Ion Exchange in Biodiesel Production

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Resins used in Biodiesel Production

Catalysis

Strong Acid Resin for Esterification of Fatty Acids (Developing)

Strong Basic resins for trans-esterification (Not efficient)

Biodiesel Purification

Absorption of

- Free Glycerin
- Waters and Methanol

Ion Exchange of Salts, Soaps and Catalyst

Glycerin Purification

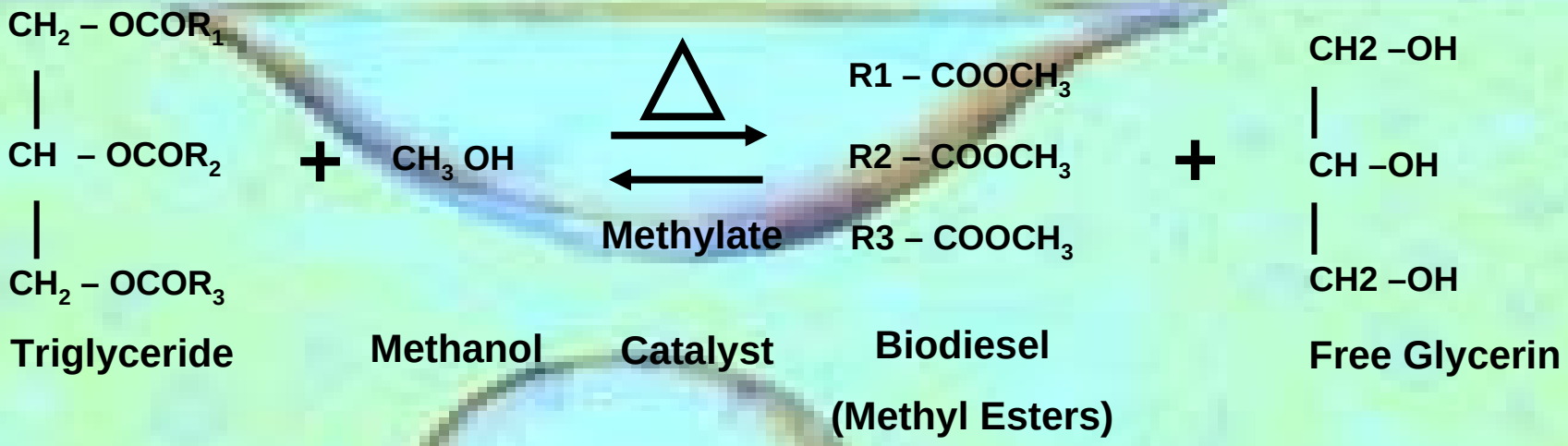
Chromatographic separation of salts (Not used at this time)

Color and ash removal (Not used at this time)

Trans-Esterification

Transesterification Converts Triglyceride (animal of vegetable oils) to Methyl-ester (BIODIESEL)

Soybean
Canola
Palm
Rape seed
Jatropha
Sunflower
Coconut
Used cooking
Animal fats



- Temperatures of 60-70 °C (140-160 °F), at atmospheric pressure
- Crude glycerin and crude biodiesel are separated

