P&G

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Natural and Synthetic Surfactants

Which one is better?

Summary

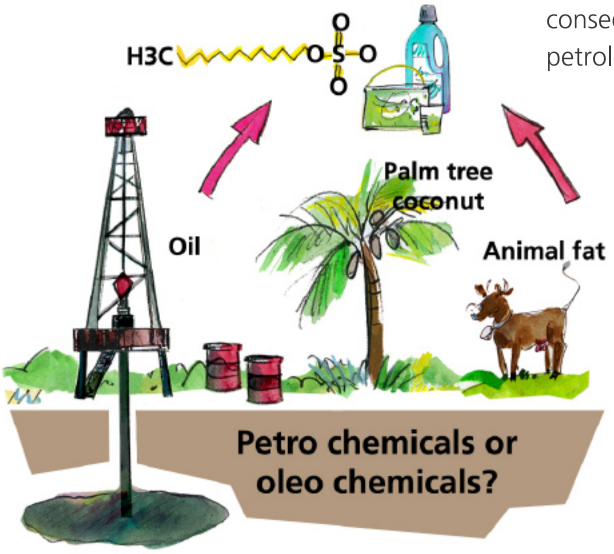
Due to the popular perception that "natural" is by definition and always better for the environment than "synthetic," it has been suggested that petrochemical surfactants should be replaced with oleochemical ones because this would improve the environmental profile of detergents. As this will be discussed in more detail in the following pages, a total substitution is not recommended for many reasons:

- The wide range in consumer needs (wash conditions) would be more difficult to meet with oleochemical surfactants alone.

- Data from biodegradation, removal by sewage treatment, toxicity and LCA studies support that petrochemical and oleochemical surfactants are of comparable environmental quality.

- Replacement of petrochemical by oleochemical surfactants would not lead to any significant reductions in water or air emissions, nor would it reduce energy consumption across the life-cycle of the surfactants.

- Colder wash temperatures will result in energy savings during the consumer use phase of the surfactant life-cycle. This will have positive consequences for the environment: reduced air emissions, conservation of petroleum stocks, reduced waste.



Ideally, both oleochemical and petrochemical surfactants are available to detergent formulators. Having the flexibility to use both oleochemical and petrochemical surfactants allows our formulators to create products that maximize the value in the bottle of detergent, so to speak, by optimizing cleaning ability under a variety of laundry conditions while keeping the price low in the current market. These days, our formulation scientists focus quite a lot on developing detergents that perform well at lower wash temperatures. This approach will continue to yield energy savings during the consumer use phase, hence a reduction of CO_2 emissions.

Introduction

A considerable amount of research goes into the formulation of a laundry detergent. In addition to the obvious concerns about performance in the wash and safety to the consumer and the environment, we study – among other things - how different ingredients interact with one another under various conditions, how stable the new product is under extreme conditions of shipping and storage, and what modifications need to be made to the manufacturing process.

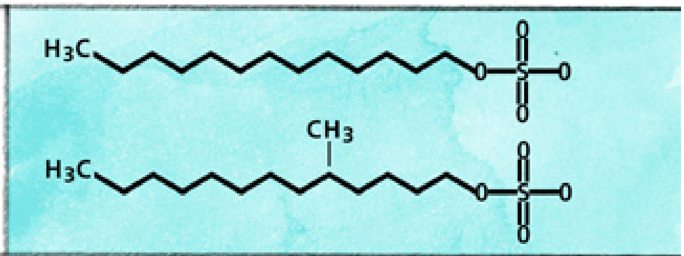
Detergents are formulations made up of several ingredients, including surfactants, enzymes and builders. Formulators ideally have access to a broad range of surfactants, which gives them more flexibility with which to achieve optimum detergent performance under a broad range of circumstances.

All surfactants currently available can be separated into two groups: those that have a "natural" origin and are derived from crops, animal fats or trees, and those that are derived from crude oil. Over the past decade, there has been a lot of debate about the pros and cons of these two types of sourcing. Oleo-based surfactants are often perceived as being better for the environment and should therefore be selected first. But is that really true? Are oleochemicals necessarily better for the environment because they are derived from plant and animal fats?

