

# ***TULSION***<sup>®</sup>



## **BIODIESEL PRODUCTION: METHANOL, METALS AND MONOGLYCERIDES**

### ***T-45 BD & T-45 BD Macro***

#### **Methanol:**

A considerable amount of debate exists on whether or not to remove methanol (MeOH) prior to removing the contaminants such as soap, glycerin, trace metals and monoglycerides. For producers using the water wash method this is clearly the case and for a number of suppliers using dry wash methods some try to lower the MeOH concentration to less than 0.5%, while others have operated successfully at higher methanol concentrations.

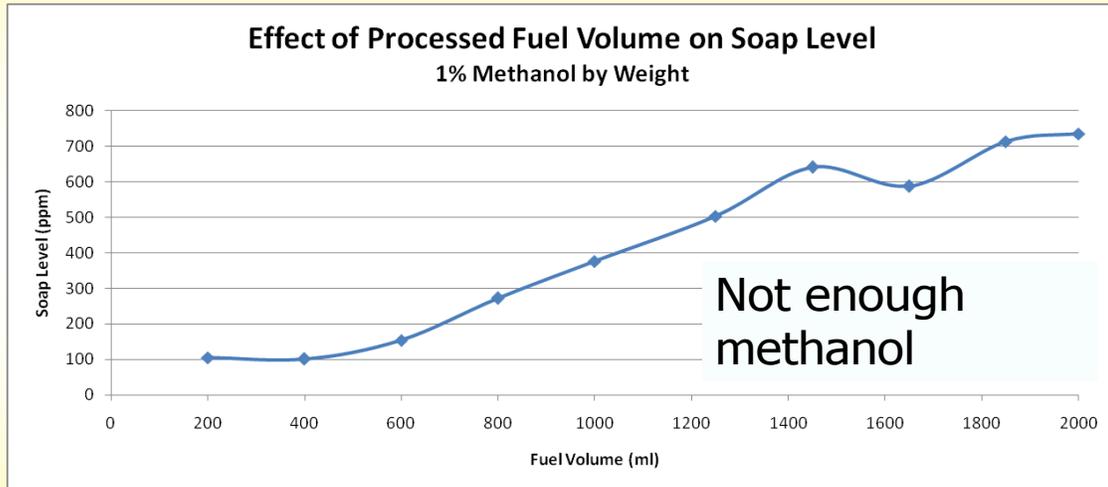
For dry wash systems in which ion exchange resins and / or cellulose are used or even in systems incorporating inorganic substrates such as magnesium silicate (e.g. Magnisol<sup>®</sup> XL) for the purification step, experience has shown that methanol is definitely required because it acts as both a transport agent for the contaminants and serves to inhibit the formation of the “glycerin sheet” that often forms on top of the resin bed, particularly when using gellular resins. It should be noted that the “glycerin sheet” either did not form or took much longer to form when producers used a macroporous resin such as T-45 BD Macro.

To quantify the effect methanol concentration has on the ability of ion exchange resins to function properly, Thermax commissioned a study at University of Idaho, College of Engineering under the auspices of Dr. Jon Van Gerpen to determine how best to operate dry wash systems. Graph 1 demonstrates the resins performance if only 1% methanol is used, while the curve in Graph 2 shows the expected effluent curve if an adequate concentration of methanol is employed.

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Graph 1

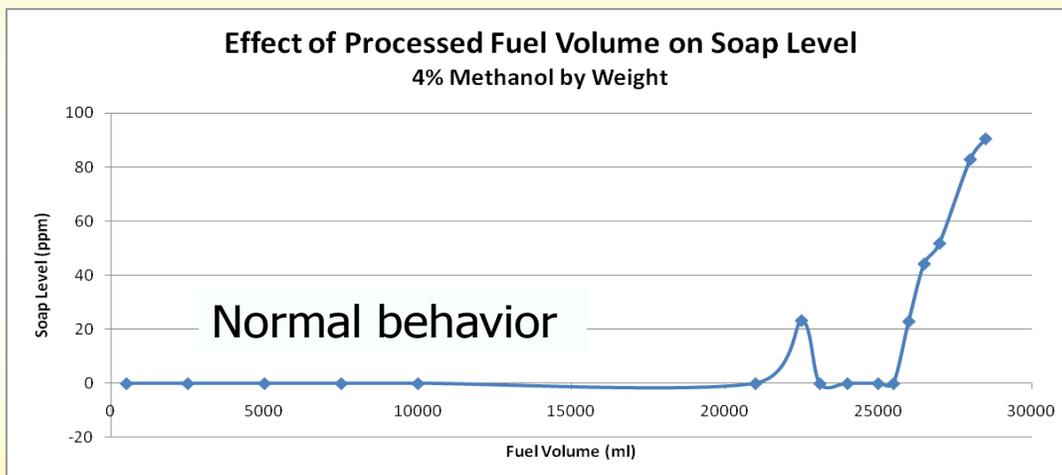
## Effect of methanol (1%)



