# Heterogeneous Guanidine Catalyst for Lipid Conversion to Sustainable Biofuel

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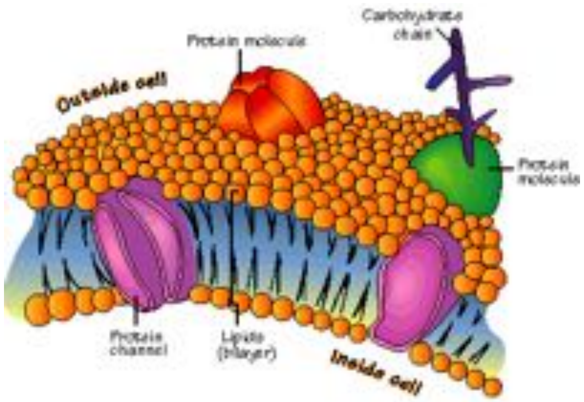



**AICHE Fall 2013**

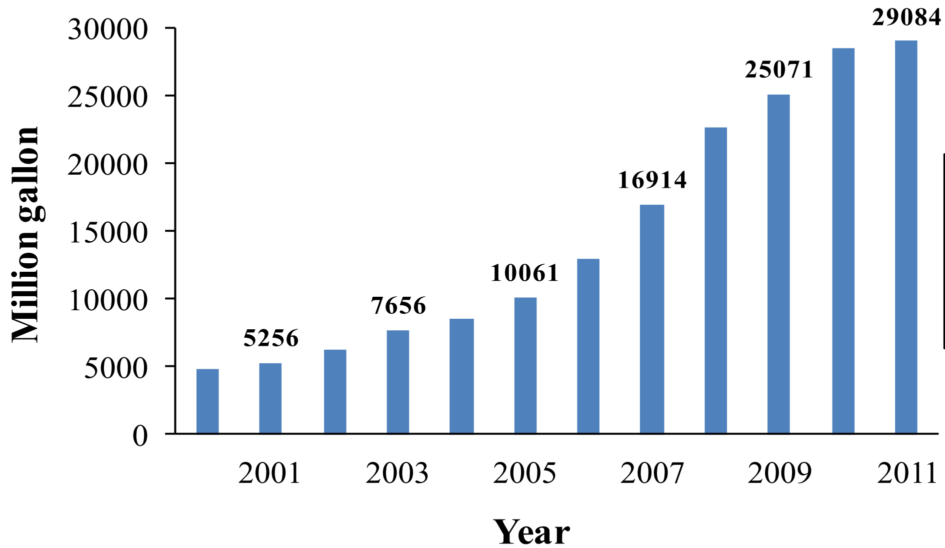
# Back to the Origin of Biodiesel

**Already in 1895 Rudolph Diesel tested vegetable oils (peanut oil) as fuel for his engine.**

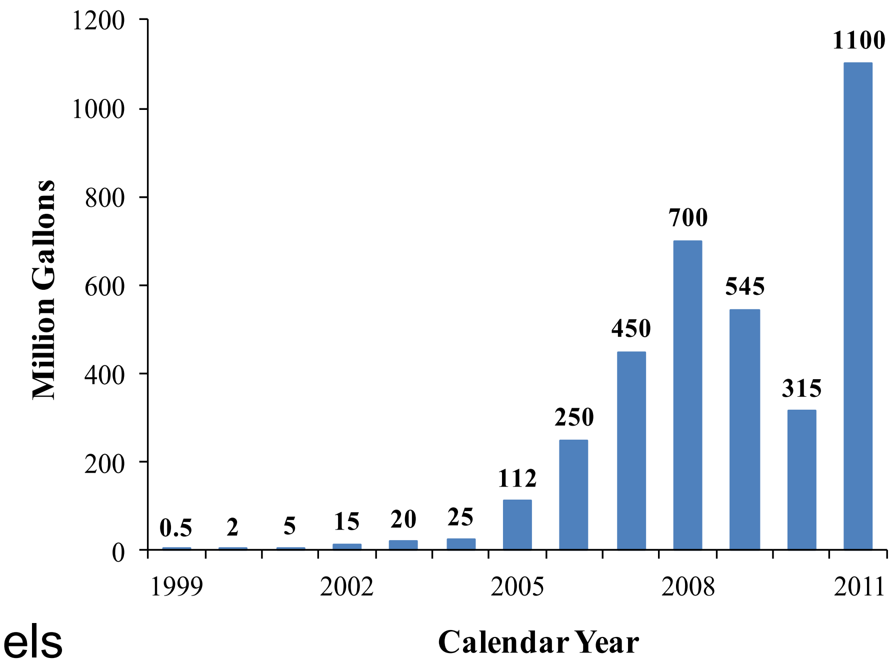
*"The use of vegetable oils for engine fuels may seem insignificant today.
But such oils may become in the course of time as important as the petroleum and coal tar products of the present time"*

*Rudolph Diesel, 1912*

# Biofuel Production Trend




Total biofuel (biodiesel and bio-ethanol) production in the world from 2000-2011. Source: US EIA.




The US biodiesel production from 1999-2011. Source: National Biodiesel Board, 2012.

**USA Biofuels Targets**

Federal RFS – 36 billion gallons by 2022

22 Billion Gallons from “2nd Generation” Fuels

# Biodiesel

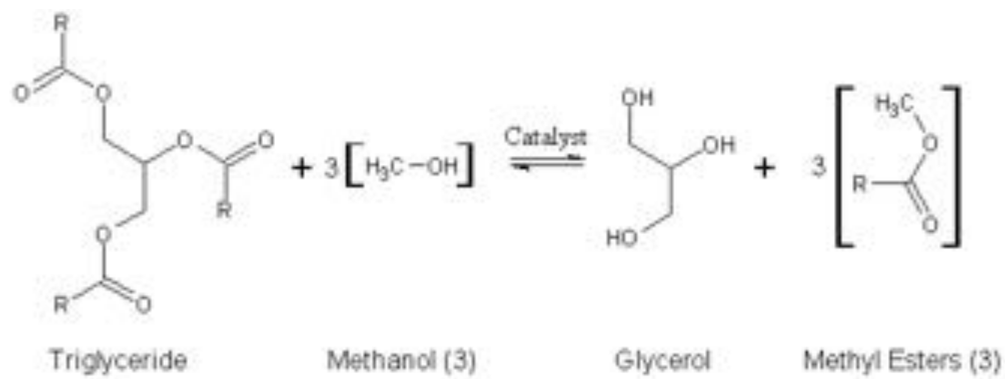
❖Fatty Acid Methyl Esters (FAME's) - Produced from triglyceride oils

❖Current Feedstocks

  - ❖Row-crop oils such as soy, canola, peanut and sunflower
  - ❖Animal fats such as tallow

❖Future Feedstocks

  - ❖Microbial sources such as algae, fungi, yeast




# Motivation for this Work

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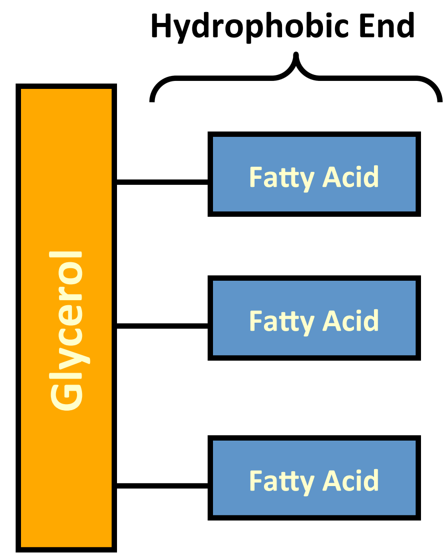
Revella
Revella

