Final Report

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

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Running period:

11/03/2009 - 30/07/2009

Funded by:

American Soybean Association (ASA)

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Index of contents

Executive Summary

The increasing use of Fatty Acid Methylester (FAME, "Biodiesel") as a blend component for mineral oil based diesel fuels shows a remarkable impact of this component on the filterability of the final fuel. Some minor components of the FAME derived from vegetable oils like sterol glucosides (SG) and acylated sterol glucosides (ASG) have been identified as the main cause for this behaviour.

The project has the aim to record the typical situation along the process chain and to identify technological steps of the oil milling and refining with a high reduction potential for SGs/ASGs.

Results

It is more challenging to process soybean oil to a low ASG/SG containing final product in comparison to processing rape seed oil to the same target. However along the process chain the differences between the oils blur. Not only SGs but also ASGs can cause filterability problems of the FAME.

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 raw oils or less processed oils. If raw or less processed oils are intended for biodiesel

production, the industrial FAME plant compulsorily needs an additional step for oil pre-processing, similar to that of an oil mill. The biodiesel process also reduces the remaining concentration of these minor components, but in case of risk-entailing raw materials this reduction potential is not big enough: Already comparatively low SG/ASG concentrations can lead to a remarkable negative impact on filterability.

Further work

Filterability will become one of the most important challenges for the use of FAME as a blend component in the future. Additional work is needed to develop standardized test methods for filterability and for the content of minor components with good precision data for low concentration ranges.

Another issue will be to get a better understanding for the correlation between the concentration of minor components and filterability.

Very important is also to check possible improvements in purification technologies. This should include both the oil mill process as well the FAME production.

We thank the American Soybean Association for funding this project.

Berlin, 30/07/2009

1 Introduction

Since 10 years increasing amounts of vegetable oils are used for the production of biodiesel. Improved standards (like EN 14214 and others), QA systems and regular monitoring led to a reduction of problems in the use of biodiesel. Nevertheless the last years have shown that a biodiesel can fail in application by precipitations, although the specifications are met.

The main[1] reason for this behaviour, which can be observed in the case of B100 but also in blended mineral oil based fuels, is the presence of sterol glucosides in the biodiesel. Sterol glucosides are a common component of plants (and finally of the generated vegetable oils like soy, rape seed and palm oil) and find the path to biodiesel industry via oil processing (milling and refining).

Normally moderate sterol glucoside concentrations in vegetable oils are not conspicuous due to the fact that originally the sterol glucosides occur mainly as acylated sterol glucosides (ASGs). This substance class is up to middle range concentrations soluble in vegetable oils, but after transesterification (the chemical part of the biodiesel process) ASGs are decomposed chemically by removing the fatty acid side chain and (partial) conversion to sterol glucosides (SGs). This substance class is not soluble in biodiesel, but the crystallization is extremely slow and depends on the temperature, on impurities as crystallization nuclei and surface effects. This leads to the situation, that a freshly produced biodiesel meets the specification, but after some days of storage/transportation the precipitation of SGs begins or the filterability of the fuel, including thereof produced blends, is bad. Another appearance is the spontaneous clogging of the loading filter in the biodiesel plant without any pre-announcement or similar situations later in the supply chain – also at public and fleet filling stations (already observed at the B2 blending level in Minnesota/USA and at several other places in the world at B5 blending level). The precipitates do not contain only SGs but also ASGs and other substances. In some cases of high source concentrations of ASGs it seems to be possible that also ASGs could be the cause for the deposits.

The remaining concentration of sterol glucosides (including ASGs) in the vegetable oil depends on the kind of raw material and the process technology of the oil mill.

It is well known from literature that soybean oil (and palm oil) has got the highest concentrations of SGs/ASGs among the traditional vegetable oils. In opposite the general level in the case of rapeseed oil seems to be comparatively low. But also the process technology of oil production has a big impact: The solvent extraction step in industrial oil mills (using hot hexane) leads to the transfer of the SGs/ASGs into the “extraction oil”. Some types of refining steps can reduce the SG/ASG concentration, but others have less influence.

2 Scope of work

The project is directed to get reliable information, by means of which process steps or modifications the concentration of SGs/ASGs 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 the rapeseed to the finished oil.

The proposed project consists of the following three parts:

[1] Other known reasons are: Wax content, content of monoglycerides of saturated fatty acids and polymers

1. Monitoring of existing oil mill technologies
2. Stability checks on best/typical cases
3. Lab based generation of biodiesel and testing

For the execution of part 1, an unified technology schema is prepared which covers all typical oil mill process steps in an anonymous way. By means of this definition the monitored oil mills can assign each taken sample to the right process step.

Samples identified as “low concentration SG/ASG” or as “taken after a step with high reduction potential” will undergo a series of repeated tests to check the stability at this position (part 2).

For part 3 biodiesel shall be made from different selected samples by means of a standardized lab procedure. The sample selection should represent typical present technology situations including best and worst cases. The biodiesel has to be characterized as follows

- Standard parameters according to EN 14214 (parameter set reduced to relevant parameters)
- Content of SG/ASG
- Filterability tested by means of a modified “cold soak” IP 387 (according to the draft proposal for an European filterability test)
- Filterability of a B7 Blend (based on a defined hydrocarbon mixture as fuel substitute)

The project report contains

- the anonymized monitoring results assigned to technology steps
- the stability check results of the best cases
- a complete report on biodiesel behaviour, prepared from selected samples
- a summary of identified steps with a high reduction potential and conclusions for possible changes in technology (if successful a following project could deal with this issue)

3 Part I: Study of the oil mill’s process impact

To make sure to get the same type of samples a general oil mill processing schema according to fig. 1 was set up. This diagram contains the sampling points in terms of the specific processing unit. In the very beginning the opportunity of a physical refining of the vegetable oil has also been considered as a parallel process type for purification. In fact after taking all samples it became clear, that no monitored company is using this kind of process.

