Heterogeneous Guanidine Catalyst for Lipid Conversion to Sustainable Biofuel

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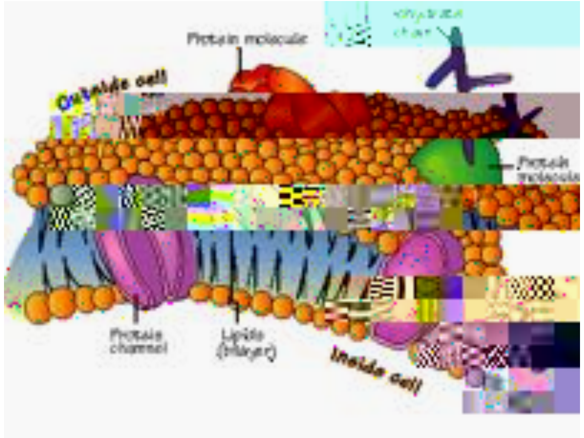

Back to the Origin of Biodiesel

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

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! Fatty Acid Methyl Esters (FAME’s) - Produced from triglyceride oils
! Current Feedstocks

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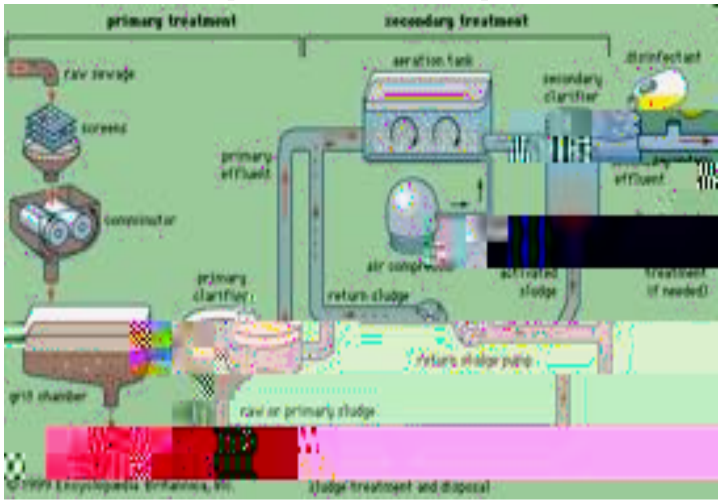
Conversion of wastewater treatment plant to a lipids factory



