# Sterol Glucoside Content in Vegetable Oils as a Risk for the Production of Biodiesel – Study of the Technological Chain Impact

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**Abstract:** The impact of the oil milling and refining process on the concentration of steryl glucosides (SG) and acylated steryl glucosides (ASG) in rapeseed and soybean oil was determined. Technological steps with a high reduction potential of SG and ASG were identified. After neutralisation and bleaching the content of SG and ASG is reduced to a level which can be tolerated for biodiesel synthesis. The differences in SG and ASG content in crude soybean and rapeseed oil are reduced to nearly the same level by the oil milling process.
**Key words:** Steryl Glucosides, Oil Milling Process, Biodiesel Process, Filterability

## Introduction

Increasing amounts of vegetable oil are used for the production of biodiesel. Improved standards (like EN 14214) and regular monitoring led to a reduction of problems in the use of biodiesel, but it is possible that biodiesel can fail in applications by precipitation although all specifications are met. The precipitation can lead to unspecific filter clogging and problems with the utilisation of biodiesel.
A possible reason for filter clogging problems apart from wax content, content of saturated monoglycerides and polymers is the presence of SG in biodiesel and diesel blends containing biodiesel. SG are common components of vegetable oils and find the path to biodiesel industry via the oil milling and refining process.
SG and ASG are better soluble in vegetable oil than in biodiesel. ASG can be converted during the biodiesel process to SG. The crystallisation is extremely slow and depends on temperature, crystallisation nuclei and surface effects. Freshly produced biodiesel can meet the specification, but during transport and storage crystallisation begins and the filterability can become bad.
The concentrations of SG and ASG in vegetable oil have therefore an important impact on the quality of the biodiesel. If it is possible to reduce SG and ASG significantly on the level of the starting material, biodiesel with low levels of SG and ASG can be produced, and problems with filter clogging should decrease.

## Scope of the work

The project is directed to get reliable information by which process step or modification in the oil mill the concentration of SG and ASG in vegetable oils intended for the production of biodiesel can be reduced. To get comparable data the chain beginning from the soybean seed to the finished oil shall be studied as well as the chain beginning from rapeseed to the finished oil.

## Part I: Study on the oil mill impact

A general oil mill processing scheme was set up with sampling points in terms of the specific processing unit (fig. 1).

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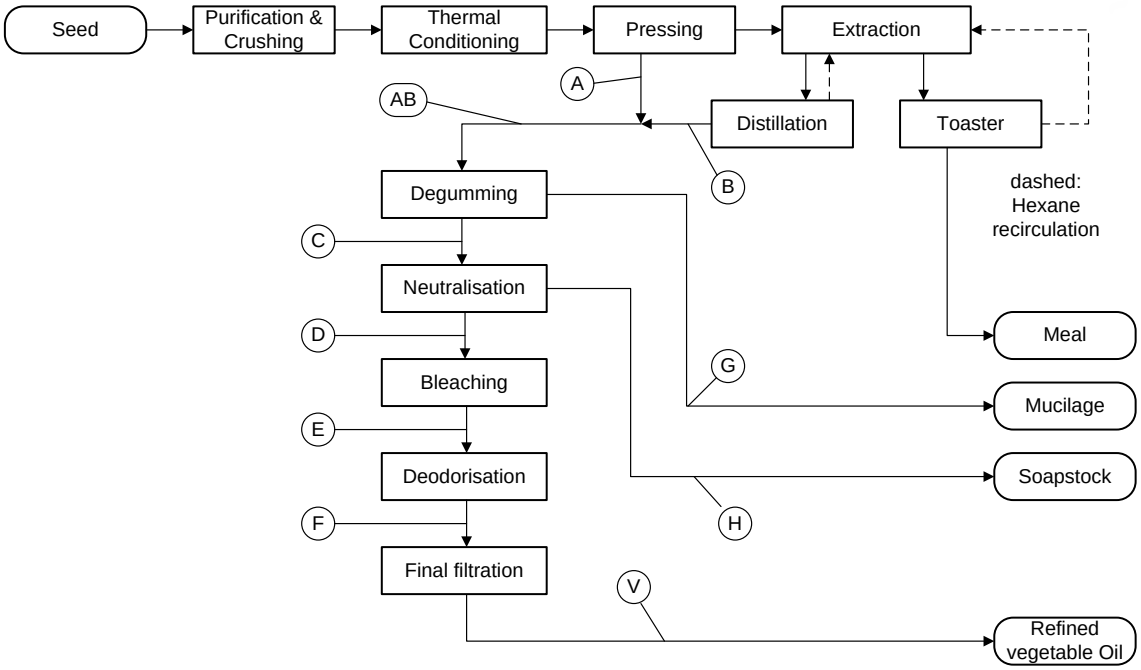


Fig. 1: Oil mill process and sampling points (A – H and V)

Fig. 2 shows the change of the SG concentration during the whole process. The columns for OM (Oil mill) 1 to 4 represent soybean oil processing, the others stand for rapeseed oil processing.