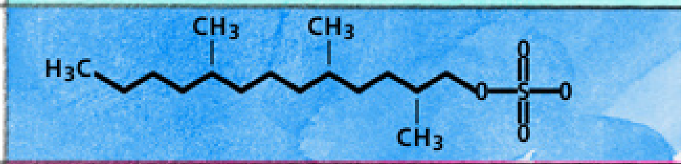
As with most scientific questions, there is no easy answer to this. In this article, we will provide facts and figures and try to provide answers to some of the most frequently asked questions about this controversial topic. We hope this information will help you make up your own mind; if you don't agree, please tell us.

Surfactant Structures
Alkyl chains can be

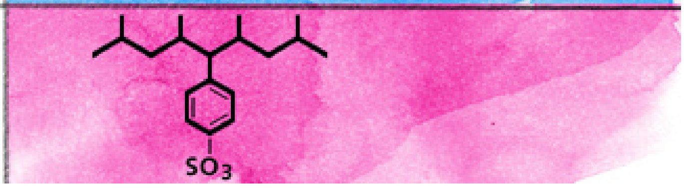
Linear or Essentially Linear
(Olechemical as well as petrochemical; Rapidly Biodegradable)



Multiple Substitution
(Petrochemical; Rapidly Biodegradable)



Highly Branched
(Not used in detergents; Non-Biodegradable)



What's the difference between a natural and a petro-based surfactant?

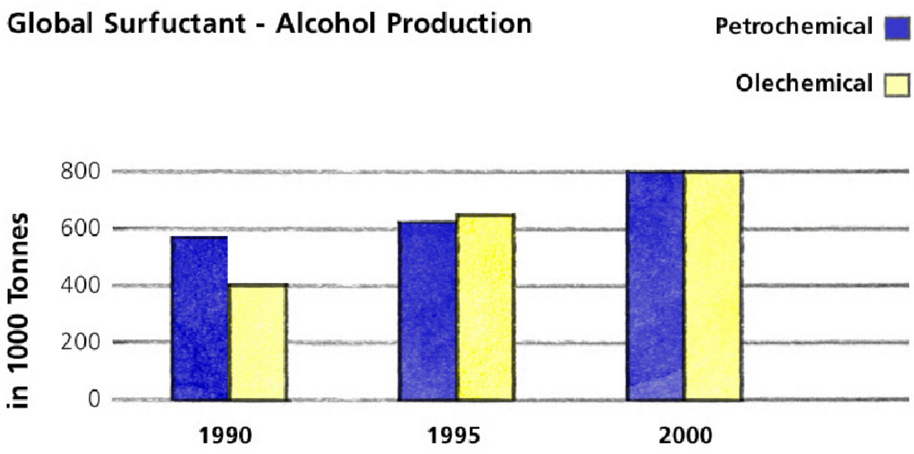
All surfactants have the same basic structure: a hydrophilic (water-loving) "head" and a hydrophobic (fat-loving) "tail," which is always a long chain of carbon atoms. The tail binds to and mobilizes soil particles, and the head works to pull the soil-surfactant couple to the water phase, to be removed with the wastewater of the washing machine.

Oleochemical surfactants, also referred to as "natural," are derived from plant oils such as palm, palm kernel or coconut oil, or from animal fats such as tallow, lard or fish oil. Fish oil is no longer used as an oleochemical feedstock, and animal fats have lost ground in recent years. In contrast, vegetable oils have been gaining ground.

Petrochemical surfactants are derived from crude oil and are also known as "synthetic" surfactants. The surfactant industry currently uses roughly equal amounts of "natural" oleochemicals and "synthetic" petrochemicals.

There are, however, some apparently minor differences between the two surfactants. The carbon chains of natural feedstocks are always linear and even-numbered, while synthetic feedstocks may have branched carbon chains and contain even or odd numbers of carbon atoms. These differences may seem subtle, but they can have a significant impact on cleaning performance, especially in mixed surfactant systems.