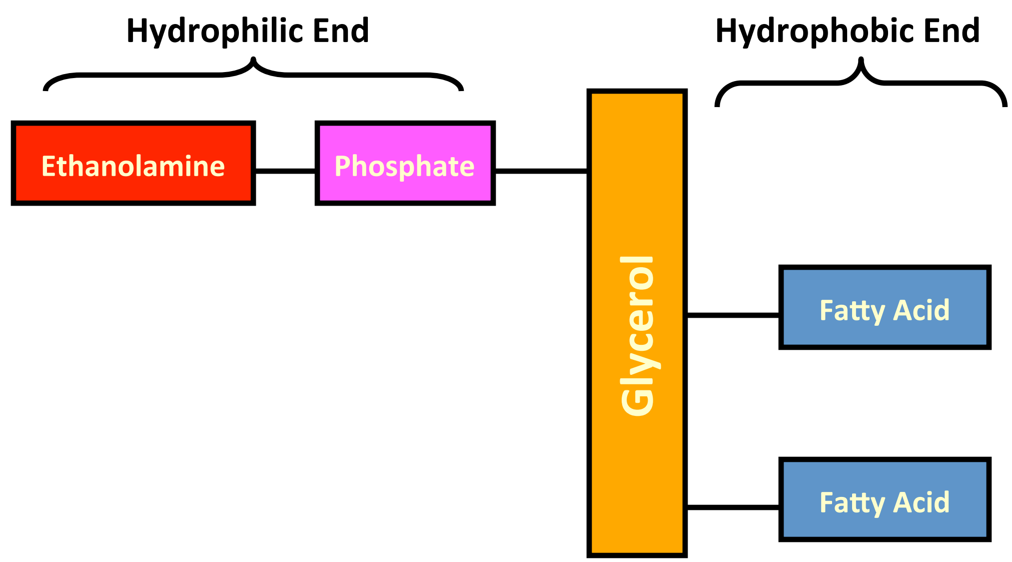

ms

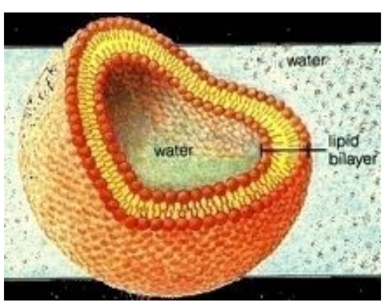
# Lipid Building Blocks

**Triglyceride**
**(plants and animals)**



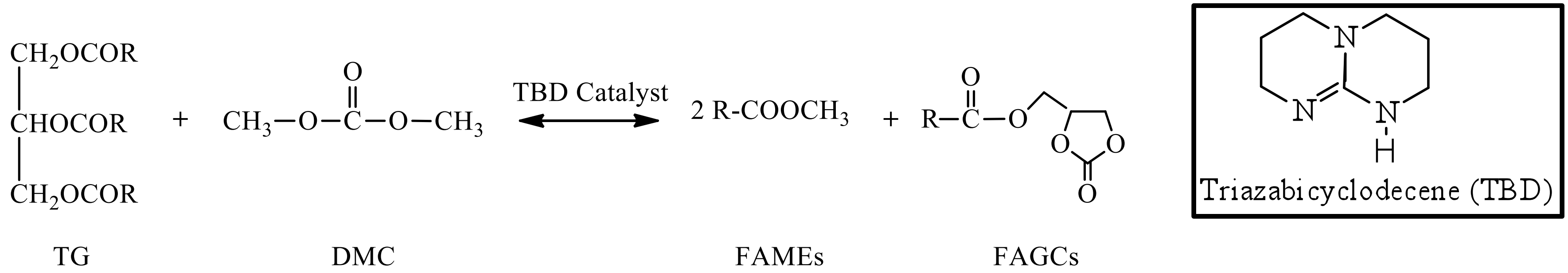

**Phospholipid**
**(bacteria)**



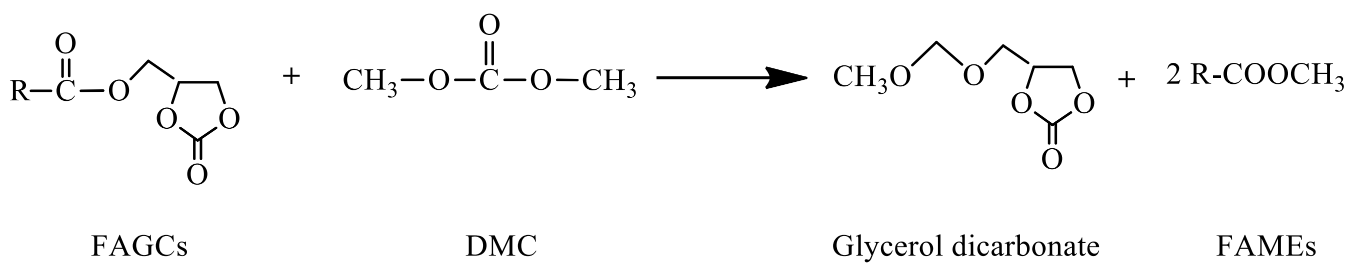



# Reaction Route for Glycerol-free Biodiesel

(a)




(b)




**Reasons for Alternant Methylating Agent**

- Glycerol is an unwanted byproduct
  - ✓1 lb of glycerol produced for every 10 lb biodiesel produced
- Complex processing (water washing, crude glycerol, biodiesel finishing)
  - ✓Crude glycerol – catalyst salts, water
- Free Fatty Acids + water + NaMeO = Soap

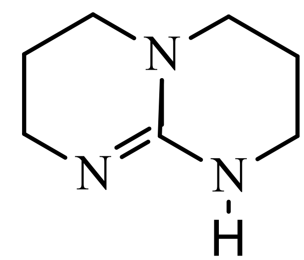
# Comparison of Biofuels

| Parameters | MeOH-Biodiesel | DMC-Biofuel (Our Process) |
|---|---|---|
| Feedstock | Vegetable oil | Vegetable oil (Canola) |
| Products | FAME | FAME and FAGC |
| Byproduct | Glycerol (10 wt.%) | GDC (< 1wt.%) |
| Catalyst | NaOH/KOH | TBD |
| Maximum yield (%) | 100 | 109.7 |
| Neutralization | **Required** | **Not required** |
| Water washing | **Required** | **Not required** |

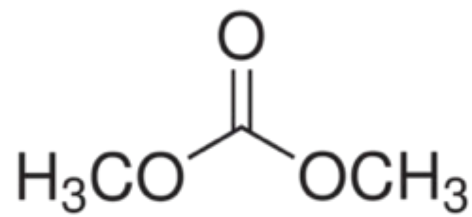
$$\text{Yield (\%)} = \frac{\text{Final weight of FAMEs} + \text{Final weight of FAGCs}}{\text{Initial weight of oil}} \times 100\%$$

