Production and Purification of Biodiesel Using Ion Exchange Resins: A new Strategy for Cleaner Biodiesel

Mohamed Mahmoud Nasef[1,2], Masoumeh Zakeri[2] and Zuriati Zakaria[1*]

[1]Department of Environmental Engineering and Green Technology, Malaysia-Japan International Institute of Technology,

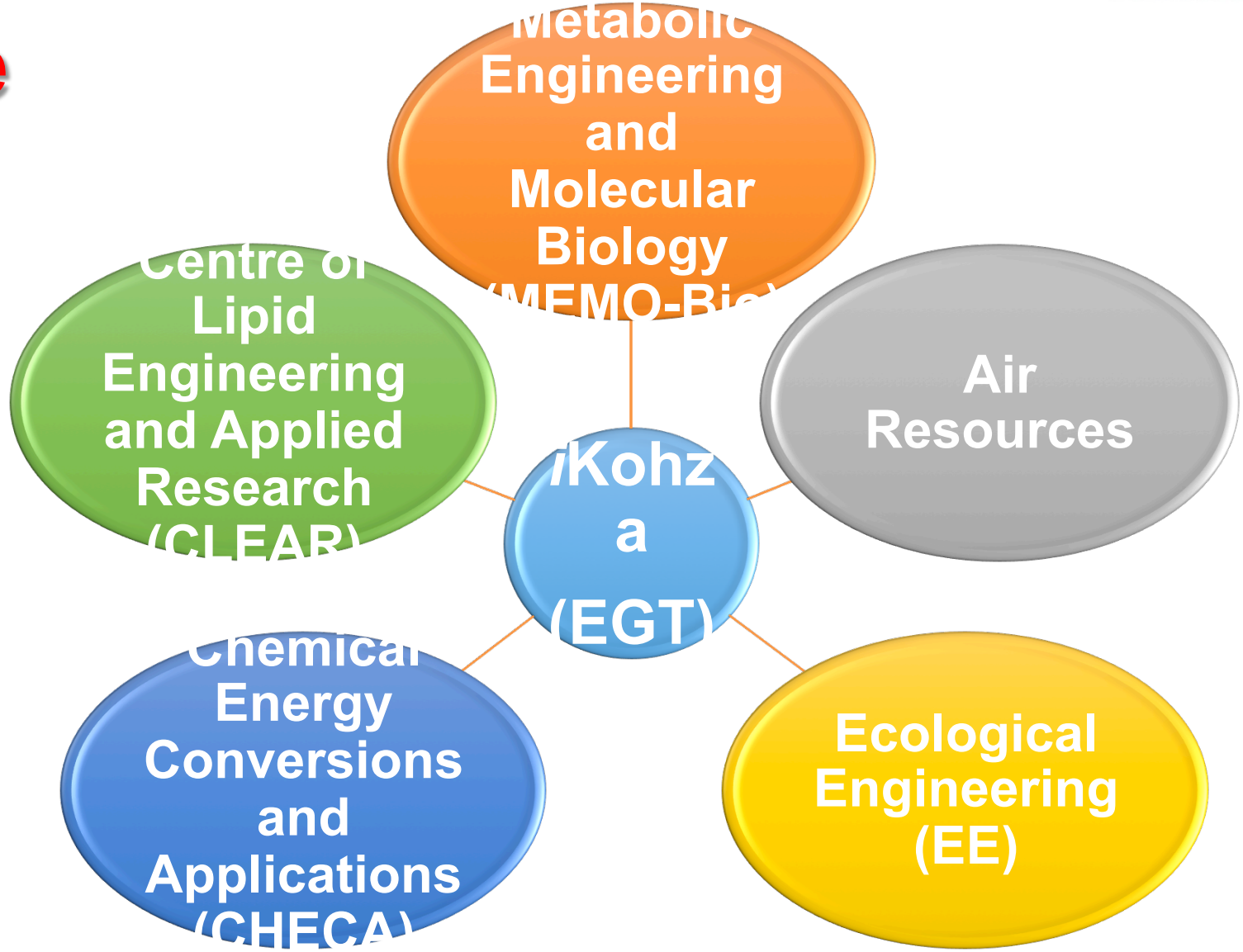
[2]Institute of Hydrogen Economy, International Campus,

Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia

MALAYSIA JAPAN INTERNATIONAL INSTITUTE OF TECHNOLOGY

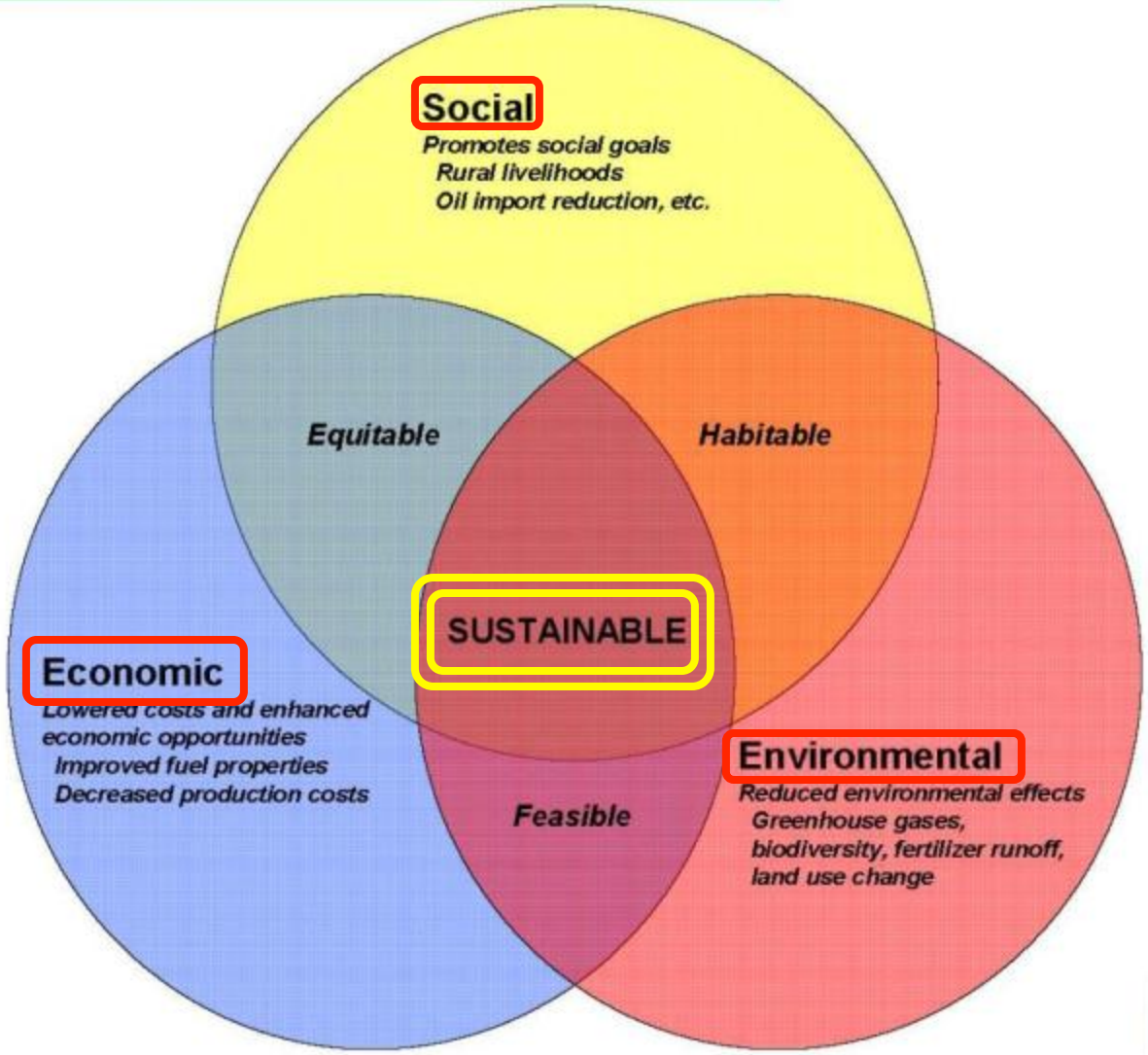
1. A G-G Project aimed to set up an educational Institute in Malaysia offering Japanese Style Engineering Education blended with Malaysia distinctiveness for sustainable industry and society
2. Leading in **academic and research excellence** in Electronics, Precision, Environmental & Green Engineering and Management of Technology

Innovative Kohza (*i*Kohza)



A Sustainable Biofuels Industry

DOE

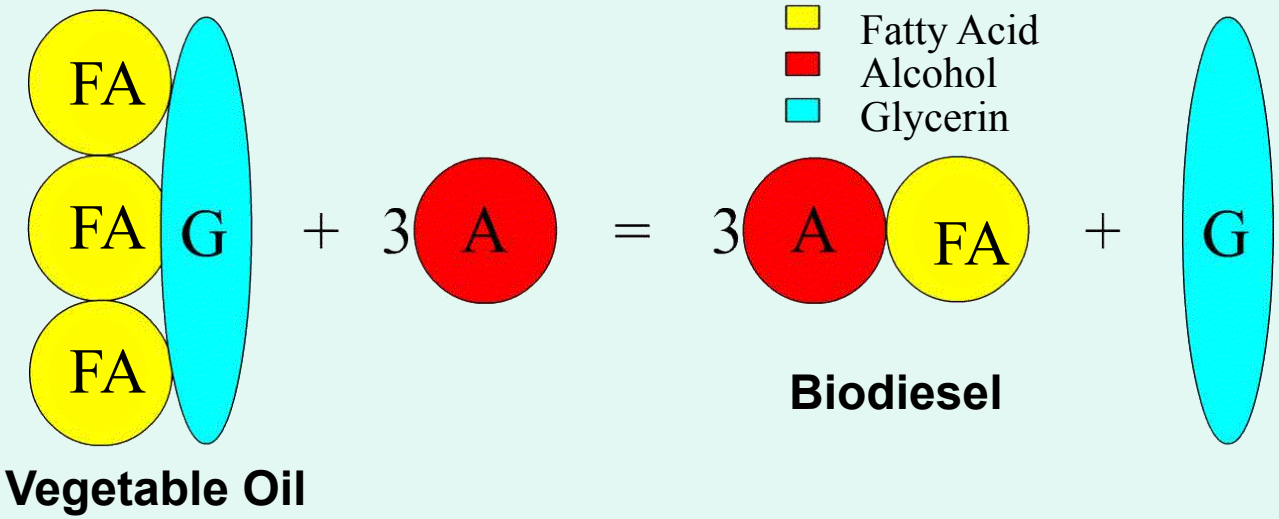


Biomass

http://biomass.ucdavis.edu/materials/forums%20and%20workshops/f2008/1.3_%20Alison%20Goss%20Eng.pdf