For this reason only the impact of the chemical refining can be studied in this project.

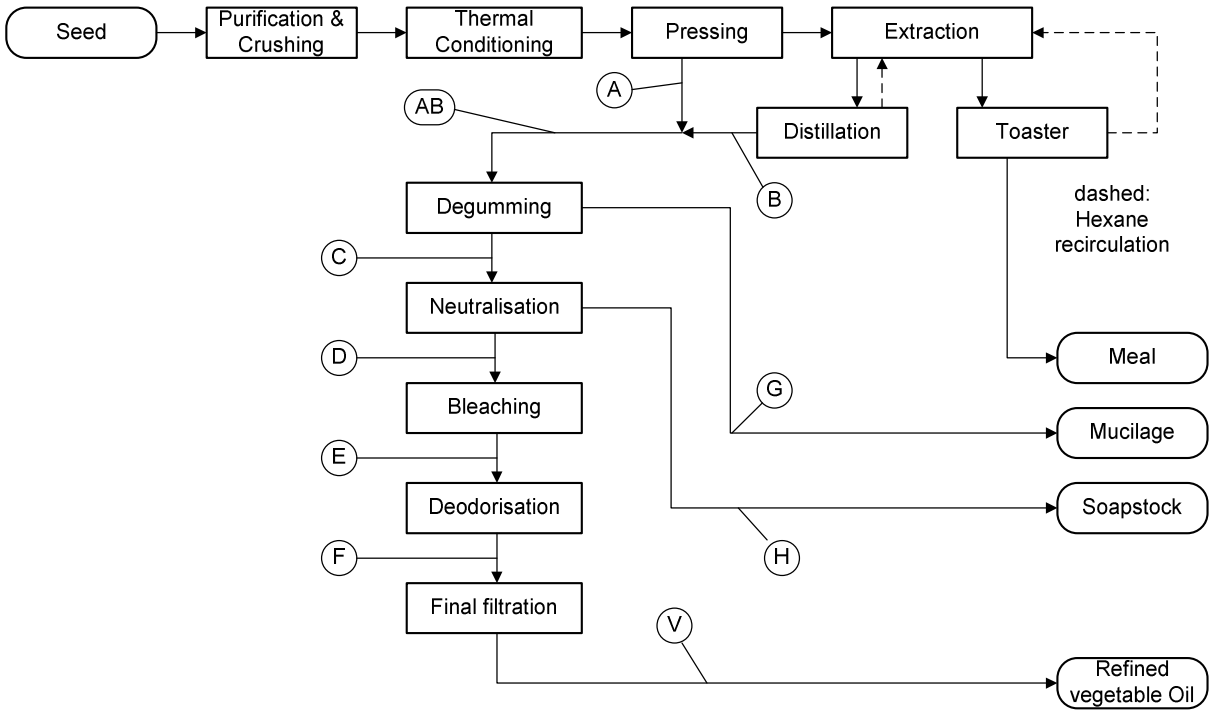


Fig. 1 Oil mill process and sampling points (A – H and V)

One of the aims of this project was to identify the main source of the SG and ASG (pressing or extraction). In the case of soybean processing a pressing step is normally not used: The crushed material goes directly to the extraction. This explains the missing data from sampling point A in case of processing soybeans.

3.1 SG contents

Fig. 2 shows the change of SG concentrations during the whole process. The columns for OM (Oil mill) 1 to OM 4 represent soybean oil processing; the others stand for rape seed 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. For an evaluation it must be considered, that in the case of rape seed processing only about 40% to 45% of the vegetable oil comes from this step however in the case of soybean oil the extraction is the whole oil source. So it is more challenging to reduce the SG concentration in the case of soybean oil.

Supposing that SG concentration > 15 mg/kg can (!) cause critical filtration behaviour of biodiesel it seems to be clear that 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. However after neutralisation, better after bleaching the risk for too high SG concentrations is reduced remarkably.

But not only the free SGs can cause problems: A remaining concentration of ASGs is a hidden risk due to the conversion of ASGs to SGs in the biodiesel process. The gathered results of this study give the impression that the conversion can happen in the oil mill process too. We observe sometimes a “recovery” of SGs at the sampling point V which could be explained by a partial conversion of ASGs.

