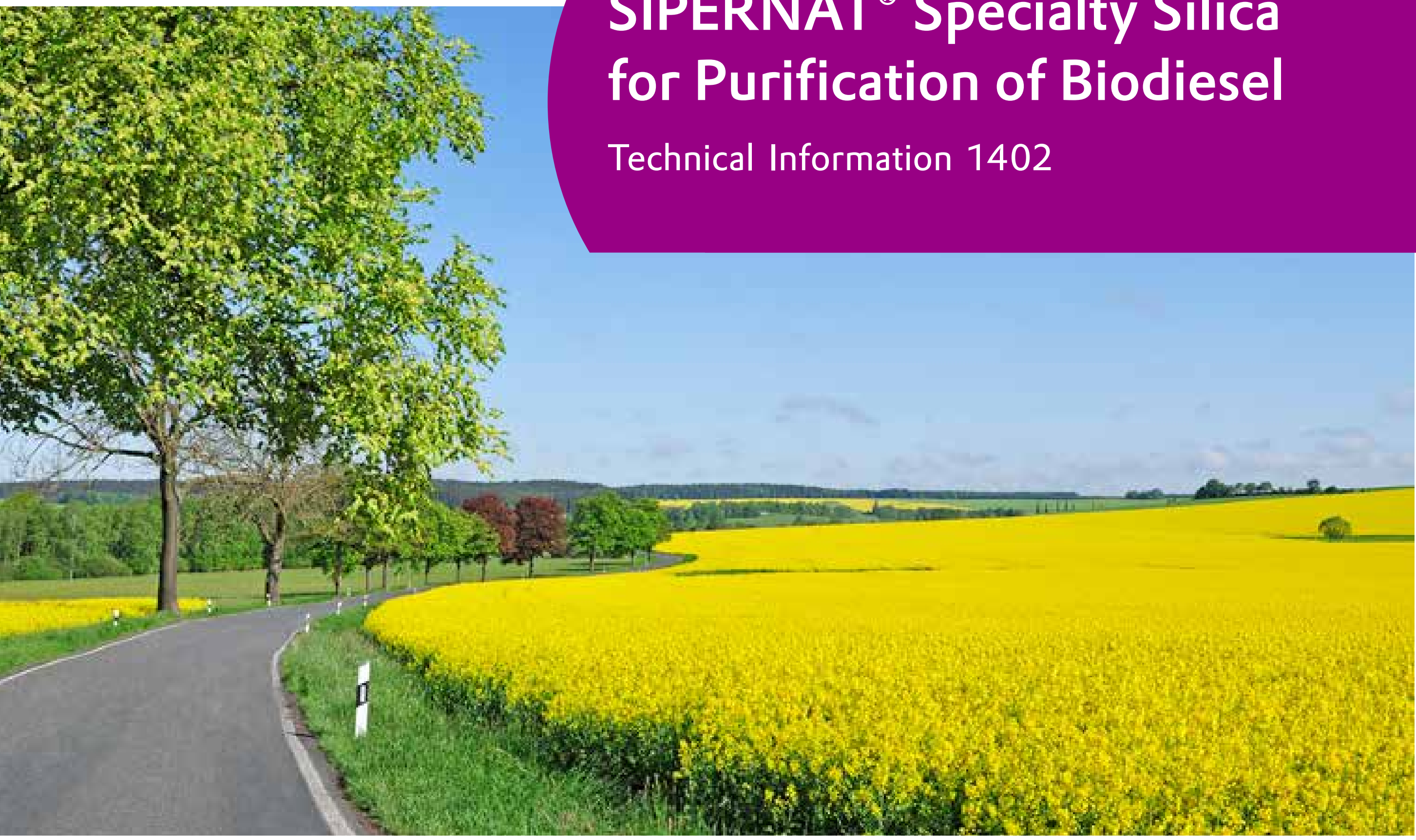
SIPERNAT® Specialty Silica for Purification of Biodiesel

Technical Information 1402



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Economical way to improve biodiesel filtration

Introduction

SIPERNAT® Specialty Silica has been independently confirmed to work as well or better than other absorbents available on the market to purify biodiesel from soaps, glycerin, free fatty acids, and methanol. Out of these potential contaminants, recent research of Evonik has revealed that SIPERNAT® Specialty Silica products perform extremely well at lowering the soap amount. Not only are SIPERNAT® Specialty Silica products great biodiesel purification agents, but they also allow the producer to improve their production flow rates, and reduce the amount of dry wash material in the final product.