1500 ppm initial soap level

Graph 2

## Effect of methanol (4%)



1000 ppm initial soap level

Regardless of the alkali catalyst used in trans-esterification of virgin or reclaimed oils to alkyl esters, the primary metals found in raw biodiesel fuel will be phosphorous primarily from the raw oil and sodium or potassium depending on the alkali catalyst used in the trans-esterification reaction. Trace quantities of other metals are present but the concentrations are so low, they are not listed in the B100 American Standard of Testing Materials specification (i.e. ASTM D-6751-07a).

While providers of inorganic purification media report moderate success in reducing the metal content of B100 fuel, it should be noted that the historical reason ion exchange media have been used for centuries was their metal removal capabilities. Today, there are hundreds of synthetic ion exchange resins with the vast majority being sulfonic acid functionalized – all used to capture metals. The basic property of cationic ion exchange resins is their ability to reduce metals to the “part per billion” (or  $\mu\text{g/l}$ ) level, well below the maximum concentration stated in D-6751-07a.

### Monoglycerides:

The last area this technical document will address is the ability of ion exchange resins to remove glycerin and monoglycerides. Figures 1 and 2 are gas chromatograph spectra of raw biodiesel before and after purification using Tulsion T-45 BD Macro.

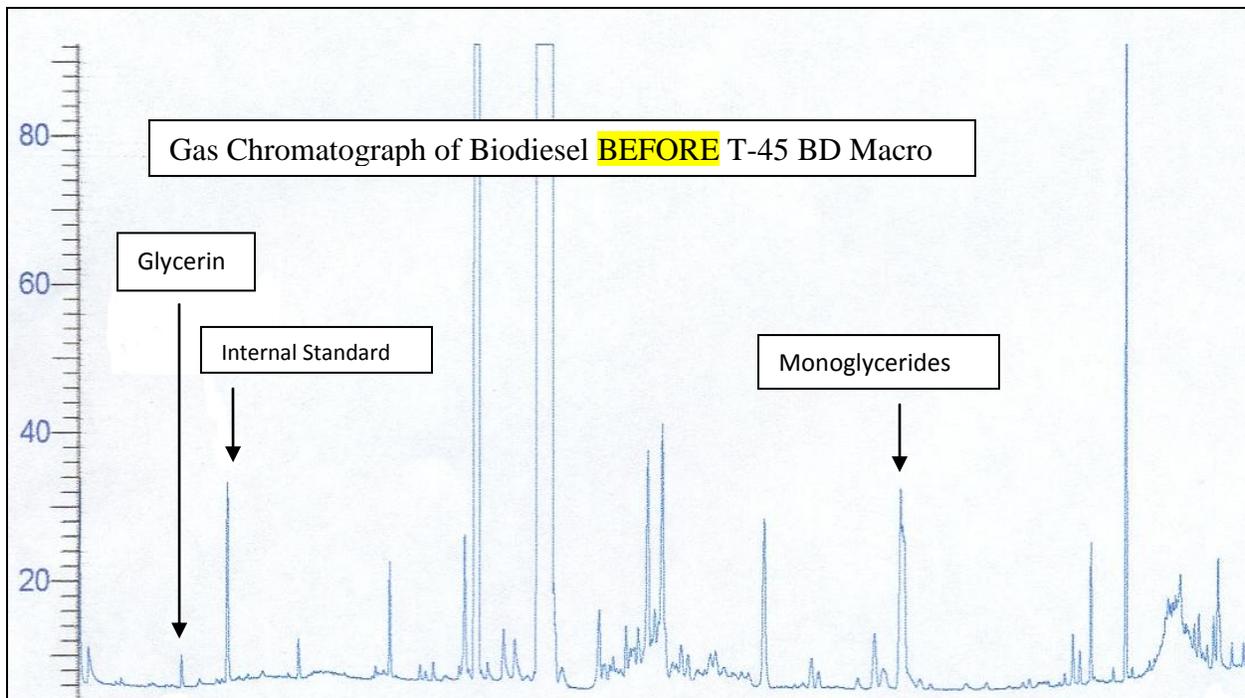


Figure1

It is well known that ion exchange and other dry wash media are able to remove free glycerin to below the 0.020% specified in the B100 standard. What is less well known is that ion exchange resins, particularly the macroporous version, are able to remove trace quantities of monoglycerides. Though it is uncertain if the mechanism is purely ion exchange or a combination of ion exchange and adsorption, the fact remains that producers of high quality B100 want to minimize or eliminate the concentration of this contaminant. See Figure 2 where the glycerin and monoglycerides peaks are barely above the limit of detection of this powerful analytical tool.

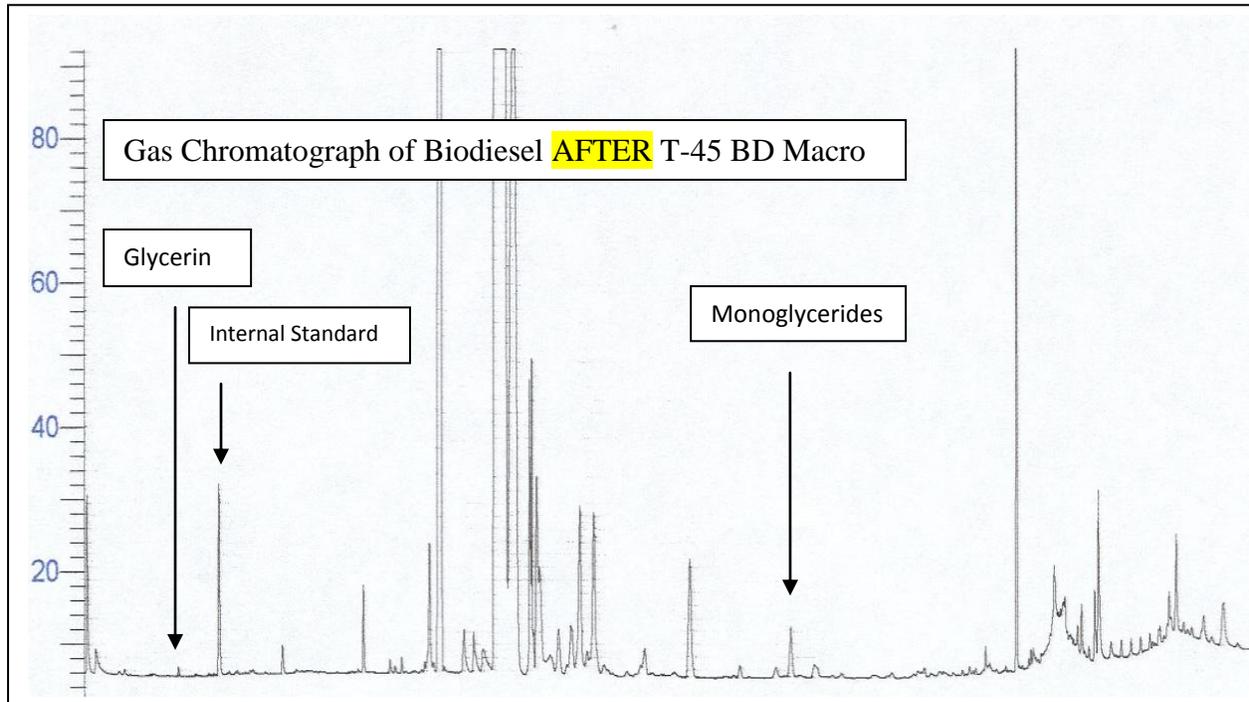


Figure 2



**THERMAX INC.**  
40440 Grand River Avenue, Novi,  
Michigan 48375, USA  
Tel# 248-474-3050, Fax# 248-474-5790

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