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THE STATISTICAL WORLD OF RAW MATERIALS, FATTY ALCOHOLS AND SURFACTANTS

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Surfactants make the world go round. The aim of this presentation is to illustrate that this is not just a catchy advertising slogan for this Congress, but that surfactants are also of real substantial importance in the world.

Both quantities and magnitude, from the raw material resources crude oil, natural gas, coal and biomass via the raw material bases of surfactant fatty alcohols - ethylene, olefin, paraffin and the oils and fats - right up to the surfactants themselves, divided into the individual product groups anionics, nonionics, cationics and amphoterics, are described.

1. Resources

The resources are immense. 3,500 mill. mt of oil were produced worldwide last year. The quantity of gas produced, converted into the equivalent quantity of oil, amounted to 2,300 mill. mt. A total of 2,400 mill. mt of coal, which is now also used as a raw material for the manufacture of fatty alcohols, were produced in 2003. Facing these production quantities of the three fossil raw materials is the huge amount of 180,000 mill. mt of biomass.

According to this statistic, with consumption stagnating reserves of oil are sufficient for the next 40 years, should no new sources be discovered. Gas will still be available for another 61 years, assuming consumption remains the same, and there is enough coal to last for more than 400 years.

Resources in mill. mt, 2003	
Production	
Oil	3,500
Gas (oil equivalent)	2,300
Coal	2,400
Biomass	180,000
Reserves	
Oil	143,000
Gas (oil equivalent)	140,000
Coal	984,500

Figure 1: Resources of raw materials

Consumption figures are not stated as they correspond roughly with production in a worldwide consideration.

Generally it can be said that the consumption of primary energy in Europe and Japan is stagnating quickly, likewise in South and Central America consumption is stagnating. Africa and the Middle East could record slight growth. Rates of increase of above 10 % are to be observed in Asia Pacific – excluding Japan, South Korea and Australia. The highest jump with an increase in primary energy consumption of almost 20 % can be established in China.

2. Raw Materials

The products made from these resources are manifold. We want to concentrate on those raw materials, which are suitable for the manufacture of fatty alcohols and are also used in part for this purpose. Altogether, 89 mill. mt of ethylene and olefin, 3 mill. mt of n-paraffin and 120 mill. mt of oils and fats are available.

Both source types are suitable for the manufacture of fatty alcohols. Altogether, 5 % of the fossil raw materials and 3 % of renewable raw materials were used to manufacture this base material of several surfactant types last year.

Raw Materials, 2003

Production	
Ethylene / Olefin	89 mill. mt
n-Paraffin	3 mill. mt
Natural Oils and Fats	120 mill. mt
Usage for fatty alcohols	
Ethylene / Olefin	1 %
n-Paraffin	4 %
Natural Oils and Fats	3 %

Figure 2: Raw material production and usage for fatty alcohol

The following chart shows, as an example, the **annual** average price of coconut oil, tallow, ethylene, crude oil and diesel in Euros per 100 kg cif Rotterdam.

Here are some noteworthy comments on the past:

In 1973/74 and the early 1980s there are two price peaks in the otherwise moderate price trend:

- The 73/74 peak was caused by the oil crisis (car-free Sundays), and
- the 1980s peak was caused by a second oil crisis and the New York stock exchange crash, with the resulting drop in value of the dollar.

These events could almost be considered as freak occurrences, but unfortunately they reflect tough reality, indicating how difficult and price-sensitive the oils and fats market used to be:

- The highest noted **day** price for coconut oil is 242.99 € per 100 kg, and
- the lowest price is 19.81 €.

Overall, the annual rate of price increase between 1962 and 2003 was 0.3 % p.a. Compared with the development of other raw material prices, coconut oil is characterized by a very stable, accurately calculable production basis, viewed in the long term.

The moderate price development of oils and fats is attributable to the fact that this world market is relatively crisis-free now, and that the raw materials are available in ever greater amounts.

Nor are steep price rises to be expected in the future. This will further increase the market opportunities for fatty alcohol based products.

