Calcium stearate - its production, its sustainability and generation of data for a LCA - One vision [1]

Michael Schiller (HMS Concept e.U.), Hitesh K. Singh (Platinum Industries Ltd.)

Abstract:
Calcium stearate consists of natural fatty acids and calcium. It is used by the rubber and plastic industries as an effective elastomer processing aid, release agent, acid scavenger and lubricant. Calcium stearate is also used as a flow agent in powders including some foods (such as Smarties), a surface conditioner in hard candies such as Sprees, a waterproofing agent for fabrics, a lubricant in pencils and crayons. The concrete industry is using calcium stearate for efflorescence control of cementitious products used in the production of concrete masonry units i.e. paver and block, as well as waterproofing. In paper production, calcium stearate is used as a lubricant to provide good gloss, preventing dusting and fold cracking in paper and paperboard making. In polyolefins, it can act as an acid scavenger or neutralizer at concentrations up to 1000 ppm. It may be used in plastic colorant concentrates to improve pigment wetting. Applications in the personal care and pharmaceutical industry include tablet mold release, anti-tack agent, and gelling agent. Calcium stearate is a component in some types of defoamers. The production of it is well know. Calcium stearate is made of a natural fatty acids and a calcium component. However, there is not any life cycle assessment (LCA) of calcium stearate available even if it is considered as an important additive in several industries on one hand and as a substance with high sustainability potential on the other hand. The recent paper is an attempt to create data on which a LCA which might be created close to reality by considering its raw materials, production, packaging and transportation under the view point of sustainability.

Keywords: metal soap, metal stearate, calcium soap, calcium stearate, sustainability, LCA, life cycle assessment

1. Background

Fatty acids, C16-18, calcium salts (CAS: 85251-71-4; Synonyms: calcium distearate, calcium stearate) belongs to a group of substances called Calcium soaps, which are widely used.
Calcium stearate is used by the rubber and plastic industries as an effective elastomer processing aid, release agent, acid scavenger and lubricant. Calcium stearate allows for complete product dispersion in elastomers. Calcium stearate accelerates the gelation of rigid PVC compounds when used it is used during the processing of profiles, pipes, sidings and injection molded fittings. Calcium stearate is also used as a flow agent in powders including some foods (such as Smarties), a surface conditioner in hard candies such as Sprees, a waterproofing agent for fabrics, a lubricant in pencils and crayons. The concrete industry is using calcium stearate for efflorescence control of cementitious products used in the production of concrete masonry units i.e. paver and block, as well as waterproofing. In paper production, calcium stearate is used as a lubricant to provide good gloss, preventing dusting and fold cracking in paper and paperboard making. In polyolefins, it can act as an acid scavenger or neutralizer at concentrations up to 1000 ppm. It may be used in plastic colorant concentrates to improve pigment wetting. Applications in the personal care and pharmaceutical industry include tablet mold release, anti-tack agent, and gelling agent. Calcium stearate is a component in some types of defoamers.
Calcium stearate consists of natural fatty acids and calcium. Fatty acids are natural constituents of the human body and essential components of a balanced human nutrition.

Fatty acids are generally judged as not representing a risk to human health. Calcium as essential trace element is also vital. Adverse health effects of calcium stearate are unlikely as both components are vital and effectively processed and regulated in the human body by natural physiological mechanism. The non-toxicity of calcium stearate is proved by extensive testing data which showed no adverse health effects.
The database for environmental effects, ecotoxicology and toxicology of Calcium distearate is extensive, allowing a robust evaluation of its hazard properties. Because of the lack of hazards the substance can be handled safely. However, it is interesting enough that no life cycle assessment (LCA) of this substance is available today. This paper is an attempt to find the reason why and to create a LCA which might be close to reality.