# Catalysts used in Biodiesel Production

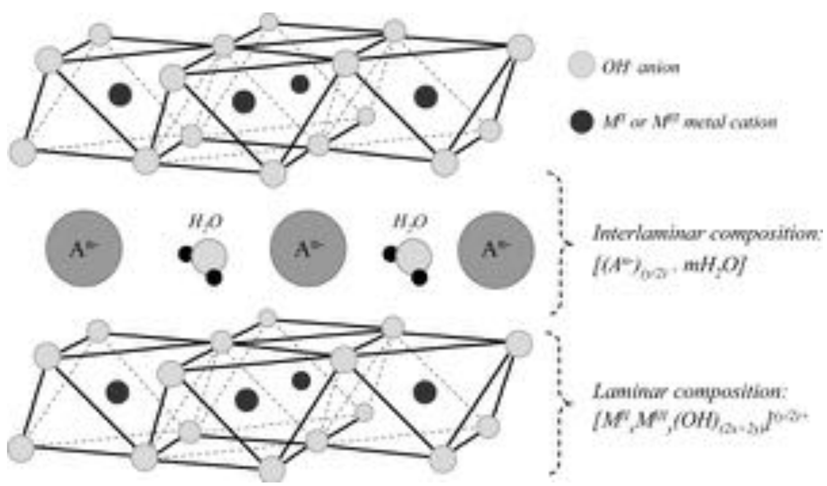
| Catalyst | Homogeneous | Heterogeneous |
|---|---|---|
| Basic | NaOMe, KOMe | Zeolites |
| | $Na_2CO_3$, $K_2CO_3$ | Oxides |
| | Guanidine | Hydrotalcite |
| Acid | $H_2SO_4$ | Amberlyst 15 |
| | HCl | Sulphated $Al_2O_3$-$ZrO_2$ |
| | $H_2PO4$ | |



Triazabicyclodecene (TBD)



Dimethyl Carbonate



# Methods and Materials

☼ Canola oil and DMC → 1:3 mole ratio

☼ 2.5 wt% TBD catalyst (based on oil weight)

☼ Continuous stirring

☼ Reaction Temperature was 60°C

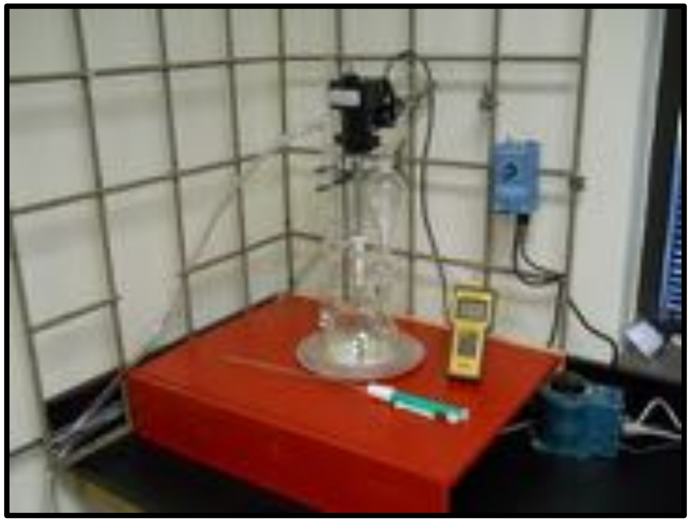
☼ Duration of reaction was 6 hours

☼ Sample extraction and preparation

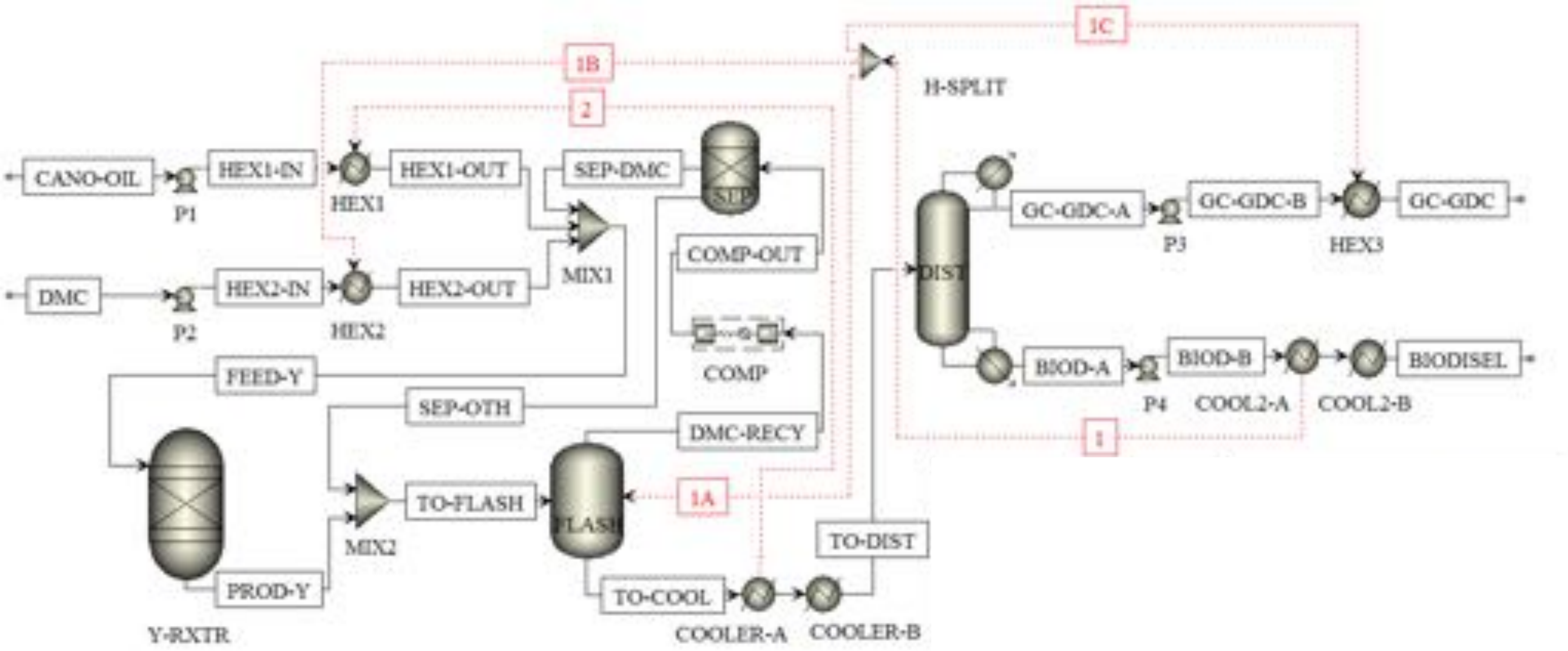
☼ Product testing –

  ☼ GC-MS, GC-FID, FTIR

  ☼ ASTM (RBFuels)