Filtration is a Necessity for Biodiesel Production

Common Contaminants:

Biodiesel is produced from multiple feedstock sources such as soy, canola, palm, jatropha, waste vegetable oil (WVO), or animal fats. Each feedstock has different contaminates that must be removed to adhere to ASTM D6751, EN 14214 and other standards for B100 fuel and blending. Programs such as BQ 9000 help promote the commercial success and public acceptance of biodiesel by assuring the fuel is produced following ASTM D6751. Contaminates that must be removed to fulfill these requirements include:

- **Virtual Elimination of Soap**
  - Lab tests show nearly total removal of soaps which results in less emulsions and more productivity.
- **Free and Total Glycerin**
  - Free glycerin refers to the remaining glycerin in the biodiesel that is produced as a by-product of the fat hydrolysis that has not been removed. Total glycerin is the sum of the free and bound glycerin. Bound glycerin refers to the mono-, diglycerides, or the unreacted/partially reacted reactants, of the reaction.
  - Removal is important because when heated, or exposed to alkaline pH, glycerol tends to polymerize by condensation with other molecules of glycerol or glycerides. Once polymerized, the molecules form gums that foul injection systems, prevent proper fuel atomization and plug fuel filters.
  - Too high glycerides content has a negative impact on the Cold Filter Plugging Point (CFPP) and other cold flow properties.
- **Free Fatty Acids (FFA)**
  - FFA slowly oxidize in the presence of atmospheric oxygen. The oxidized material can cause motor damage.
- **Metals**
  - Metals catalyze oxidation and polymerization reactions of hydrocarbons. Heavy metals promote auto oxidation of fatty acids. Alkali metals (Sodium, Potassium) form sediments and cause injector failure, form soaps and contribute to insolubles.
- **Additional contaminants:** Alcohol, Calcium, Magnesium, Phosphorus, Sulfur, and others.

Purification Technologies:

Ensuring that a processed feedstock can meet BQ9000 purity specifications is vital, but can prove a challenge for producers who frequently change their feedstock. Purification techniques typically include water washing, resin ion-exchange columns and dry washing.

- Water washing removes water soluble contaminants, but may leave behind emulsions or soaps. The advantage is simplified waste disposal in the form of wastewater, however, a large amount of wastewater is produced. Water can be difficult to separate if soaps are present. Water washing will not remove oil soluble contaminants such as monoglycerides. SIPERNAT® Specialty Silica can improve water washing by removing more contaminants from the biodiesel than water alone. SIPERNAT® Specialty Silica can also remove soaps, proteins and sulfur.
- Resin ion-exchange columns are an upgrade from water washing, however there are two major concerns: contamination of the resin column resulting in high cost of replacement and difficulty in disposing of the spent resin column. SIPERNAT® Specialty Silica can protect the resin column from contamination prolonging its life.
- Dry washing removes impurities by absorbing them on highly porous precipitated silica. The advantage is the ability to remove a wide range of contaminants. While a disadvantage to this process is the possible loss of biodiesel on the silica, with the use of SIPERNAT® Specialty Silica dry washing is very efficient and the drying step can be eliminated in most cases.

Using Silica as a Filtration Aid

When added to the oil after glycerin extraction, SIPERNAT® Specialty Silica has the ability to absorb impurities. The very high surface areas of SIPERNAT® Specialty Silica products have a high concentration of hydroxyl groups. These OH-groups will absorb many of the contaminants that are present in unpurified biodiesel including soaps, glycerin, free fatty acids, methanol, and heavy metals. Dry washing, unlike water washing, does not add water to the system and eliminates the need for the extra drying step. Dry washing also has the ability to filter high contaminant feed stocks in a single pass, as opposed to the multiple water-washes needed if a water wash system was used.

