Synthesis, Characterization and Evaluation of Sulphated Zirconias for Biodiesel Production by Triglyceride Cracking

Elizabeth J. Eterigho, J. G. M. Lee & A. P. Harvey

School of Chemical Engineering and Advanced Materials
Newcastle University, UK

Bioenergy III: Present and New Perspectives on Biorefineries Lanzarote, May, 2011

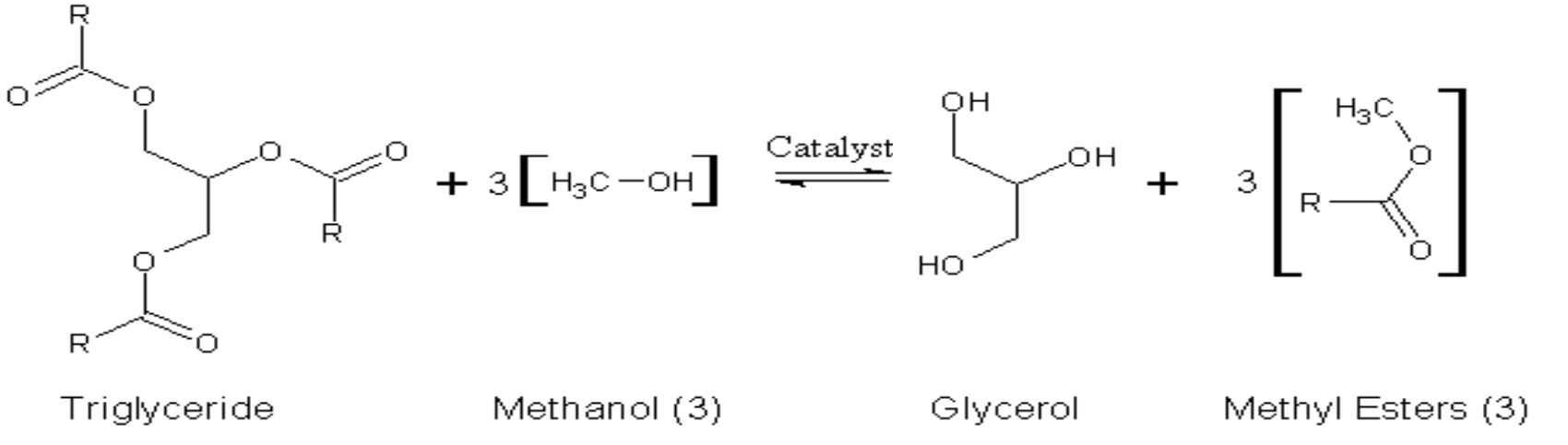
Outline

- Introduction
- Motivation of study
- Objective
- Experimental
- Results
- Conclusions