2. Consideration of processes and raw materials

Calcium salts can be produced in different ways [2]. One way is the neutralization of the acid (HAc) by a Calcium (hydr)oxide (CaO resp. $Ca(OH)_2$); Equation 1 and 2.

$$CaO + 2\,HAc \Longrightarrow CaAc_2 + H_2O \qquad (1)$$

$$Ca(OH)_2 + 2\,HAc \Longrightarrow CaAc_2 + 2\,H_2O \qquad (2)$$

Based on this reaction mechanism three production ways are possible :
- Reaction 1: a direct and dry conversion of acid and calcium compound without solvent (e. g. water) in a high speed mixer. (According to the knowledge of the authors calcium hydroxide is mainly used for the production of calcium stearate.)
- Reaction 2: a melt process at temperatures depending on the melt temperature of the metal soap and the acid which is applicable when calcium stearate is produced in combination with other metal soaps like zinc, magnesium or lead stearate or laurate.
- Reaction 3: a precipitation reaction in two steps; Equation 3 and Eq. 4. In a 1st step an alkaline (mainly Sodium) salt is formed. In a 2nd step a solution of the soluble metal salt (e.g. Calcium chloride) is added. In the case of reaction 4 an alkaline salt is formed as by-product (e.g. Sodium chloride), which is dissolved in water.

$$NaOH + HAc \Longrightarrow NaAc + H2O \qquad (3)$$

$$CaCl_2 + 2\,NaAc \Longrightarrow CaAc_2 + 2\,NaCl \qquad (4)$$

Already the variation of the calcium source and processes is complicating the preparation of an LCA of calcium stearate. However, it will not become easier while considering the source of the fatty acid. The chemically pure Stearic acid is a saturated fatty acid with C18-carbon chain. The IUPAC name is octadecanoic acid. It is a waxy solid, and its chemical formula is $CH_3(CH_2)_{16}CO_2H$. Its name is derived from the Greek word στέαρ "stéar", which means tallow. Stearic acid is one of the most common saturated fatty acids found in nature following palmitic acid. The so-called and commercially available Stearic acid occurs in many animal and vegetable fats and oils. It is more abundant in animal fat (<30%) than vegetable fat (<5%). Commercially available stearic acid is prepared by treating these fats and oils with hydrogen for conversion of unsaturated fatty acids to saturated at a high pressure and temperature and the hydrolysis of saturated triglycerides. The resulting mixture of fatty acids with different chain length (Table 1) is then distilled. By-products are mainly glycerine, sulphuric acid contaminated pre-purification waste and some shorter chain fatty acids. Already Table 1 is showing that based on the source (either tallow or palm oil) a wide variation of chain length of the fatty acid is available which makes the preparation of an LCA for Calcium stearate very difficult. Nevertheless, the author will try to create an LCA for Calcium stearate based on:

- Calcium hydroxide which is assumed to be the standard raw material
- One based tallow (assumed molecular weight 274 g/mol)
- Another one based on palm oil assumed molecular weight 269 g/mol)
- Based on Reaction 1 which is assumed to be the easiest, cheapest and probably the most used for the production of Calcium stearate in PVC industry.

Table 1 Composition of the fatty acids in tallow and palm oil and the resulting saturated fatty acids after hydrogenation in percent

3. Input and output flows for 1000 kg (1 mt) of calcium stearate based on tallow

3.1. Input flows

According to Eq. 2

- 126.27 kg calcium hydroxide and
- 935.15 kg tallow based stearic acid are necessary.

61.43 kg water are formed as a by-product. However, in some cases are "catalysts" are used like <1% of formic acid, acetic acid, hydrochloric acid or water. This might be neglected in this consideration.

acid	Carbons	Tallow minimum	Tallow maximum	Tallow source	Palm oil Mean average	Palm oil source
Octanoic	8-0	0.0	0.5	[3]		
Decanoic	10-0	0.0	0.5	[3]		
Lauric	12-0	0.0	1.5	[3]	0.2	[4]
Myristic	14-0	2.5	3.5	[3]	1.0	[4]
Palmitic	16-0	22.0	27.0	[3]	43.4	[4]
Stearic	18-0	18.0	23.0	[3]	4.6	[4]
Oleic	18-1	37.0	43.0	[3]	40.5	[4]
Linoleic	18-2	3.0	5.0	[3]	10.7	[4]

Linolenic	18-3	0.5	1.0	[3]	0.4	[4]
Arachidic	20-0				0.3	[4]
Octanoic	8-0	0.0	0.5			
Decanoic	10-0	0.0	0.5			
Lauric	12-0	0.0	1.5		0.2	
Myristic	14-0	2.5	3.5		1.0	
Palmitic	**16-0**	**22.0**	**27.0**		**43.4**	
Stearic	**18-0**	**58.5**	**72.0**		**56.2**	
Arachidic	20-0				0.3	