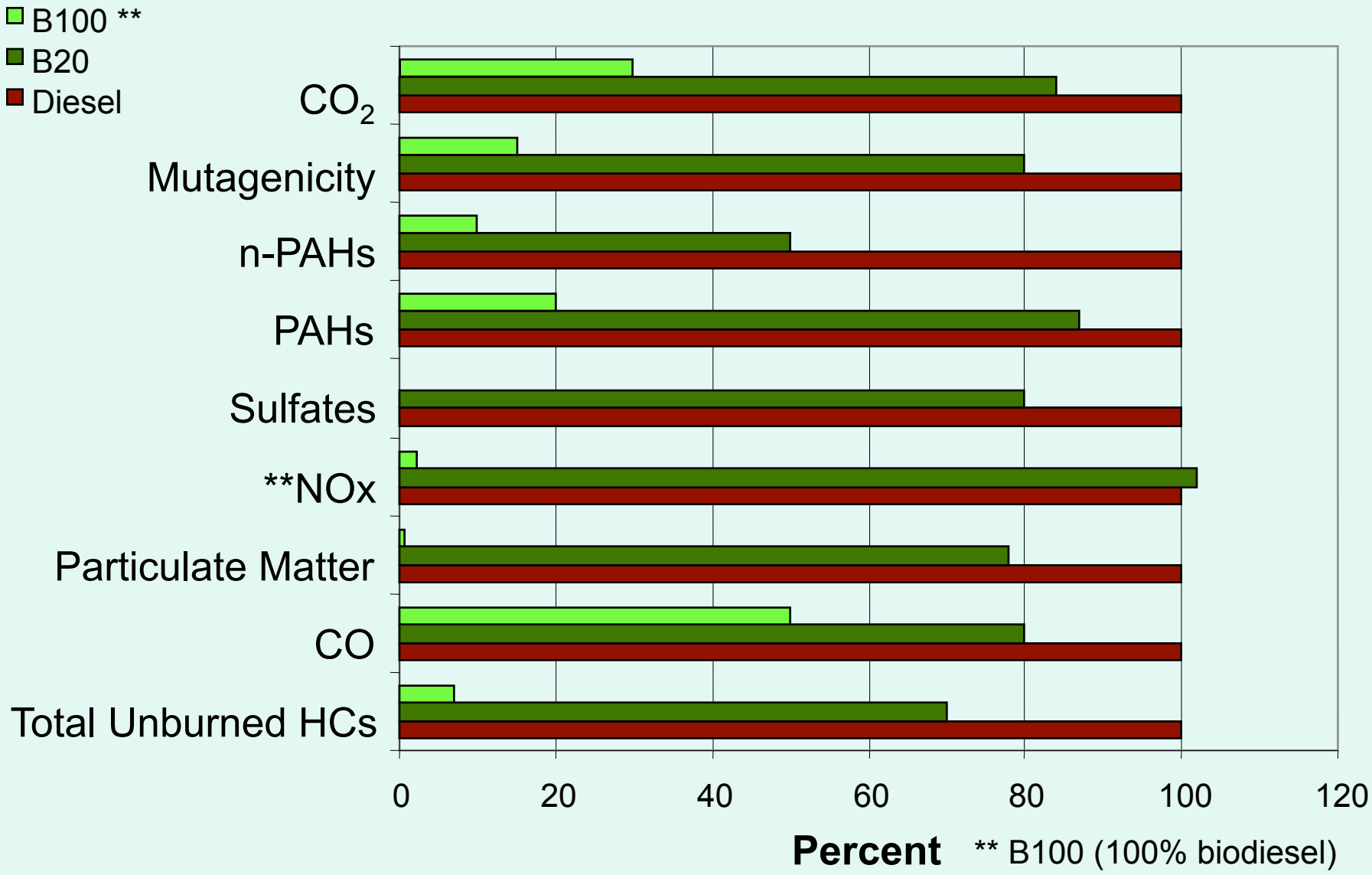
Biodiesel

- Alternative fuel for diesel engines
- Made from vegetable oil or animal fat
- Meets health effect testing (CAA)
- Lower emissions, High flash point (>300F), Safer
- Biodegradable, Essentially non-toxic
- Renewable
- It can be blended in any concentration with diesel-oil
- Chemically, biodiesel molecules are mono-alkyl esters produced usually from triglyceride esters



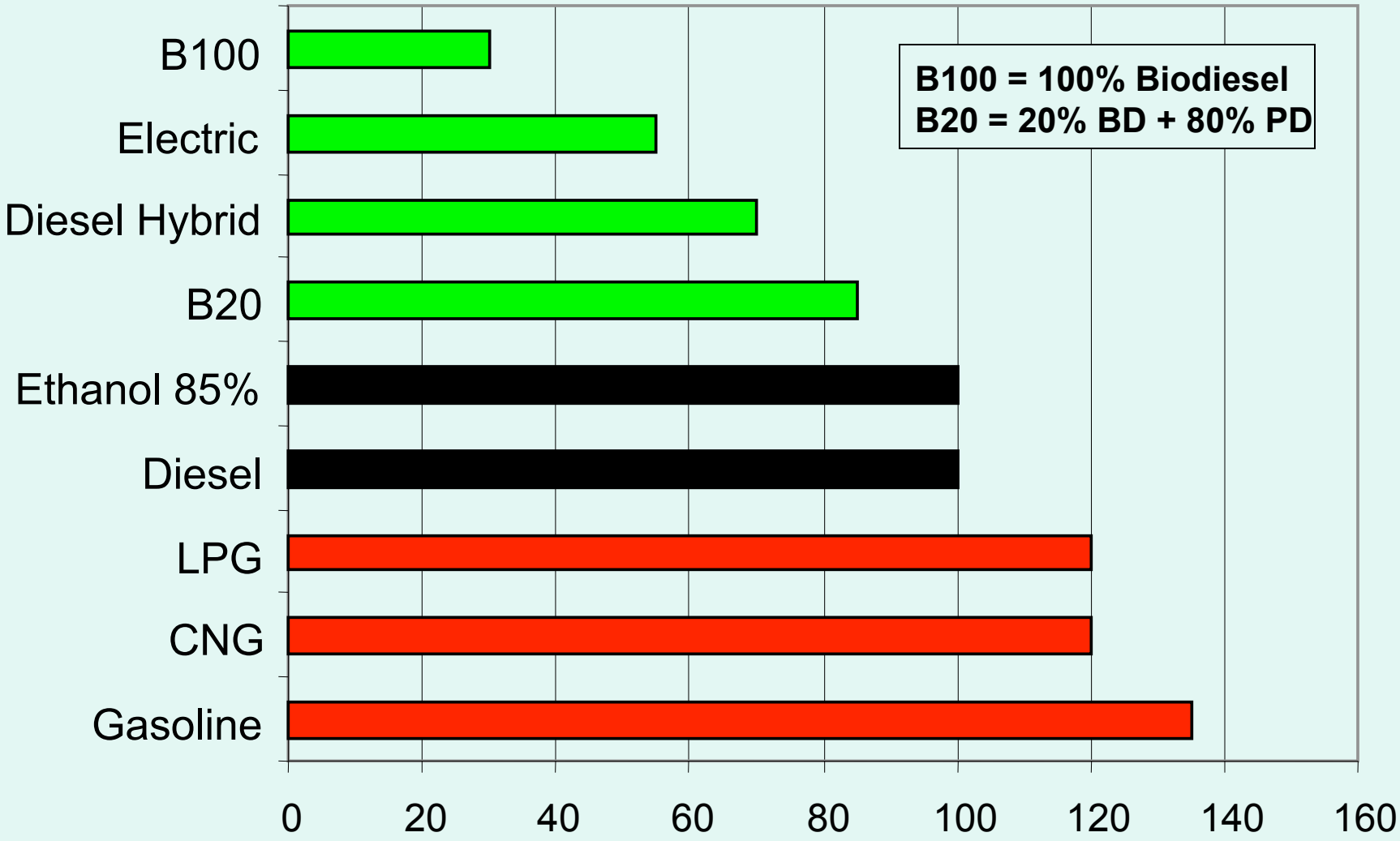
http://www.slideshare.net/saurabhkumarverma19/biofuel-33608124

Relative Emissions: Diesel and Biodiesel



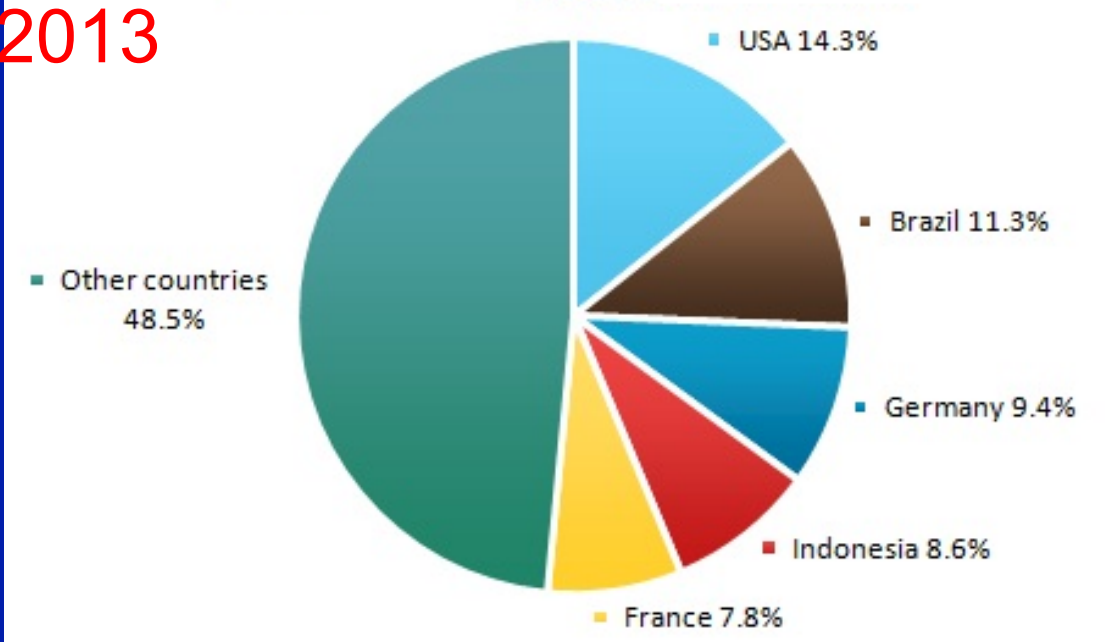
http://www.slideshare.net/saurabhkumarverma19/biofuel-33608124