Added benefits of SIPERNAT® Specialty Silica include:

SIPERNAT® Specialty Silica is easy to add to existing production facilities:

- The material can be added before transesterification to remove soaps, or protein, or to remove traces of glycerin in the methyl ester. All that is required is agitation of the tank and filtration of the material on a leaf filter or filter press.
- It can be added on a column or leaf filter so that the oil can be filtered in a continuous process. As one column is saturated, the flow can be switched to a second column, while the first one is discarded and replaced.

Added benefits from Dry Washing with SIPERNAT® Specialty Silica:

- SIPERNAT® Specialty Silica is synthetic amorphous silicon dioxide. Since it is synthetic, it has reproducible physical and chemical properties which insures reliable performance.
- Currently, producers are using 2 or 3 different solid filtration materials to solve various problems. SIPERNAT® Specialty Silica may replace one or more of these dry wash systems or it can supplement systems to improve performance or reduce dependency on any one system such as resins. This may improve performance and save money over the current systems.

Soap Removal:

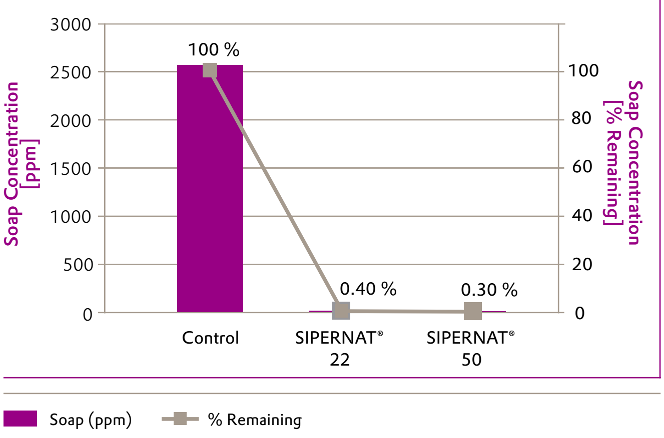
Biodiesel made from WVO was measured for soap content using an acid titration. The biodiesel is diluted in isopropyl alcohol and a bromophenol blue pH indicator is added. Hydrochloric acid is titrated into the solution until the color changes. It was then filtered with SIPERNAT® Specialty Silica products and the soap content was measured again. The result showed near total removal of soaps well below ASTM limits.

Table 1 Soap removal from WWO by SIPERNAT® Specialty Silica

Grade	Soap (ppm)	% Reduction
Control	2,570.4	
SIPERNAT® 22	10.43	99.6 %
SIPERNAT® 50	8.07	99.7 %

Soap limits for biodiesel according to ASTM D664 are 41 ppm for NaOH reacted biodiesel and 66 ppm for KOH reacted biodiesel.

Figure 1 Soap Concentration after filtration with SIPERNAT® silica products



Total Glycerin Reduction:

Glycerin removal has been tested in both a continuously stirred batch system and in a vertical filtration column. The biodiesel filtered was analyzed by gas chromatography in accordance to ASTM D6584.

Biodiesel produced from a variety of feedstocks was dry washed with SIPERNAT® Specialty Silica to reduce the total glycerin content. The three grades of SIPERNAT® Specialty Silica, which have shown the most promising purification results are SIPERNAT® 22, SIPERNAT® 50, and SIPERNAT® 2200. All three grades are hydrophilic silica with high absorption capacities. **Tables 2** and **3** below show the results of stirred experiments in which 0.5 % and 1.0 % of silica by weight of biodiesel were tested. This testing was done with two WVO sources of varying contamination levels; note that the second source had significantly higher contamination.