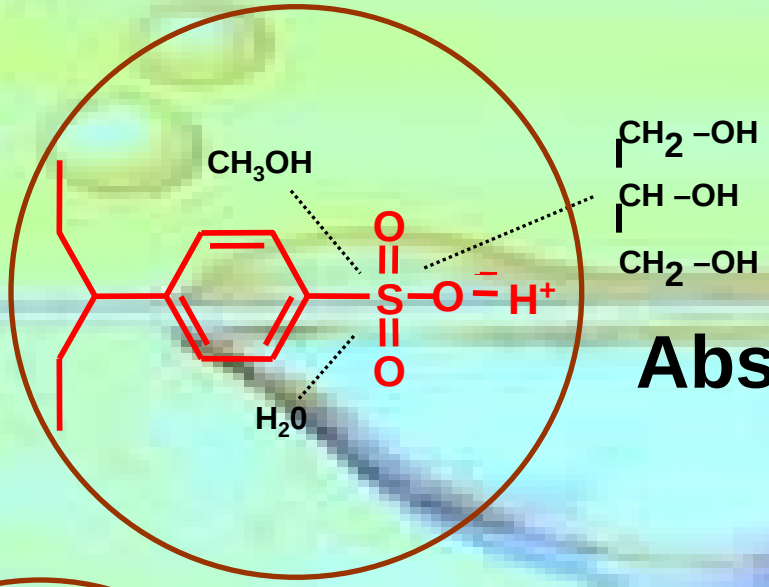
Purolite® PD206 Advantages

Purolite PD206	Water Wash	Inorganic Anhydrous Salts
Operating Cost $0.014/gal ($0.0037/litre)	Reported cost $0.08/gal ($0.021/litre) for water and disposal	Reported cost $0.12+ /gal ($0.032/litre) due to filter equipment needed
Low maintenance dry system	Medium to High maintenance Multiple washes, difficulty attaining < 500 ppm water	High maintenance replacing filters and removing sludge
No need to filter	Minimal filtration still necessary	Heavy Filtration needed
Low energy	High pumping and drying energy	Medium energy to circulate, settle and filter solids
No waste disposal costs	Waste water treatment or water disposal issues	Disposal costs for spent media plus fire hazard
No water required	Several water wash stages required.	No water required

General Technical Data

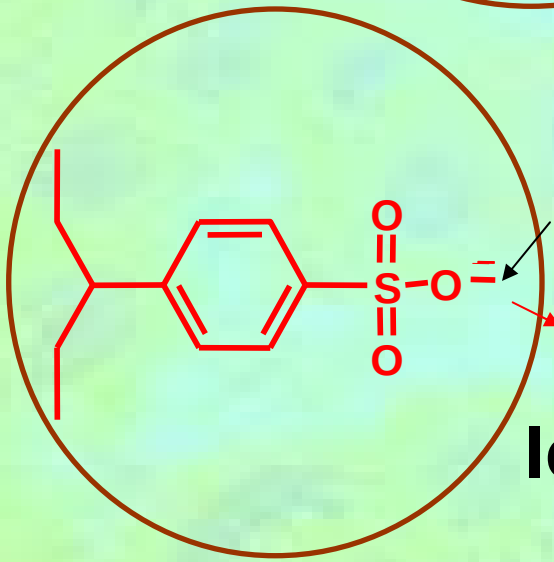
PUROLITE® PD 206 PHYSICAL AND CHEMICAL PROPERTIES	
Appearance	Hard spherical beads
Functional Group	$R\text{-}SO^-_3$
Ionic form (as shipped)	H^+
Moisture Holding Capacity	<3 %
Bulk Density	800-830 g/dm^3 (litre) (48-50 lbs/ft^3)
Specific Gravity	1.20
Chemical Resistance	Insoluble in all common solvents
Operating Temperature	<150 ºC (<300 ºF)

