critical value can be assumed to be the same for both the original and new product, the shear rate needs to decrease as viscosity increases, to maintain the same droplet size. In other words, in the production of the new lotion, the colloid mill should be operated at a lower shear rate condition, that is, lower rotor speed and/or smaller gap width (Wieringa et al., 1996).

Conclusions

Chemical-based consumer products, such as pharmaceuticals, personal care, and health care products, continue to gain significance in the global chemical industry. Product quality is the key issue for the manufacture of such products. However, manufacturing cost, as well as research and development expenses, which constitute about 30–35% of product cost (Reisch, 2000), are equally important. In order to minimize these costs, and to keep up with the increasing pressure towards shorter development time, it is desirable to perform process and product development in an effective and efficient manner. It is necessary to consider issues in different aspects and scales, and integrate them in a systematic way.

To meet this need, we have presented a systematic procedure for synthesizing chemical-based consumer product processes, the entirety of which is depicted in Figure 10. Based on market trends, the desired quality factors are identified and related to the product ingredients and microstructure, and then to the process flowsheet and operating conditions. The entire workflow is considered so as to ensure successful development of the product from the laboratory to commercial production. Heuristics as well as mathematical models are used to assist decision-making at each step of the procedure. These are based on an understanding of the fundamental interactions between the product ingredients, as well as the physicochemical phenomena which occur during product manufacturing and application.

The manufacturing process discussed here mainly covers mixing, blending, solids handling, and filling. While it is common for manufacturing companies to purchase the ingredients from suppliers, some key ingredients may be synthesized in-house. For example, the process in pharmaceutical companies usually spans all the way from reaction to dosage formulation. For such a case, it is desirable to integrate the manufacturing process with the upstream production and isolation steps.

Another important issue in such a product-centered development process is information management. The availability of databases and software tools, as well as hierarchical proce-

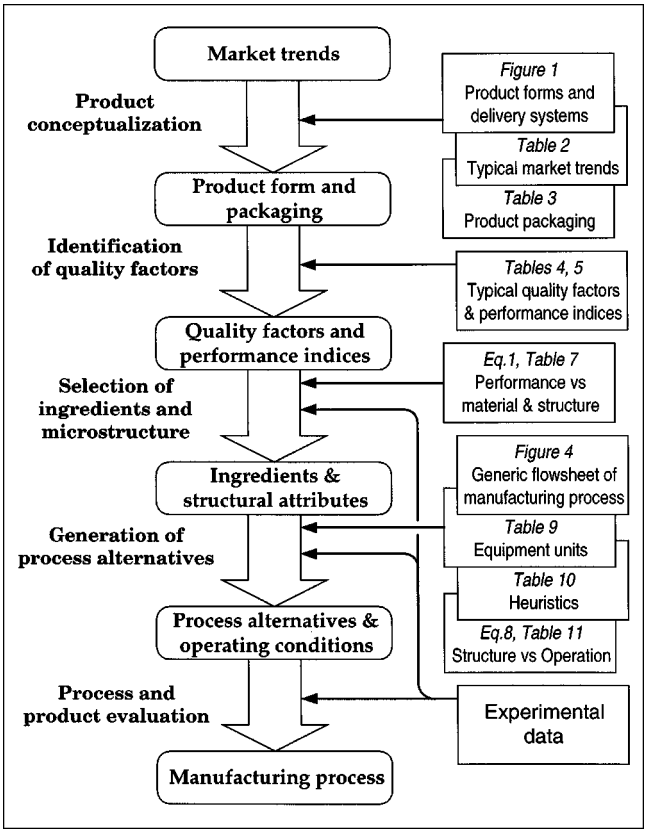

Figure 10. Systematic procedure for product-oriented process synthesis and development of chemical-based consumer products.

dures, greatly assists a development project. Integration of such tools into a coherent environment would further improve the development process. Efforts in this direction are now underway.

Acknowledgment

Financial support from the National Science Foundation (Grant No. CTS-9908667) is gratefully acknowledged. We thank George Stephanopoulos of Mitsubishi Chemical for suggesting the term "Product-Centered Processing."

Notation

A = Hamaker constant, J
b = dimension of screen opening, μm
c = diameter of screen wire, μm
C_1 = constant in Eq. 15, $m\cdot(kg\cdot m^{-1}\cdot s^{-2})^{\alpha}$
C_2 = constant in Eq. 15, m
d_d = droplet size from atomizer, m
d_p = droplet or particle diameter, m
D = impeller diameter, m
$\mathfrak{D}$ = diffusivity, $m^2\cdot s^{-1}$
g = gravitational constant, $m\cdot s^{-2}$
h = homogenizer valve gap width, m
H = tablet size, m
k = constant in breakage function (Table 13), dimensionless
k_c = constant in Eq. 10, dimensionless
k_e = constant in Eq. 13, dimensionless
K = pre-exponential factor of non-Newtonian fluid viscosity, $Pa\cdot s^n$
m_s = surfactant concentration, $kg\cdot m^{-3}$
m_t = tablet mass, kg
M = mass-flow rate, $kg\cdot s^{-1}$
n = constant in power-law viscosity model, dimensionless
n = screen parameter (Table 13), dimensionless
N = rotational speed, rpm or s^{-1}
N_{Ca} = capillary number, dimensionless
N_{Fa} = fragmentation number, dimensionless
N_{Fw} = flow number, dimensionless
N_{We} = Weber number, dimensionless
p = homogenization pressure, Pa
p_i = parameter (Eq. 9), various dimension
r = size interval ratio, dimensionless
t = penetration time, s
T = vessel diameter, m
u_f = air velocity in fluid jet mill, $m\cdot s^{-1}$
v = particle volume, μm^3
v_r = relative air velocity, $m\cdot s^{-1}$
w = pore diameter, m
W = weight, N
w_L = liquid content, $kg\cdot kg^{-1}$
y = roller crusher gap width, mm
z = depth of penetration, m
z_0 = constant, $4\cdot 10^{-10}$ m
α, β = parameters in Eq. 15, dimensionless
$\dot{\gamma}$ = shear rate, s^{-1}
Γ = excess surface concentration of surfactant, $kg\cdot m^{-2}$
ϵ = porosity, dimensionless
ϵ = turbulence energy dissipation rate (Eq. 12), $W\cdot kg^{-1}$
ϵ_{av} = average power density (Eq. 13), $W\cdot kg^{-1}$
ϵ_p = particle porosity, dimensionless
η = roughness factor for van der Waals force, dimensionless
θ = angle of inclination of a pan granulator, rad
κ = viscosity ratio, dimensionless
μ = viscosity, Pa·s
ρ = density, $kg\cdot m^{-3}$
σ = interfacial tension, $N\cdot m^{-1}$
σ_c = compressive pressure, Pa
σ_t = tensile strength, Pa
τ = residence time, s
τ_0 = yield value, Pa
ϕ = internal phase volume fraction, dimensionless
ω = angular velocity, s^{-1}
ω = mass fraction (Table 13), dimensionless

Subscripts

c = continuous phase
d = dispersed phase
e = emulsion
s = suspension
G = gas
L = liquid
m = maximum
0 = initial value

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Manuscript received July 18, 2001, and revision received Nov. 12, 2001.