Table 2 Total Glycerin Levels (wt %) in WVO based biodiesel after dry washing with SIPERNAT® Specialty Silica:

Washing Material Used	Total Glycerin content wt%
Unwashed B100 (**source 1**)	0.483
0.5 % SIPERNAT® 50	0.200
0.5 % SIPERNAT® 22	0.200
0.5 % SIPERNAT® 2200	0.190

Table 3 Total Glycerin Levels (wt %) in WVO based biodiesel **with different sources** after dry washing with SIPERNAT® Specialty Silica:

Washing Material Used	Total Glycerin content wt%
Unwashed B100 (**source 2**)	0.833
1 % SIPERNAT® 50	0.330
1 % SIPERNAT® 22	0.307
1 % SIPERNAT® 2200	0.407

* Values for the washed waste vegetable oil (WVO) samples were calculated independently by Paradigm Sensors in a blind study. B100 specification ASTM 6751-11a: limit for total glycerin is in accordance to ASTM D 6584 is 0.240 max

Table 2 shows that SIPERNAT® Specialty Silica performs well at dropping the glycerin level to an acceptable range within the B100 specification of 0.240 wt%. The second WVO source was quite contaminated and although the silica amount required in the wash step would have had to be used above 1 % by weight in order to meet B100 specifications, SIPERNAT® Specialty Silica still performed well, removing approximately 60 % of the glycerin.

Mono- and Diglyceride Removal:

The reduction of the mono-, and diglycerides were examined in a soy methyl ester (SME) feedstock. This filtration was performed in a vertical filtration column. Approximately 300 mL of biodiesel was passed through 15g of each grade of silica. **Table 4** below displays bound glycerine levels remaining in the biodiesel. It is this value that would be added to the percent glycerin in the biodiesel to determine the value of the Total Glycerin. All three grades reduce the amount of bound glycerin in the biodiesel well below the B100 specification of 0.220 wt%.

Table 4 Bound Glycerin Levels in SME Source 3 at Room Temperature

Washing Material Used	Total Bound Glycerin (wt%)
Unwashed B100	0.101
SIPERNAT® 50	0.063
SIPERNAT® 22	0.063
SIPERNAT® 2200	0.072

B100 specification ASTM 6751-11a: limit for bound glycerin in accordance to ASTM D 6584 is 0.220 weight-% max

Concentration studies were done with SIPERNAT® 22 and diatomaceous earth to measure the influence of concentration on removal efficiency. **Table 5** shows the weight percent of monoglycerides, the glyceride, which adds most significantly to the total bound glycerin count, in the biodiesel after going through a stirred dry wash system. These tests were performed by varying the amount of dry wash material that the biodiesel came in contact with.

Table 5 Bound Monoglyceride Levels in SME Source 3 with varying concentrations of dry wash material in a stirred system at 20 °C

Concentration of dry wash material in Biodiesel (g/mL)	Bound Monoglycerides (% by wt) Material: SIPERNAT® 22	Bound Monoglycerides (% by wt) Material: diatomaceous earth
0	0.133	0.133
0.040	0.101	0.108
0.049	0.098	0.108
0.060	0.095	0.112
0.100	0.085	0.109

B100 specification ASTM 6751-11a: limit for bound glycerin in accordance to ASTM D 6584 is 0.220 max

The removal with SIPERNAT® 22 was shown to be almost linear. The test performed with diatomaceous earth demonstrated only a slight removal and no trends were observed with increasing the overall concentration. As predicted the lack of surface functionality in the form of hydroxyl groups in the diatomaceous earth cause this material to not be a suitable choice when bound glycerin filtration is necessary.

Acid Number:

The presence of large amounts of free fatty acids (FFA) formed from the hydrolysis of ester linkages causes a high acid number in biodiesel. As previously said, the presence of these FFA cause motor damage and must be maintained at the ASTM specification of 0.5 (mg KOH/g of biodiesel). Various feedstocks were tested for their Acid Value post trans-esterification and glycerin extraction. **Table 6** shows the results of biodiesel purified with SIPERNAT® Specialty Silica.