Relative Greenhouse Gas Emissions



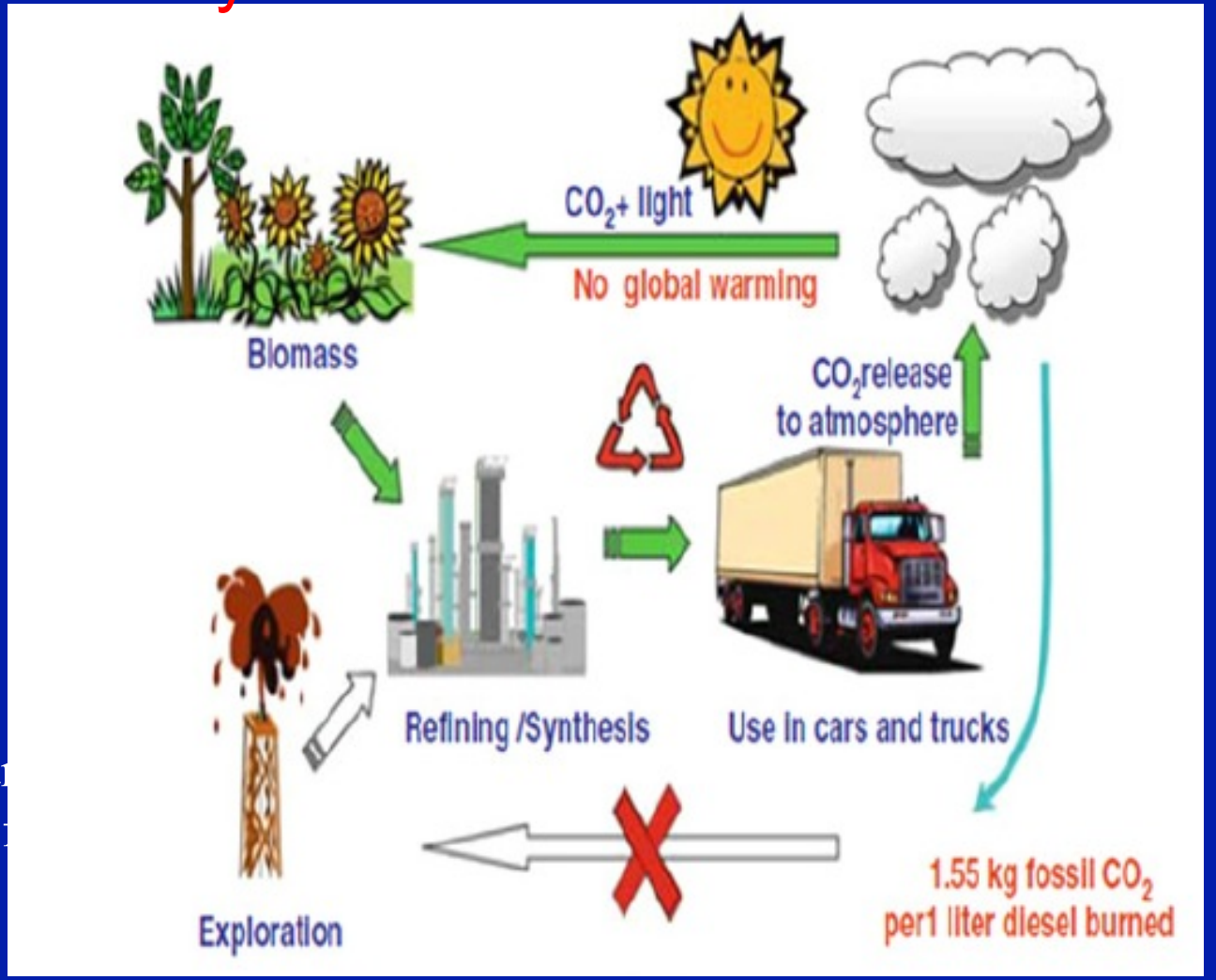
Data from “A Fresh Look at CNG: A Comparison of Alternative Fuels”, Alternative Fuel Vehicle Program, 8/13/2001

World biodiesel production in 2013



In 2013, the world biodiesel production stands at about million cubic meters distributed. USA, Brazil, Germa Indonesia followed by France are the five producers biodiesel with 51.5% of the total world production

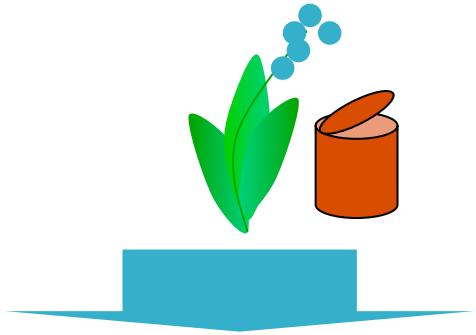
Life cycle of diesel versus biodiesel



"Biodiesel: 2014 World Market Outlook and Forecast up to 2018," Jan, 2014.

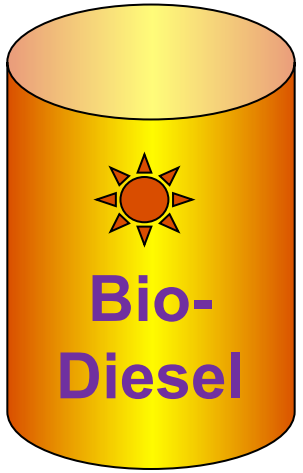
Biodiesel production

Raw oil sources of biodiesel



Palm oil
Rape seed oil,
Soyabean oil,
Sunflower oil,
Canola oil,
Coconut oil,
Jatropha nut oil,
Used Cooking Oil,
Animal fats

Conversion



- High viscosity
- Poor combustion properties

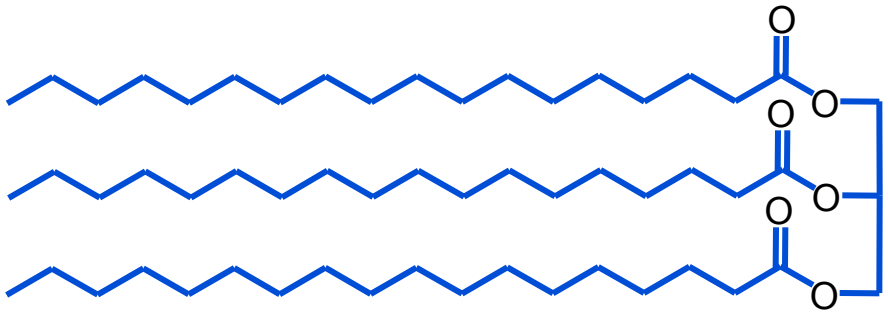
- **Low viscosity**
- **Excellent combustion properties**

http://www.macquarieoils.com/

Raw oils chemical composition

Triglycerides

> 95%



Fatty-Acids:

0.1- 5%

Others:

< 1%

Micelles, phospholipids, proteins, mineral salts

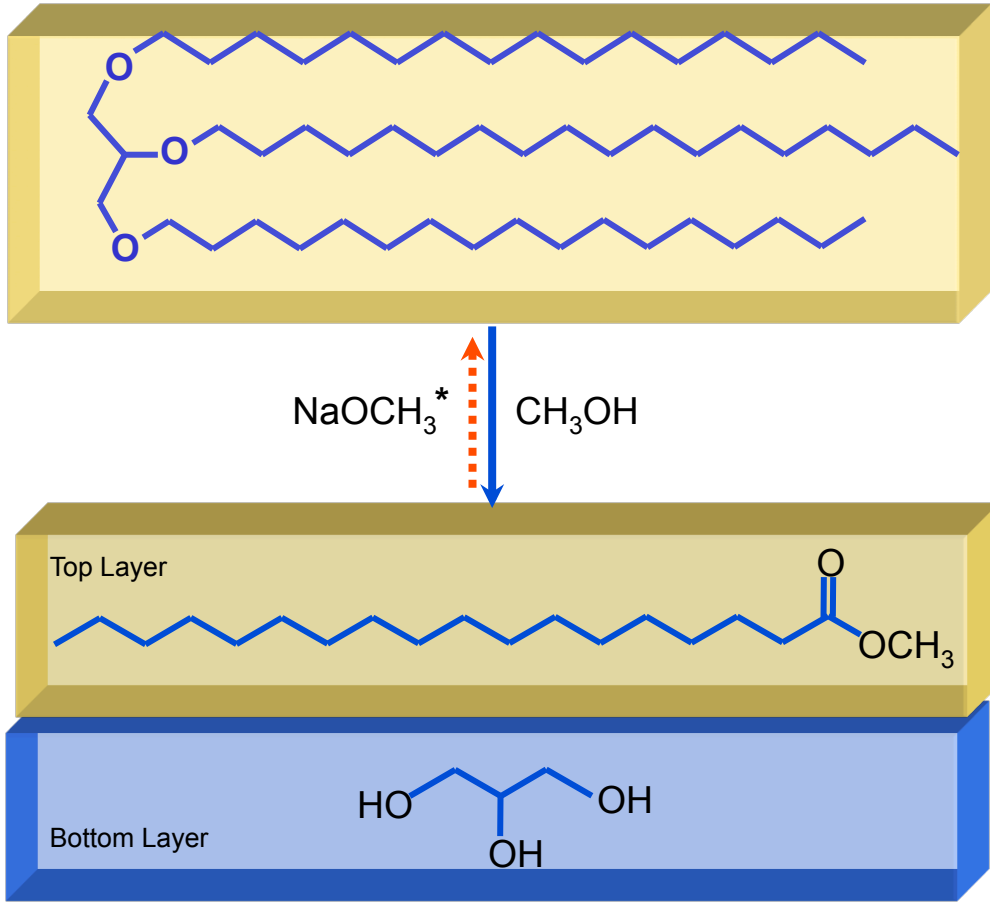
http:// www.picse.net/CD2011/biodiesel/convertingFatsToBiodiesel.htmlable

Four main production methods

- Direct use and blending
- Micro emulsions
- Thermal cracking
- Transesterification

Transesterification

- Most common production method
- Uses vegetable oils and animal fats as feed stocks
- The reaction of a fat or oil with an alcohol to form esters (biodiesel) and glycerol



* The catalyst Na-methoxide is also a drying agent and should be used instead of NaOH to suppress the formation of soap

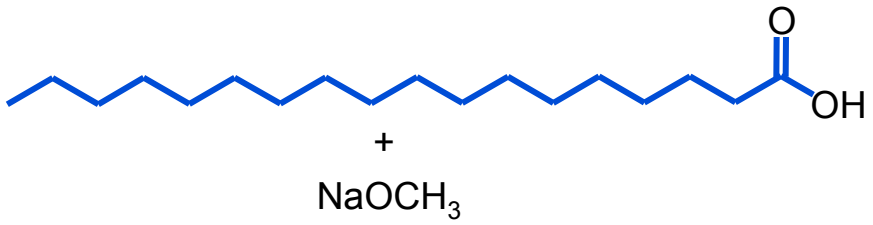
Journal of Sustainable Energy & Environment 3 (2012) 35-47

The main obstacle for biodiesel preparation with hemogeneous base:

