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Letter to the Editor

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Comment on "Life Cycle Carbon Footprint of Linear Alkylbenzenesulfonate from Coconut Oil, Palm Kernel Oil, and Petroleum-Based Paraffins"

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D. R. Shonnard et al.[1] reported on the life cycle carbon footprint (LCCF) of linear alkylbenzenesulfonate (LAS) and concluded that the replacement of petroleum-based paraffins with biobased paraffins will facilitate a significant reduction of the greenhouse gas emissions (GHG) from the production of LAS. This correspondence aims to highlight that the mandatory transitioning from petroleum-based to renewable-based products is not a panacea and will not resolve the problem of GHG for all chemical products, especially for commodity chemicals like LAS. Here are some of the highlights which warrant comment. To facilitate our discussion, the italicized texts below are directly quoted from Shonnard's paper.

1. GREENHOUSE GAS CONTRIBUTION

The authors claim "*that the greenhouse gas emissions from the production of LAS can be reduced between 45 and 50% by replacing petroleum based paraffins with coconut or palm kernel oil derived paraffins.*" From their analysis, highlighted in Figure 2,[1] the main greenhouse gas contribution difference comes from end of life process (EoL). In the text, we can find the origin of such difference: "*The processes that convert the n-paraffins to LAB are the same for both sources of n-paraffins, with EoL CO_2 emissions handled differently due to the source of the carbon in the LAS. In our study, fossil carbons will be counted toward the GHG total, while renewable carbon will not count, assuming carbon neutrality*···.". It should be mentioned that the paraffin part (ideally between C10 and C13)[2] represents between 47 and 54% of the mass of LAS. Apart from this classical consideration (i.e., CO_2 emissions should be considered differently if the paraffin is biobased or petroleum-based), the authors do not find any other way of improving the carbon footprint for LAS, however, some issues should not be overlooked (vide infra).

2. FATTY ACID COMPOSITION

Coconut oil (CO) and palm kernel oil (PKO) belong to the so-called lauric oils, which are characterized by their high lauric acid (C12) content of approximately 45−50%.[3] Therefore, about 55% of the oil (C10−C12 fraction) could be used for LAS synthesis since the paraffin length should be ideally between C10 and C13.[2] The remaining carboxylic acid should be evaluated in the LCCF, but in Table S6, a mass allocation factor of 0.47 was calculated according to equation S2 for PKO suggesting that the entire oil fraction could be used for LAS synthesis. Oil mill effluent seems to be also forgotten (see issue 5).

3. AVAILABILITY OF THE C10−C12 FRACTION

CO and PKO comprise around 5% of the total natural fats and oils, but are now an important feedstock of the oleochemical industry. These oils have the unique advantage of having their fatty acid composition falling within the carbon chain spectrum highly desired by the oleochemical industry where C12 and C14 fatty acid fractions are sought after. Since about 80% of the fatty alcohol market is in the range of C12−C14 alcohols, lauric oils are the main raw materials. Various surfactants are already produced using fatty acid fractions or from fatty alcohols obtained by hydrogenation.[4] The current world supply of fatty alcohols is equally divided between natural and synthetic;[5] thus, the use of CO and PKO for the synthesis of LAS ("*more than 3 millions of metric tons per year*") will have impact on the oleochemical industry and this should be evaluated in the LCCF of LAS. The authors "*... assume that sustainability principles (...) will be adhered to during commercialization of this new product so as to avoid competition with food*···". The competition with other biobased surfactants should also be taken into account.

4. OIL (TRIGLYCERIDES), FATTY METHYL ESTER, OR FATTY ACID TRANSFORMATION IN *N*-PARAFFIN

The conversion of CO, PKO, or oil fraction to *n*-paraffin could not be simply performed using H_2, electricity, natural gas, and water as in Figure 1 and the text "*Converting these biorenewable oils to normal paraffins requires a catalytic deoxygenation process that consumes hydrogen, natural gas, water, and electricity and generates coproducts of renewable fuels: diesel, fuel gas, LPG, and naphtha.*[15]". The yield of the process used in the LCCF could not be known since it refers to confidential data (Table S5 in the Supporting Information). A closer look to reference 15 of the paper,[6] did not provided further information, but yield below 50% is expected due to the CO and PLO composition (see issue 2). However, the high H_2 consumption associated with this process (1.5−3.8 wt % H_2 of the incoming feed stream for vegetable oil upgrading)[6] is the main drawback of such a process. Since H_2 is not currently available in large quantities from renewable resources, H_2 is made primarily from steam

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reforming of natural gas. CO_2 is the byproduct and should have been mentioned in Figure 1 and the text. An alternative lipid processing route such as catalytic hydrothermal processing might possibly have been envisioned.[7]

5. EXTRACTION PROCESS

"*The extraction process produces coconut meal and palm kernel meal in addition to the oils.*" The extraction of oil from the fruits involves a number of processing stages. During this process, a large quantity of water is required. I have no specific information on water use during CO or PKO processing. It is however estimated that for each ton of crude palm oil, 5 to 7.5 ton of water are required and more than 50% of this water ends up as palm oil mill effluent (POME).[8] If the untreated effluent is discharged into watercourses, it is certain to cause considerable environmental problems due to its high COD (up to 50,000 mg/L), high BOD (up to 25,000 mg/L), and high polyphenols content.[8]

A conventional and common method for treating POME is the open type lagoons treatment, and such a process emitted biogases (methane, CO_2, ...). Several projects have been initiated in order to achieve zero-effluent discharge by the use of biogases for heat or electricity, recovery of nutriments that could be reused as fertilizer, and recycling water, but to my knowledge, the economics of this approach needs to be further addressed for commercial uptake.[9]

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Notes

The author declares no competing financial interest

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