Presently, about 50% of the surfactants used in surfactant industry are derived from petrochemical raw materials, with the other 50% are derived from oleochemical raw materials. The most important surfactants used in consumer detergents are the so-called anionic and nonionic surfactants; the alcohols used are linear or essentially linear. This results in a rapid and complete biodegradation of both oleochemical and petrochemical derived detergent surfactants



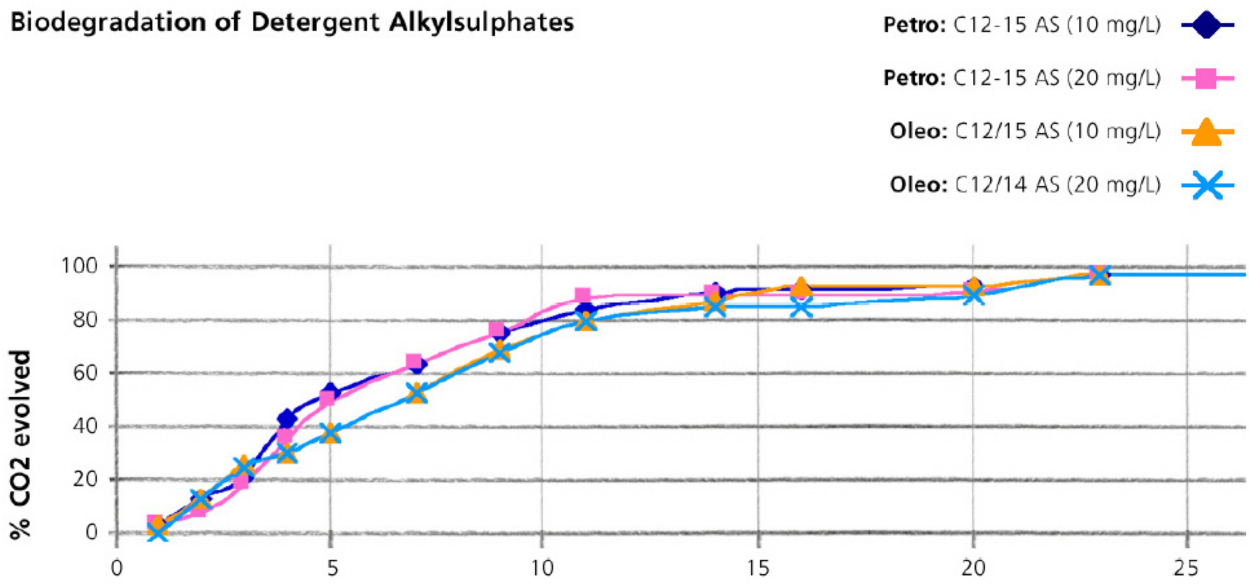
The use of the terms "natural" and "synthetic" to describe the origin of surfactants has led to some confusion. Technically, these are not accurate descriptions for these materials. Petrochemical and oleochemical surfactants both come from natural sources, since crude oil is extracted from the earth and originates from plants. On the other hand, both types of surfactants are "synthetic" in that both oleochemical and petrochemical feedstocks require further chemical processing before they become the surfactants we use.

Aren't oleochemical surfactants more biodegradable?

The answer is clearly no. The biodegradability of a material is related to its chemical structure and its solubility, not its origin. Surfactants that share the same structure will biodegrade equally well, regardless of whether they were derived from oleochemical or petrochemical alcohol feedstocks.

To illustrate this point, four surfactants (two oleochemical and two petrochemical) with similar chemical structure (same chain lengh; all essentially linear alcohol sources) were tested side by side in the laboratory using the same method and the same bacterial source. The results clearly show that their biodegradation curves largely overlap. Each of the four surfactants biodegraded quickly and completely (see graph below).

Tests such as these are routinely used to ensure that all the surfactants in P&G products biodegrade rapidly and completely. Rapid biodegradation leads to rapid elimination from the environment.



Graph: Results of biodegradation test, expressed as CO_2 production over time. Test method is OECD Guideline 301.

In addition to biodegradation testing, studies are done to ensure that detergent surfactants will be effectively removed by sewage treatment. One such study compared the removal efficiency of the four most used types of surfactants in seven sewage treatment plants. No significant differences in removal were observed. Either type of surfactant was effectively removed, which means that very little surfactant reaches the rivers.