Table 6 Acid Values of B100 biodiesel based on various Feedstock Pre & Post Dry Wash(mg KOH/g of biodiesel)

Washing Material Used	WVO*	Soybean Oil	Canola Oil
Unwashed B100	0.710	0.731	1.477
1 % SIPERNAT® 50	0.085	–	–
1 % SIPERNAT® 22	0.077	0.031	0.084
1 % SIPERNAT® 2200	0.060	0.030	0.029

* Values for the washed waste vegetable oil (WVO) samples were calculated independently by Paradigm Sensors in a blind study.
B100 specification ASTM 6751-11a: limit for acid number in accordance to ASTM D 664 is 0.5 max

Samples were tested at identical weight percent in unwashed B100 samples in a blind study. Every silica grade reduced the Acid Value to below the ASTM requirements.

Methanol Content:

Methanol is one of the reactants used to produce biodiesel. While most of it is consumed in the reaction, trace amounts will remain in the system. SIPERNAT® Specialty Silica has also proved to successfully reduce the methanol content of biodiesel.

Table 7 Methanol Content in WVO Post Dry Wash: weight %

Washing Material Used	Methanol
Unwashed B100	0.3
1 % SIPERNAT® 50	0.1

* Values for the washed waste vegetable oil (WVO) samples were calculated independently by Paradigm Sensors in a blind study.
B100 specification ASTM 6751-11a: limit for methanol content in accordance to EN 14100 is 0.2 max

Processing and Production Effects of Silica

Filter column systems:

Physical characteristics affect the flow rate of the system and how glycerides are absorbed. High density products can significantly drop the flow rate of the oil through production. An excess of small particles can lead to a drop in pressure as the column becomes plugged.

Table 8 Physico-chemical properties of SIPERNAT® Specialty Silica grades particularly suitable for dry wash biodiesel purification

Products	d_{50} Particle Size, laser diffraction µm)	Tapped Density (g/L)	DOA Absorption (ml/100 g)	Loss on Drying (%)
SIPERNAT® 50	50	180	295	≤ 7
SIPERNAT® 22	120	260	235	≤ 7
SIPERNAT® 2200	320	250	225	≤ 7

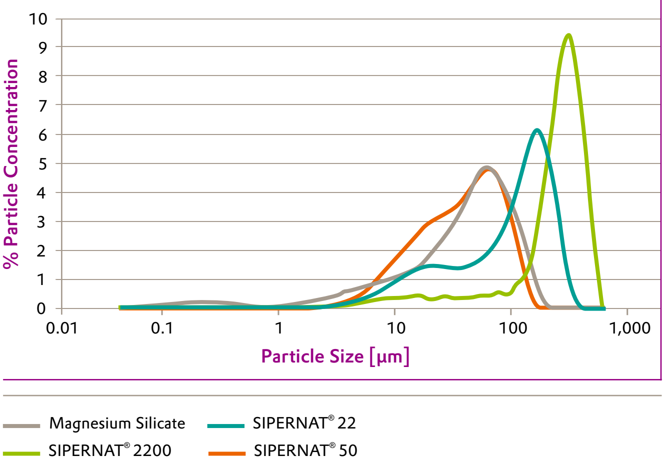
To measure the difference in flow rates 0.2 grams of glass wool was placed on the bottom of a 50 mL filter column. Two grams of each SIPERNAT® Specialty Silica grade were added on top of the glass wool. B100 from a WVO source was then poured onto the dry wash material to simulate a purification column. The amount of B100 in the centrifuge tube was kept constant in order to keep the pressure on the dry wash material consistent. The gravity flow rate was calculated for the different samples tested. In comparison to a commercial magnesium silicate, SIPERNAT® 50 had equal filtration flow rate while SIPERNAT® 22 had 46 % better flow rate and SIPERNAT® 2200 had 692 % better flow rate.

For users looking to use dry wash in a column the best silica with regards to flow is SIPERNAT® 2200. Due to its large particle size and lower density the material is able to substantially increase the production rate compared to other grades.