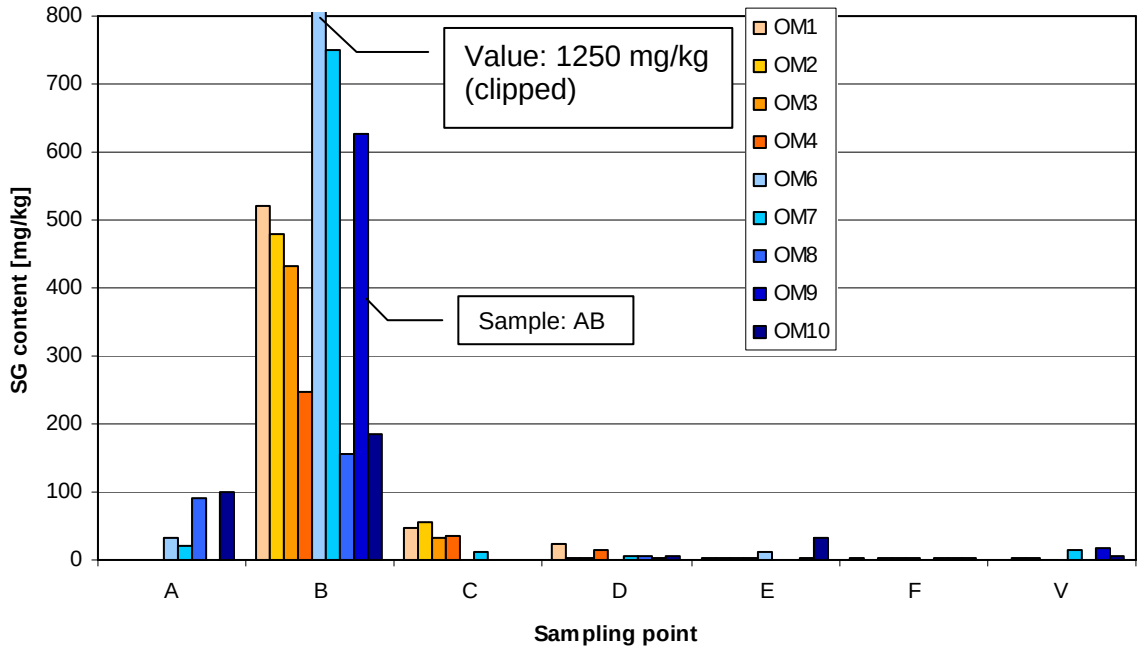


Fig. 2 Sequence of SG contents during the oil mill process (the sample B value for OM 6 is clipped)

As expected a large amount of SGs is concentrated in the mucilage and in the soapstock as well (see tab. 1).

Tab. 1 SG contents in mucilage and soapstock

Plant	SG content		Unit
	Mucilage	Soapstock	
OM1	2810	4440	mg/kg
OM2	7610	4020	mg/kg
OM3	8830	2070	mg/kg
OM4	11200	4650	mg/kg
OM6		7290	mg/kg
OM7		5330	mg/kg
OM8		7520	mg/kg
OM9	5370	4250	mg/kg
OM10	330	3700	mg/kg

The ASG's decrease is similar to that of the SGs but the residual concentrations after processing are by trend higher compared to those of SGs (fig. 2 compared to fig. 3).

Nevertheless the results of this study show that the existing purification processes have enough power to do the required work.

As already discussed for SGs it seems to be not sufficient to use a degummed oil as a raw material for biodiesel production without additional pre-cleaning steps in the biodiesel plant.

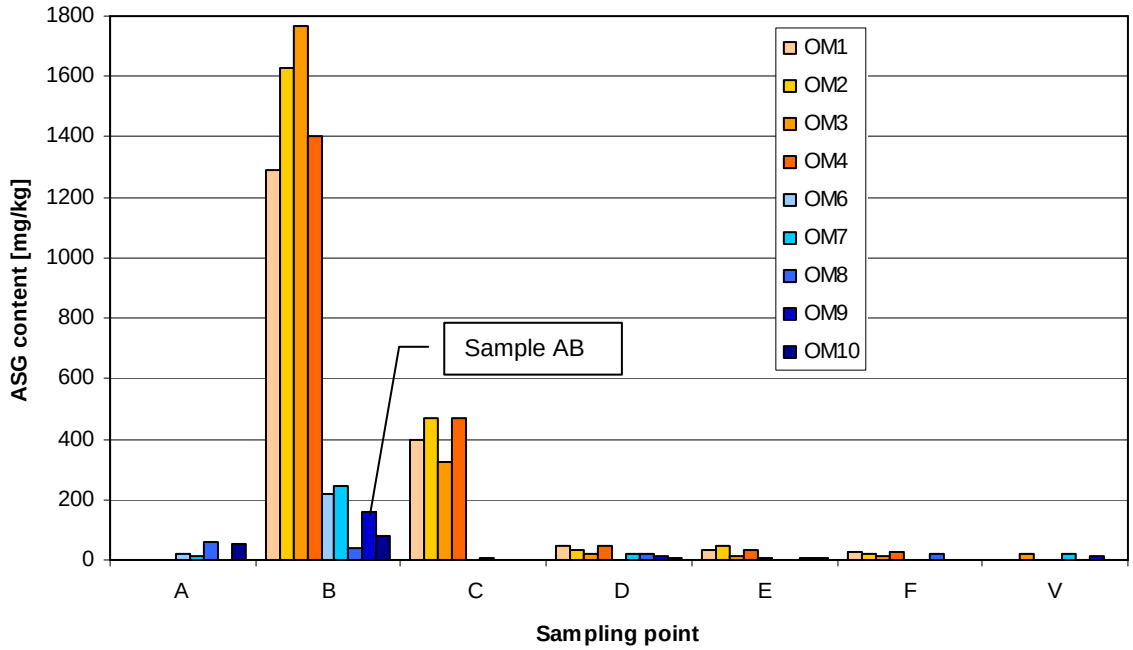


Fig. 3 Sequence of ASG contents during the oil mill process

We find very high concentrations of ASGs in the mucilage and the soapstock – the largest values occur in case of soy bean processing (see tab. 2).

Tab. 2 ASG contents in mucilage and soapstock

Plant	ASG content		Unit
	Mucilage	Soapstock	
OM1	9200	9770	mg/kg
OM2	21800	14900	mg/kg
OM3	32600	3310	mg/kg
OM4	37000	9630	mg/kg
OM6		3310	mg/kg
OM7		4480	mg/kg
OM8		4550	mg/kg
OM9	686	3410	mg/kg
OM10	119	1900	mg/kg

A remarkable difference in the behaviour of ASGs and SGs is the inversion of the concentration ratio between ASGs and SGs while processing soybean oil or rapeseed oil (see fig. 4).