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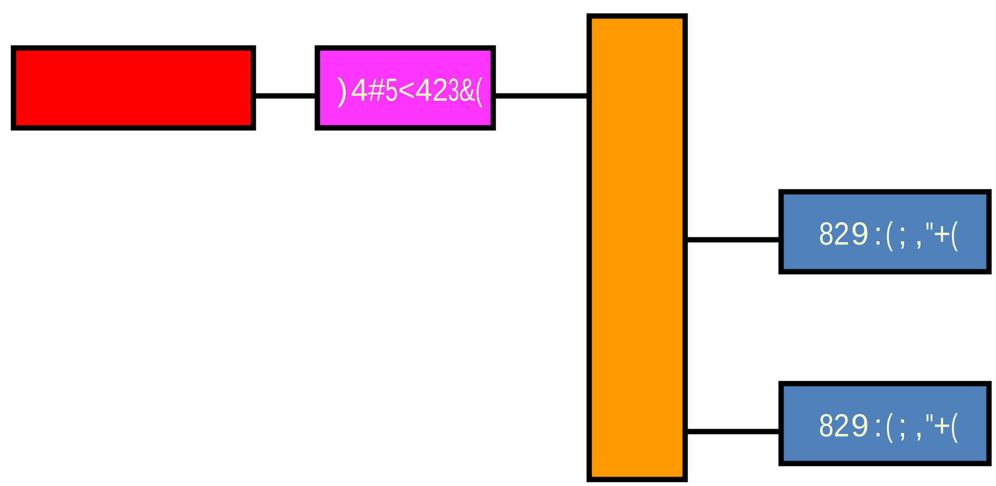
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Parameters	MeOH-Biodiesel	DMC-Biofuel (Our Process)
Feedstock	Vegetable oil	Vegetable oil (Canola)
Products	FAME	FAME and FAGC
Byproduct	Glycerol (10 wt.%)	GDC (< 1wt.%)
Catalyst	NaOH/KOH	TBD
Maximum yield (%)	100	109.7
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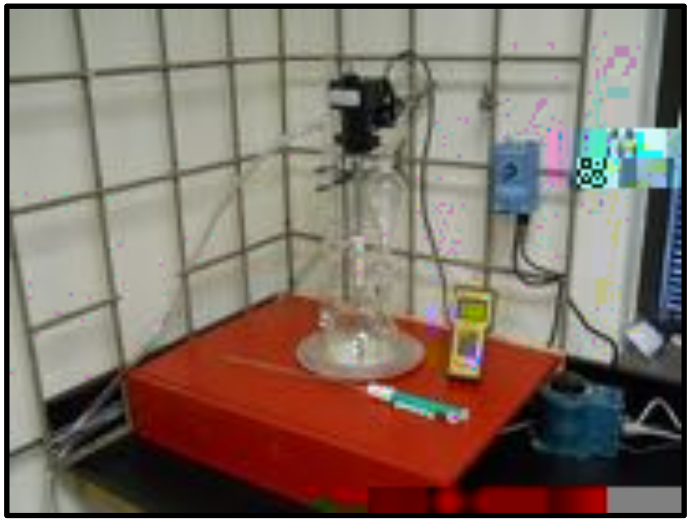
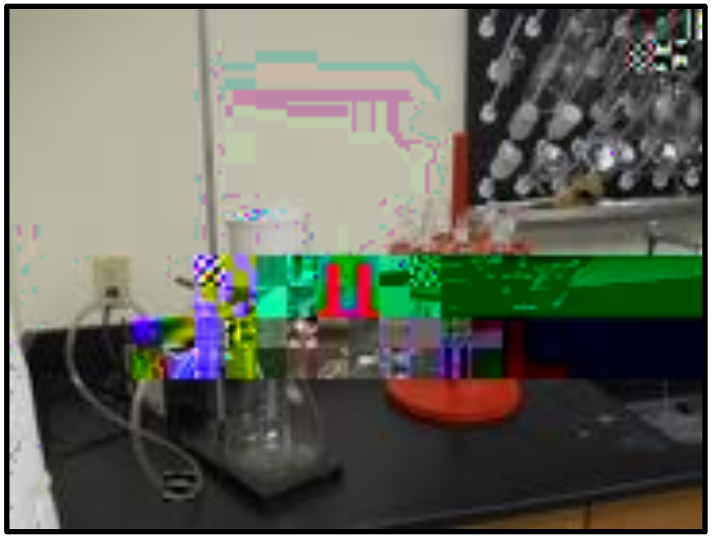
Methods and Materials