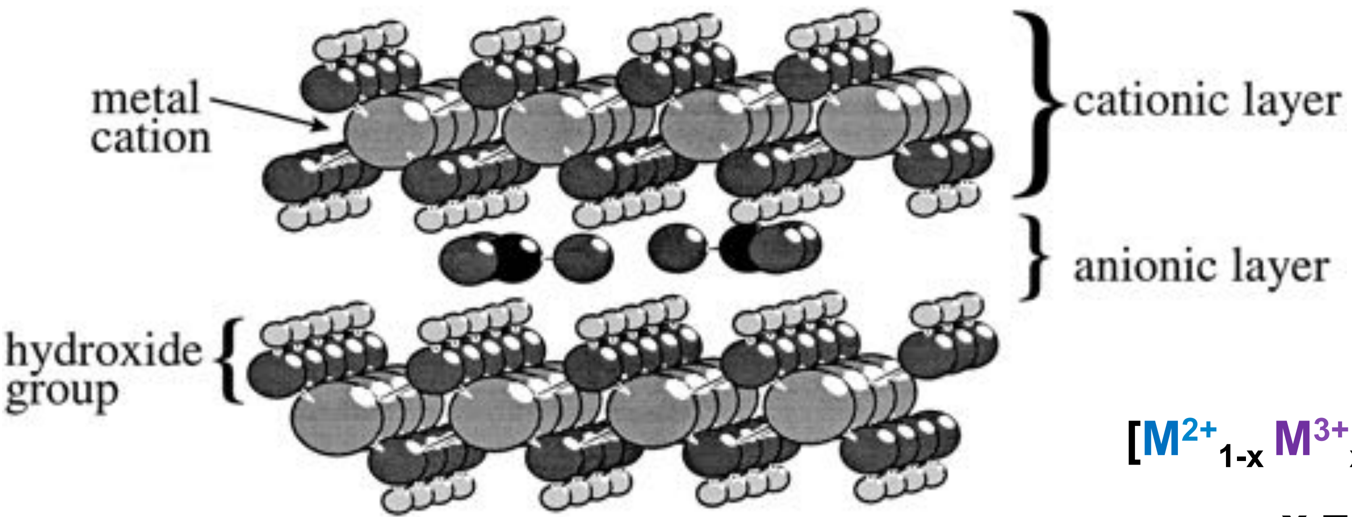


# Process Developed in this Work




| Specification | Value | Unit | Specification | Value | Unit |
|---|---|---|---|---|---|
| Flow of biofuel stream | 1098.5 | kg $h^{-1}$ | DMC, GC and GDC | 0.0052 | kg $h^{-1}$ |
| Total glycerin | 0.37 | kg $h^{-1}$ | % Impurity DMC, GC and GDC | 0.005 | % |
| % Total glycerin | 0.034 | % | Total % impurity | 0.035 | % |
| ASTM specification for glycerin | 0.24 | % | Purity of biofuel | 99.97 | % |

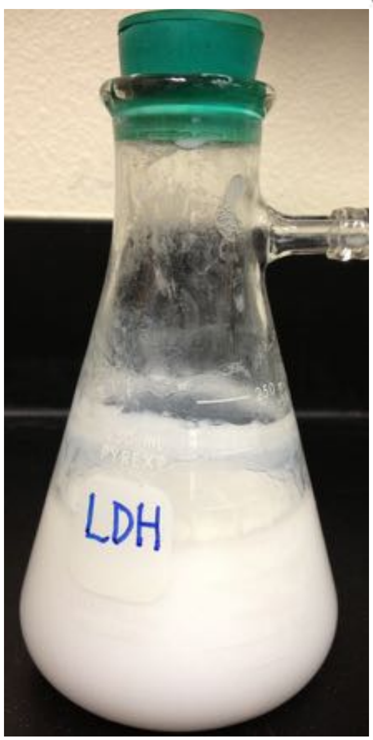
# Layered Double Hydroxides




W. Kagunya et al. *Chemical Physics* 236, 225–234 (1998)

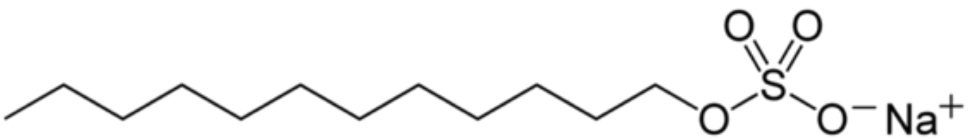
$$[M^{2+}_{1-x} M^{3+}_{x}(OH)_2]^{x+} (A^{m-})_{x/m}.nH_2O$$

$$x = M^{3+}/(M^{2+} + M^{3+})$$

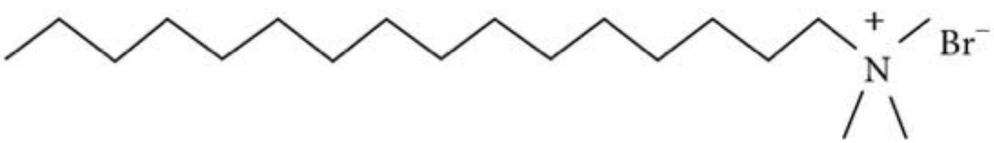



- ✓**Simplicity of the preparation at high level of purity**
- ✓**Low cost, reusability and biocompatibility**
- ✓**High dispersion property**
- ✓**Surface basic properties and structural stability**
- ✓**LDHs display very high ionic exchange capacities**
- ✓**Can be organically modified with a variety of organic anions**