The results show that extraction oil can contain remarkable amounts of SGs, but there is a broad range depending on the process parameters.

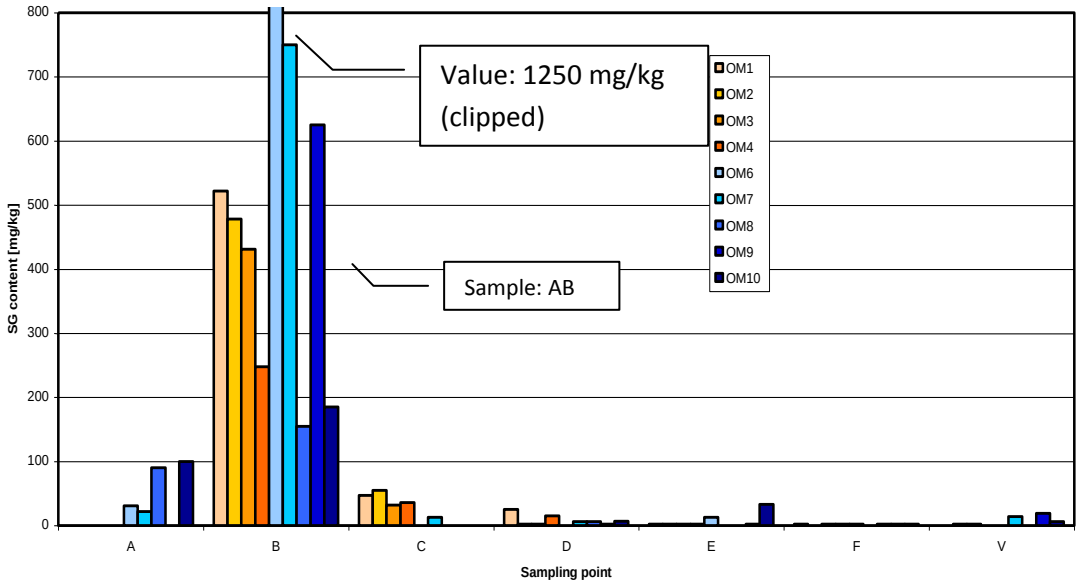


Fig. 2: Sequence of SG contents during the oil mill process (the sample B value for OM 6 is clipped)

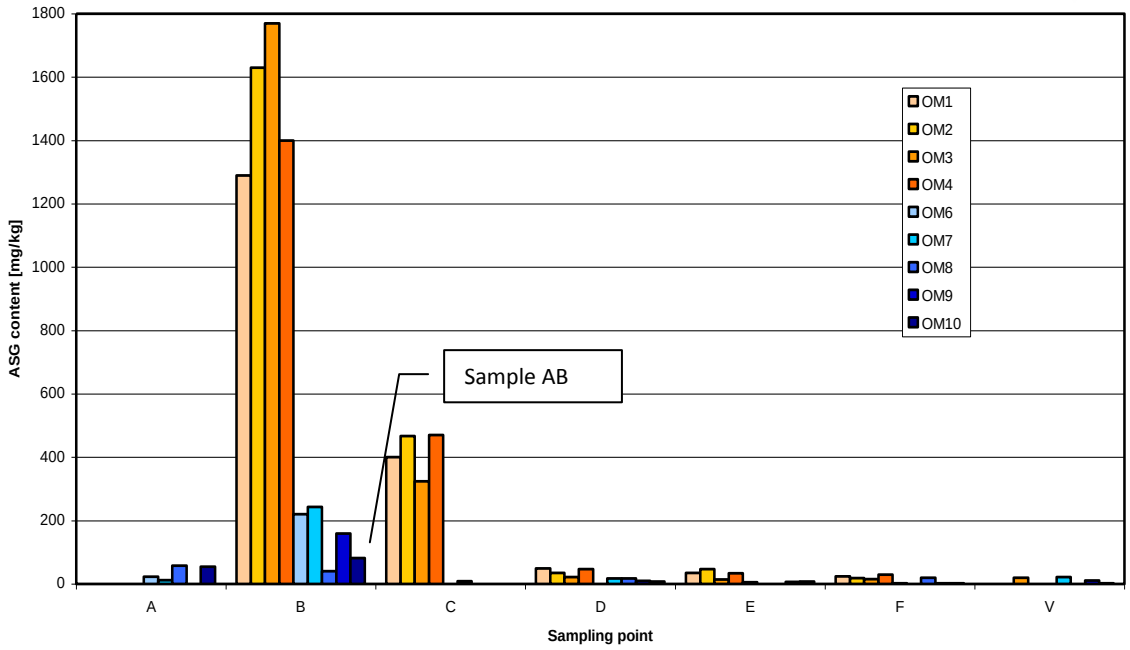


Fig. 3: Sequence of ASG contents during the oil mill process

An oil quality at sampling point C (after degumming and before neutralisation) is not sufficient for biodiesel production and requires additional steps in the biodiesel plant. After neutralisation, better after bleaching the concentration of SG and ASG is reduced remarkably.