Soap formation

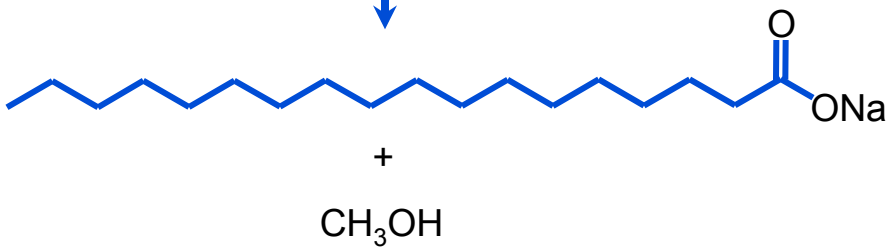
Free fatty acid (FFA)

< 5%



+

$NaOCH_3$



+

CH_3OH

Soap

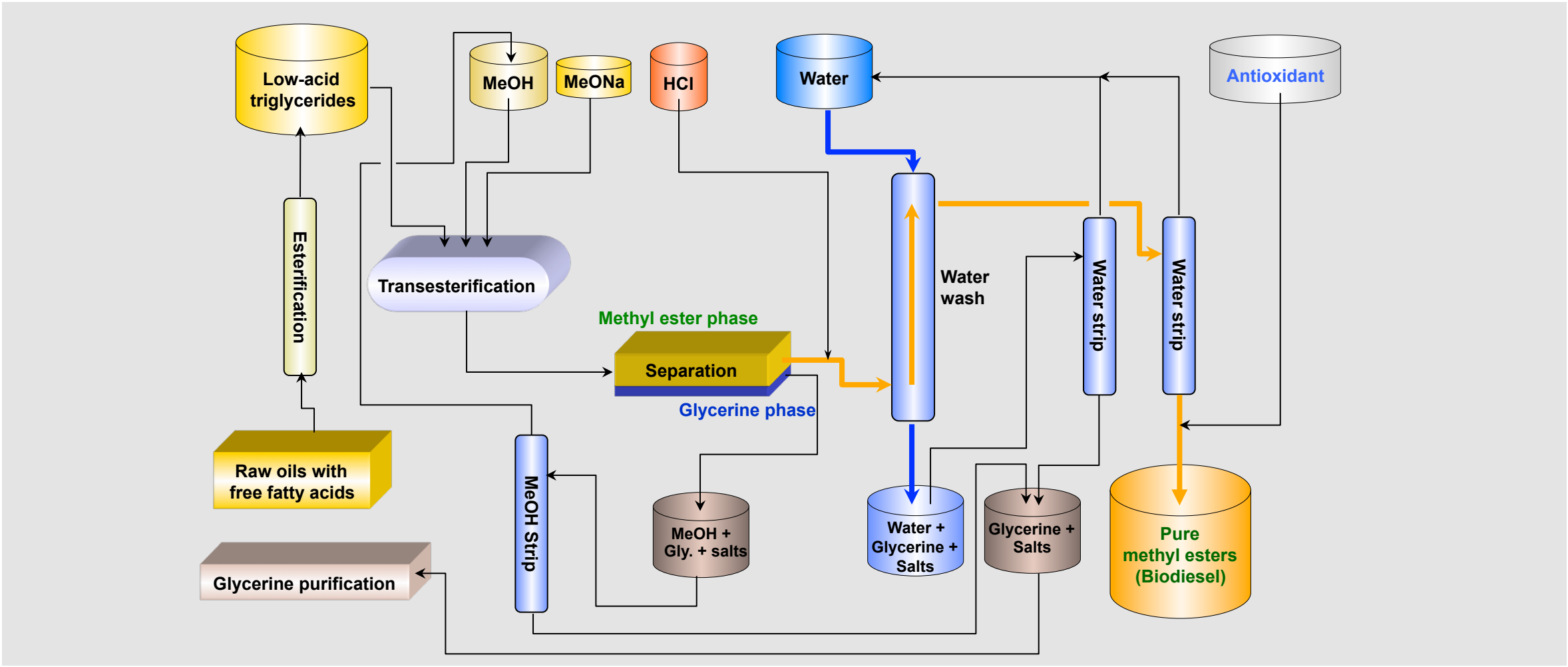
Methanol

The FFA content of the triglycerides should be maintained
below 0.5% to minimize soap formation and maximize BD selectivity

http://www.picse.net/CD2011/biodiesel/convertingFatsToBiodiesel.html

LEWATIT® THE BETTER CHANGE

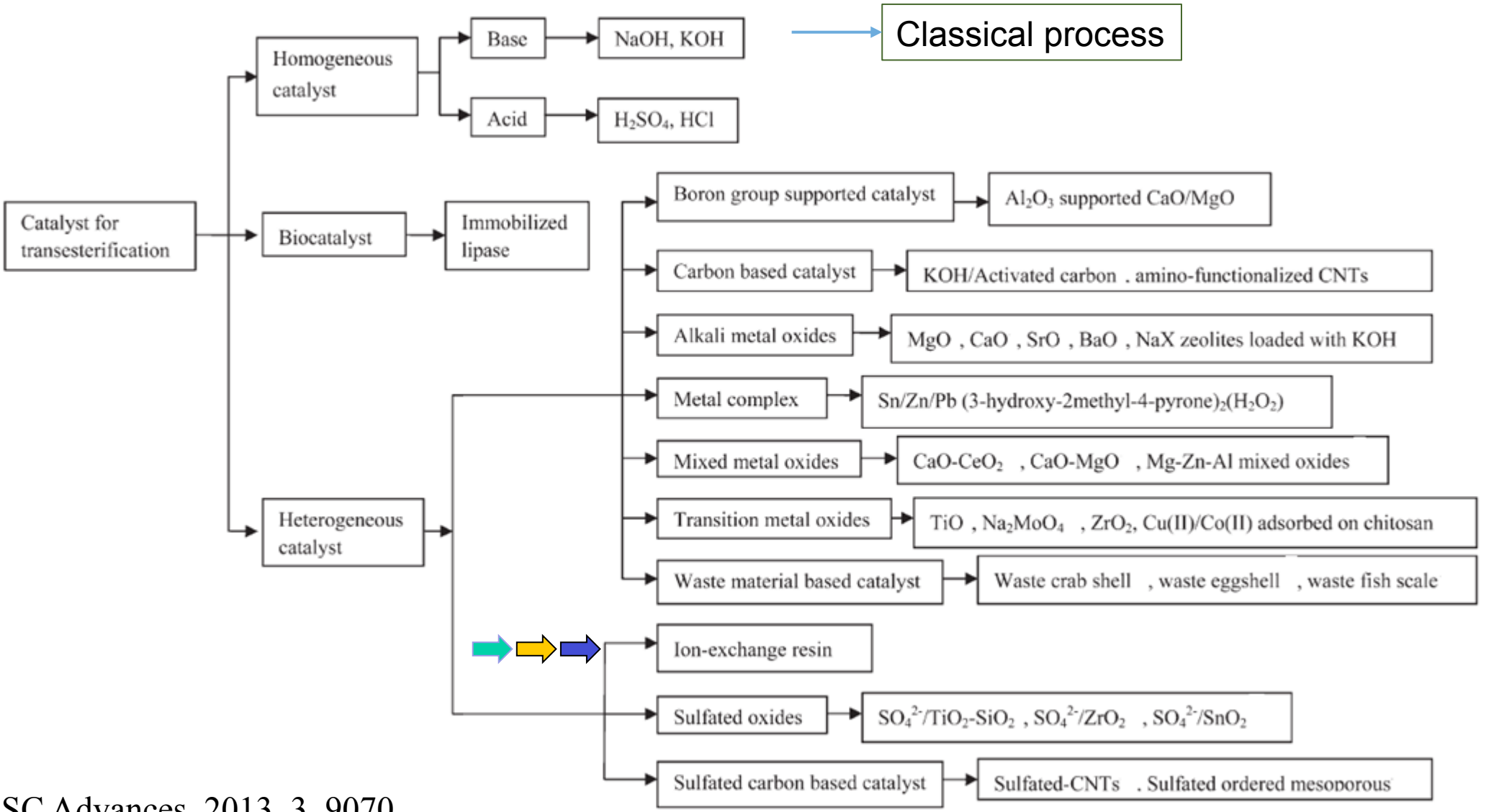
Classical biodiesel production process



http:// www.picse.net/CD2011/biodiesel/convertingFatsToBiodiesel.htmlable

LANXESS

Catalysts used in transesterification reaction for biodiesel production



RSC Advances, 2013, 3, 9070

Disadvantages of Homogenous Basic Catalyst Technologies for Biodiesel Production

Disadvantages:

- Large amount water
- Acid usage in product separation
- Saponification occurs
- Residual KOH in biodiesel creates excess ash content in the burned fuel/engine deposits/high abrasive wear on the pistons and cylinders
- Addition separation process to remover catalyst traces

Alternative solid polymer heterogeneous catalyst can eliminate/reduce such problems

Ion Exchange Resins as Heterogeneous Catalyst

Commercial ion exchange resins are usually based on the polystyrene crosslinked with divinylbenzene, which are classified based on the type of functional group and % of cross-linkages

Anionic Exchangers

- Strongly basic – functional groups derived from quaternary ammonia compounds, R-$NH_2^+OH^-$.
- Weakly basic - functional groups derived from primary and secondary amines, R-NH_3OH or R-R'-NH_2OH.

Cationic Exchangers

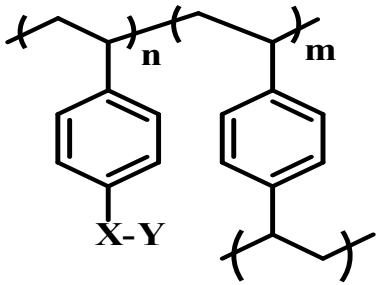
- Strongly acidic: functional groups derived from strong acids e.g., R-SO_3H (sulfonic).
- Weakly acidic – functional groups derived from weak acids, e.g., R-COOH (carboxylic).