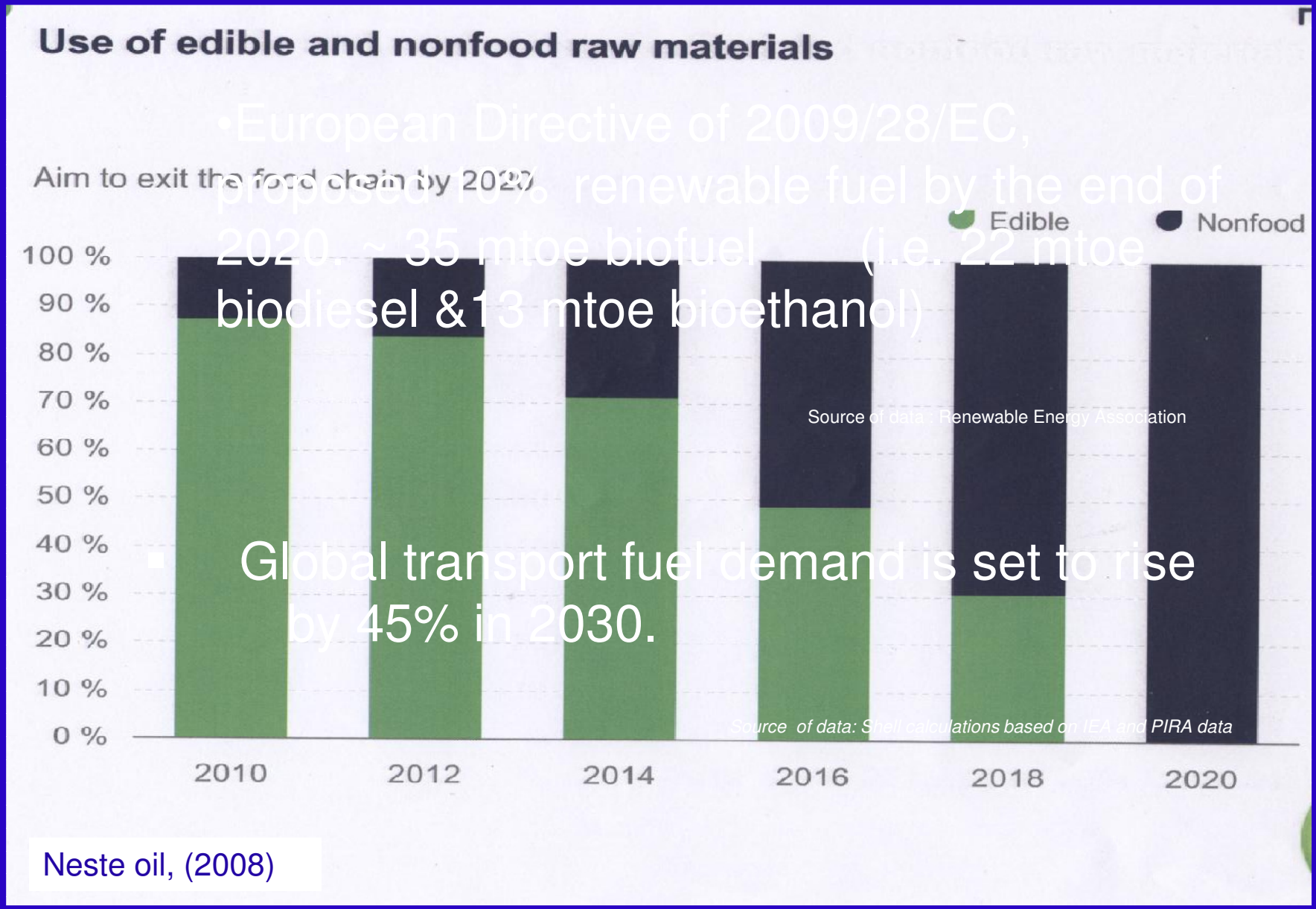
Introduction

- Biodiesel are mono-alkyl esters of fatty acids derived from natural oils. (FAMEs)
  - renewable,
  - Carbon neutral i. e. Not adding to the global warming crisis
  - it is sustainable