- 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)(





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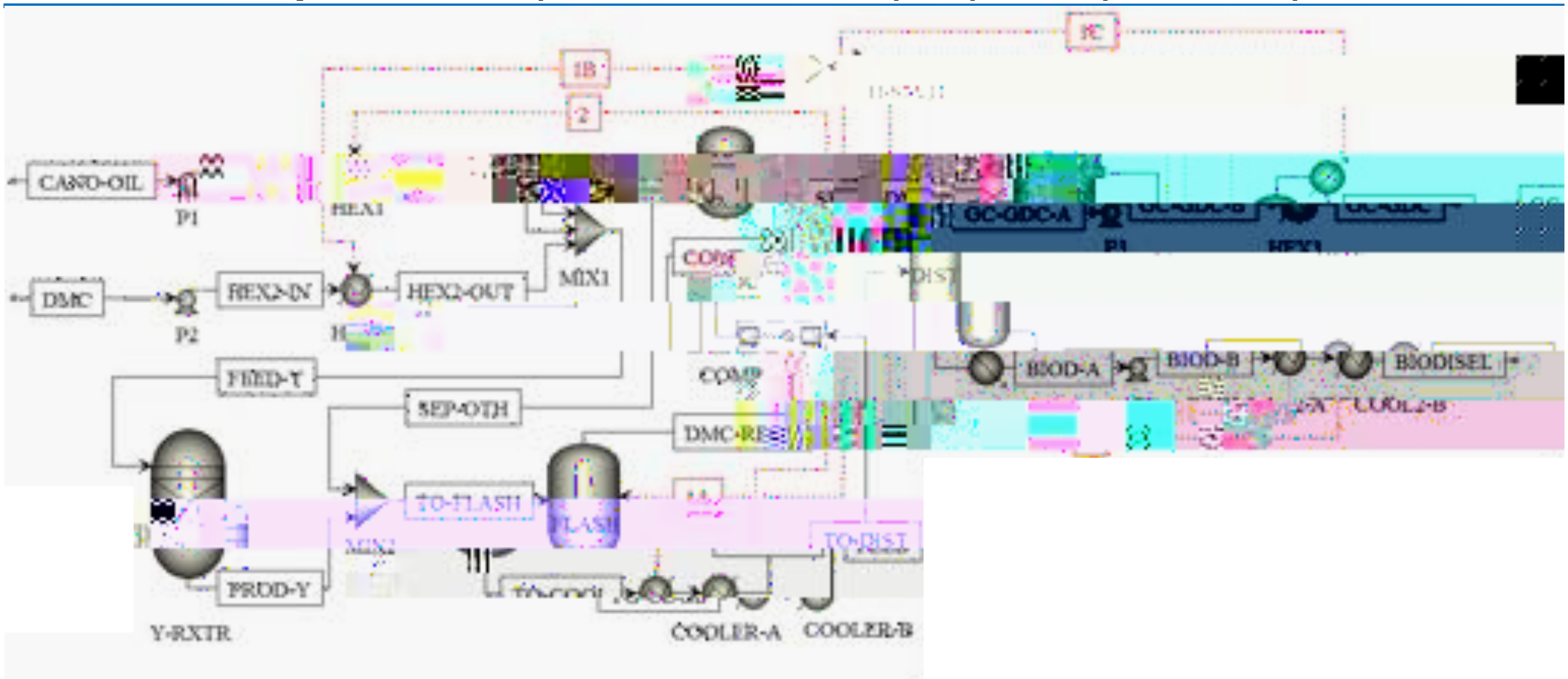

Specification	Value	Unit	Specification	Value	Unit
Flow of biofuel stream	1098.5	kg h^{-1}	DMC, GC and GDC	0.0052	kg h^{-1}
Total glycerin	0.37	kg h^{-1}	% Impurity DMC, GC and GDC	0.005	%
% Total glycerin	0.034	%	Total % impurity	0.035	%
ASTM specification for glycerin	0.24	%	Purity of biofuel	99.97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

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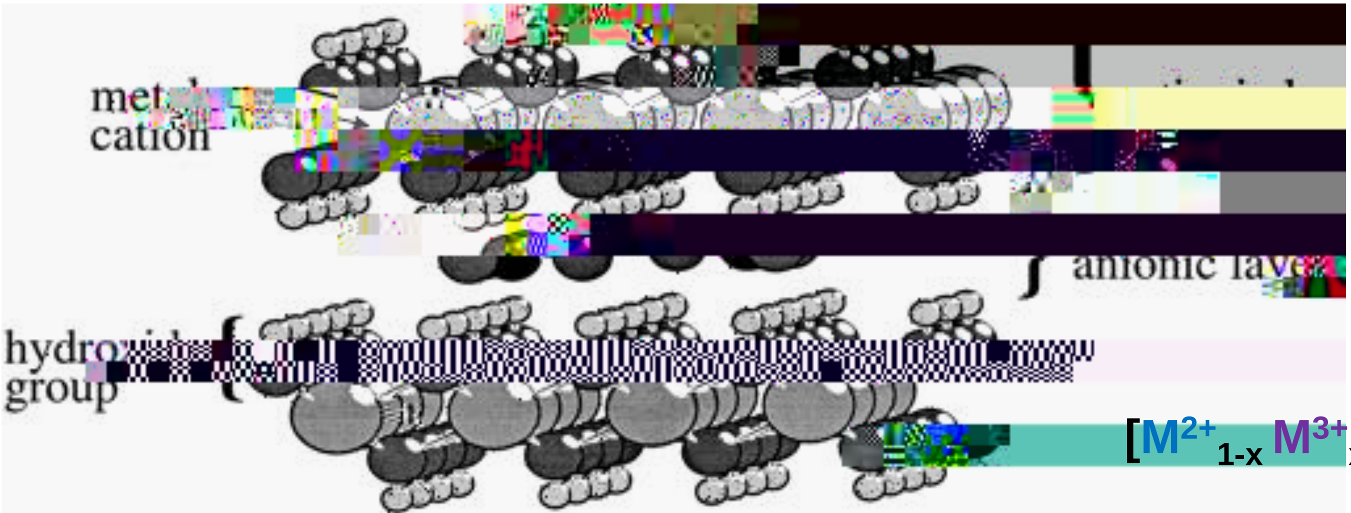