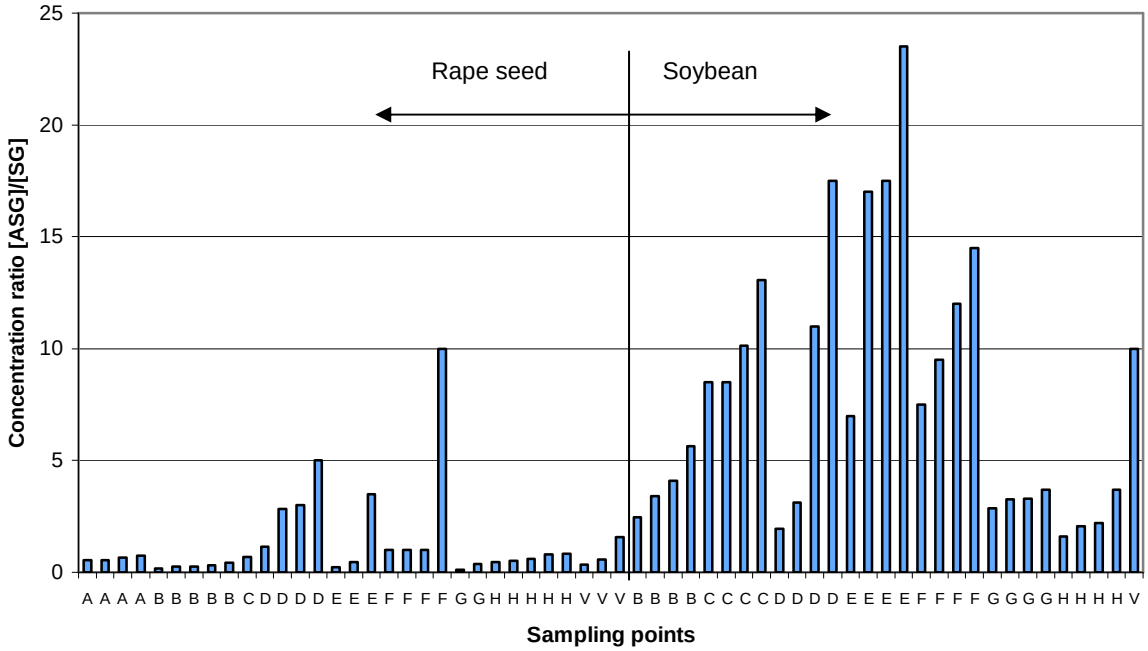


Fig. 4 Concentration ratio between ASG and SG depending from the kind of raw material

This is the reason for a potential higher risk of soybean oil when the ASGs convert to SGs by chemical reaction.

4 Part II: Reproducibility Test

A main task of the project was to evaluate the stability of the found ASG and SG concentration levels. This is part of the question which factors influence these values mainly:

- Technology
- Process parameters
- Raw material

For this purpose some selected samples are taken after some time at the same sampling points as before. A comparison of the ASG and SG concentrations gives fig. 5 and 6.

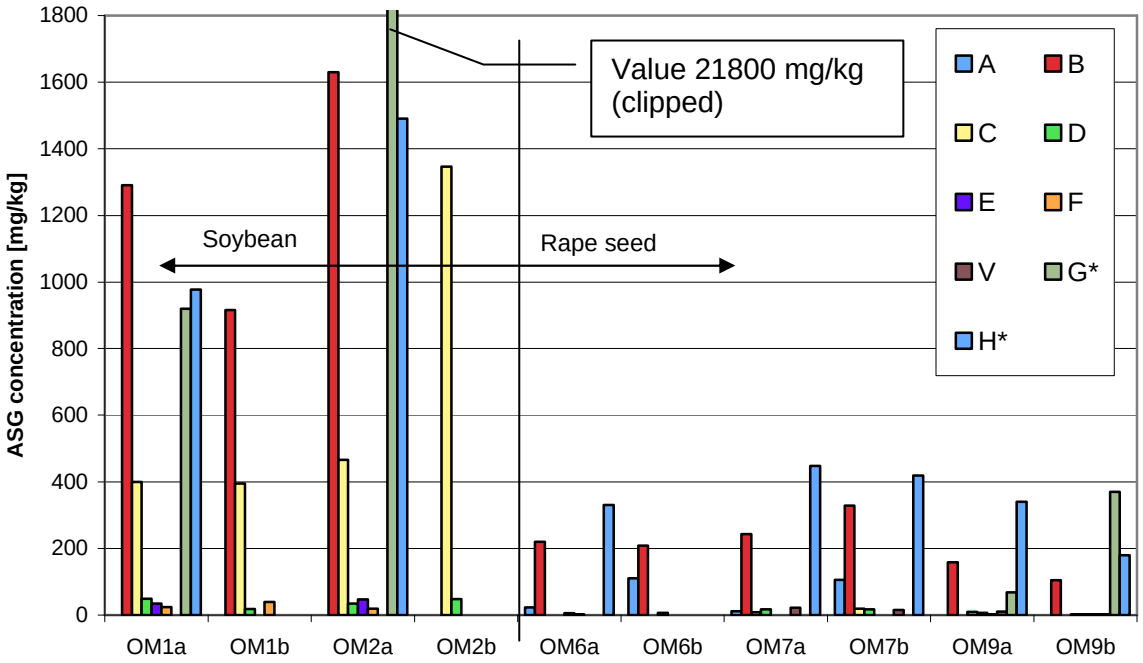


Fig. 5 ASG concentrations: Results of repeated sampling at the same positions in several oil mills (OM1 and OM2 represent soybean processing, but OM 6, OM7 and OM9 rapeseed processing; *a* representing 1st and *b* 2nd sampling)
Please note: The concentrations for mucilage (G) and soapstock (H*) read from this diagram have to be multiplied by 10.)*