Conventional method



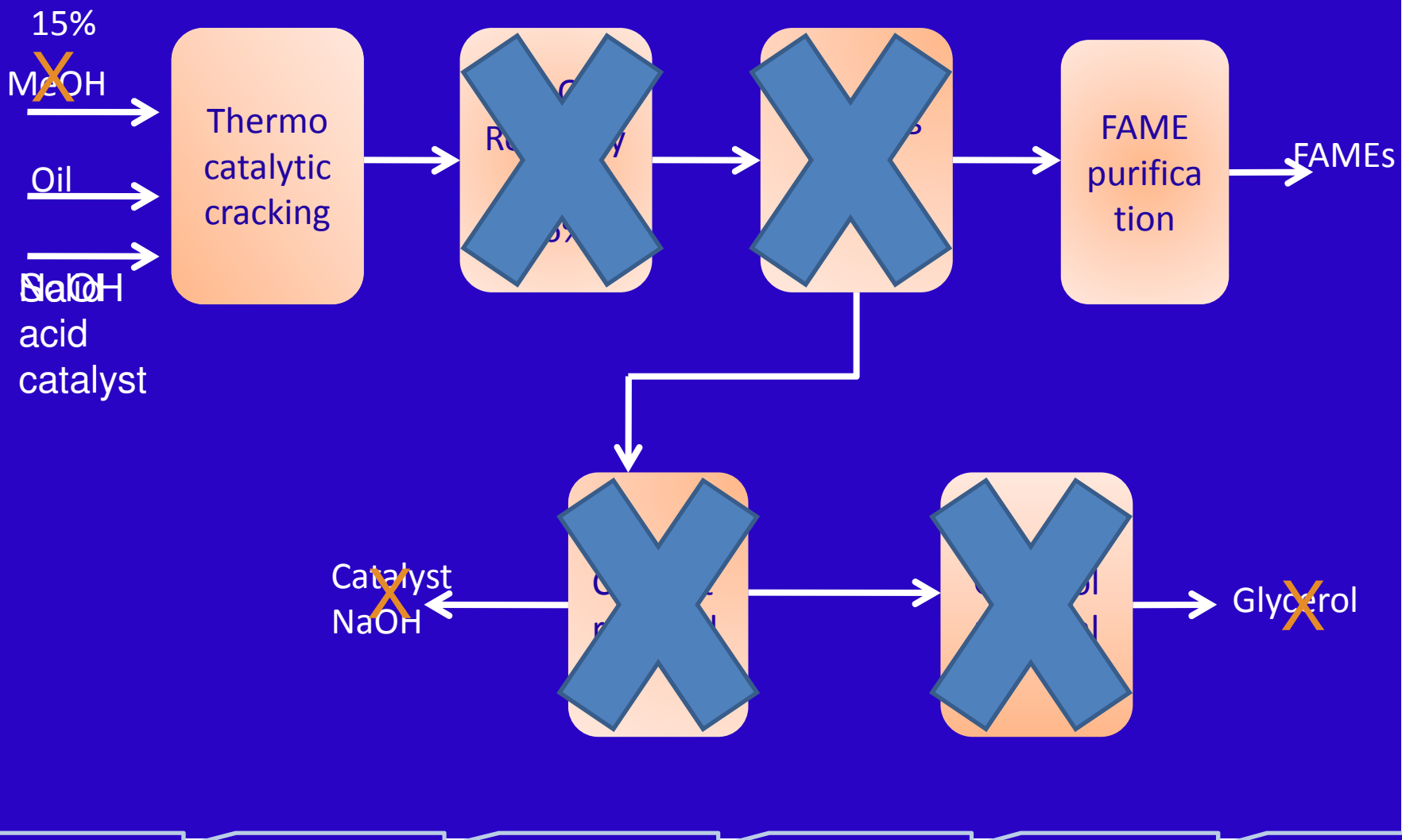
Motivation



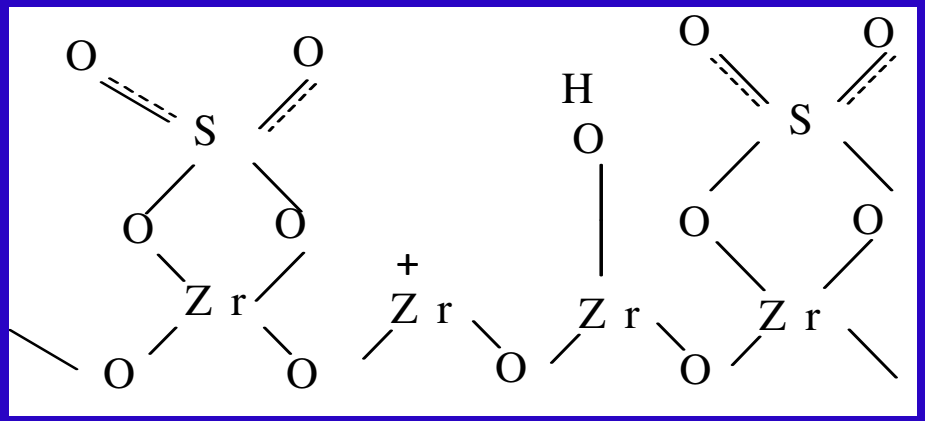
- European Directive of 2009/28/EC, proposed 10% renewable fuel by the end of 2020. ~ 35 mtoe biofuel (i.e. 22 mtoe biodiesel &13 mtoe bioethanol)
- Global transport fuel demand is set to rise by 45% in 2030.

Neste oil, (2008)

Transesterification Process



Sulphated zirconia



Sulphated zirconia is:

- ✓ super-acid catalyst with acidity 10^4 times stronger than 100% sulphuric acid
- ✓ good for organic reactions

Drawbacks:

- ✓ a relatively small surface area
- ✓ rapid deactivation and
- ✓ sulphate leaching,