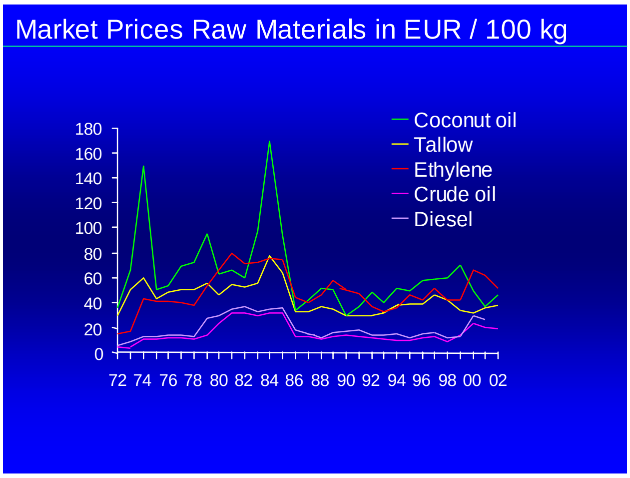

Figure 3: Market prices of raw materials

If we now concentrate on oils and fats, we can establish that the available quantity has more than quadrupled in the last 45 years. The 32 mill. mt in the year 1960 have meanwhile increased to well over 120 mill. mt.

The clearest changes as a percentage are with palm oil, heavily influenced by activities in Malaysia particularly and with rapeseed oil through the notably increased cultivation in Europe.

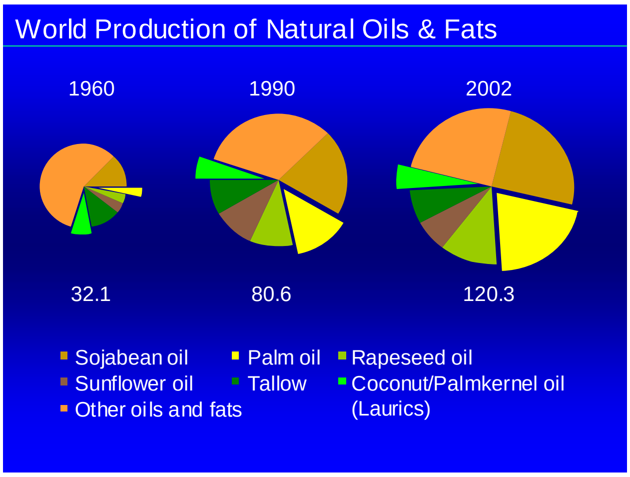

Figure 4: World production of oils and fats

- **Soybean oil** is the oil that is extracted in the greatest quantities. Most of it is used for food.
- **Palm oil** is used in both the oleochemical industry and the food industry.
- **Rapeseed oil** is available on the world market in two varieties: **low erucic acid** and **high erucic acid**. Low erucic acid rapeseed oil is used in the food industry and for the production of biodiesel. The high erucic acid variety is used for technical purposes.
- **Sunflower oil** is also available in two varieties: a **high linoleic acid** type (conventional sunflower oil) and a **high oleic acid** type (HOSO – high oleic sunflower oil).
- **Tallow**, which is unsuitable for human consumption, is an interesting raw material source. However, diseases in animals raised for slaughter, such as BSE and foot and mouth disease, brought animal-based raw materials into discredit, so that it is not longer used in the cosmetic field. Nevertheless, the high temperatures used during production, and the production methods in general, continue to satisfy the legal requirements for the certification of these products as safe for use.

- **Laurics** are the two medium-chain oils (oils with a high proportion of C12-C14 chains), i.e. coconut oil and palm kernel oil.
- **Others** include olive oil, sesame oil, fish oil, train oil, etc., which are of minor importance for Cognis.

The laurics are of major importance for the Industry, since many of the fatty alcohols obtained from these oils are basic materials for the production of surfactants. Fatty alcohol sulfates and ether sulfates and fatty alcohol ethoxylates are the main bulk surfactants obtained from the laurics.

Asia is the most important area of cultivation of oil plants that yield the most suitable oils and fats for the oleochemical sector. Malaysia, Indonesia and the Philippines are the main source countries of palm kernel oil and coconut oil, the two laurics.

As we said, 120.3 mill. mt of oils and fats were produced worldwide in 2002. Of these, 97.7 mill. mt were vegetable oils and 22.6 mill. mt were animal fats. What are they used for?

- 81 % (97.4 mill. mt) are used for food.
- 19 % (22.9 mill. mt) are used by industry, namely
- the animal feed industry (6.1 mill. mt) and
- the chemical industry (16.8 mill. mt).

The worldwide chemical industry therefore uses only 14% of the total production of oils and fats. More than 10 mill. mt are processed into soap. Around 4.5 mill. mt are used annually in oleochemical processes.