Crosslinking to make ion exchange resin

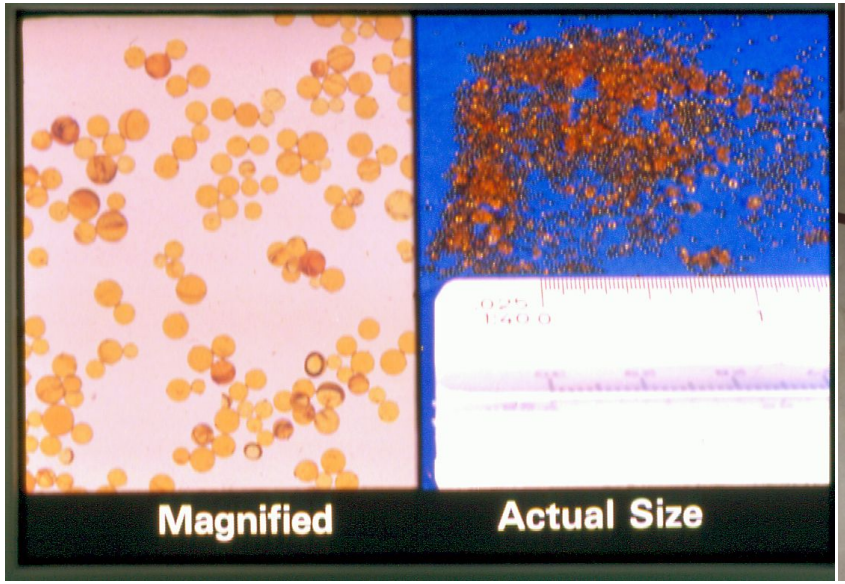
Chem. Rev. 2008, *109*, 515

Advantages of using ion exchange resins in biodiesel production
Low-cost
Chemical stability
Durability and physical strength
Adaptable in any type of reactors
Negligible to low metal leaching
Ease of catalyst recycle especially for macroporous resins
Commercially available in several varieties
Defined amounts of anchoring sites
Ease regenerated and separated because of their relatively large particle size
Applied as catalysts at large scale
Activity, selectivity and catalyst efficiency are comparable with homogeneous catalysts
Ease of handling
Ease immobilization procedure
Compatible with many reaction solvents including water

General structure of ion exchange resin



X	Y
SO_3^-	H^+
$N(CH_3)_3^+$	Cl^-
CO_2^-	Na^+
NH_3^+	OH^-



Chem. Rev. 2008, *109*, 515

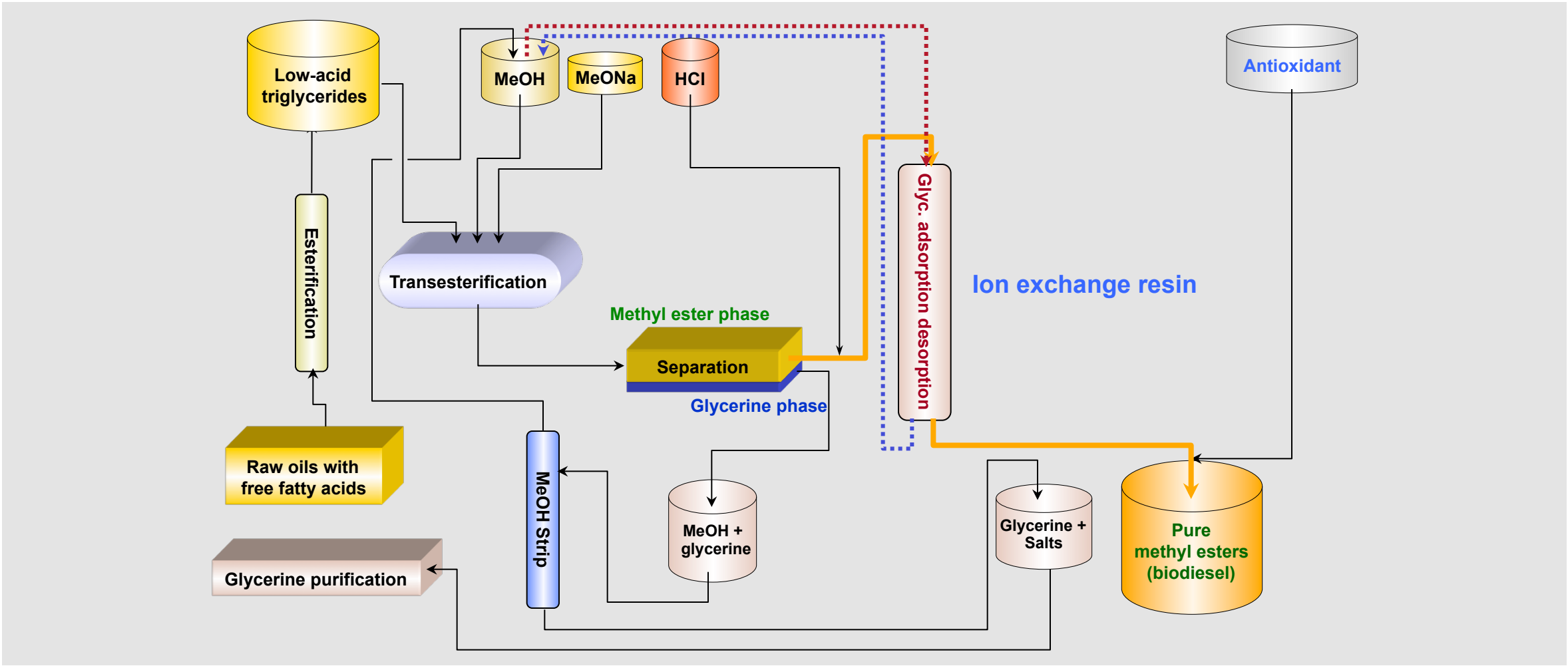
3. Purification of biodiesel

Effects of impurities on biodiesel production

Impurity	Effect
FFA	Corrosion Low oxidation stability
Water	Hydrolysis (FFA formation) Corrosion Bacteriological growth (filter blockage)
Methanol	Low values of density and viscosity Low flash point (transport, storage and use problems)
Glycerides	Corrosion of Al and Zn pieces High viscosity Deposits in the injectors (carbon residue)
Metals (soap, catalyst)	Crystallization Deposits in the injectors (carbon residue) Filter blockage (sulphated ashes)
Glycerol	Engine weakening Settling problems
	Increase aldehydes and acrolein emissions

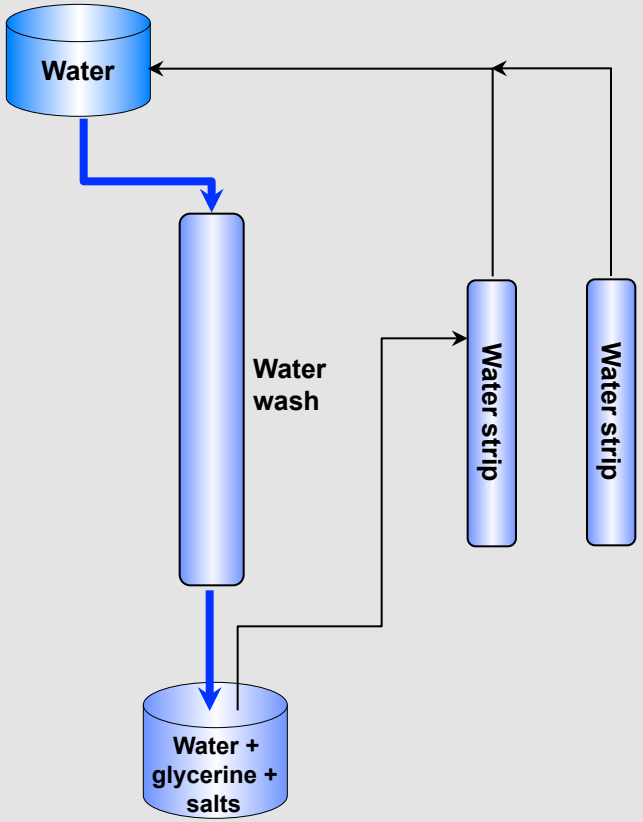
Chemical Engineering Journal 2008, *144*, 459

Purification with Lewatit as a ion exchange resin

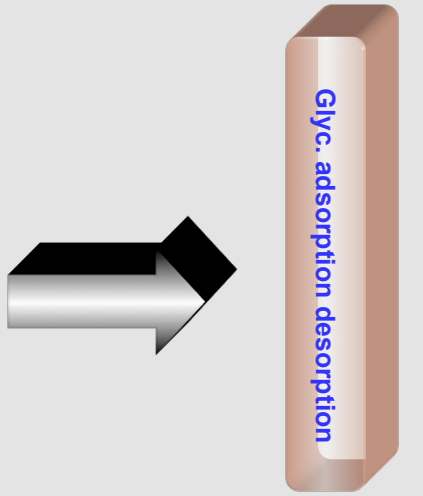


Ion exchange resin *vs* water wash

Purification with water wash



Purification with ion exchange resin



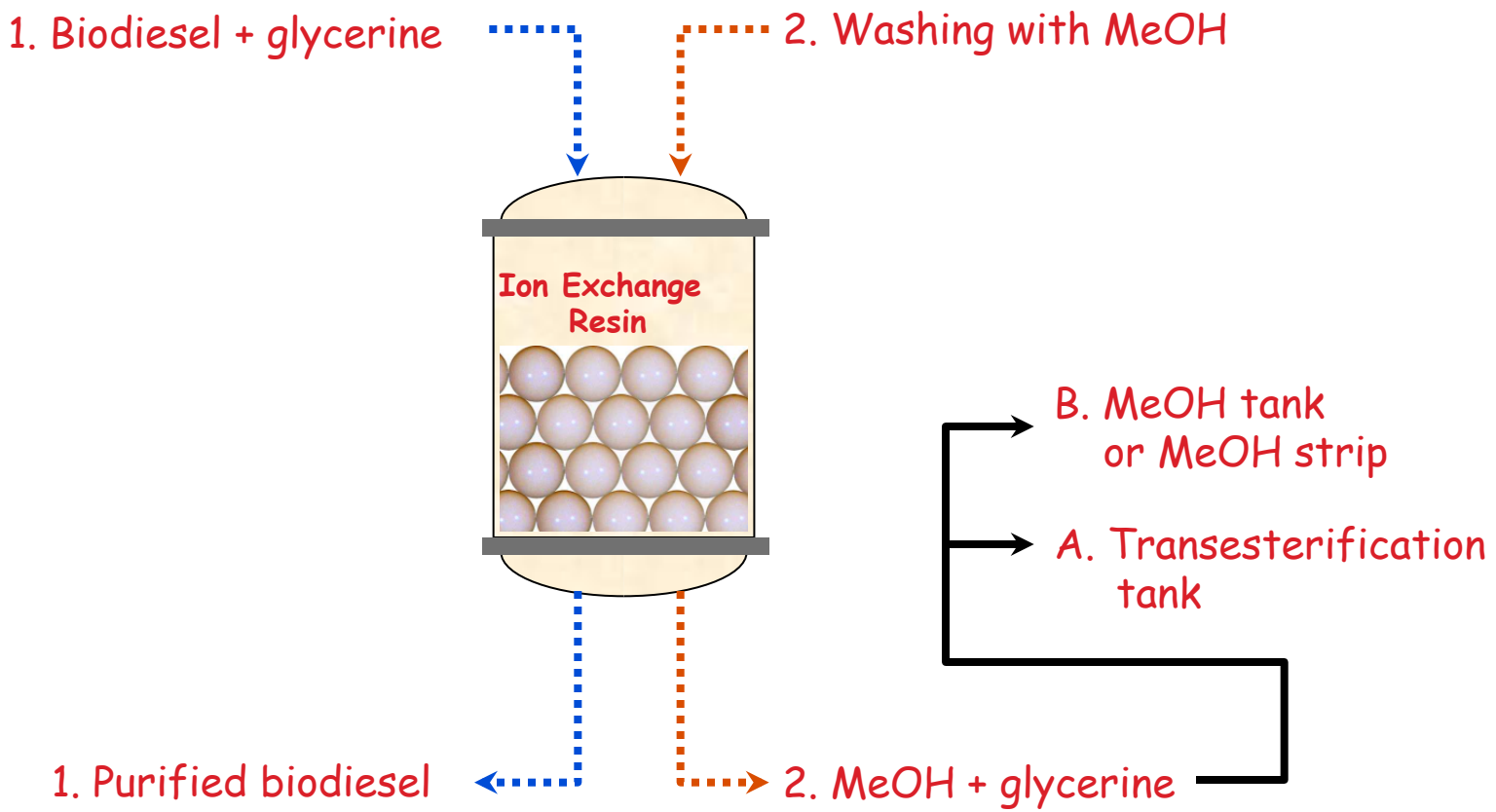
One column of resin completely replaces the water washing system!!