Purolite® PD206 functions



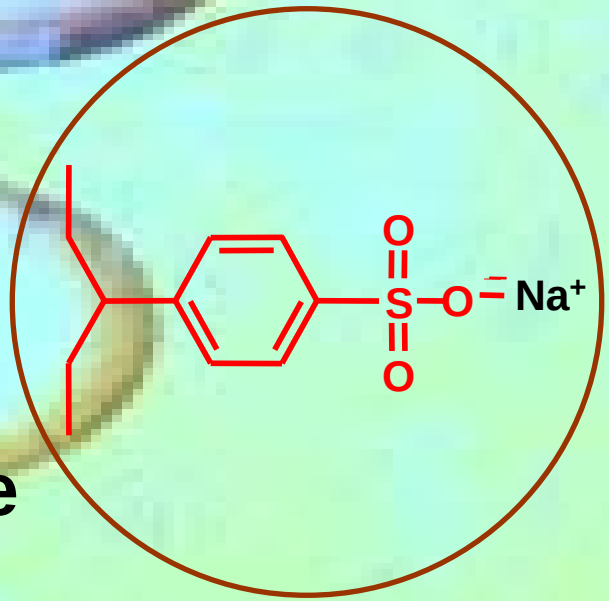
CH_2 –OH
CH –OH
CH_2 –OH

Absorption



Soap
and
Na-OCH_3

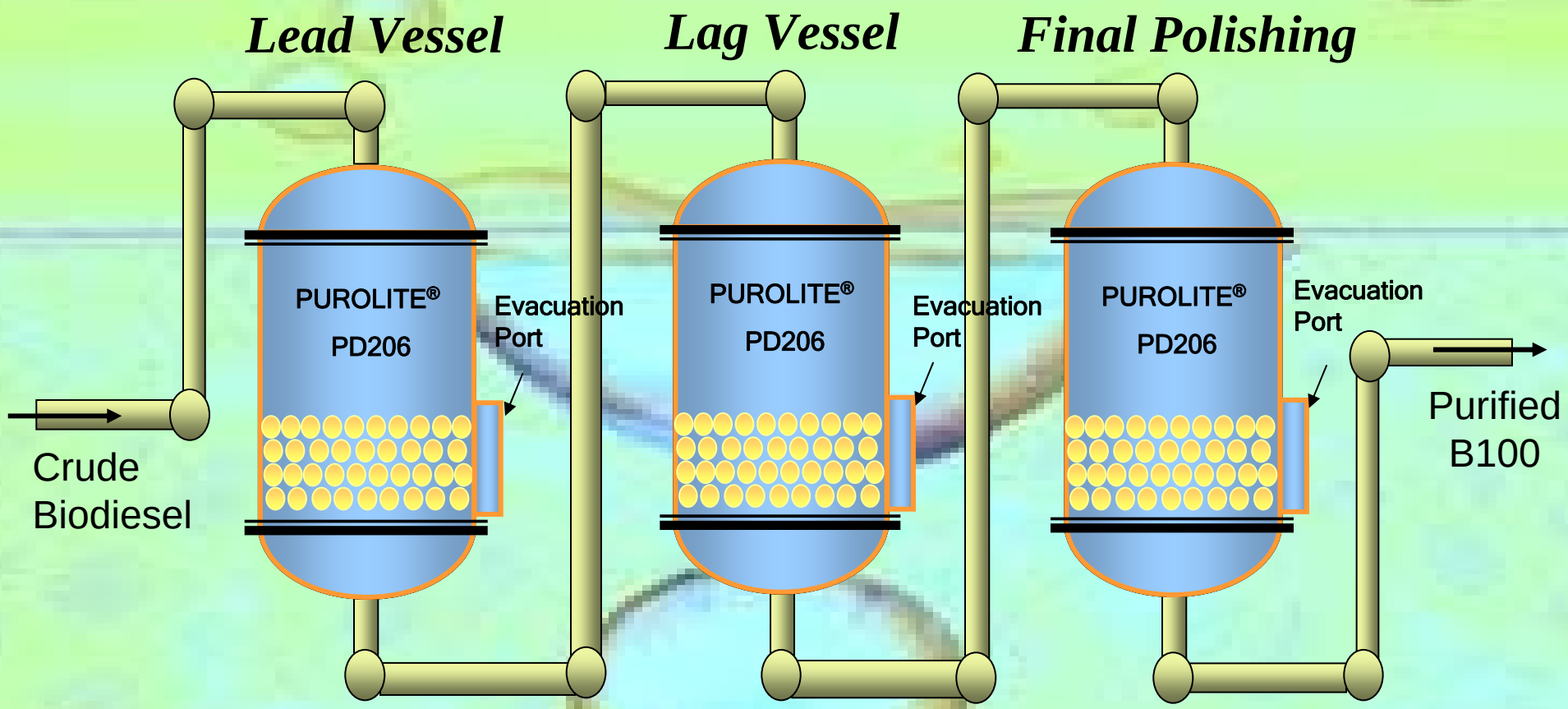