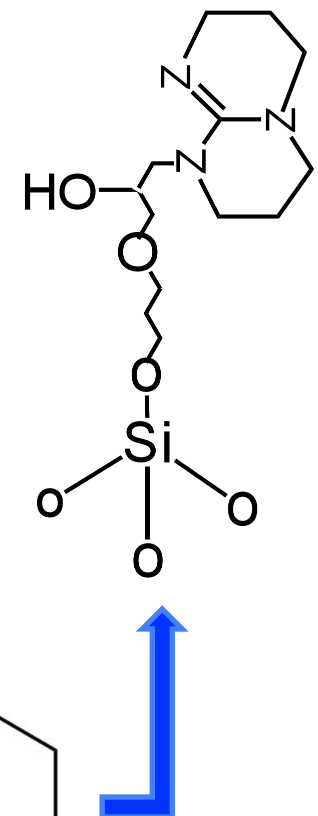
# Chemical Structures

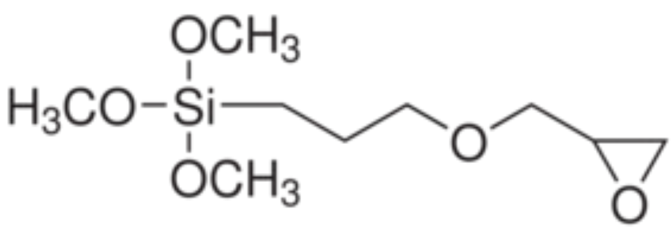



**Sodium Dodecyl Sulfate (SDS)**



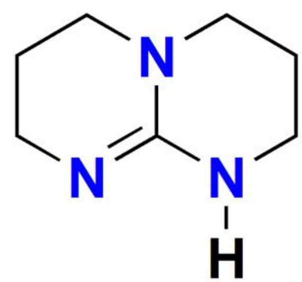

**Cetyl Trimethyl Ammonium Bromide (CTAB)**



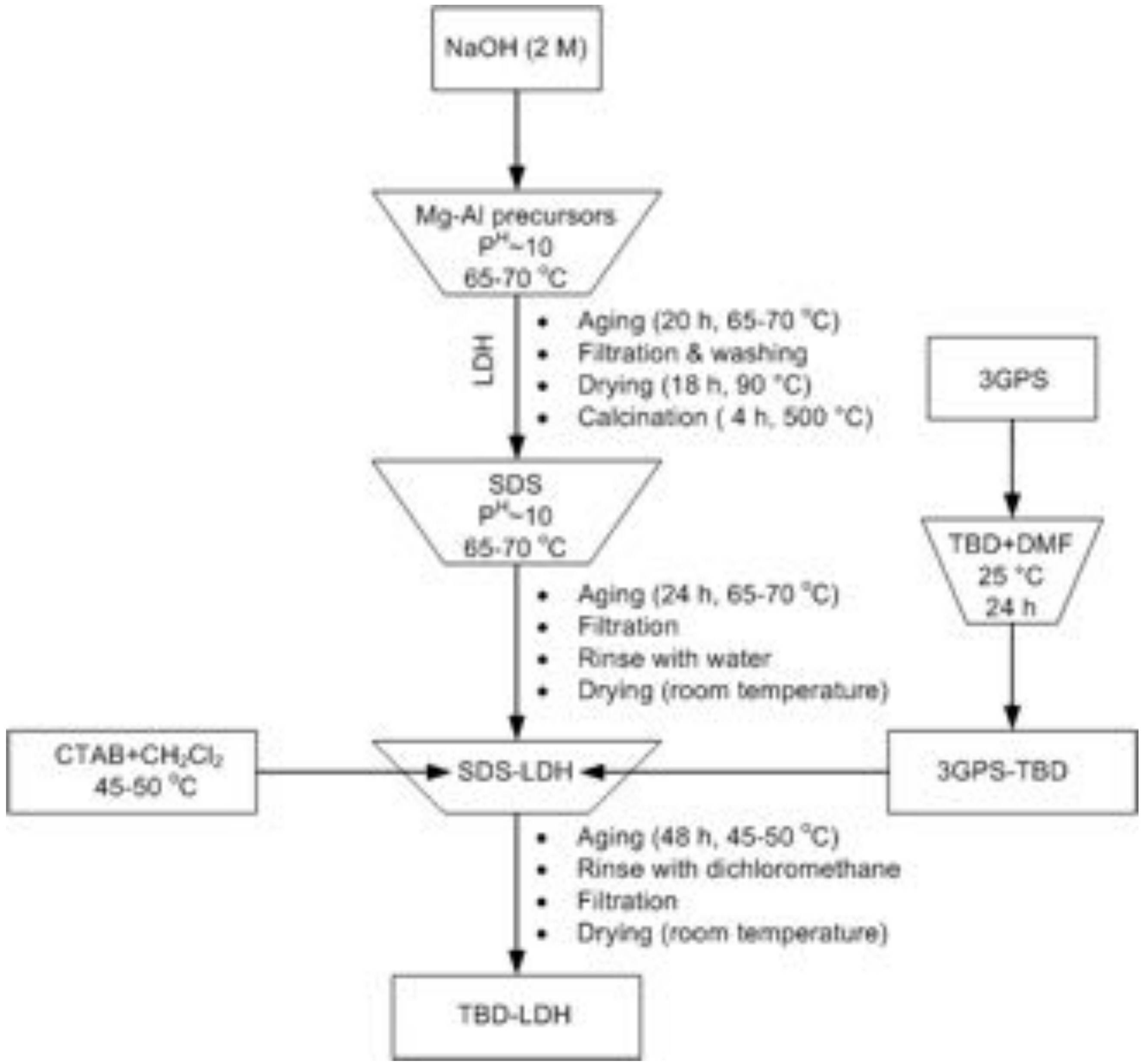

**(3-Glycidyloxypropyl) trimethoxysilane (3GPS)**

+

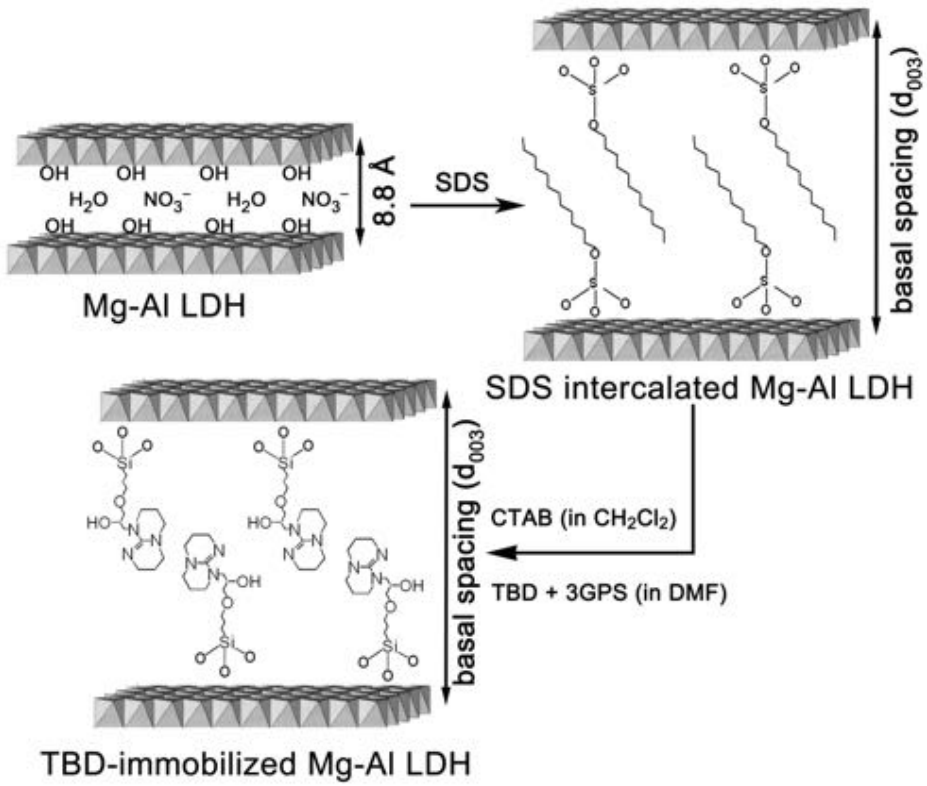


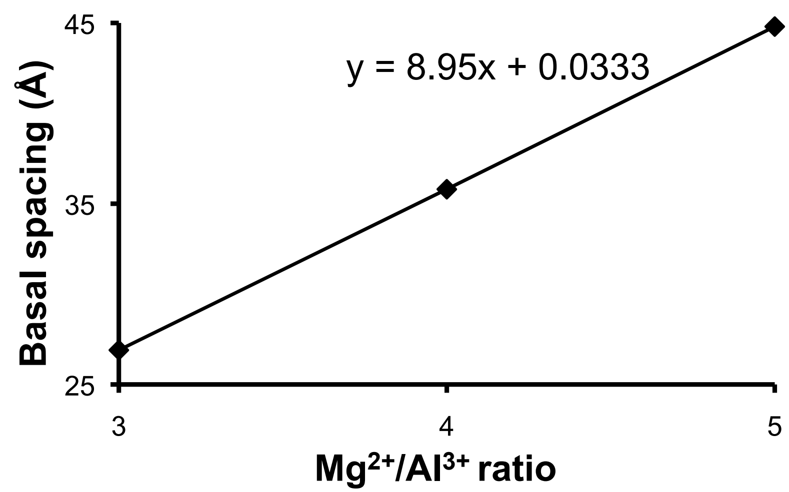

**Triazabicyclodecene (TBD)**

# Preparation by Coprecipitation Method



# Structure of Modified and TBD Immobilized LDHs




$$LDH.SDS + CTAB + X^{n-} \longrightarrow LDH.1/n\,(X^{n-}) + CTAB.SDS$$

(where, X = 3GPS.TBD)

