



BIODIESEL PRODUCTION: MACRO vs. GEL Why do Macro resins work better than gels?



This scanning electron microphotograph below is perhaps the easiest way to explain why macroporous resins are far more effective in removing contaminants such as glycerin, soap, residual metals and mono-glycerides from raw biodiesel. **It's the holes!** The contaminants to be removed have a known physical size and therefore a limitation if the moieties such as glycerin, soap, monoglycerides and metals are unable to penetrate into the interstitial spaces.



Figure 1: Scanning Electron Microscope photo of Tulsion T-45 BD Macro magnified 100X.

The "holes" or macropores evident in the above photo extend throughout the entire bead matrix. The large macroporous transport pores, non-existent in gellular resins, allow the inner area of the bead to be accessed for adsorption of polar molecules such as glycerol, monoglycerides and soap. See Figure 2.





The photomicrograph on the illustrates right the macroporous structure of T45 BD Macro. Transport pores, evident throughout the entire bead structure. facilitate adsorptive removal of contaminants by utilizing the entire internal surface area of the bead. The dramatically macro-pores increase the surface area of T45 BD Macro exposing the contaminants to a surface area 1000x greater than that measured in gel resins.



Figure 3: 100X magnification showing crosssectional scanning electron microphotograph of Tulsion T-45 BD Macro

For contaminant ions, such as residual metals from the catalyst that have an ionic charge, the transport pores allow the internal functional groups to be utilized. Since 90% of the

exchange sites are located within the bead and only 10% of the exchange sites located on the outside surface of the bead, it is imperative that a path exist to these exchange sites. Macro pores offer that path, which is not apparent with gel resins. Access to transport pores, internal functional groups and a large surface area are the key reasons why macroporous resins are more efficient than their gel counterparts.

While the contaminants to be removed are known and can be measured, the mechanism that describes how these contaminants are removed from the raw biodiesel is not known. It has been postulated that a number of mechanisms are used in combination regardless of the feedstock or method chosen to purify the raw fuel. Research funded by Thermax at University of Idaho, College of Agricultural and Life Sciences under the direction of Dr. Jon Van Gerpen, has identified four possible mechanisms "at play" during the purification of raw biodiesel. See data in Graph 1.



Graph 1: Adsorption vs. Ion Exchange

Generating these data allowed four mechanisms to be postulated, which are:

- 1. Mechanical filtration by the ion exchange resin bed.
- 2. Adsorption of polar moieties onto the surface area of ion exchange resins, cellulosics or inorganic substrates such as magnesium silicate.
- 3. Ion exchange of the weakly associated sodium ion (Na+) of a free fatty acid (FFA) molecule with the mobile counter-ion (i.e. H+) of T45 BD or T45 BD Macro.
- 4. A layer of glycerin coats the resin surface externally in the case of a gel resin; internal <u>and</u> external in the case of macroporous resin such as T435 BD Macro. The glycerin layer then captures the soap from the raw biodiesel solution.

Graph 1 illustrates that both ion exchange <u>and</u> adsorption are critical in the purification process regardless of the influent soap level. The key feature to note is that adsorption appears to be 30-35% of the purification process and as such, surface area then becomes of utmost importance.



Figure 4: 1500X magnification SEM photo of a gel resin showing surface characteristics. Left side of SEM shows stress fracture of weaker gellular structure. Right side of SEM shows no discernable transport pores to access internal surface area required for adsorption reactions to occur.



Figure 5: 1000X magnification of Tulsion T-45 BD Macro

The key differences between gel and macroporous resins can be attributed to large transport pores which allow the contaminants to have access to a large internal surface area where both adsorption and ion exchange reactions may take place. The high degree of cross-linking characteristic of macroporous resins makes them more robust and less susceptible to bead breakage under elevated temperatures and pressures often encountered when purifying raw biodiesel fuel.



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