Filter bag systems:

Fine particles are a concern when using a solid material as a purification agent. If the dry wash material is so small that it can pass through the filter mesh, then, there will be solid particulates in the biodiesel, further contaminating it. A high percentage of these solid particles will lead to problems downstream. **Figure 2** displays the particle size distribution for SIPERNAT® Specialty Silica along with Magnesium Silicate, a material also used in biodiesel purification.

Figure 2 Particle size distribution using light scattering of various SIPERNAT® Specialty Silica grades recommended as dry wash materials in comparison to Magnesium Silicate



Evonik supplies products over multiple particle sizes and particle size distributions. Unlike magnesium silicate the SIPERNAT® products for biodiesel do not have a high level of fine particles. Using a 3 micron filter would ensure that dry wash purification material is not present in the biodiesel. **Table 9** below shows the percent by volume that would pass through this size filter. It demonstrated that SIPERNAT® products should perform much better than the competition.

Table 9 Percent by volume that would pass through a 3 µm mesh filter

Dry Wash Material	% Volume Through 3 µm Mesh
Magnesium Silicate	5.73
SIPERNAT® 22	0.08
SIPERNAT® 2200	0.37
SIPERNAT® 50	0.18

Filter Efficiency:

Efficiency of the filter is determined by the amount of material it can filter before losing selectivity. The efficiency value for the three different grades of silica was tested using SME Source 3. In this test, biodiesel was run through a filter made with SIPERNAT® Specialty Silica in order to determine at which point the filter would be completely saturated with the target contaminants, and no longer an effective filter. Resin or diatomaceous earths were not used in making the filter. The point where the filter no longer removes contaminants was recorded. This was determined by testing for target compounds such as soaps and identifying the failure point. When the failure point was reached, the contaminant content rose sharply. **Table 10** shows these results.

Table 10 Efficiency of dry wash filters

Dry Wash Material	Biodiesel/Silica (mL/g)
SIPERNAT® 50	34.5
SIPERNAT® 22	20.5
SIPERNAT® 2200	22.5

SIPERNAT® 50 silica, which has the highest surface area and the highest standard absorption capacity, is predicted to be the best choice to filter out the undesired compounds from the biodiesel. This is demonstrated by the highest efficiency value out of all SIPERNAT® Specialty Silica grades tested in this study. The conditions of your filtration and the use of other filter materials will allow you to use SIPERNAT® products to polish biodiesel to the required blend standards.

When systems such as resins, chilling, oxygen removal, temperature and pressure, are combined under realistic industrial settings, additional efficiencies should be realized. Blends of SIPERNAT® Specialty Silica products and other products can result in even higher performance making use of the strong points and price of each type of product.

Summary

Purification of biodiesel is a requirement to meet BQ9000 specification. There are multiple ways to purify biodiesel, for example, water washing, resin ion exchange and dry wash. SIPERNAT® Specialty Silica can complement and enhance these methods. Producers can benefit greatly by using SIPERNAT® Specialty Silica as their dry wash purification agent because it removes a wide range of contaminants such as soaps, glycerin, methanol, mono- and di-glycerides, and others such as proteins and sulfur.

When used with water washing, SIPERNAT® Specialty Silica can be used to "polish" the biodiesel, remove water, and remove soaps alone or in combination with other filter materials.

Resin filtration can be improved by using SIPERNAT® Specialty Silica to protect the resin column.

The choice of silica depends heavily on the purity and the source of the feedstock. SIPERNAT® 50 has proved to be effective at removing bound glycerin. SIPERNAT® 2200 is not only efficient at reducing the total glycerin content but it is also the most efficient at reducing the acid value while increasing the process flow rate. SIPERNAT® 22 is an excellent choice for producers looking for a mid-range performance across all characteristics.

SIPERNAT® Specialty Silica products are excellent biodiesel purification agents. They allow the producer to improve their production flow rates, reduce the amount of dry wash material from the final product, and enable the flexibility of working with different feedstocks.

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