**Standard Lab synthesis and testing of the prepared Biodiesel**

Biodiesel was produced from selected soybean and rapeseed oils on laboratory scale. The FAME produced from the selected crude soybean oil shows a very good conversion degree (low concentrations of glycerol and glycerids) but an unexpected high value of total contamination and acid number. To improve the FAME quality adsorbents had to be used for a final purification. The behaviour of the rapeseed oil in the process and the rapeseed oil derived FAME was as expected. The SG and ASG concentrations of the starting vegetable oil and the resulting biodiesel are summarised in Table 1.

| No. | Sample | SG [mg/kg] | ASG [mg/kg] |
|---|---|---|---|
| 1 | Soybean oil | 98 | 1346 |
| 2 | FAME from 1 | 55 | 55 |
| 3 | FAME from 1 after use of adsorbents | < 5 | 38 |
| 4 | Rapeseed oil | 201 | 19 |
| 5 | FAME from 4 | < 5 | < 5 |

Tab. 1: SG and ASG concentration of vegetable oils and FAME

The analysis of the biodiesel show that the biodiesel process already has (without special measures) a remarkable potential to reduce the remaining ASG and SG concentrations. However if the transesterification process starts with crude materials containing ASG (or SG) in high concentration this behaviour is not sufficient to reduce concentrations to an acceptable level in the final product. Adsorbents can help to improve the situation but they may influence only some of the critical substances.

**Filterability of methyl esters and blends**

The filterability of FAME and FAME blends is an important property for the application as fuel. The filterability of a soybean oil based and a rape seed oil based FAME were determined as well as the filterability of the corresponding B7 blends. The results are summarised in Table 2.

| No. | Sample | FBT (IP 387 (B)) |
|---|---|---|
| 1 | FAME (soybean oil based) | 10.3 |
| 2 | FAME (rapeseed oil based) | 1.02 |
| 3 | B0 (Diesel fuel w/o FAME) | 1.00 |
| 3 | B7 using No. 1 | 7.57 |
| 4 | B7 using No. 2 | 4.40 |

Tab. 2: Filter blocking tendencies (FBT) of different fuels/blends

Low values of filter blocking tendencies (FBT) in FAME are not a guaranty to get a proper FBT value of the blended fuel.

**Conclusions**

The project leads to some fundamental approaches in understanding the sources of ASGs and SGs and the impact of the oil refining and transesterification process. Soybean oil and rapeseed oil cause different levels of ASG and SG contents. The ASG/SG ratio is a typical characteristic of the different kinds of oil.

It is more challenging to process soybean oil to a low ASG/SG containing final product in comparison to processing rapeseed oil to the same target. However along the process chain the differences between the oils blur. Properly degummed and bleached oil contains low or not determinable concentrations of ASGs and SGs. A high risk for an ASG/SG caused bad FAME filterability comes from the use of crude oils or less processed oils.

In the case of risk-entailing crude materials the reduction potential of the biodiesel process is not big enough. If crude or less processed oils are used for biodiesel production, the industrial FAME plant compulsorily needs a special step for oil pre-processing, similar to that of an oil mill. The concentration of SG and ASG in biodiesel seems to have an impact on the filterability, but for a generalization more data are needed.

**Literature**

[1] Elbein A. D., Forsee W.T., "Biosynthesis and structures of glycosyl diglycerides, steryl glucosides and acylated steryl glucosides", Lipids 10(7), 427-436, 1975.
[2] Philips K. et al., "Analysis of sterol glucosides in foods and dietary supplements by solid-phase extraction and gas chromatography", J. Food Lipids 12, 124-140, 2005.
[3] Bondioli P., "Identification and quantification of steryl glucosides in biodiesel", Eur. J. Lipid Sci. Technol. 110 (2), 120-126, 2008.
[4] Verleyen T. et al., "Analysis of free and esterified sterols in vegetable oils", J. American Oil Chem. Soc. 79(2), 117-122, 2002.
[5] Lacoste, F. et al., “Quantification of free and esterified steryl glucosides in vegetable oils and biodiesel”, Eur. J. Lipid Sci. Technol., 111, 822-828.
[6] Haupt, J., Brankatschk, G., Wilharm, T., Sterol Glucoside Content in Vegetable Oils as a Risk for the Production of Biodiesel – Study of the Technological Chain Impact; 2010; www.agqm.de