Comparison between ion exchange resin and water wash for biodiesel purification

Ion exchange resin (Purolite)	Water Wash
Operating Cost ($0.0037/litre)	Reported cost ($0.021/litre)
Low maintenance dry system	Medium to High maintenance Multiple washes
No need to filter	Minimal filtration still Heavy Filtration needed necessary
Low energy	High pumping and drying energy
No waste disposal costs	Waste water treatment or water disposal issues
No water required	Several water wash stages required

Heller, T. "Ion Exchange in Biodiesel Production". Purolite Company

Alternate loading and washing



Preparation of alternative ionic resins in fibril form

Commercial ion exchange resins having microporous structure have following disadvantages:

- Diffusion limitation when used in packed-bed column
- Slow kinetics
- Slow regeneration process
- High cost

It is interesting to develop solid polymer/ionic catalyst in fibril form to be used for catalysis of triglycride and purification of crude

Also, It interesting to develop fibril ion exchange resin for purification of biodiesel

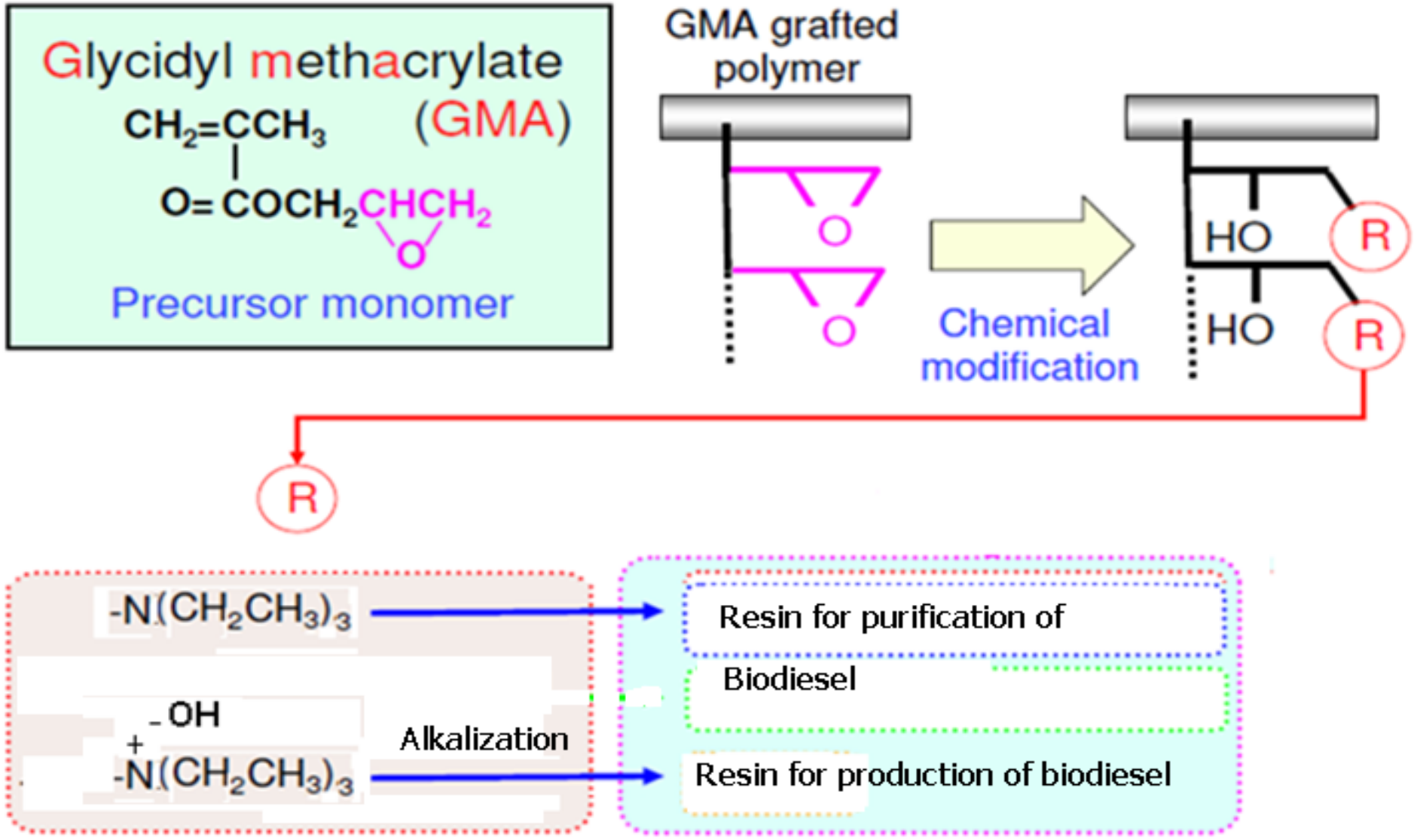
Motivation for Research

- Growing environmental concern
- Majority of commercial resins are in microporous beads (granular) form.
- Diffusion (mass transfer) limitation.
- Long regeneration process.

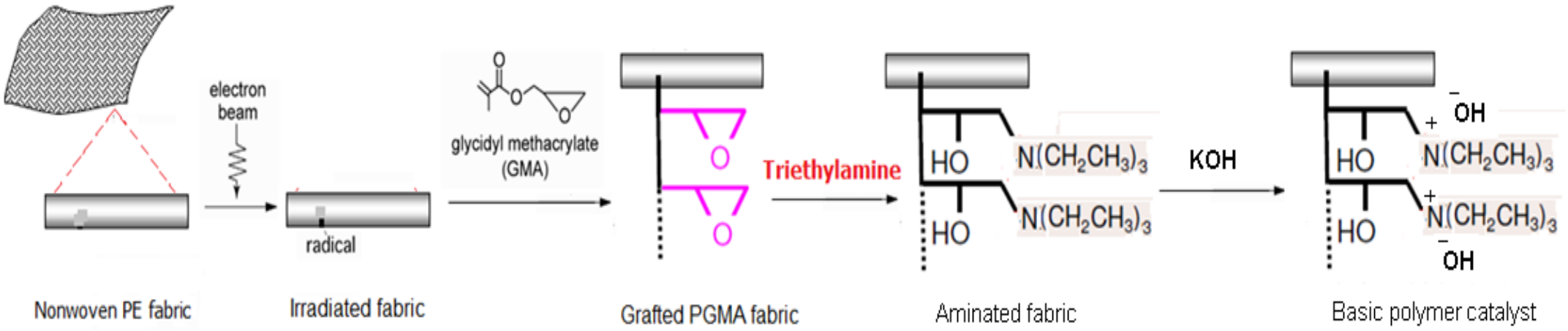
New materials with high selectivity, stability and cost effectiveness are needed.

- Fibrous functional polymeric materials provide a solution to overcome conventional resins limitations.
- Grafting of gylcidylmethacrylate onto polyethylene non-woven fabric provides potential alternative fibrous adsorbents for heavy metal removal.