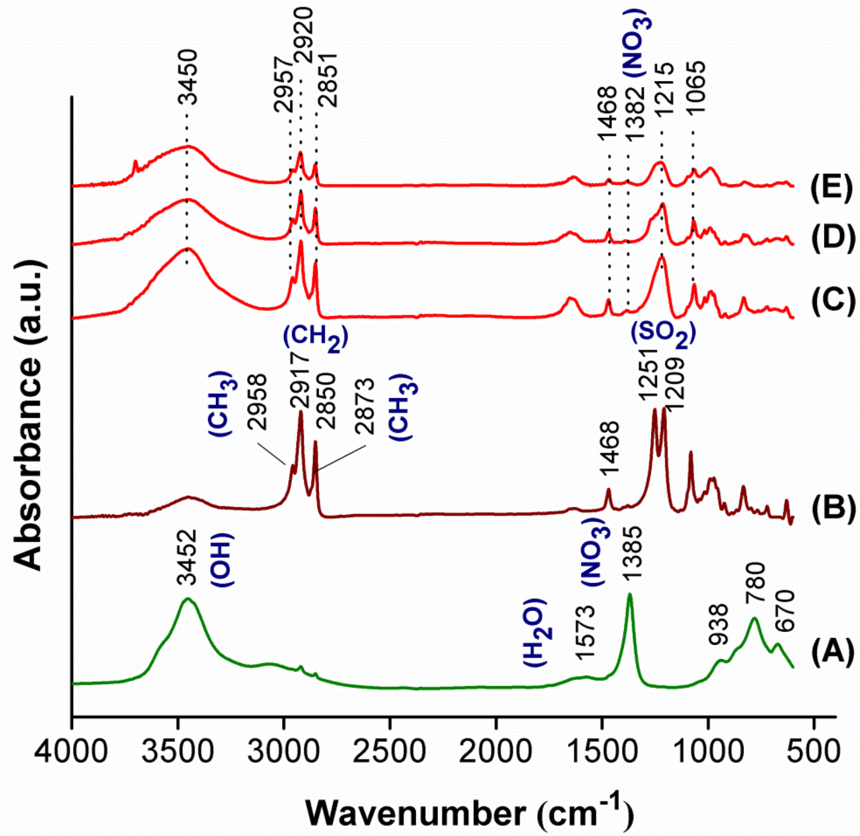
Schematic representation of SDS and TBD arrangement in Mg-Al LDH structures (not in scale).

# EDS analysis

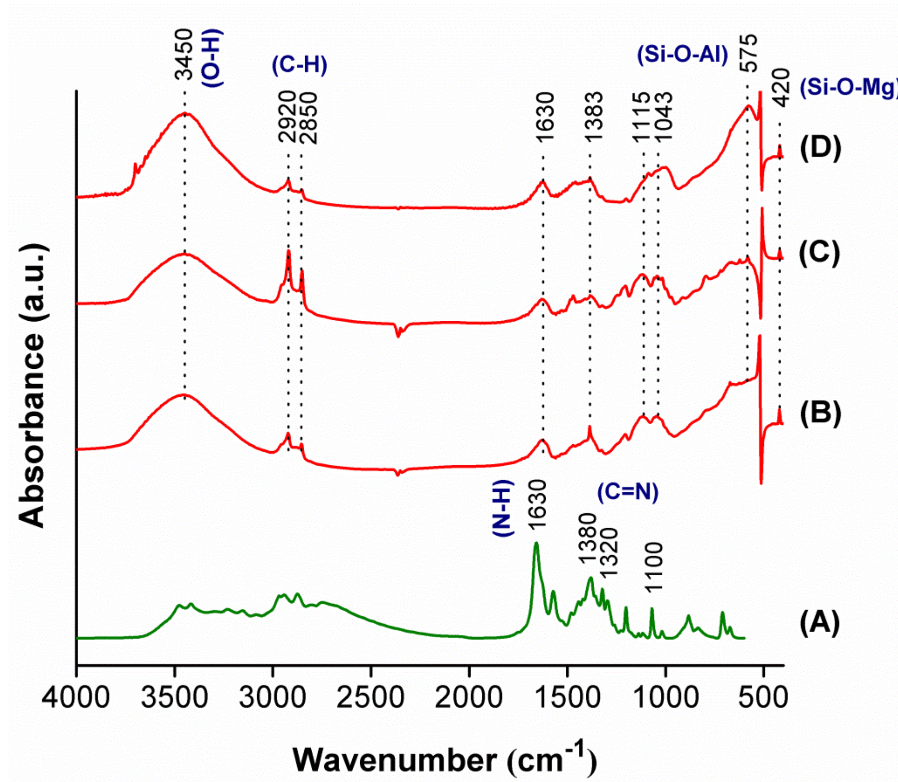
| Samples | Element % by mass[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **C** | **N** | **O** | **Na** | **Mg** | **Al** | **S** | **Si** | **Cl** |
| SDS | 59.86 | -- | 18.13 | 9.22 | -- | -- | 12.79 | -- | -- |
| LDH-3 | -- | 2.54 | 41.83 | 1.68 | 40.67 | 13.27 | -- | -- | -- |
| LDH-4 | -- | 9.03 | 46.72 | 2.17 | 34.08 | 7.99 | | | |
| LDH-5 | -- | 3.73 | 41.41 | 2.88 | 42.86 | 9.13 | | | |
| SDS-LDH-3 | 60.15 | 1.64 | 18.16 | 0.85 | 5.58 | 1.20 | 12.42 | -- | -- |
| SDS-LDH-4 | 48.11 | 2.49 | 23.56 | 0.35 | 10.40 | 4.08 | 11.01 | -- | -- |
| SDS-LDH-5 | 34.97 | 2.32 | 28.73 | 0.08 | 10.06 | 11.84 | 11.94 | -- | -- |
| TBD-LDH-3 | 44.60 | 4.38 | 27.40 | 1.27 | 8.33 | 6.43 | 1.14 | 4.11 | 2.33 |
| TBD-LDH-4 | 54.74 | 4.00 | 20.06 | 0.28 | 5.98 | 4.24 | 1.36 | 5.42 | 3.92 |
| TBD-LDH-5 | 30.69 | 3.27 | 28.30 | 0.58 | 17.67 | 4.11 | 0.43 | 8.32 | 6.63 |

- ✓ SDS intercalated LDH samples contain around **12 mass% of S**.
- ✓ TBD immobilized samples show around **1 mass% S** remaining on the samples.
- ✓ We suggested TBD was linked with surface by a silicon coupling agent and EDS data shows the presence of Si in TBD-LDHs.