Calcium hydroxide is a very cheap product. Long transportation ways will increase the costs. That's why we can assume that the average transportation is 500 km maximum by heavy trucks probably 40 mt per shipment.
Regarding tallow-based stearic acid the transportation is more difficult to judge. Some calcium stearate producers are also producing stearic acid like e.g. Peter Greven GmbH & Co. KG [5]. In such cases the transportation is <1 km. Other producers of calcium stearate are purchasing stearic acid from different source. In these cases we can assume a maximum seaway distance of 15'000 km [6] plus 1'000 km by heavy trucks. The second category of producers is the minority. We assume that only 10% (or even less) of all Calcium stearate which is produced in Europe is produced by manufacturers who are not producing stearic acid themselves.
The final calcium stearate is either packed in 40 paper bags (25 kg each) or in 50 paper bags (20 kg each) or in 2 bigbags (PP; 500 kg each). For the paper bags is one wooden pallet per mt necessary. In the case of the bigbags are 2 wooden pallets are used per mt. We can assume that the ratio is 25% 25 kg paper bags, 25% 20 kg paper bags and 50% bigbags. Regarding the wooden pallets we can assume that the pallets of Calcium hydroxide and of stearic acid are re-used for this purpose and only 0.5 wooden pallet
Even if we focus in this paper on Reaction 1 it will require some compromises regarding energy input. The 1st obstacle is that calcium stearate can be slightly acidic or neutral or slightly over-basic. The reaction time will be increased in this order and according to the reaction time the consumed electrical energy will be increased. Furthermore, the reaction time is also depending on the quality and reactivity of the calcium hydroxide and the fatty acid (like particle size, degree of carbonatization of calcium hydroxide), presence or absence of catalyst, on reaction temperature, mixer speed, mixer volume, filling grade of mixer, mixer tools, insulation of reactor etc.; see e.g. According to Eq. 2 about 6% water is formed during the reaction. This requires a drying step for the reaction product before packaging. The drying process can be done in many different ways with different sources of energy. Last but not least a milling step depending on the particle size of the raw product and the final product might be necessary… However, there are many small things which will influence the energy input. There is no real and practical chance to elicit these data from single producers… Due to this misery the authors will create (Table 2) and calculate

3 different scenarios regarding the energy input and its final influence on the LCA of calcium stearate. We assume in scenario:

- 1 a comparably short reaction time and no addition of water or any catalyst which might represent the minimum energy input during production of calcium stearate
- 2 an example which was published in literature/patent and which might represent a process which is close to reality
- 3 a similar process without the addition of any catalyst or water but with longer reaction time compared to scenario 1.

Table 2a Used energy values taken from literature

	Value	Unit	Value	Unit	Source
melting energy of stearic acid	198.9	kJ/kg			[7]
spec. heat capacity of water	4.187	kJ/K·kg			[8]
spec. heat capacity of stearic acid	1.830	kJ/K·kg	501.5	J/kmol·k	[9]
spec. heat capacity of calcium hydroxide	1.000	kJ/K·kg	87.5	kJ/kmol·k	[10]
vaporization energy of water	2260.0	kJ/K·kg			[11]
Neutralisation energy acid-base reaction			-50 to -58	kJ/mol H_2O	[12]

In these scenarios we assume that the reaction is finished at 100°C. So we have to heat up the reaction mixture from 20°C to 100°C which is the boiling temperature of water added as a catalyst resp. formed during the reaction. The specific heat capacity of calcium stearate was not available. So, we used that of the raw materials, both stearic acid and calcium hydroxide. We also neglected the exothermic energy of the reaction which would reduce the total energy on one hand. On the other hand we also nearly neglected the energy loss of the reactor to environment which would increase the energy balance.