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$$[M^{2+}_{1-x} M^{3+}_{x}(OH)_2]^{x+} (A^{m-})_{x/m}.nH_2O$$

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

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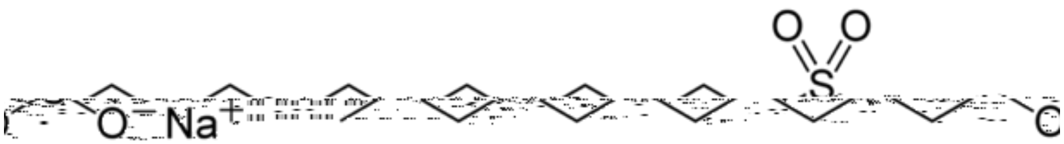
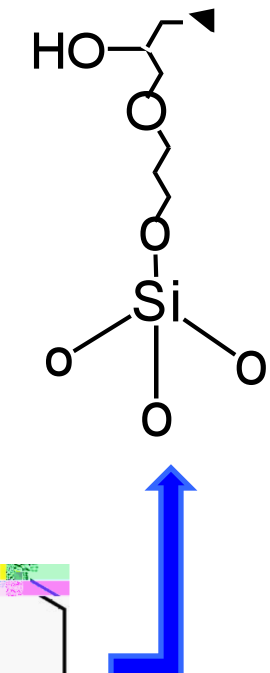
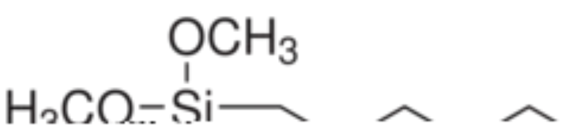


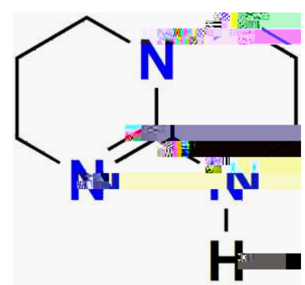
Sodium Dodecyl Sulfate (SDS)

Cetyl Trimethyl Ammonium(Bromide (CTAB)





(3-Glycidyloxypropyl) trimethoxysilane (3GPS)



Triazabicyclodecene (TBD)

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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	28.7399128.7399128.7399128.7H34.97						
TBD-LDH-3									
TBD-LDH-4									
TBD-LDH-5									

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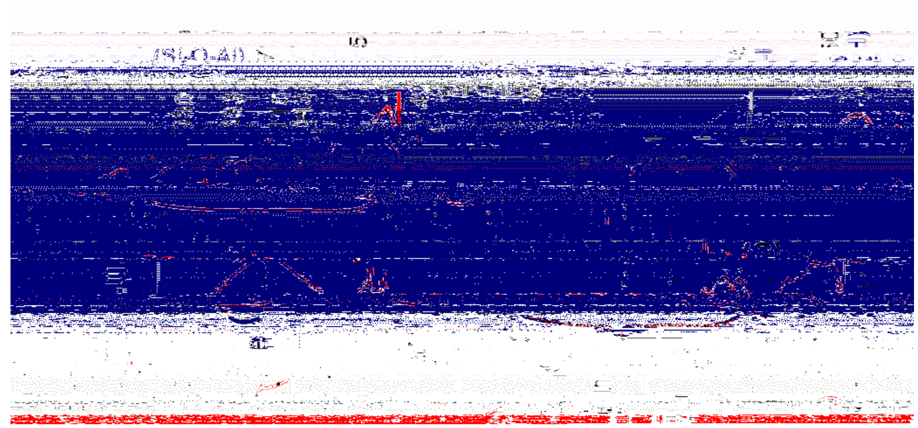

Infrared spectra of (A) LDH-3, (B) SDS, (C) SDS-LDH-3, (D) SDS-LDH-4, and (E) SDS-LDH-5.