# FTIR Results

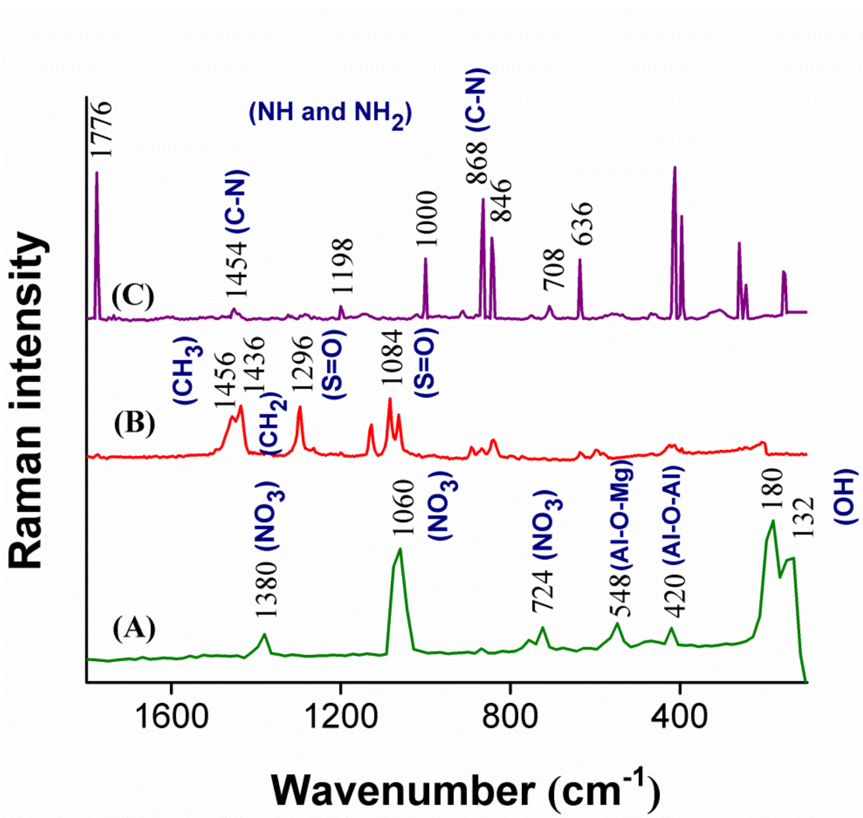



Infrared spectra of (A) LDH-3, (B) SDS, (C) SDS-LDH-3, (D) SDS-LDH-4, and (E) SDS-LDH-5.

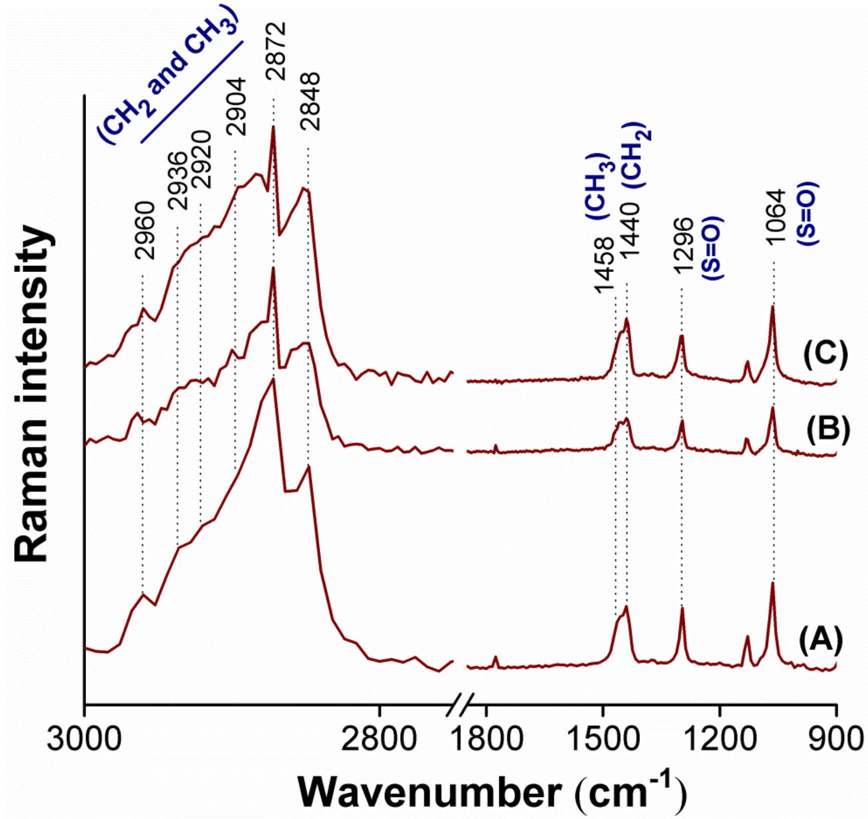



Infrared spectra of (A) TBD, (B) TBD-LDH-3, (C) TBD-LDH-4, and (D) TBD-LDH-5.

# Raman Results

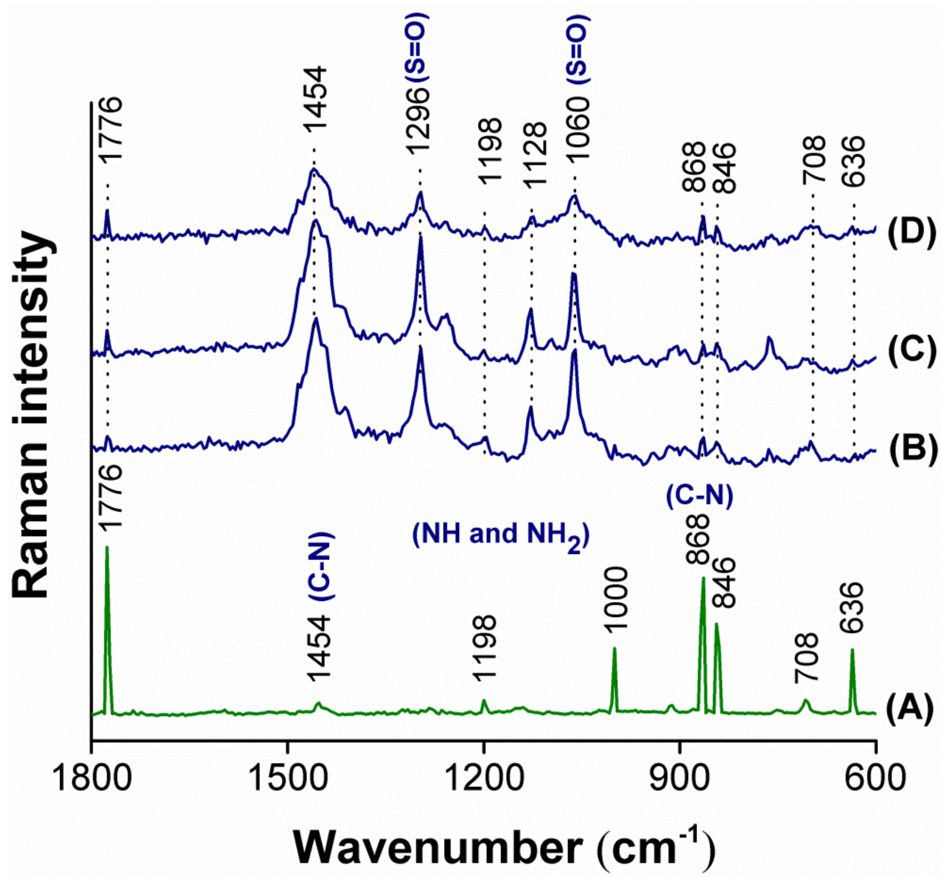



Raman spectra of (A) LDH-3, (B) SDS, and (C) TBD.




Raman spectra of (A) SDS-LDH-3, (B) SDS-LDH-4, and (C) SDS-LDH-5.

# Raman Results




Raman spectra of (A) TBD, (B) TBD-LDH-3, (C) TBD-LDH-4 and (D) TBD-LDH-5.

