

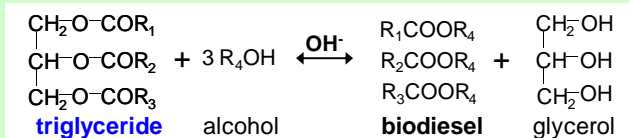
A Novel Process for Continuous Production of High Quality Biodiesel with Ion-exchange Resin Catalysts

Naomi Shibasaki-Kitakawa and Toshikuni Yonemoto

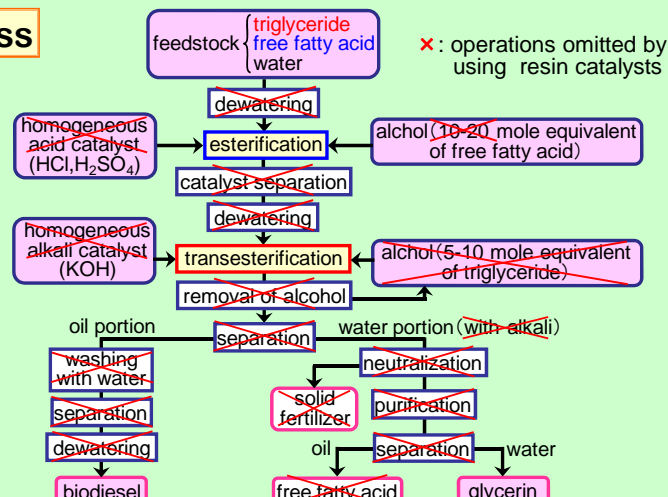
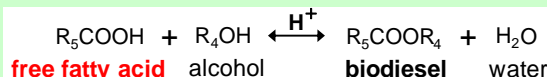
Department of Chemical Engineering, Tohoku University, Aoba-yama 6-6-07, Aoba-ku, Sendai 980-8579, Japan

Problems of industrial biodiesel production process

- Biodiesel is mainly produced via transesterification of **triglyceride** with homogeneous alkali catalyst from refining edible oils with **free fatty acid (FFA) content of less than 0.5 wt%**.



- The restriction of **FFA** content in feedstocks causes an increase not only in **production cost of biodiesel** but also in **price of edible oils**.
- Alternative pretreatment method** converting **FFA** to biodiesel by esterification with homogeneous acid catalyst has been proposed.

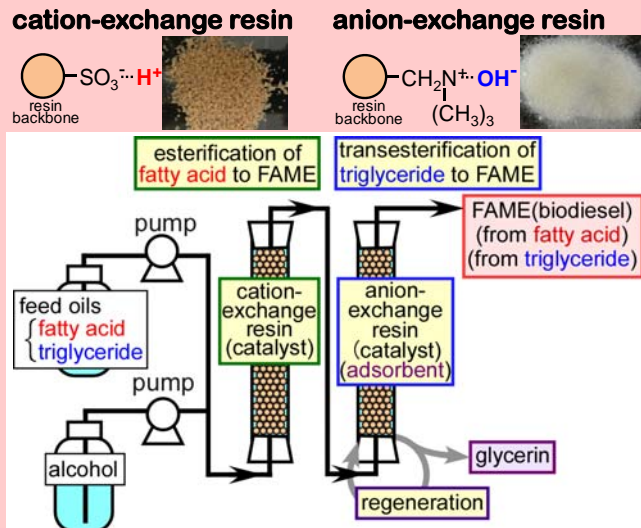


Process flow of biodiesel production combining esterification of **FFA** and transesterification of **TG**

The process using homogeneous acid and alkali catalysts is very complicated and has not been realized in an industrial scale up to now.

A new simple production process without up- and down-stream processing

- The process removes the restriction of feedstocks and enables efficient biodiesel production from **various cheaper waste oils with high FFA content up to 100 wt%**^{1,2}.
- Esterification and transesterification catalyzed by resins (50°C) irreversibly progress, therefore **adding excess alcohol are unnecessary**².
- Anion-exchange resin has abilities to remove by-products (glycerin and water) and impurities³, so that **refining process of product is unnecessary**.
- Glycerol is recovered at high purity** during regeneration of anion-exchange resin and more than 100 time regenerations do not cause irreversible decay of the catalytic activity.



Schematic diagram of new production process

1)N. Shibasaki-Kitakawa et al., *Bioresour. Technol.*, **98**, 416(2007), 2)N. Shibasaki-Kitakawa et al., *Energy Fuels*, **24**, 3634(2010), 3)T. Tsuji et al., *Energy Fuels*, **23**, 6163(2009), 4)N. Shibasaki-Kitakawa et al., *Bioenerg. Res.*, **4**, 287(2011)

Application to various feedstocks

Triglyceride rich oil

crude *Jatropha curcus* oil:
 { **FFA** content of 2-20 wt%
 { water content of 3300 mg/kg

- Byproduct, transparent glycerol without any catalysts is also obtained in methanol solution (60-80 wt%).

(a) biodiesel (b) glycerol



Photographs of products obtained without purification

Free fatty acid rich oil

rice bran acid oil:
 { **FFA** content of 95 wt%
 { water content of 750 mg/kg

- The final product, (c) fully met all the standard values without purification.



Photographs of (a) acid oil, (b) effluent from 1st column with **PK208LH** and (c) effluent from 2nd column with **PA306S**

High quality biodiesel, fully meeting with European and Japanese standards can be continuously produced by the simple process with neither pretreatment of feed oils nor purification of products from various oils with high **FFA** content up to 100 wt%.

Physical properties of used resins

properties	PK208LH	PA306S
character	cation	anion
cross-linking density [%]	4	3
diameter [mm]	0.40-0.60	0.15-0.43
ion-exchange capacity [mol/m ³ -resin]	1.2 × 10 ³	0.79 × 10 ³

※Resins were donated by Mitsubishi Chemical Co.,Ltd., Tokyo, Japan.



Photograph of fully automated pilot plant for 50 L/day installed last month (Now test operations are being performed.)