H-OCH_3 & FFA



+ CH3OH + FFA

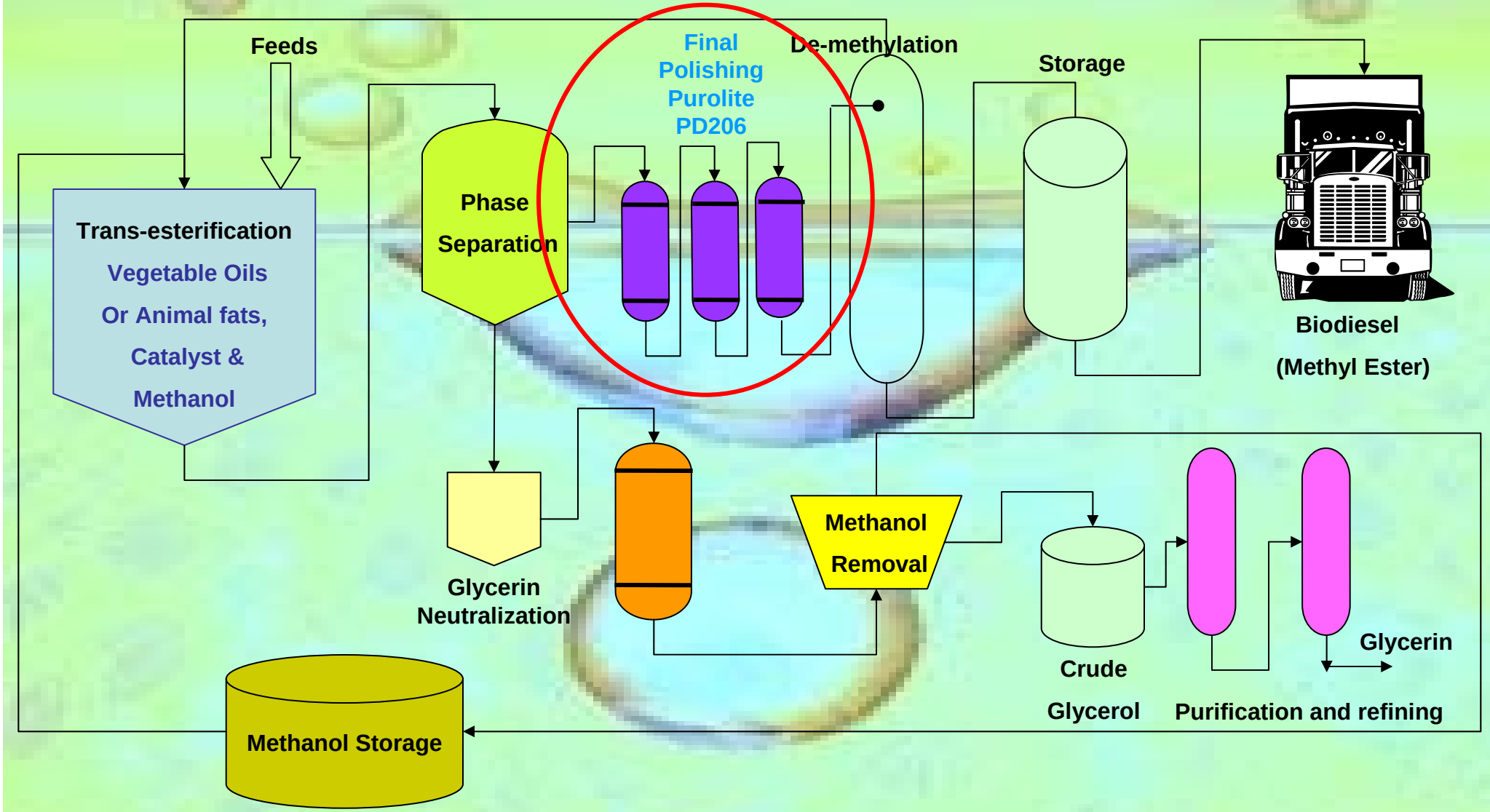
Ion Exchange

Purification Towers

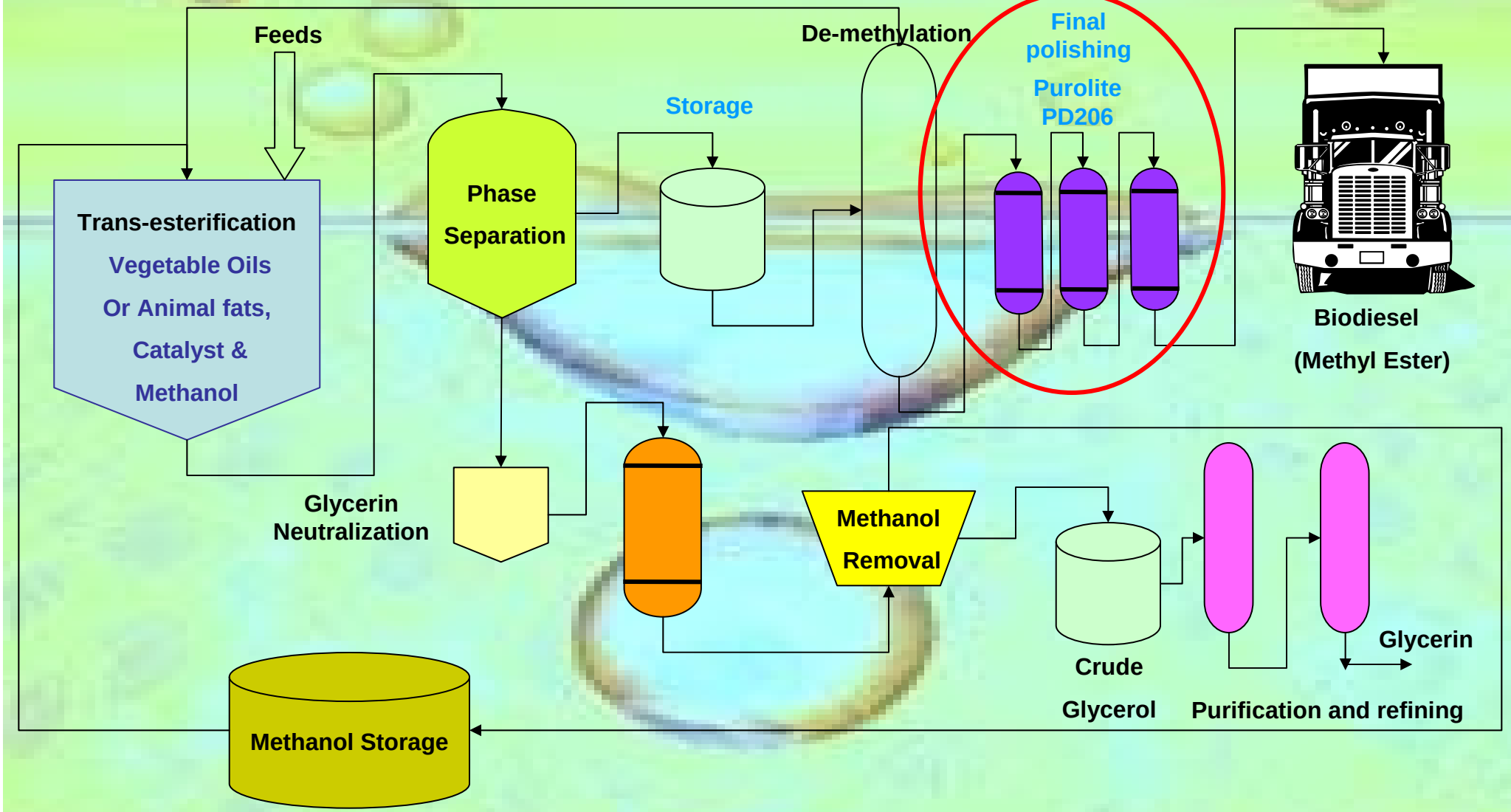


OPERATING INFORMATION	
Freeboard	>150%
Flow rates	2.5-3.0 BV/h
Temperature	Ambient to 60º C (140 ºF)
Minimum bed depth	60cm (24 inches)
Screen size	<150 microns