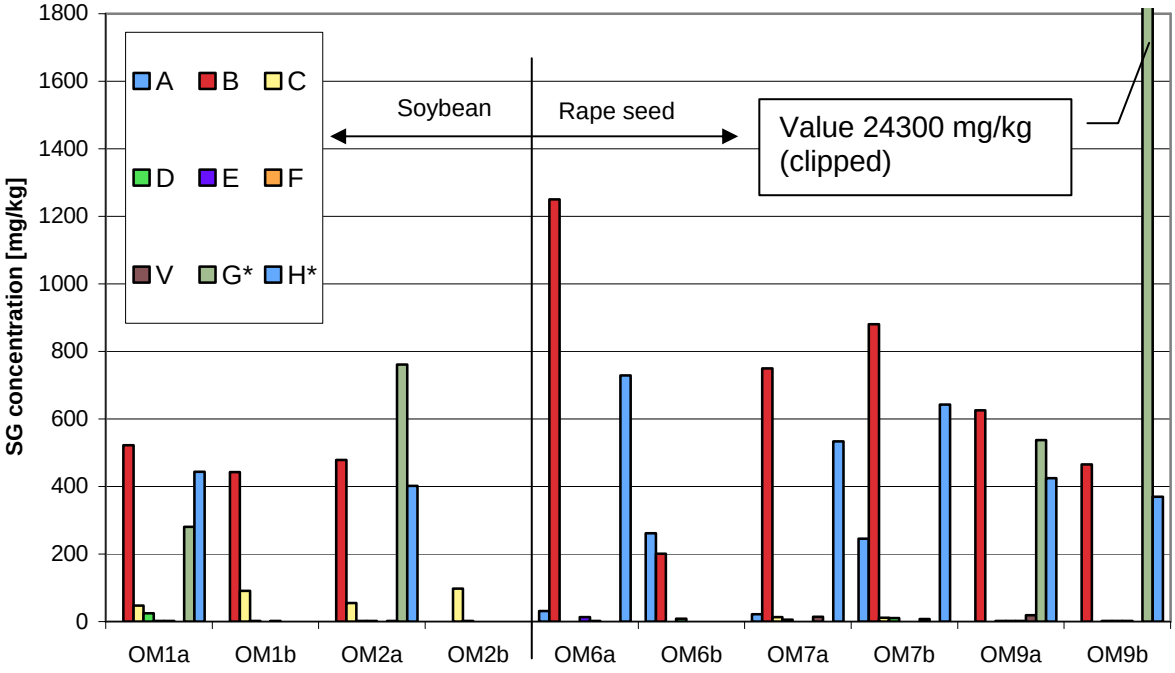


Fig. 6 SG concentrations: Results of repeated sampling at the same positions in several oil mills (OM1 and OM2 represent soybean processing, but OM 6, OM7 and OM9

rapeseed processing; *a* representing 1st and *b* 2nd sampling)
Please note: The concentrations for mucilage (G) and soapstock (H*) read from this diagram have to be multiplied by 10.)*

The results show possible deviations by repeated sampling almost in a range of 1:2 or 2:1 but always in the same concentration level. The reason for this behaviour is not clear up to now. However it must be considered that process control in oil mills is not optimized for lowering SG or ASG concentrations but for good results in other control parameters which are common quality features for the oil and meal.

After a complete run through all process steps the differences blur more and more – also the differences between soybean oil and rapeseed oil.

5 Part III: Standard Lab Synthesis and Testing of the prepared Biodiesel

5.1 Standardized Lab Procedure for Transesterification

5.1.1 Laboratory Equipment

The transesterification is done in common double mantle vessels with a volume of 2 L or 5 L. It is possible to heat and cool the vessels very exactly to +/- 1 ℃. Furthermore a cooler on top is installed to make sure that methanol vapour can not leave the reaction. The vessels are equipped with curved bottoms and in the centre taps are installed for draining. Fig. 7 shows an example of a reactor with 2 L volume.

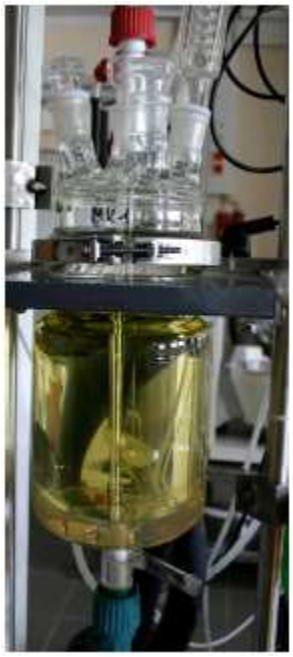


Fig. 7 Laboratory double mantle vessel (2 L)

In the vessels the two-step transesterification reaction and subsequent acidic and neutral washing steps are realised. After that the raw biodiesel is dried with a rotary evaporator that is shown in fig. 8.

Fig. 8 Rotary evaporator for raw biodiesel drying

5.1.2 Detailed description of transesterification

Before the FAME is produced, the acid value of the vegetable oil has to be determined to calculate the additional amount of catalyst needed. In general the recipe uses a molar excess of 1.45 of methanol and 1 %(m/m) of catalyst with respect to the weighted sample of vegetable oil. The calculated amounts of catalyst and methanol are divided in a ratio of 4:1 between the first and second transesterification step. The reaction is carried out at 55 ℃ and within 60 minutes per step. The settling time for the glycerol separation is 30 minutes. After the glycerol is drained completely out of the vessel, the remaining FAME is washed twice with 16.5 %(m/m) of a low concentrated phosphoric acid (1 %(m/m)). After that the mixture is washed twice with 7 %(m/m) deionised water. All washing steps are done at 55 ℃. The mixtures are stirred for 5 min each and the settling time is always 30 min.