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

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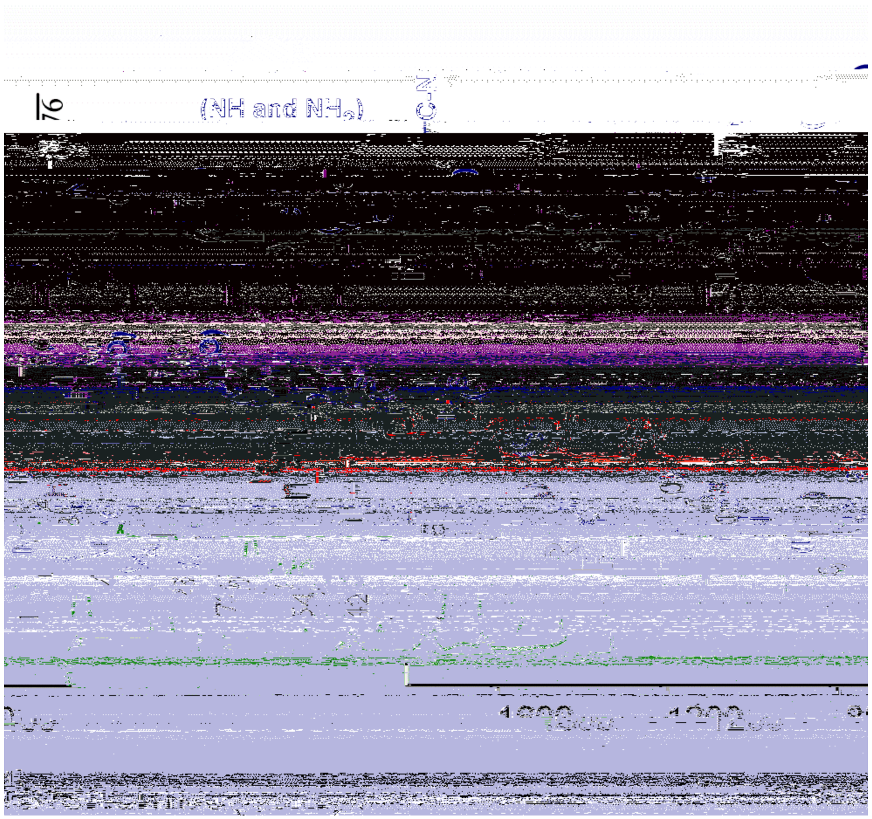
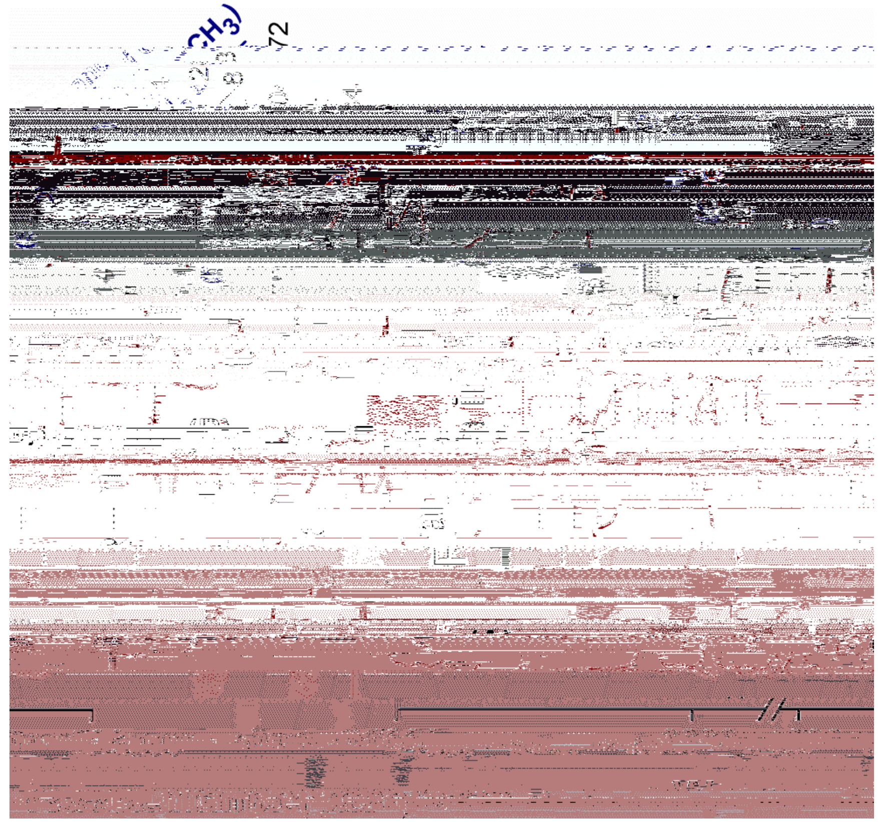


Raman spectra of (A) LDH-3, (B) SDS, and (C) TBD.