Polish before demethylation



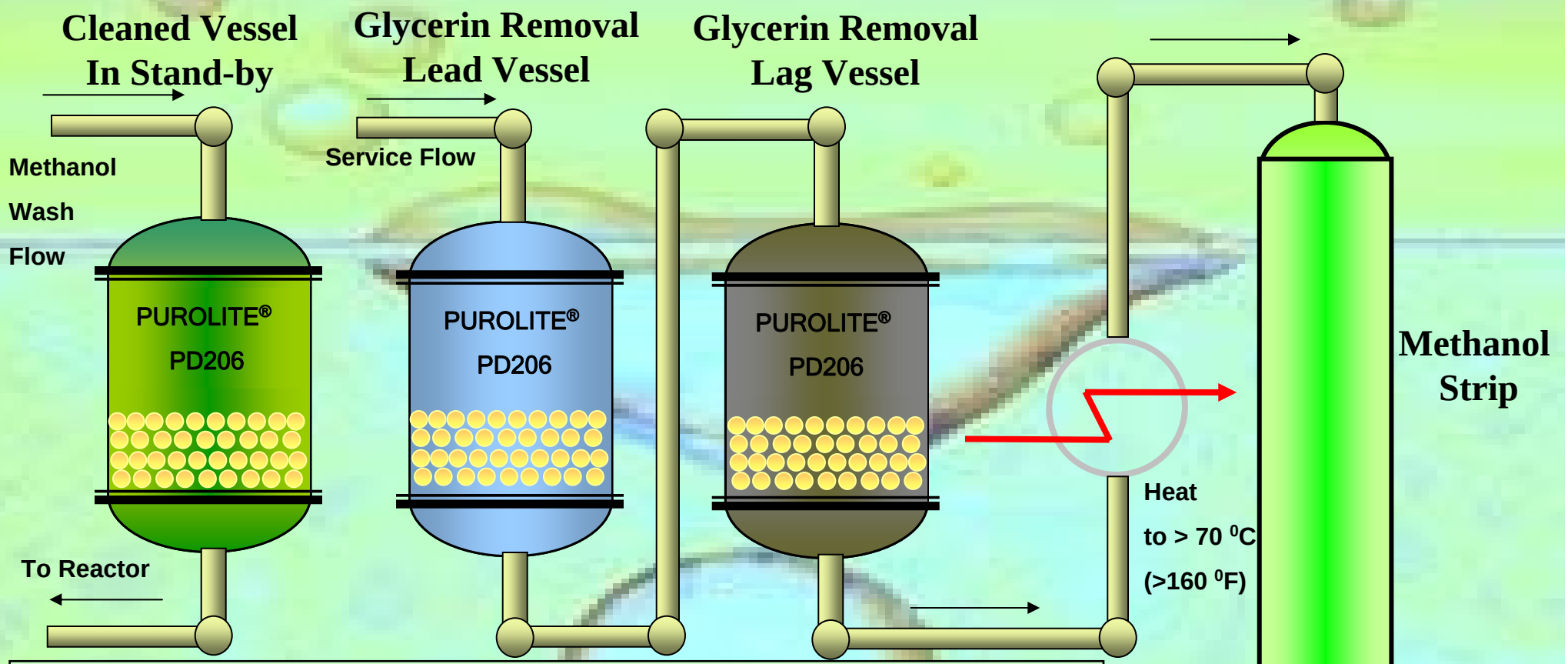
Polish after Demethylation



Operating Cost for Purolite® PD206

- Polishing Vessels **Before Demethylation**
  - Influent glycerin is commonly **2000ppm** (0.2%)
  - Lead tower
    - Washed with Methanol every **5-6 days**
    - Replaced with new or regenerated resin every **2-3 months**
  - Attrition is **<5-15%** due to handling
  - Capacity loss negligible
    - Resin life estimated **5-7 years**.
  - Operating cost will be **$.014/gal ($0.0037/litre)** biodiesel using regenerated PD206
- Polishing Vessels **After Demethylation**
  - No Methanol washing only replacement of resin due to flashpoint criteria
  - Columns in final position **after Demethylation** has been reported to cost greater than $0.10/gal ($.026/L)

Methanol Wash removes free Glycerin



Vessel Operation

- Lead Vessel washed with methanol to remove glycerin at breakthrough
- After methanol wash lag vessel moves to lead position
- Methanol and glycerin are returned and used in the Transesterification process
- Catalyst loading on PD206 will reduce its holding capacity for free glycerin.
- Ionic exhaustion of resin is indicated by elevated sodium or pH in the biodiesel.
- Exhausted resin should be removed from the vessel and replaced with new or regenerated Purolite PD206