Thereafter the raw biodiesel is dried in a rotary evaporator which is operated at 50 mbar for 45 min. The water bath temperature is 90 ℃ and the flask is aerated with Argon. Finally the biodiesel is filtered through a coarse filter paper comparable to the typical police filters in biodiesel plants.

In case of unexpectedly high values of total contamination, high element contents or acid numbers the biodiesel should be purified additionally using adsorbents. This procedure causes the risk of a remarkable reduction of SG and ASG contents which cannot be transferred to typical plant designs. Therefore the SG and the ASG concentrations have to be determined before and after the purification step to prevent any kind of misinterpretation.

5.2 Results

To show the behaviour and possible change of ASG and SG concentrations during the biodiesel process we have chosen not to take the “best cases” as raw material for transesterification. The reason is an analytical one: If the test would start with concentrations already near or lower than the detection limit there is no chance to see the real impact of the transesterification step.

The general FAME properties of the biodiesel generated from oil mill samples are as follows:

Tab. 3 Characterization of the generated Biodiesel

Parameter	**Method**	**Results**			**Unit**
		Biodiesel from soybean oil (raw)	Biodiesel from soybean oil (purified)	Biodiesel from rapeseed oil	
CFPP	DIN EN 116	-7		-16	℃
Water content	DIN EN ISO 12937	227		363	mg/kg
Oxidation stability 110℃	DIN EN 14112	5.1	5.4	6,9	h
Acid number	DIN EN 14104	1.09	0.87	0.489	mg/g KOH
Iodine number	DIN EN 14111	130		114	g Iod/100g
Free Glycerol	DIN EN 14105	0.01		< 0.01	% (m/m)
Monoglycerides		0.34		0.29	% (m/m)
Diglycerides		0.07		0.07	% (m/m)
Triglycerides		< 0.01		< 0.01	% (m/m)
Total glycerol		0.10		0.09	% (m/m)

(Tab. 3 Characterization of the generated Biodiesel, cont.)

Na+K content	DIN EN 14108/14109	10.7	1.7	0.8	mg/kg
Ca+Mg content	DIN EN 14538	19.8	13.8	0.5	mg/kg
Phosphorus content	DIN EN 14107	14.0	3.2	0.6	mg/kg
Total contamination	DIN EN 12662:1998	125	<1	3	mg/kg
Ester content	DIN EN 14103			>99	% (m/m)
Sulfur content	DIN ISO 20846	0.4		2.3	
Fatty acid profile C12:0	DIN EN 14103	< 0.1		<0.1	
C14:0		< 0.1		<0.1	
C16:0		10.7		4.2	
C16:1		0.1		0.2	
C18:0		3.1		1.6	
C18:1		24.2		62.1	
C18:2		54.0		18.9	
C18:3		6.3		10.1	
C20:0		0.3		0.5	
C20:1		0.2		1.4	
C22:0		0.5		0.3	
C22:1		< 0.1		0.3	
C24:0		0.2		<0.1	
C24:1		< 0.1		0,1	

The FAME produced from the selected 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. The aggregates (leading to the total contamination value) seem to contain also residuals like earth alkaline and alkaline fatty acid salts. To improve the FAME quality adsorbents had be used for a final purification.

The behaviour of the rape seed oil in the process and the rape seed oil derived FAME was as expected.

The tests show the following change of ASG and SG concentrations:

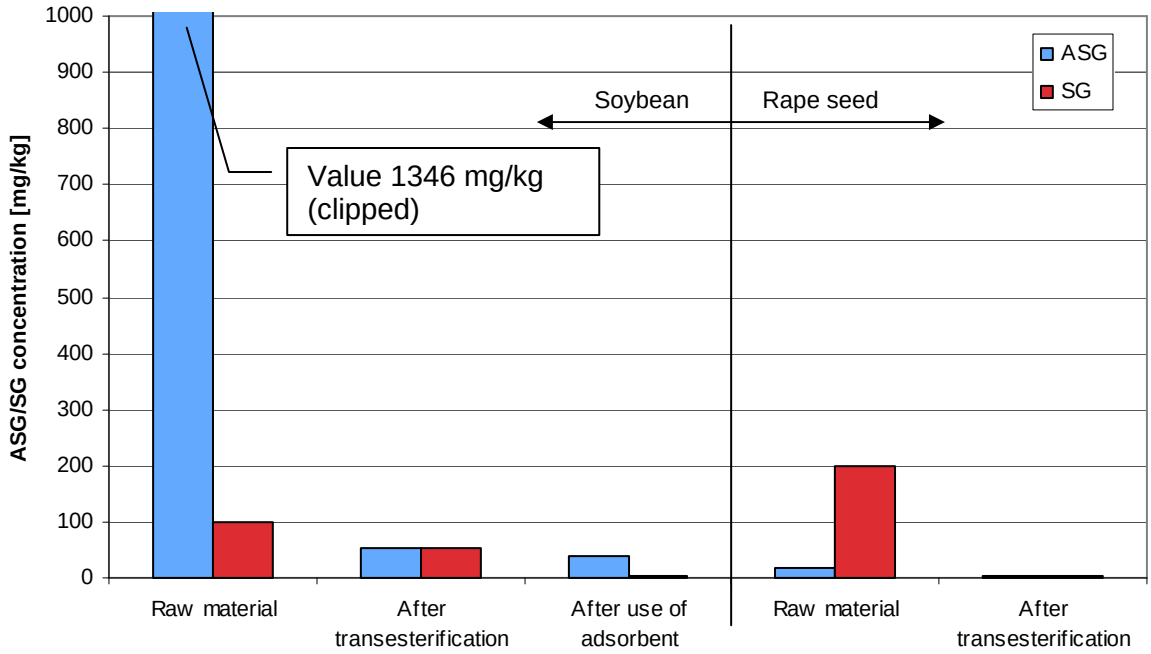


Fig. 9 Tendency of ASG and SG concentrations before and after transesterification

The tests 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 raw 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.