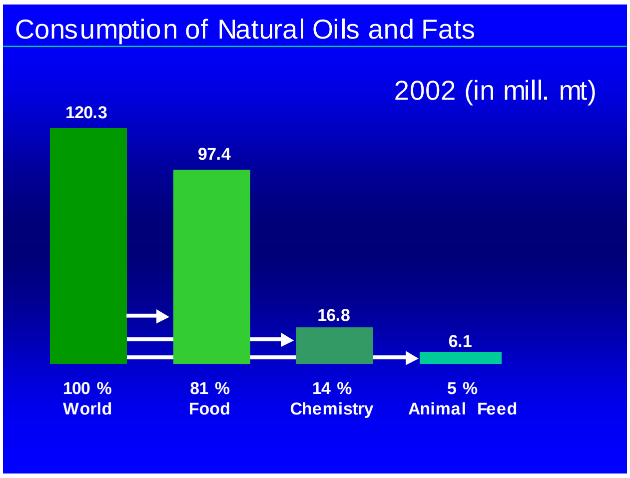

Figure 5: Consumption of oils and fats

The picture is totally different for crude oil. 90 % are used for energy and only 8 % for chemical processing. In actual figures, however, only 8 % amounts to 280 mill. mt, twice the quantity of all oils and fats produced.

The difference between producing countries and consumption regions is even greater for crude oil than for oils and fats. The small producing states in the Middle East export their black gold for the most part to the main consumers North America, Europe and increasingly Asia.

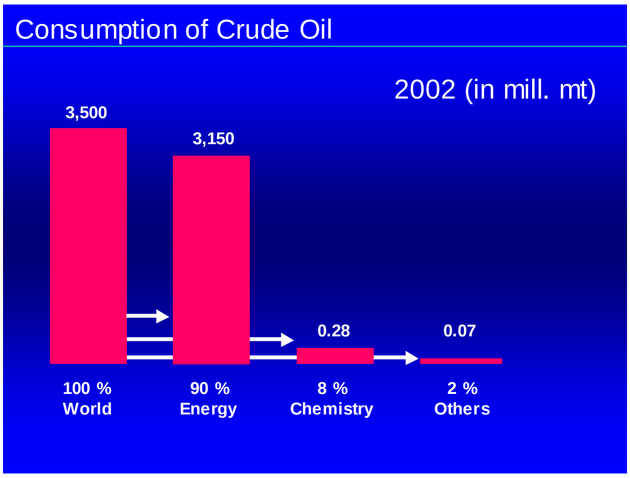

Figure 6: Consumption of Crude Oil

The ratio for coal is even more dramatic. Most of it is used to provide energy. Only a very small percentage of 0,01% is processed in the chemical industry. However this is not such a small amount when expressed as 460,000 mt instead of as a percent.

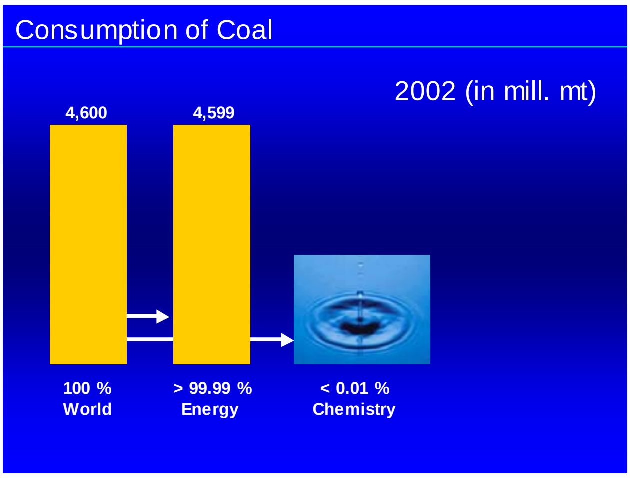

Figure 7: Consumption of Coal

As already mentioned at the beginning, altogether we are talking about almost 5 mill. mt of resources that are used for the manufacture of fatty alcohols and thus as raw material for the manufacture of fatty alcohol-based surfactants.

3. Fatty Alcohols

The production of fatty alcohols has quite a long history. Between 1925 and 1930 several study groups independently developed the catalytic high pressure hydrogenation to yield fatty alcohols from natural feed stocks such as edible oils. The first commercial plant was built in 1931 with a capacity of 2,000 t/a.

Another milestone was the development of the oxo-reaction (hydroformylation) for the manufacture of aldehydes from olefins, carbon monoxide and hydrogen by Otto Roelen in 1938. Ruhrchemie, BASF and Henkel built the first commercial plant for the manufacture of oxo-alcohols in 1944 in Oberhausen. The discontinuously operating plant had a capacity of 10,000 t/a and was designed to produce short-chain alcohols for plastic additives.