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

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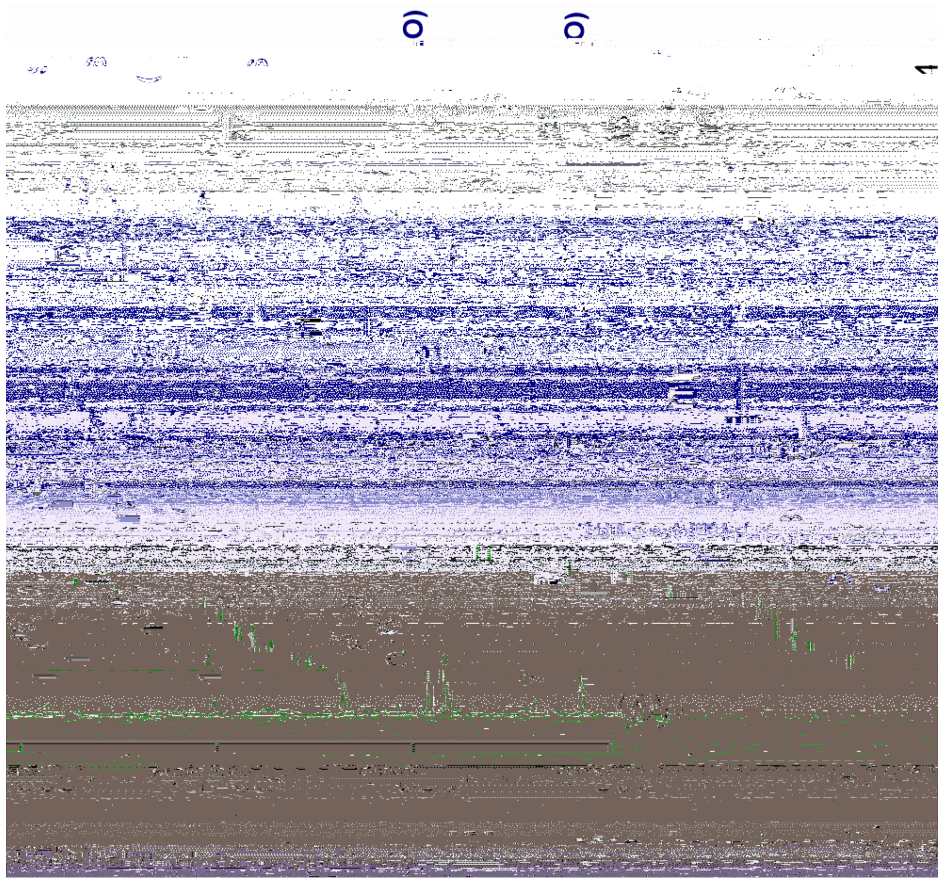

Raman spectra of (A) TBD, (B) TBD-LDH-3, (C) TBD-LDH-4 and (D) TBD-LDH-5.

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Calcined LDHs present basic sites that are associated to structural hydroxyl groups as well as strong Lewis basic sites associated to O^{2-}M $^{+}$ 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
[illegible]	$C_{12}H_{25}SO_4^-$	10.41	0.16
3	TBD-$C_9H_{20}O_2SiO_3^-$	10.44	[illegible]
4	TBD-$C_9H_{20}O_2SiO_3^-$	[illegible]	[illegible]
5	TBD-$C_9H_{20}O_2SiO_3^-$	[illegible]	0.33

[a]Suspension of 0.3g of Mg-Al LHD in 20 ml [illegible]

[b]0.15g Mg-Al LDH, suspended in 5 ml tolu[illegible]

was titrated with 0.01M benzoic acid dissolved in toluene.