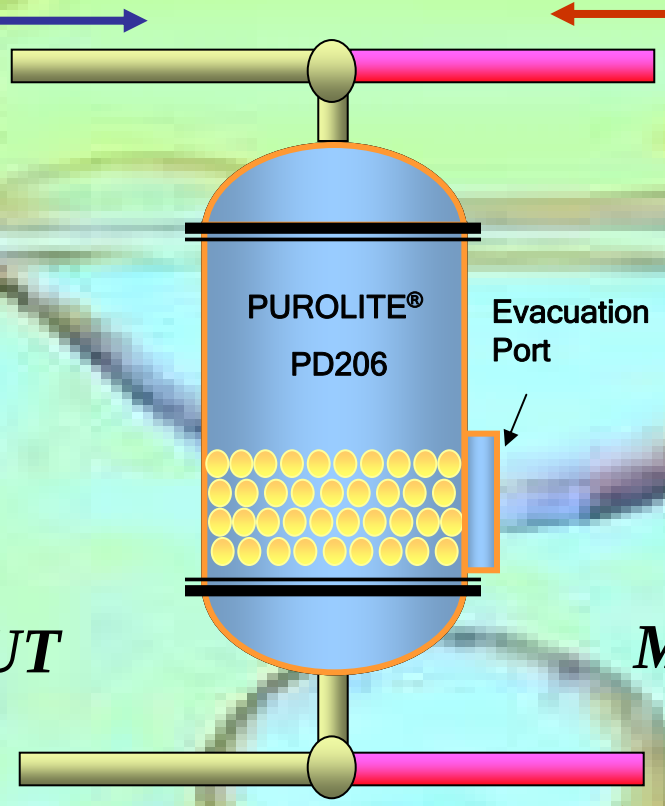
Washing Glycerin from Resin

Service Cycle - IN

Biodiesel with trace Glycerin

MeOH Wash Cycle - IN

Dry MeOH



Service Cycle- OUT

Biodiesel “FREE” of Glycerin and catalyst goes to demethylation

MeOH Wash Cycle - IN

MeOH + Glycerin

To MeOH stripping or Transesterification

After several methanol washes Purolite PD206 will exhaust on Sodium and will no longer remove trace soaps and catalyst. The resin is either disposed of or regenerated

H^+ form vs. Na^+ Form Resin

Property	H^+ Form	Na^+ Form
Viscosity of glycerin	Reduces viscosity for better absorption into the bead	High Viscosity glycerin absorbs on resin surface
Catalyst removal	Absorption with glycerin then ion exchanges in bead	Absorption only with free glycerin
MeOH requirement for washing	2-3 BV for 95% free glycerin removal	4 BV suggested due to thicker glycerin
MeOH wash frequency	Approx 3-5 days depending on glycerin loading	For similar sized towers Approx. twice as often as H^+ form resin
H^+ Regeneration	Approximately 3-6 months to restore performance	None
Capacity	.4-.6 g Free Glycerin / g dry PD206	.1-.1.5 g FG / g Wet resin
Process downtime	good	Fair

Meet ASTM / EN Specifications

Before

Turbidity high

Glycerin .05 - .4%

Water .05%

Methanol 1-5%

Catalyst 25-300 mg/kg

Soap .1 - 3.0 mgKOH/g

After

Turbidity low

Glycerin .001 - .01% (ASTM .02%)

Water .002% (ASTM .05%)

Methanol 1-5% no change

Catalyst <2 mg/kg

TAN = Soap (ASTM .5 mg KOH/g)

Returning Resin for Regeneration

- When PD206 exhausts with catalyst of soap functional sites are converted to Na of K.
- Conversion back to H form not possible at plant
- Where regeneration facilities are convenient as in the eastern USA resin can be returned to Purolite and convert to H form
- This reduces operating cost by approx 25%
- Reduces solid waste generation
  - Resins can be used several years with negligible lose of operating capacity
  - No solid or liquid waste disposed at the plant.
- Shipping used resin requires flamable solid placard.

Summary / Status

- Ion Exchange is a **prominent** component for purification of Biodiesel
  - Primarily for Dry polishing Process
- Best application is free glycerin removal before demethylation
- A **3 tower lead lag** application is most effective
- **Methanol wash** will extend operating life of resin and reduce cost
- **Catalyst removal** is achiever with resin polishing before and after demethylation
- **Regeneration** offered (USA and Canada)
  - **reduce waste** resin
  - Purolite recognized as a **full service supplier**
  - Handling and shipping details must be followed
  - **Green Technology** reduces demand on petroleum based raw materials