In 1954 Karl Ziegler made the invention that linear primary alcohols can be obtained by the oxidation of trialkyl aluminium to aluminium alcoholates followed by a hydrolysis. Commercial plants were built in 1963 by Continental Oil Company, in 1964 by Condea and in 1965 by Ethyl Corporation.

Since 2002 in South Africa a coal-based alcohol is produced by the hydroformylation of olefins obtained in the Fischer-Tropsch process with subsequent hydrogenation.

In this article fatty alcohols are defined as alcohols containing twelve or more carbon atoms per molecule and having a carbon backbone with a high degree of linearity.

Today the worldwide installed capacities for fatty alcohols are 2,150 kt/a, of which 1,130 kt/a are referring to alcohols based on natural feedstock. Approximately 75 % of all consumed fatty alcohols are used for the production of surfactants.

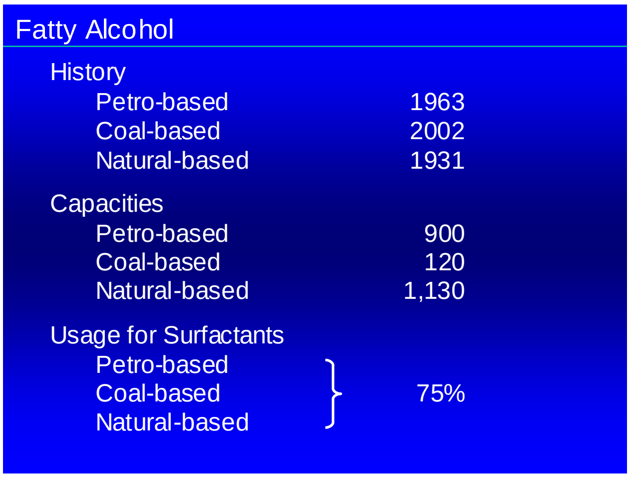

Figure 8: Fatty alcohols – history and worldwide capacities

Fatty alcohols derived from fats and oils are normally produced by the hydrogenation of the corresponding fatty acid methylesters (FACME). Most of the methanol is recovered in this process and is recycled for use in the ester exchange step. Another route of manufacturing is the hydrolyzation of fats and oils to the corresponding fatty acids followed by a subsequent catalytical reduction to the alcohols. In both processes coconut and palm kernel oils as well as tallow fat are the major feed materials.

A number of synthetic routes have been developed for producing detergent-range alcohols from petroleum-derived raw materials. Ethylene, olefins, or n-paraffins are the basic chemical starting materials and the Ziegler chemistry and oxo process are the most important routes.

In the Ziegler process ethylene is added to triethyl aluminium to build a mixture of high-molecular-weight trialkyl aluminiums known as the ethylene growth product. After the oxidation with air the corresponding aluminium alkoxides are formed. The subsequent hydrolysis of these alkoxides leads to a mixture of linear primary alcohols having the same number of carbon atoms as the alkyl groups in the trialkyl aluminium growth product. Ziegler alcohols have even-numbered carbon chain lengths just like natural oil-based alcohols. In fact, alcohols made by the Ziegler process can be used as across-the-board replacements for their natural oil-based counterparts.

The oxo reaction as applied to the synthesis of detergent-range alcohols is currently employed commercially in a variety of modifications. Although each of these processes represents unique technology, they all involve the reaction of olefins with synthesis gas (CO/H_2) in the presence of an oxo catalyst to yield higher alcohols. The major differences among the processes are the type and source of the olefin, catalyst and process conditions. Most of the oxo plants in the world use processes in which first the intermediate aldehydes are isolated, purified and then hydrogenated in a second reactor.

The Shell SHOP process is a major modification of the oxo process. The use of a modified cobalt type catalyst allows that the hydroformylation and hydrogenation of the intermediate aldehyde occur in the same reactor.

Oxo-alcohols, which contain 20-40% branching of the alkyl chain, consist of both even- and odd-numbered carbon chain lengths. These alcohols also compete directly in some markets with natural oil-based alcohols. The interchangeability of surfactants made from ethylene-based alcohols with those from natural oil-based alcohols is particularly true in the household detergent market.