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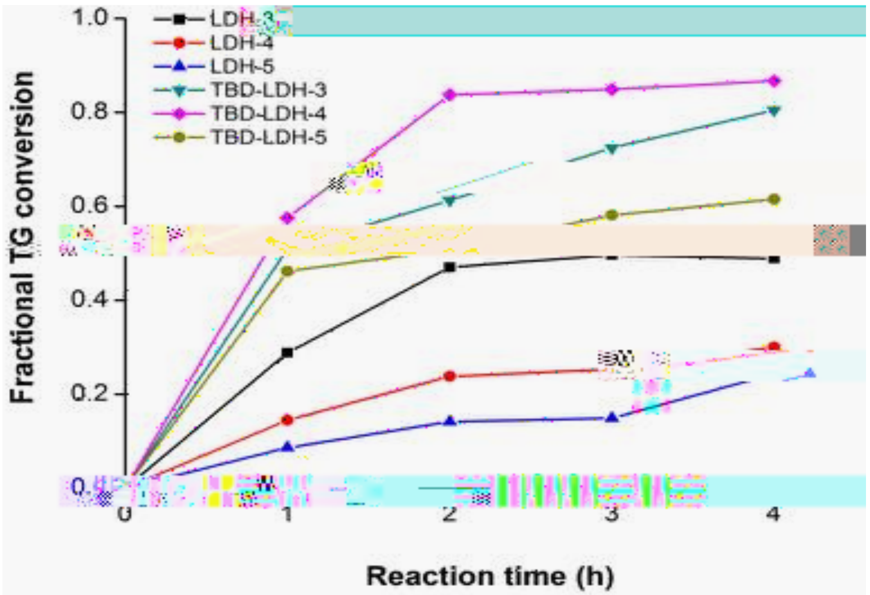
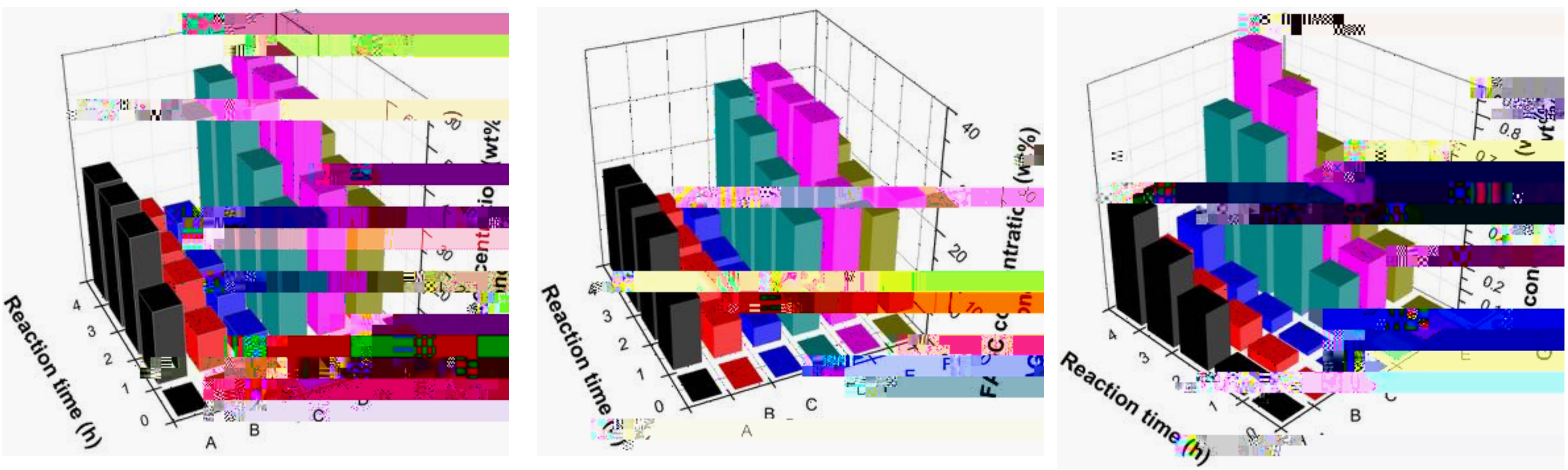


Catalysts	TG conversion (%)
LDH-3	48.92
LDH-4	30.07
LDH-5	24.39
TBD-LDH-3	80.47
TBD-LDH-4	86.71
TBD-LDH-4	61.53

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