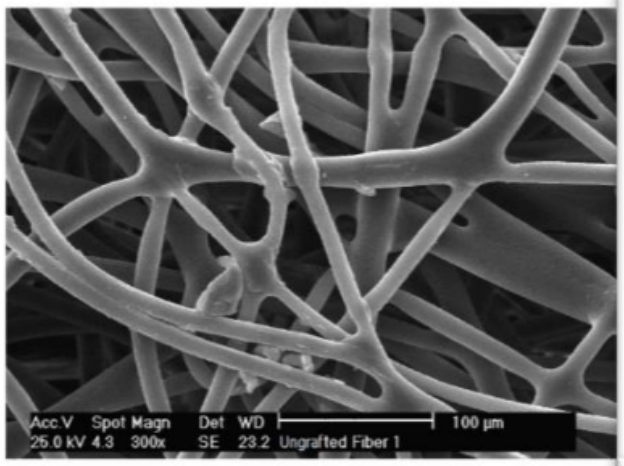
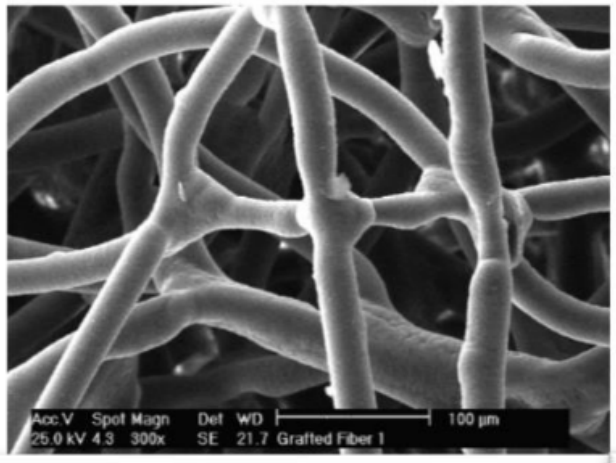
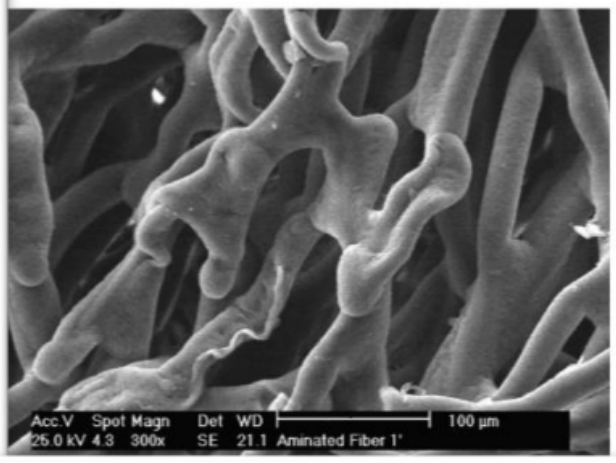
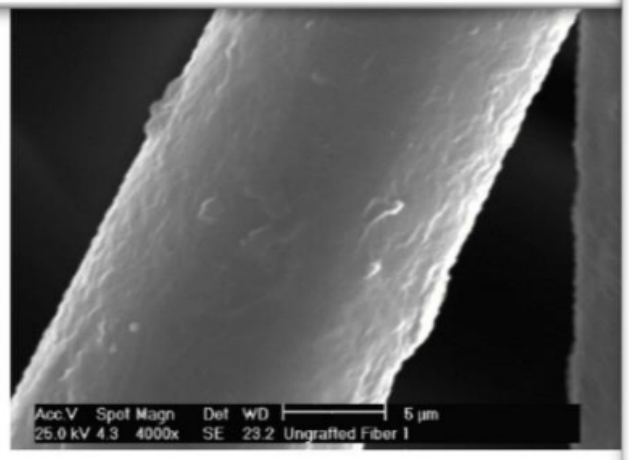
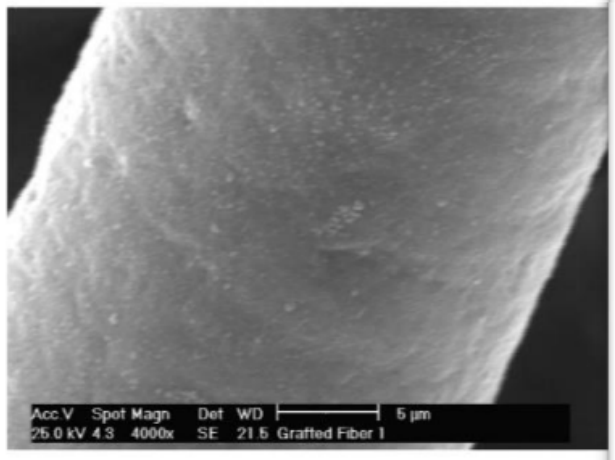
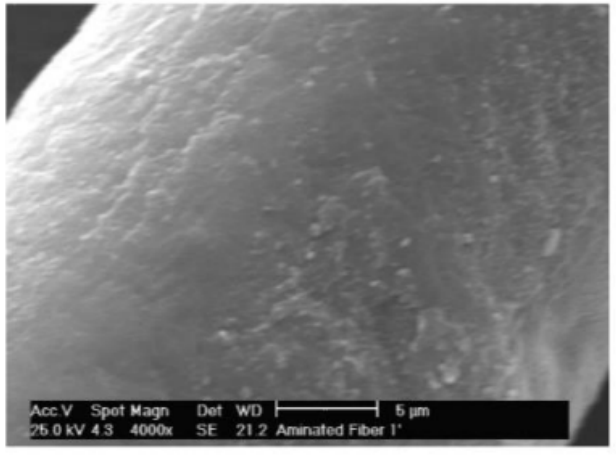
Single route to prepare polymer catalyst and ionic resin by radiation grafted absorbent



New solid basic polymer catalyst

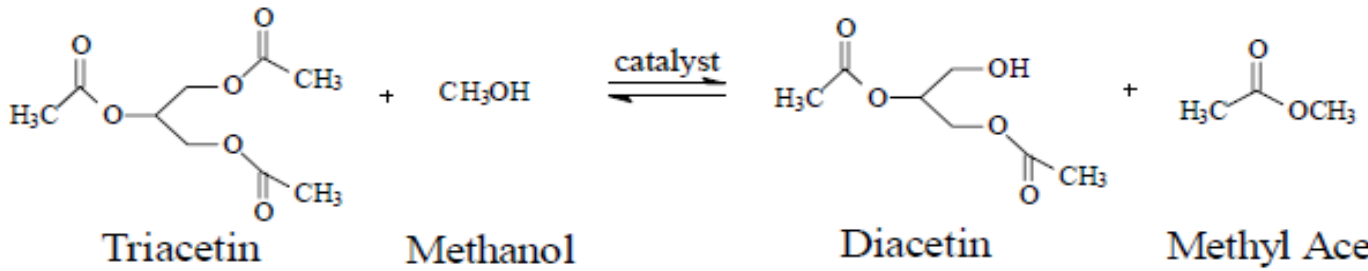


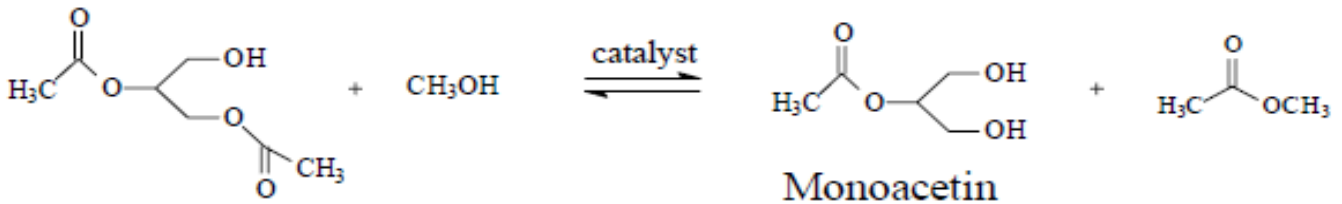
Morphology of new fibrous basic polymer Catalyst

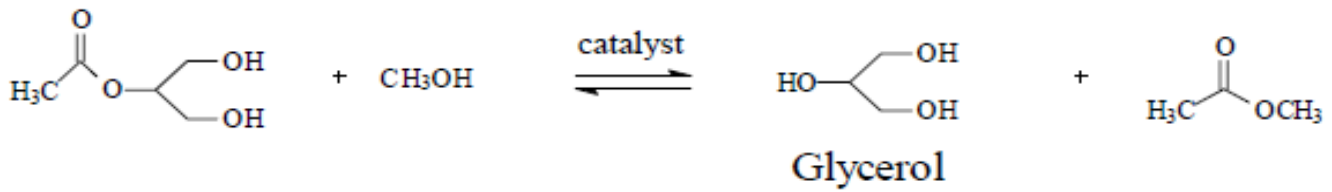
	A) Before Grafting	B) After Grafting (Before amination)	C) After amination
100 μm			
5 μm			

Transesterification of triacetin (model compound for triglycride)

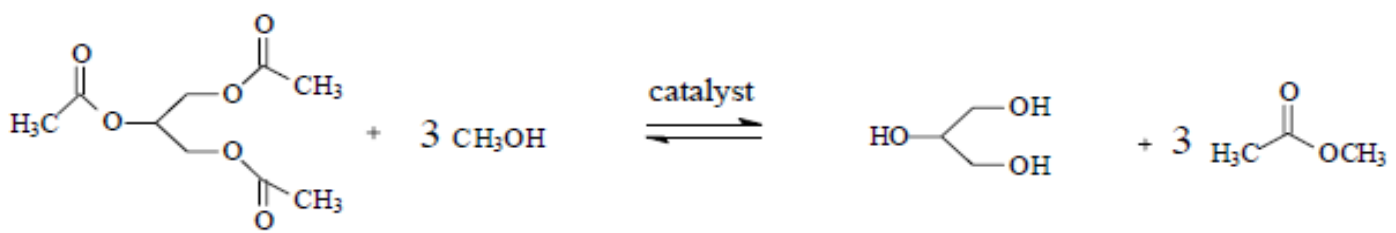
Stepwise reactions:

1. 

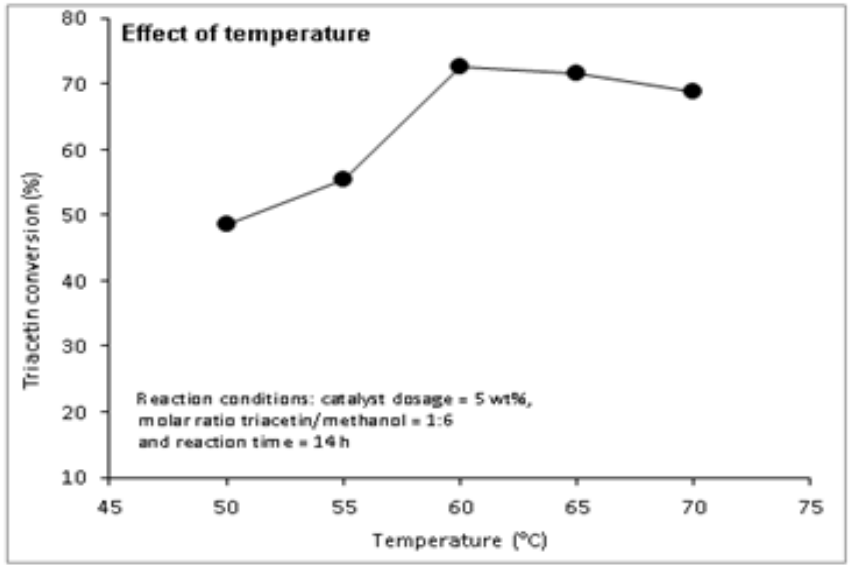
2. 

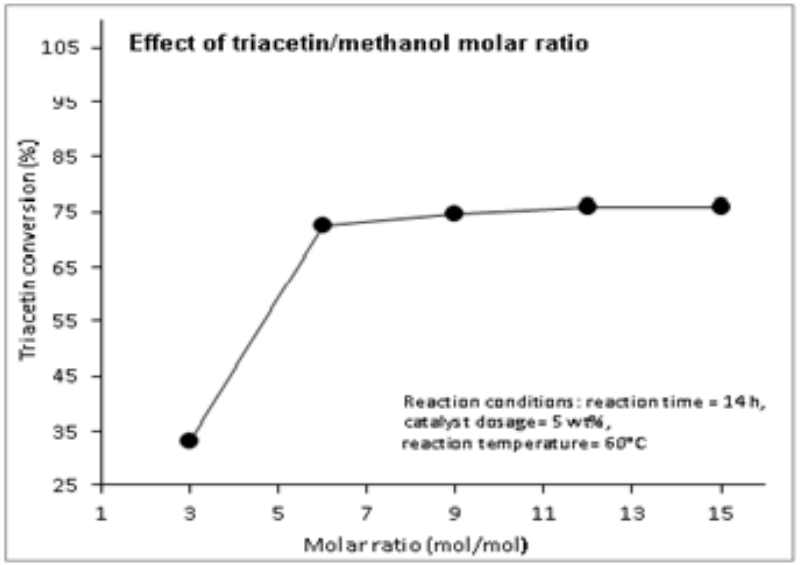
3. 