Surfactant	Influent (mg/L)	Effluent (mg/L)	Removal (%)
LAS[1)]	5.2	0.039	99.2
AES[2)]	3.2	0.007	99.6
AE[3)]	3.0	0.006	99.8
AS[4)]	0.6	0.006	99.2
Soap[5)]	28.0	0.174	99.0
BOD[6)]	221.0	3.200	98.1

[1)] Linear Alkylbenzene Sulphonates[2)] Alcohol Ethoxy Sulphates
[3)] Alcohol Ethoxylates
[4)] Alcohol Sulfates
[5)] Soaps, or salts of fatty acids
[6)] BOD or Biological Oxigen Demand, the sum of all organic substances in wastewater
Ref.: Matthijs et al. (1999). Env. Toxicol. Chem. 18: 2634-2644.

What about toxicity? Aren't petrochemical surfactants more toxic?

Again, the answer is no. The toxicity of a surfactant is related to its chemical structure, not its origin. We extensively study the toxicity of our surfactants to aquatic organisms, and numerous other researchers have done so before us. Many good summaries exist.

In general, the longer the fatty chain, the more toxic the surfactant is to aquatic organisms. Conversely, the shorter the fatty chain, the lower the toxicity. This phenomenon is well known in scientific literature and is linked to hydrophobicity, or the degree to which a surfactant dislikes water and dissolves in fats. More hydrophobicity correlates with higher toxicity, but this relationship only holds true as long as the surfactants are water-soluble. When the alkyl chain becomes so long that the surfactant is barely water-soluble, the surfactant will appear to be less toxic. This is because it can no longer be taken up by living organisms, in other words it is "biologically inert".

Assessing environmental impact using Life Cycle Analysis

If we want to truly compare two options, we should take into account all of the environmental effects associated with each one. The desire to make better, fully informed decisions about such choices has resulted in the emergence of a scientific discipline called "environmental life cycle assessment". A thorough discussion of the life cycle of oleochemical vs. petrochemical surfactants is beyond our current scope, but one only has to think about some of the factors that are taken into account during a life cycle assessment to gain an appreciation for the environmental trade-offs associated with different technologies:

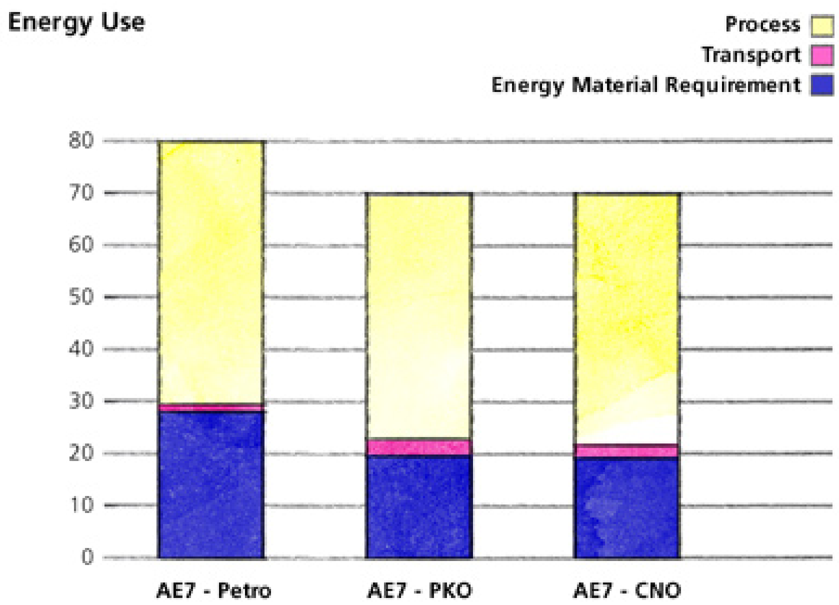
- Issues associated with land use, i.e., the effects of deforestation to make room for plantations to produce oleochemical feedstocks.
- Pollution (solid waste, wastewater, air pollution) associated with transport and processing of different raw materials [1].
- Total use of chemicals per wash load (i.e., a better performing surfactant blend may result in a lower total chemical usage).