The 3 Types of Fatty Alcohols

Name	Raw Material	Intermediate	Process
Natural			
Cognis	Oils & Fats	FACME	Hydrogenation
Lurgi	Oils & Fats	Fatty Acid	Hydrogenation
Synthetic			
Ziegler	Petrol	Ethylene	Oligomerisation
Oxo	Petrol	Ethylene	Oxo (SHOP)
Oxo	Petrol	Olefin	Hydrogenation
Sasol	Coal	Olefin	Hydroformylation

Figure 9: Three types of fatty alcohols

The world surfactants alcohol production has increased over the last ten years significantly. Especially the production and capacities for oleochemicals in Asia have undergone an annual increase of approx. 5%. This naturally takes cultivable land away from other uses on a planet that is currently sufficient for food needs, but is plagued by growing worries regarding deforestation, devastation, climatic changes and other similar concerns. Today, about 50% of the alcohol consumed worldwide for the production of surfactants is from natural origin.

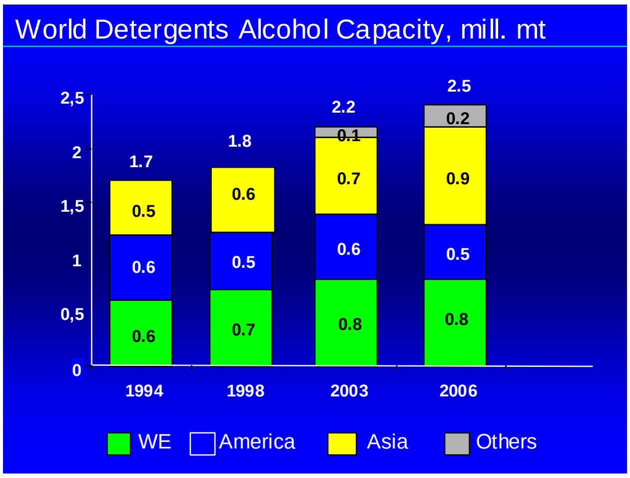

Figure 10: World detergents alcohol capacity

Approximately 75% of the detergent alcohols (natural and synthetic) are used as raw materials for the production of surfactants, which are mainly used in household detergents. The use in cosmetics represents another major outlet.

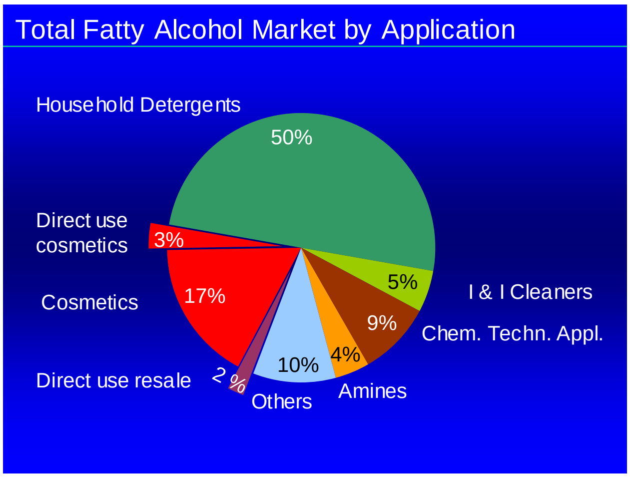

Figure 11: Fatty alcohol market by uses

Concerning environmental issues, the alcohols are generally considered to be products of low acute toxicity. They are well tolerated by human skin and have been used in personal care and pharmaceutical formulations for many years. Both the free alcohols and their common surfactant derivatives biodegrade rapidly and fully under both aerobic and anaerobic conditions.

The rapid growth in the use of fatty alcohols during the 1990s can partly be explained by the low toxicological profile and the safe use of these products, but it has also resulted from a number of other developments. The continued substitution of soap by alcohol based surfactants in the personal care industry, the strong sales of laundry liquids that use higher levels of alcohol-based surfactants than the corresponding powders, the displacement of linear alkylbenzene sulfonate (LAS) surfactants from detergent powders by alcohol-based anionic surfactants because of their better crystalline properties and compatibility with other detergent ingredients, and the substitution of alkylphenol ethoxylates by alcohol-based surfactants are some important factors explaining the strong growth of alcohols.

4. Surfactants

As many of the surfactants are sold in aqueous solutions typical markets are more regional rather than global. Therefore the world surfactants capacities are well balanced throughout the world and are mainly reflecting multi-purpose sulphonation and ethoxylation capacities. Because of the more sophisticated technology for the production of nonionic surfactants and their designed use for machine application in less developed countries anionic surfactants are predominating the market.