6 Filterability of Methyl Esters and Blends

Besides the evaluation of residual concentrations of SGs and ASGs filterability is also a main criterion of the FAME properties. Finally not only the filterability of the FAME itself must be in a proper range but also those of the blended fuels. Meanwhile several filterability test methods with different philosophies exist. Besides the ASTM draft “Cold Soak Test” the so called “Filter blocking tendency” is used increasingly. This automated test method based on a filtration by pressure reduces the operator’s influence which is typically the most critical point for filterability tests.

The study results of Filter blocking tendency (FBT) according IP 387 (B) are shown in tab. 4

Tab. 4 Filter blocking tendencies of different fuels/blends

No.	**Sample**	**FBT (IP 387 (B))**
1	FAME (soybean oil based)	10.3
2	FAME (rape seed 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

The conclusions obtained from tab. 4 are

- Both SGs and ASGs can cause bad filterability of FAME (not only SGs as often mentioned)
- ASG concentrations above the detection limit of the used method leads to a remarkable decrease of filterability
- Low values of FAME FBT values are not a guaranty to get a proper FBT value of the blended fuel

The reason for the last phenomenon is not completely clear but it can be assumed that the solubility of the ASGs and SGs in the blend is lower than in the original FAME and leads to a further aggregation of small particles which can interact with filter pores.

While up to now no proven or general accepted limit for FBT values exists the found results on FAME and blended would be considered as bad fuels. The efforts must be directed to reduce all kinds of minor components in FAME which increase the risk for filter blocking.

7 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 rape seed 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 rape seed 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 raw oils or less processed oils.

The biodiesel process also reduces the remaining concentration of these minor components, but in case of risk-entailing raw materials this reduction potential is not big enough.

If raw 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.

Not only SGs but also ASGs can cause filterability problems of the FAME. Already comparatively low concentrations lead to a remarkable negative impact.

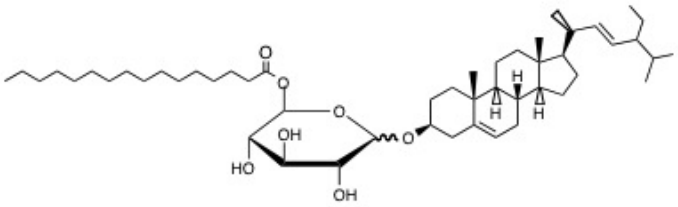
The implication of residual amounts of SGs and ASGs for the filterability of blended fuels is impressive but corresponds with former results. A mix-down of the problem can not be expected.

The use of adsorbents could be a possible solution for a post-processing of FAME. A potential technology development has to consider that ASGs and SGs can only be removed with a different efficiency. Another issue is to prevent an only one-way use of the adsorbent. The internal recycling is more favourable. This is a general economical and also ecological challenge for adsorption processes for purification of products but not easy to solve.

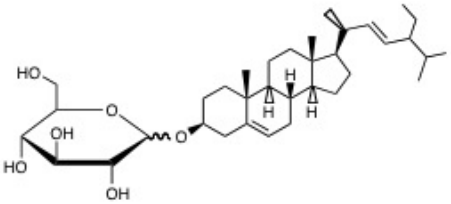
8 Description of the Determination of Sterol Glucoside Content

8.1 Introduction

At the moment there is no standard method established for the determination of sterol glucosides in vegetable oil or fatty acid methyl esters (FAME). Within the scope of the project it was decided to use a procedure on the basis of high performance thin layer chromatography (HPTLC) because with this method it is possible to determine both types of sterol glucosides. The acylated sterol glucoside (ASG) and the non-acylated sterol glucosides (SG) are quantifiable separately. Fig. 7 shows two examples of an ASG and SG.



example of an acylated sterol glucoside (ASG)



example of a non acylated sterol glucoside (SG)

Fig. 10 Examples of ASG and SG

With the commonly known gas chromatographic (GC) methods it is not possible to determine ASG and SG separately because the ASG molecules do not pass the GC system without chemical conversion. Thus it is usually necessary to saponify the ASGs first and transfer them into a non-acylated sterol glucoside. After that it is possible to determine both types as sum parameter. The alternative high performance liquid chromatography (HPLC) is quite difficult to adjust to the sterol glucosides because these components are soluble in pyridine or THF/Water mixtures only. Usually these kinds of solvents are not applied in the HPLC sector because of several reasons. The main reason is that the interactions between the solid phase and the target compounds are hindered because of the unavoidable additional interaction between solvent and liquid phase.

8.2 HPTLC – Method Description

In a first step the sample (vegetable oil or FAME) is diluted in a solvent mixture of tert-butyl methyl ether in heptane (1:2). After that it is fractionated with a solid phase extraction (SPE) column as shown in fig. 11. The column is a standard silica gel column.