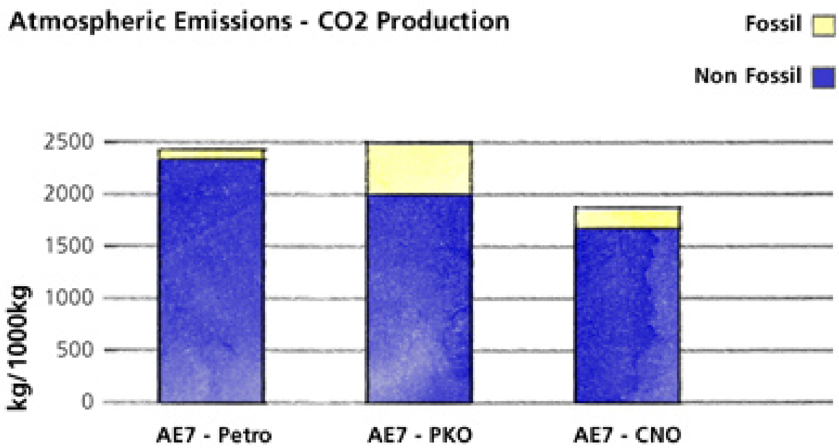
The sourcing and production of oleochemical and petrochemical surfactants alike requires natural resources (energy, raw materials) and generates polluting wastes. The scientific discipline that aims to quantify and evaluate the environmental impacts of materials and processes is called Life Cycle Assessment (LCA). The information that is collected — the most time-consuming part of the exercise - and that forms the basis for the LCA is called the Life-Cycle Inventory (LCI).

P&G participated in a Life Cycle Inventory study group composed of more than 13 surfactant producers and detergent formulators. The group's goal was to quantitatively assess resource requirements and environmental releases associated with the production of surfactants sourced from oleochemical versus petrochemical feedstocks.

The results, shown here for an oleochemically and a petrochemically derived alcohol ethoxylate (AE7), make it clear that neither surfactant can be supported as environmentally superior. Rather, there are trade-offs: lower environmental resource requirements are offset by higher emissions.

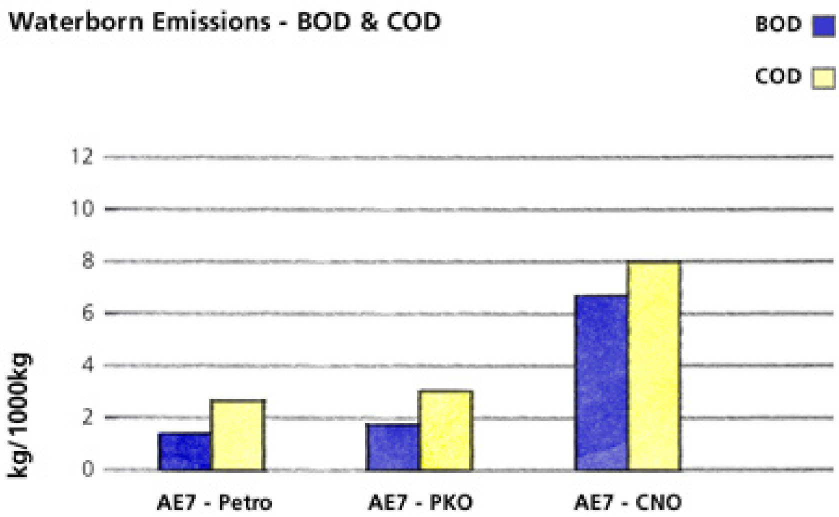
[1] A raw material is the starting point in the production of another material. Fatty alcohols are raw materials for surfactant producers.