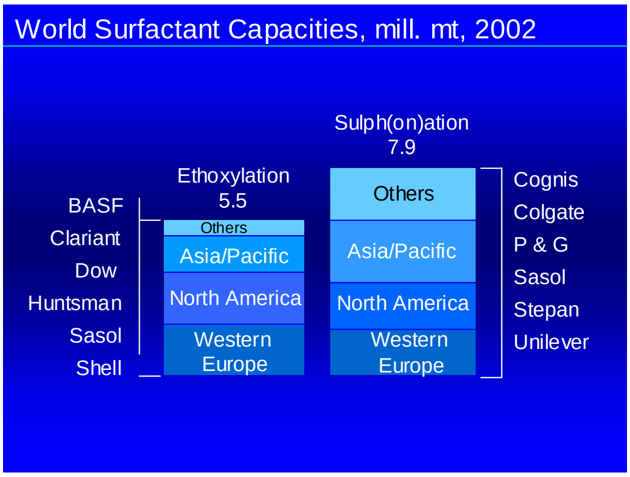

Figure 12: World surfactants capacities in 2002

The world surfactant market for 2003 can be estimated to be approx. 18.2 mill. mt of which soap represents the greatest share of 9 mill. mt. The second biggest single surfactant is LAS with 2.9 mill. mt followed by a variety of other surfactants. Together all fatty alcohol based surfactants are reflecting 2.5 mill mt.

World Surfactant Consumption in 2003

		mill.mt
Soap		9.0
Anionics		4.5
LABS	2.9	
BABS	0.2	
FAS	0.6	
FES	0.8	
Nonionics		1.7
AE	1.1	
NPE	0.6	
Quats		0.5
Amphoterics		0.1
Others*		2.4

*(incl. lignin-, petroleum sulfonates, talloil deriv.)

Figure 13: World surfactants consumption in 2003

In Western Europe and North America the principal surfactant demand is supplied by four surfactant groups - linear alkylbenzene sulfonate (LAS), fatty alcohol ethoxylates (AE), fatty alcohol ether sulfates (FES) and fatty alcohol sulfates (FAS). A different distribution is valid for Asia, where LAS is, mainly for price reasons, the dominating surfactant. In Asia most of the products on the market are designed for hand use and not for machine use. In general products for machine use require much more complicated formulations with special requirements to the surfactant and builder system. Foaming, dosing, thermal and water hardness stability are only some important parameters which must be controlled in products designed for machine use. The comparison of the data for the different regions reveals that the portion of alcohol derivatives increases as does the maturity and sophistication of the regional markets at the expense of LAS. Both Western Europe and the US rely on alcohol derivatives for 60-70 % of the major surfactants whereas in Asia and the rest of the world it is 15-30 %. This observation suggests that a move away from LAS to alcohol based derivatives will likely occur in Asia and in Latin America as these markets increase in maturity, technology, standard of living and sophistication.

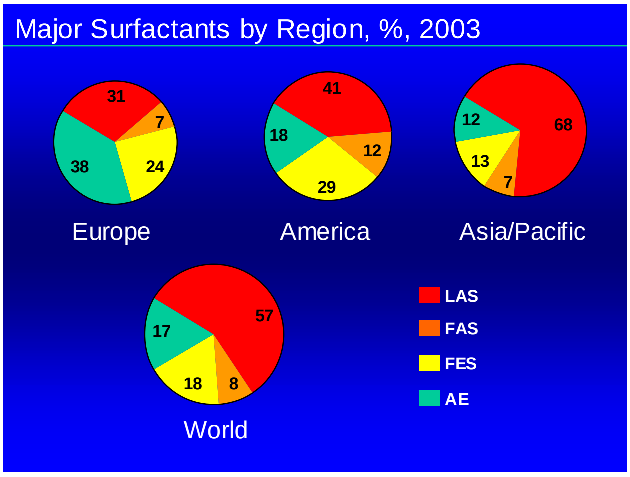

Figure 14: Major surfactants by region

Today, LAS is still the most universal and cost effective surfactant available and will continue to be the workhorse of the household detergents industry on a global basis.

Fatty alcohol based surfactants, irrespective of whether the alcohol comes from renewable or petrochemical sources, will continue to grow because of the versatile properties of the surfactants made thereof. It is a great challenge to find molecules, which meet increasing environmental as well as performance and cost / benefit requirements. Also in the future new surfactants will be based on renewable and / or petrochemical sources depending on the availability, the costs, the performance, and chemical structure of the raw materials.