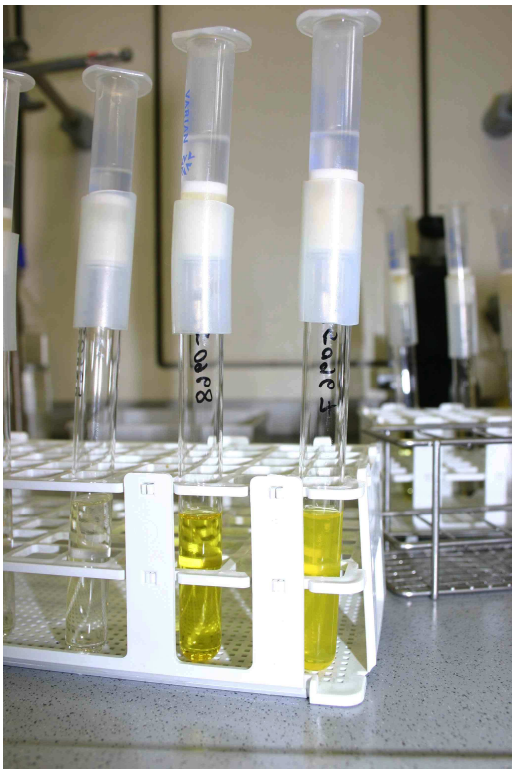


Fig. 11 Solid phase extraction of samples

The ASG-/SG-fraction can be eluted from the column with acetone and methanol. After that the solvents have to be removed to dryness of the sample before it is redissolved in THF/Water. 5 µL of each sample are applicated with a special thin layer sampler (refer to fig. 12) on a thin layer chromatography (TLC) plate. It is possible to measure up to 14 samples in parallel together with 6 calibration solutions.

Fig. 12 TLC sampler

On fig. 13 TLC plate is shown together with the marked sectors of the ASG and SG bands.

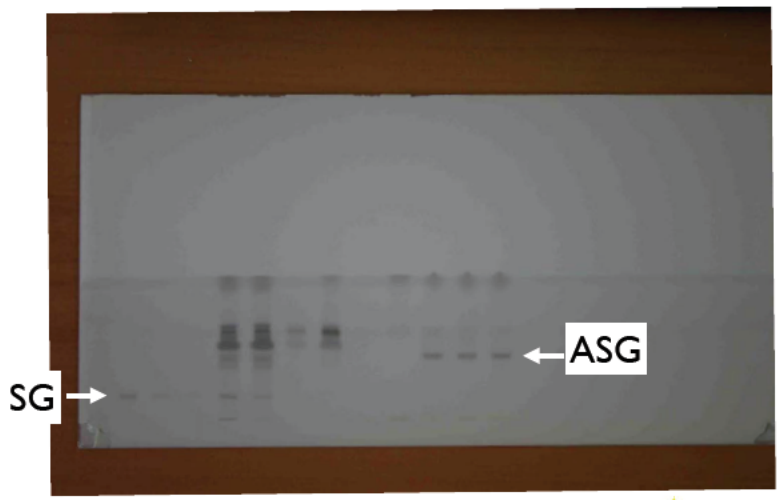


Fig. 13 TLC plate with SG and ASG bands

For the analysis a TLC scanner is used that works with visible light and is shown in fig. 14.

Fig. 14 TLC Scanner

In the end it is possible to determine the ASG/SG-contents via a software based calculation programme. At the moment the limit of quantification of the HPTLC – method is at 5 mg/kg. As an example a typical chromatogram is shown in fig. 15.

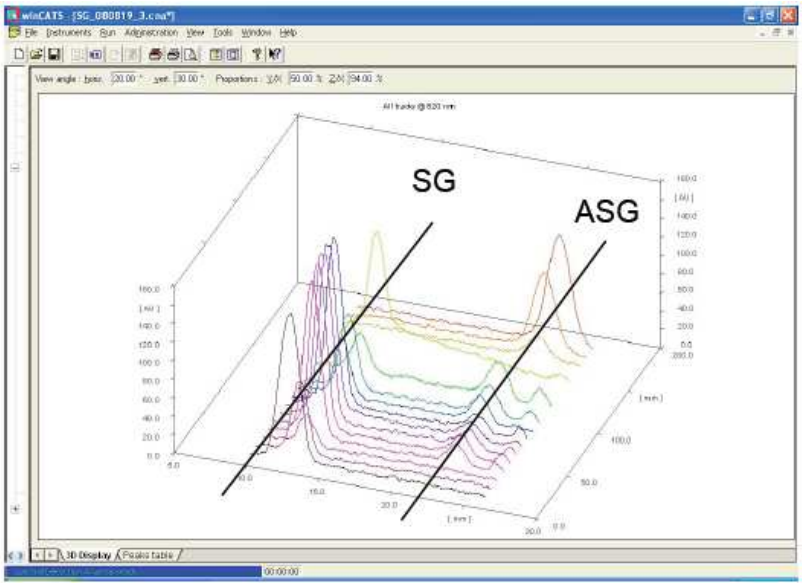


Fig. 15 Example of a HPTLC chromatogram

9 References

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10 Annex: Abbreviations

ASG	Acylated sterol glucosides
FAME	Fatty acid methyl ester (the chemical description of “biodiesel”)
FBT	Abbreviation for “Filter blocking tendency”, a test method according IP 387
HPTLC	High Performance Thin Layer Chromatography
OM	Oil mill, part of the anonymized sample source description
SG	(non-acylated) glucosides
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
% (m/m)	Concentration in percent per mass

The whole analytical work for this project was done by

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an accredited lab for biofuels testing. All photographs of test equipment in chapters 5 and 8 are provided by Analytik-Service GmbH.

Done as per 30/07/2009