# Measurement of Basic Sites

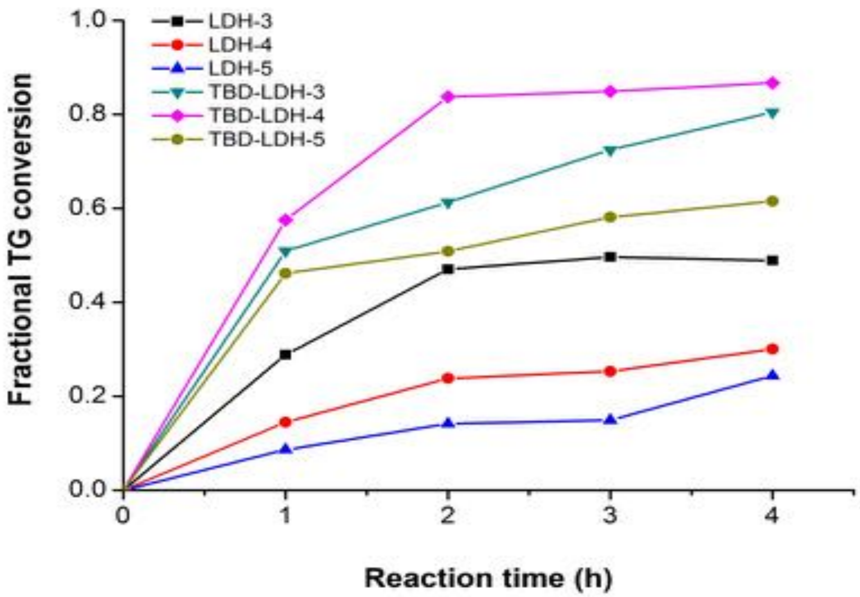
Calcined LDHs present basic sites that are associated to structural hydroxyl groups as well as strong Lewis basic sites associated to $O^{2-}M^{n+}$ acid–base pairs.

| Mg/Al molar ratio in the gel | Inorganic anion | pH of suspension in water[a] | mmol basic sites per g of Mg-Al LDHs[b] |
|---|---|---|---|
| 3 | $NO_3^-$ | 9.75 | 0.42 |
| 4 | $NO_3^-$ | 9.70 | 0.23 |
| 5 | $NO_3^-$ | 9.62 | 0.20 |
| 3 | $C_{12}H_{25}SO_4^-$ | 9.94 | 0.10 |
| 4 | $C_{12}H_{25}SO_4^-$ | 10.22 | 0.13 |
| 5 | $C_{12}H_{25}SO_4^-$ | 10.41 | 0.16 |
| 3 | TBD-$C_9H_{20}O_2SiO_3^-$ | 10.44 | 0.43 |
| 4 | TBD-$C_9H_{20}O_2SiO_3^-$ | 10.62 | 0.40 |
| 5 | TBD-$C_9H_{20}O_2SiO_3^-$ | 10.78 | 0.33 |

[a]Suspension of 0.3g of Mg-Al LHD in 20 ml deionized water.

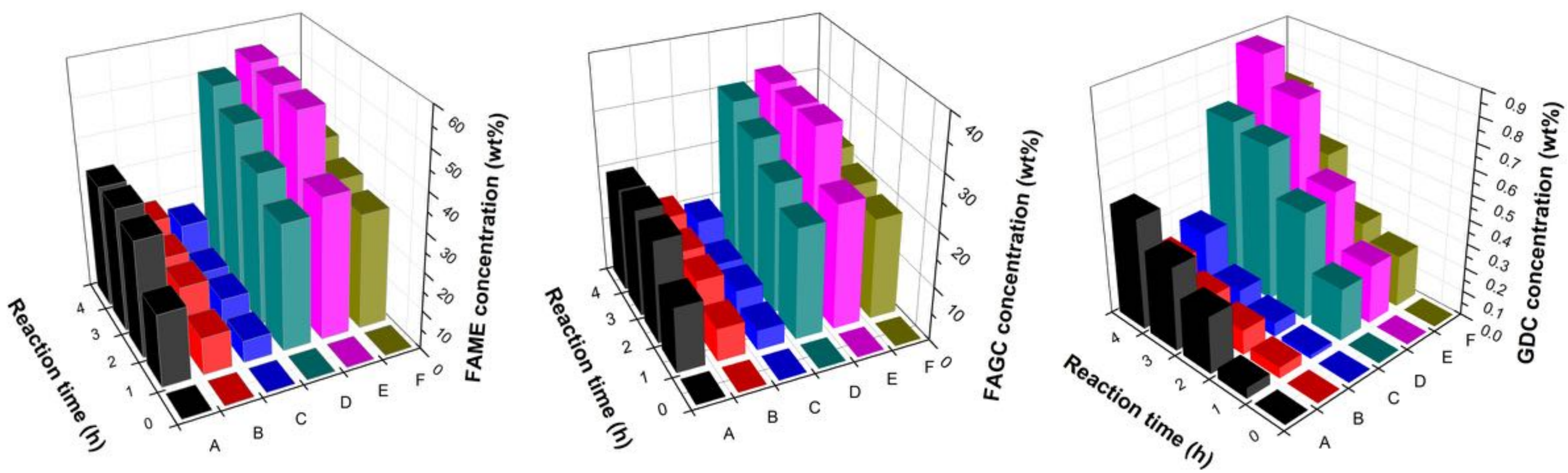
[b]0.15g Mg-Al LDH, suspended in 5 ml toluene and phenolphthalein indicator solution, was titrated with 0.01M benzoic acid dissolved in toluene.

# TG Conversion and Product Distribution




| Catalysts | TG conversion (%) |
|---|---|
| LDH-3 | 48.92 |
| LDH-4 | 30.07 |
| LDH-5 | 24.39 |
| TBD-LDH-3 | 80.47 |
| TBD-LDH-4 | 86.71 |
| TBD-LDH-4 | 61.53 |

| Time (h) | FAME (wt.%) | FAGC (wt.%) | GDC (wt.%) |
|---|---|---|---|
| 1 | 0.368 | 0.229 | 0.002 |
| 2 | 0.523 | 0.323 | 0.005 |
| 3 | 0.534 | 0.320 | 0.008 |
| 4 | 0.546 | 0.324 | 0.009 |
| Product distribution using TBD-LDH-4 | | | |




(A) LDH-3, (B) LDH-4, (C) LDH-5, (D)TBD-LDH-3, (E) TBD-LDH-4, (F) TBD-LDH-5

# Summary and Future Work

**A Homogeneous TBD catalyzed process** was developed by laboratory experiments and simulated in Aspen Plus to produce glycerol-free biofuel from canola oil using alternative transmethylating agent, DMC.

**A kinetic model** for batch canola oil and DMC reaction using TBD as homogeneous catalyst has been developed after studying oil/DMC molar ratio, temperature and catalyst loading effects on the yield of products.

**A Heterogeneous TBD-LDH** catalyst was developed to combine the advantages of homogeneous catalysis with the best properties of heterogeneous materials, and was used for canola oil transesterification with DMC.

**Ongoing Work:**

- ✓Heterogeneous reactor design and evaluation of kinetic parameters
- ✓ Catalyst robustness using real feedstock
- ✓ASPEN model development
- ✓Engine testing

# THANK YOU

- ✓ Texas Hazardous Waste Research Center
- ✓ Renewable Biofuels (RBF), Inc
- ✓ Higher Education Assistance Fund (HEAF)