Table 2b Different theoretical scenarios of energy input for the production of 1 mt tallow-based Calcium stearate based of the data in Table 2a

Scenario =>	1	2	3
T(start) at °C	20	20	20
T(end) at °C	100	100	100
reaction time in hrs	6	8	10

kg water per mt product (as catalyst added)	no	140.27	no
Energy input per mt calcium stearate			
Electrical energy input in kJ/mt product during the entire production time	**550000**	**733333**	**916667**
Theoretical energy during reaction in kJ/mt product			
heating up from 20°C to 65°C	83741	83741	83741
melting (stearic) at 65°C	186011	186011	186011
heating to 100°C in kJ	74134	94690	74134
vaporization heat (water)/kJ	138832	455848	138832
maintaining temperature for entire reaction time	78937	124902	142087
subtotal/kJ/mt	**561654**	**945191**	**624804**
Total of electrical and other energy input/kJ/mt	**1111654**	**1678524**	**1541471**

We can conclude:

- while comparing scenario 1 and 3 that the reaction time has an significant influence on total energy input
- from scenario 2 amount of water which must be evaporated can also dramatically increase the energy input

3.2.Output flows

According to Eq. 2 61.43 kg water are formed as a by-product while producing 1 mt Calcium stearate. This might be either condensed and going the waste water system or directly to air. During the reaction of stearic acid and calcium hydroxide no direct emissions of SO_x and NO_x are occurring in theory. (Indirect emissions of power input are possible and probable.) We expect small amounts of direct emissions of carbon dioxide because calcium hydroxide is absorbing carbon dioxide from the atmosphere during its shelf life. The real amount is not know because it depend on several factors (packaging, time, temperature…) However, it is not important to know because the exactly same amount is released during the reaction between stearic acid and Calcium hydroxide.
Other emissions to the air might be a very small amount of the raw materials and the final calcium stearate. These emissions can be extremely low and next to nothing when state-of-art filter technology is installed. We can assume that it is maximum 96 g calcium stearate per mt product[1]. In reality it might be factor 10 or even 100 lower. There is in theory no

[1] We assume a plant with a production of 10000 mt/year. Furthermore we assume that the emissions are at the top limit of "TA Luft" Chapter 5.2.5 [13] with a mass flow of 0.2 kg/hr.

direct emission to soil because it is produced in nearly dust free closed systems. The flooring is covered by concrete. Any possible dust will be collected by either brushing or wetting with water and following brushing or by cleaning with water which is going to the waste water system. So, the wheels for forklift trucks and the shoes of workers can transfer are an extremely small amount of raw materials However, there is a theoretical possibility that calcium stearate is going to a waste water system. The solubility of calcium stearate is very limited (2.2 mg/L resp. 2.2 g/m^3 at 20°C [13]). Even if we assume that our theoretical 10000 mt plant was treating 100 m^3 waste water per with 200 days operation per year the emission of calcium stearate to water would be 44 kg per year in total or 4.4 g per mt product in maximum. Again, this is no danger for environment because calcium stearate is biodegradable [14].

Regarding packaging materials this means of Calcium hydroxide:

- 0.126 wooden pallets which can be re-used
- 0.126 bigbag (PP) or 5.05 paper bags maybe with PP inside (25 kg)[2].

Regarding packaging materials this means for stearic acid based on tallow:

- 0.935 wooden pallets which can be re-used
- 0.935 bigbag (PP) or 37.41 woven PP bags (25 kg)[3].

Small amounts of the raw material will remain in the packaging. We can assume that this amount is 0.1%[4] or even lower [15]. This results:

- 126 g Calcium hydroxide and
- 935 g tallow based stearic acid will maximally remain in the packaging.

Depending on the country these PP bigbags and the paper bags will be incinerated and end in a landfill. The stearic acid will be converted to carbon dioxide and water during combustion and also during bio-degradation in a landfill. Calcium hydroxide will be calcined to calcium oxide which will react either with other inorganics from other waste or with Carbon dioxide from air. (In a landfill it will react with Carbon dioxide from air or any source and form Calcium carbonate.) If the waste incinerator is either producing steam for heating or electricity the recovered energy of the packaging material and the stearic acid might improve the Carbon dioxide food print slightly.