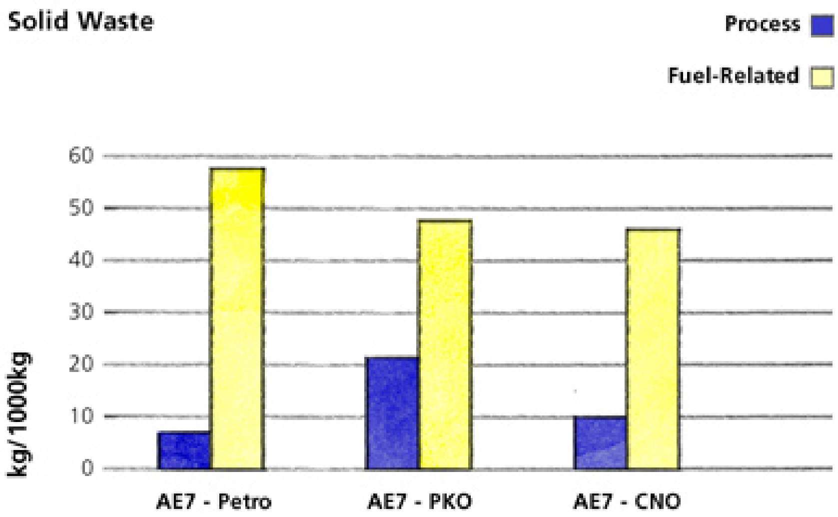




Key

AE7 – Alcohol Ethoxylates (7 Ethoxy units)
Petro - Petrochemical
PKO - Palm Kernel Oil
PO - Palm Oil
CNO - Coconut Oil





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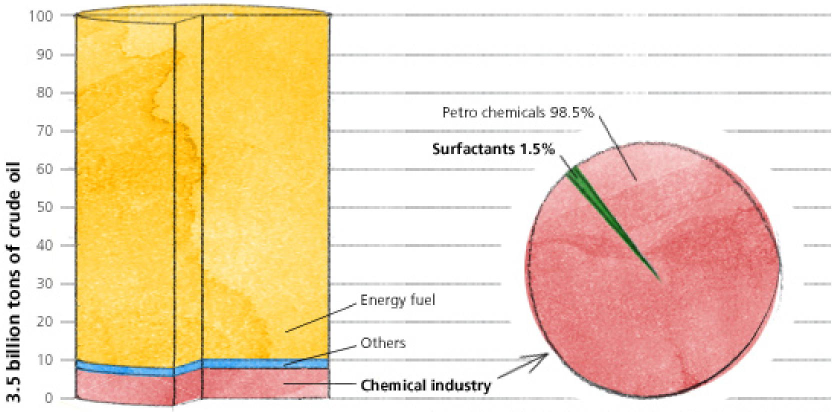
Is washing with oleochemical surfactants more energy efficient?

Because of the limited range of oleochemical alkyl structures (i.e., only even-numbered chain lengths, no branching), formulating detergents with oleochemicals alone often requires using other chemicals (additives) and/or washing with warmer water. Because our formulation flexibility is greater when we can also use petrochemical detergents, we can develop detergents that will perform well at lower water temperatures and/or reduce the total amount of chemicals needed per wash load. Since 60-80% of the energy needed for the laundry is for heating the water, the use of cooler water significantly reduces the energy requirement associated with the detergent's life cycle. The bottom line is that no major environmental improvements would be expected from a conversion from petrochemical to oleochemical surfactants, whereas the reduction in formulation flexibility may actually lead to increased energy requirements and increased pollution.

Consumption of crude oil and its use for surfactants in 2000



The global share of surfactant raw materials is in maximum 0.1% of crude oil consumption

Detergent Surfactants: Global Warming considerations

Globally, approximately 90% of crude oil is used in the energy and transporation sector. About 8% is used by the chemical industry. A fraction of this, or about 0.1% of the worldwide crude oil consumption, is used for the production of surfactants.

We studied the potential impact of a total replacement of petrochemical surfactants with oleochemical surfactants on global warming gas (CO_2) emissions. The analysis shows that such a replacement would result in a reduction in CO_2 emissions of no more than 0.1%. This is because the production and processing of oleochemical materials also consumes fossil fuel hence generates CO_2.

Why is formulation flexibility important?

Each surfactant has unique properties that make it valuable for a given application. Oleochemical and petrochemical surfactants have complementary properties. Optimal washing performance is usually obtained using a carefully balanced blend of surfactants.

Let's look at an example: oleochemically-derived alkyl sulphates with an even fatty acid chain of 12 or 14 carbons ($C_{12/14}$ alkyl sulphates) produce high suds, while alkyl sulphates with 16 or 18 carbons (C_{16-18} alkyl sulphates) are less soluble in cold water. By blending a petrochemically-derived C_{12-15} alkyl sulphate or C_{11-13} LAS with oleochemically-derived C_{16-18} alkyl sulphate, our formulators can create a surfactant system that will be soluble in cool water and not produce too many suds.

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