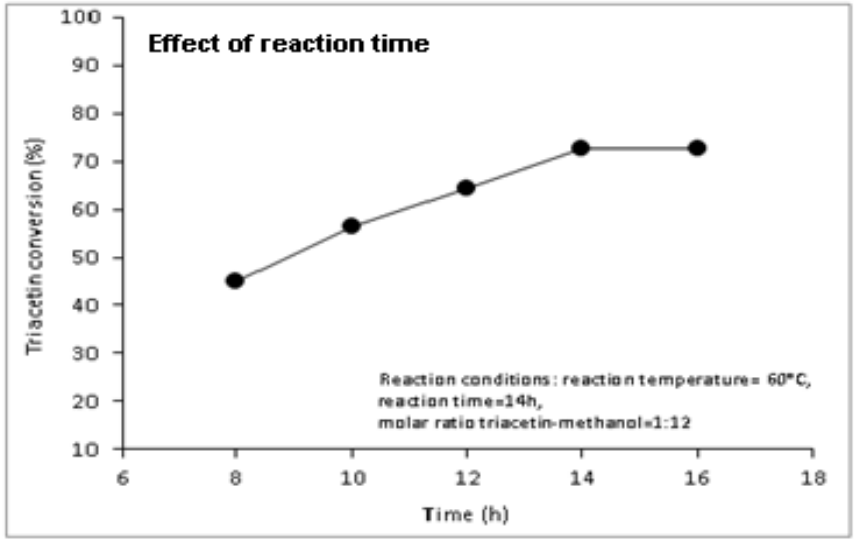
Overall reaction:

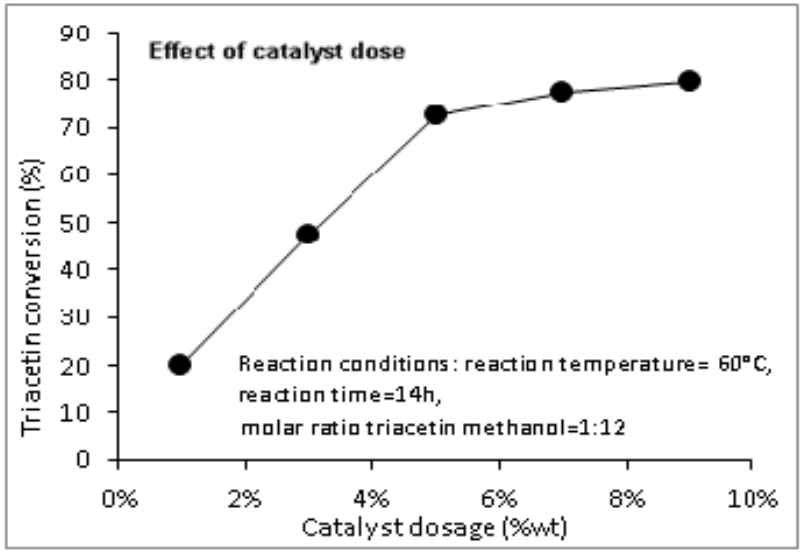


Effect of reaction parameters on triacetin conversion to biodiesel in presence of methanol using new catalyst

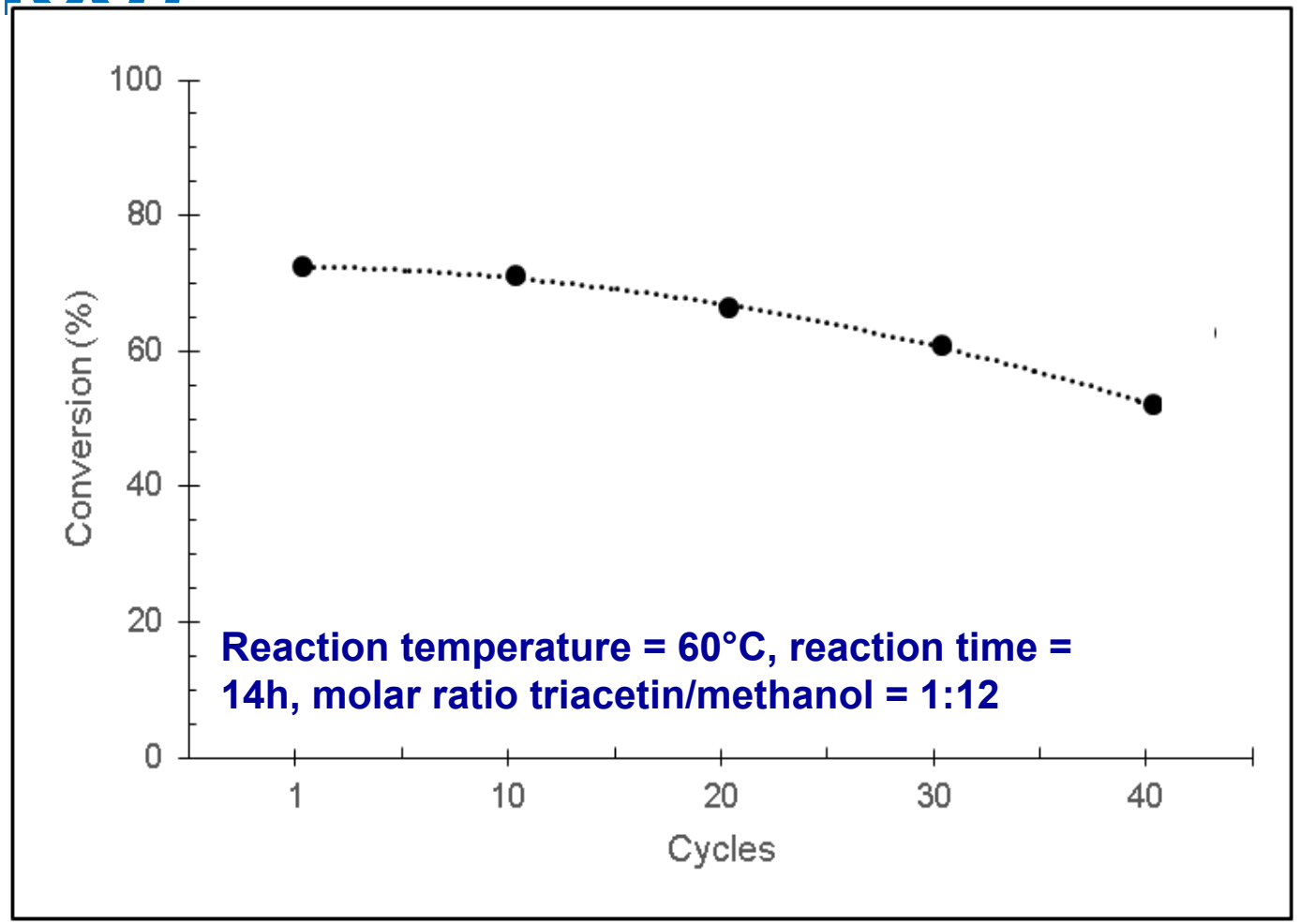




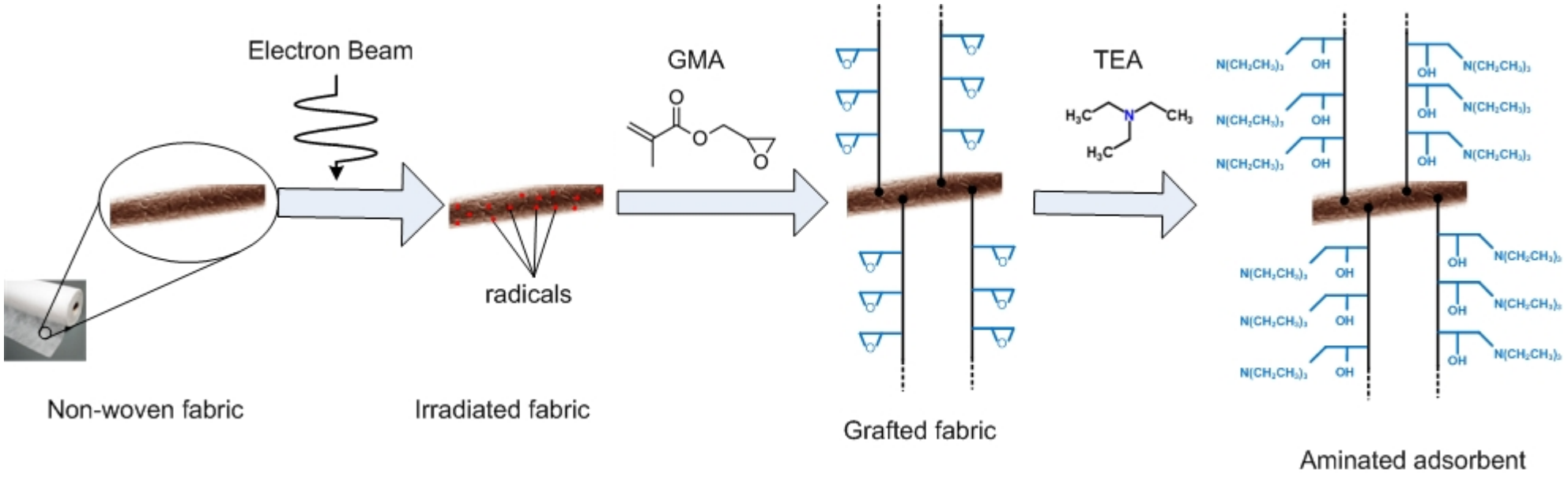




Reusability of catalyst(No of cycles)



Radiation grafted amine containing resin for purification of crude biodiesel



Purification of crude biodiesel

Sample	Soap (ppm)	K (mg/kg)	Water (mg/kg)	Methanol (%)
Crude biodiesel	1678	25	1300	2.5
Resin treated biodiesel	160	1.5	700	0.4

Note: crude biodiesel was obtain by transesterification of palm oil with KOH in presence of methanol.

Concluding Remarks

- Radiation induced grafting (RIG) is an advantageous technique for preparation of basic polymer catalyst for biodiesel production and fibrous adsorbent for purification of crude biodiesel .
- PP/PE nonwoven fabric and GMA provide an excellent combination for preparation of precursors that can be aminated and used as adsorbent in a post grafting aminated and alkalized with KOH to be sued as catalyst for biodiesel production.
- Fibrous aminated and alkalized polymer is a promising heterogeneous solid polymer basic catalyst for biodiesel production.
- The polymer catalyst can be regenerated easily by washing with methanol and KOH

Continue..

- The results of this study reveals that:
- Catalyst obtained has a strong potential for biodiesel and
- Catalyst can be recovered and regenerated easily
- The adsorbent can be effectively purify crude biodiesel
- The use of radiation grafted catalyst and adsorbent provide a combination forming a new strategy to improve the environmental impact of biodiesel production.

Acknowledgments

- The author wishes to thank:
  - The Malaysian Ministry of Higher Education (MOHE) for awarding this research grant under Research University (RU) Fund
  - Malaysian Nuclear Agency for access to irradiation facilities


THANK YOU
SAVE PLANT
SAVE ENERGY
SAVE LIFE