However, neither the emission to soil, water or are result in a real environmental problem because:

- Calcium stearate was found to be readily biodegradable [14].
- Calcium stearate finally degrades calcium carbonate, carbon dioxide and water according to Equation 5.
- The carbon dioxide formed during degradation does not increase the carbon food print because the stearate source is bio-based and renewable.
- Calcium is sustainable according [2, #19]

$$Ca(C_{17}H_{35}COOH)_2 + 52.5\ O_2 ==> CaCO_3 + 35\ CO_2 + 36\ H_2O \quad (5)$$

4. Input and output flows for 1 mt of Calcium stearate based on palm oil

4.1. Input flows

(Chapter 5.2.5 “Organic substances in dust form” says: To treat as total dust. The dust containing in the exhaust emissions in exhaust shall not exceed the following values:

Mass flow rate: 0.20 kg/h or

Mass concentration: 20 mg/m^3

Even if they meet or falls below a mass flow rate of 0.20 kg/h in the exhaust gas must not exceed the mass concentration of 0.15 g/m^3. Assuming a maximum mass flow of 0.2 kg/h, 200 days production per year and 24 hrs per day it will result in 960 kg emission per 10000 mt product resp. 96 g per 1 mt product.

[2] We can assume 50% bigbags and 50% 25 kg bags which are going to waste.

[3] We can assume 50% bigbags and 50% 25 kg bags which are going to waste.

[4] This is the maximum value which is allowed according to law [15]

According to Eq. 2

- 128.47 kg Calcium hydroxide and
- 934.03 kg palm oil based stearic acid are necessary.

These figures are very close to that of tallow based calcium stearate. The input regarding packagings and transportation of the raw material are assumed to be the same as in paragraph 3.1. In Table 3 we calculated the energy input under as the same conditions as in Table 2b but only for scenario 1 to get an information about the minimum energy input. The energy input of a palm oil based calcium stearate in scenario 1 is less than 0.6% higher compared to a tallow based calcium stearate produced under the same conditions.

Table 3 Theoretical scenario of energy input for the production of 1 mt palm oil based Calcium stearate based of the data in Table 2a

Scenario =>	1
T(start) at °C	20
T(end) at °C	100
reaction time in hrs	6
kg water per mt product (as catalyst added)	no
Energy input per mt CaStearate	
Electrical energy input in kJ/mt product during the entire production time	**550000**
Theoretical energy during reaction in kJ/mt product	
heating up from 20°C to 65°C	85195
melting (stearic) at 65°C	185788
heating to 100°C inkJ	75422
vaporization heat (water)/kJ	141250
maintaining temperature for entire reaction time	80309
subtotal/kJ/mt	**567964**
Total of electrical and other energy input/kJ/mt	**1117964**

4.2.Output flows

According to Eq. 2 62.50 kg water are formed as a by-product while producing 1 mt Calcium stearate. This might be either condensed and going the waste water system or directly to air. This slightly increased amount of water release compared to section 3.2 can be neglected. All other parameters can be considered as the same as in section 3.2.

5. Other parameters

Trace elements, especially of heavy metals, might be interesting for the evaluation of environmental impact. These are summarized in Table 4. These trace metal can be emitted to environment in extremely low amounts due to the residues in packaging and emissions to soil, air and water.

4 Examples of analytical results of ICP analysis of several trace metals in stearic acid (palm oil based) and Calcium stearate based on palm oil (BDL: Below detection limit)

metal	unit	stearic acid 1	stearic acid 2	Calcium stearate 1	Calcium stearate 2	detection limit
Sb	ppm	BDL	BDL	BDL	BDL	0.50
As	ppm	BDL	BDL	BDL	BDL	0.60
Ba	ppm	1.1	1.0	1.8	5.3	0.01
Cd	ppm	0.7	0.8	0.9	2.6	0.01
Cr	ppm	0.9	0.9	1.7	1.8	0.01
Cu	ppm	0.5	0.5	0.5	0.4	0.25
Pb	ppm	4.7	4.3	5.5	17.2	0.50
Ni	ppm	2.7	0.7	1.4	1.9	0.25
Tl	ppm	BDL	BDL	BDL	BDL	0.20
V	ppm	BDL	BDL	0.4	7.3	0.20
Hg	ppm	BDL	BDL	BDL	BDL	0.10

6. The importance of free fatty acid

The content of FFA in calcium stearate is a very important parameter in the specification. It shall be <0.5% in the most cases. Otherwise the free fatty acid can cause problems like:

- gas formation when it react with basic substances like metal oxides and metal hydroxides in the formulation
- This might result in failures in electrical performance in cable insulation or in a reduced corner weld strength in window frame applications.
- Plate out in the die and in the calibration might be another unwished side effect.

7. Sustainability

Schiller and Everard [16] considered several metals soaps which were and are still used in PVC stabilization, assessing them using tools from the TNS Framework for sustainability; Table 5.
Beside cadmium and lead all other metals including sodium, magnesium, aluminum, calcium, lanthanum, barium and zinc have a high potential to become fully sustainable if the PVC product is recycled in a closed loop.

Table 5 Overview about which metal soap has the best potential to become fully sustainable in 2022 (☹: breaching the SC, ・ : can breach the SC, ☺: will not breach the SC; left: metal, right: acid)

metal	acid	SC 1	SC 2	SC 3	SC 4	∑
Ca	Stearic and oleic acid	☺☺	😐😐	😐☺	☺☺	☺

8. Summary

We have shown that calcium stearate can be produced based on different sources of stearic acid and which influence the raw material source and the way of production have on the energy consumption. We considered emissions, packaging, transportation… and we are absolutely sure that the generated data are a serious base to create a LCA of calcium stearate what is overwhelming the skills of the authors. However, we can summarize that calcium stearate is an important chemical and additive in plastic industry with a high potential of sustainability. Charles Babbage[5], an English mathematician, analytical philosopher and the first computer scientist who originated the idea of a programmable computer should have said: "Errors using inadequate data are much less than those using no data at all." [17]

9. Literature sources

[1] F. Mercury, B. May, R. Taylor and J. Deacon; One Vision, UK (1985)
[2] M. Schiller, M. Everard; "Metal soaps in PVC Stabilization considered under the Aspect of Sustainability - One Vision" J. Vinyl & Additive Technology; in preparation
[3] Industrial Chemical Product Data Sheet "Split Tallow fatty Acid"; https://de.scribd.com/document/241405553/Split-Tallow-Fatty-Acids-PDS; accessed 27.10.2022
[4] https://oilpalmblog.wordpress.com/2014/02/03/2-fatty-acid-composition-of-palm-oil-palm-oil-fractions-and-palm-kernel-oil/; accessed 27.10.2022
[5] http://www.peter-greven.de; accessed 27.10.2022
[6] http://www.searates.com/de/reference/portdistance; accessed 27.10.2022

[5] 26 December, 1791 – 18 October, 1871

[7] http://en.wikipedia.org/wiki/Enthalpy_of_fusion; accessed 27.10.2022
[8] M. N. Riaz (Ed.); "Extruders in Food Applications"; CRC Press (2000) page 211 ISBN: 1-56676-779-2
[9] http://en.wikipedia.org/wiki/Stearic_acid; accessed 27.10.2022 (cited from D. R. Lide (ed.), CRC Handbook of Chemistry and Physics (90th ed.). Boca Raton, Florida: CRC Press. ISBN 978-1-4200-9084-0)
[10] https://en.wikipedia.org/wiki/Calcium_hydroxide_(data_page); accessed 27.10.2022 (cited from *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*. D. R. Lide (ed.) (84th ed.). Boca Raton, Fla.: CRC Press. 2003. pp. 5–10. ISBN 0849304849. OCLC 52548731)
[11] Y. A. Çengel, M. A. Boles; "Appendix 1." Thermodynamics: An Engineering Approach. 7th ed. Boston: McGraw-Hill (2011) Page 914
[12] http://www.docbrown.info/page07/delta1He.htm; accessed 27.10.2022
[13] https://gestis.dguv.de/data?name=020980; accessed 27.10.2022
[14] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/5720/5/3/2, accessed 27.10.2022
[15] OECD Series on Emission Scenario Documents Number 24; "Emission Scenario Documents on Transport and Storage of Chemicals" ENV/JM/MONO (2006) 26 page 68
[16] M. Schiller, M. Everard; "Metal soaps in PVC Stabilization considered under the Aspect of Sustainability - One Vision" J. Vinyl & Additive Technology 23 (2017) pages 127-134
[17] http://en.wikiquote.org/wiki/Charles_Babbage; accessed 27.10.2022