Objective

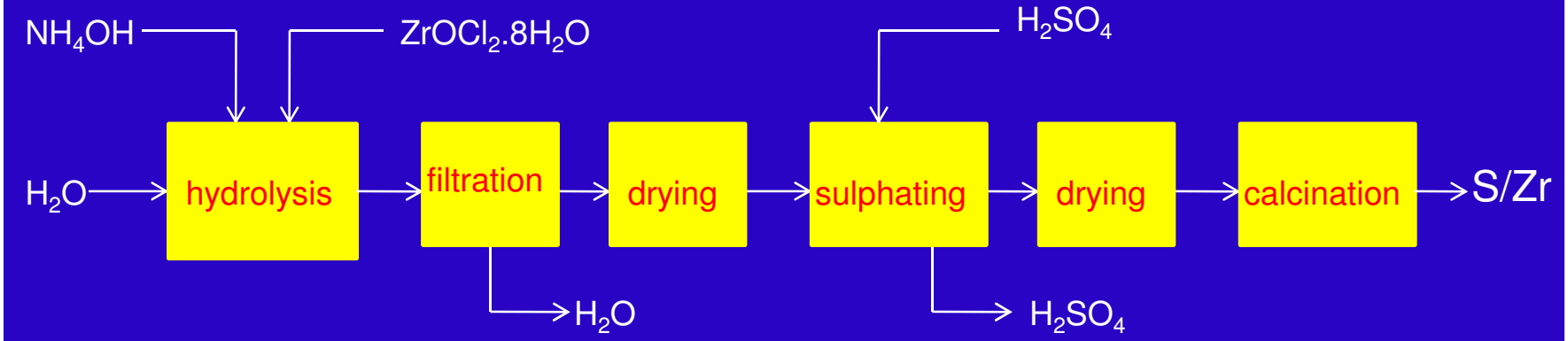
- The main objective of our research is to improve the catalytic activity of sulphated zirconia for high activity and selectivity towards desired products.

Two different methods of Preparation

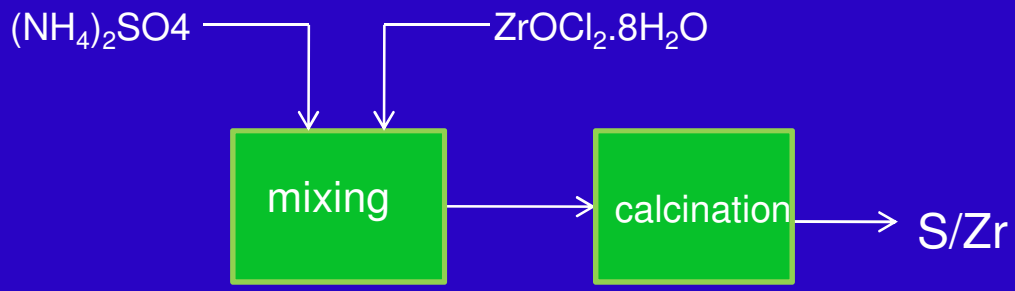
- Direct method (ds), simple calcination of $ZrOCl_2.8H_2O$ and $(NH_4)_2SO_4$ for 5 hours at 600°C
- Conventional method (cm)
  - $ZrOCl_2.8H_2O$ was hydrolysed with NH_4OH,
  - $Zr(OH)_4$ was impregnated with H_2SO_4
  - Calcination for 3 hours at 650°C .
- Characterization of catalysts

Catalyst synthesis

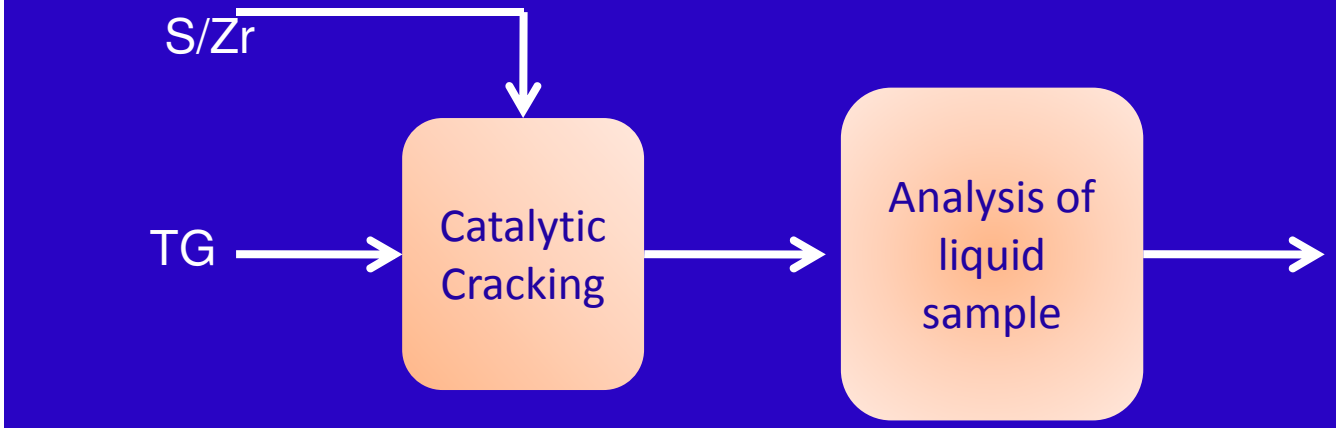
Conventional method "cm"



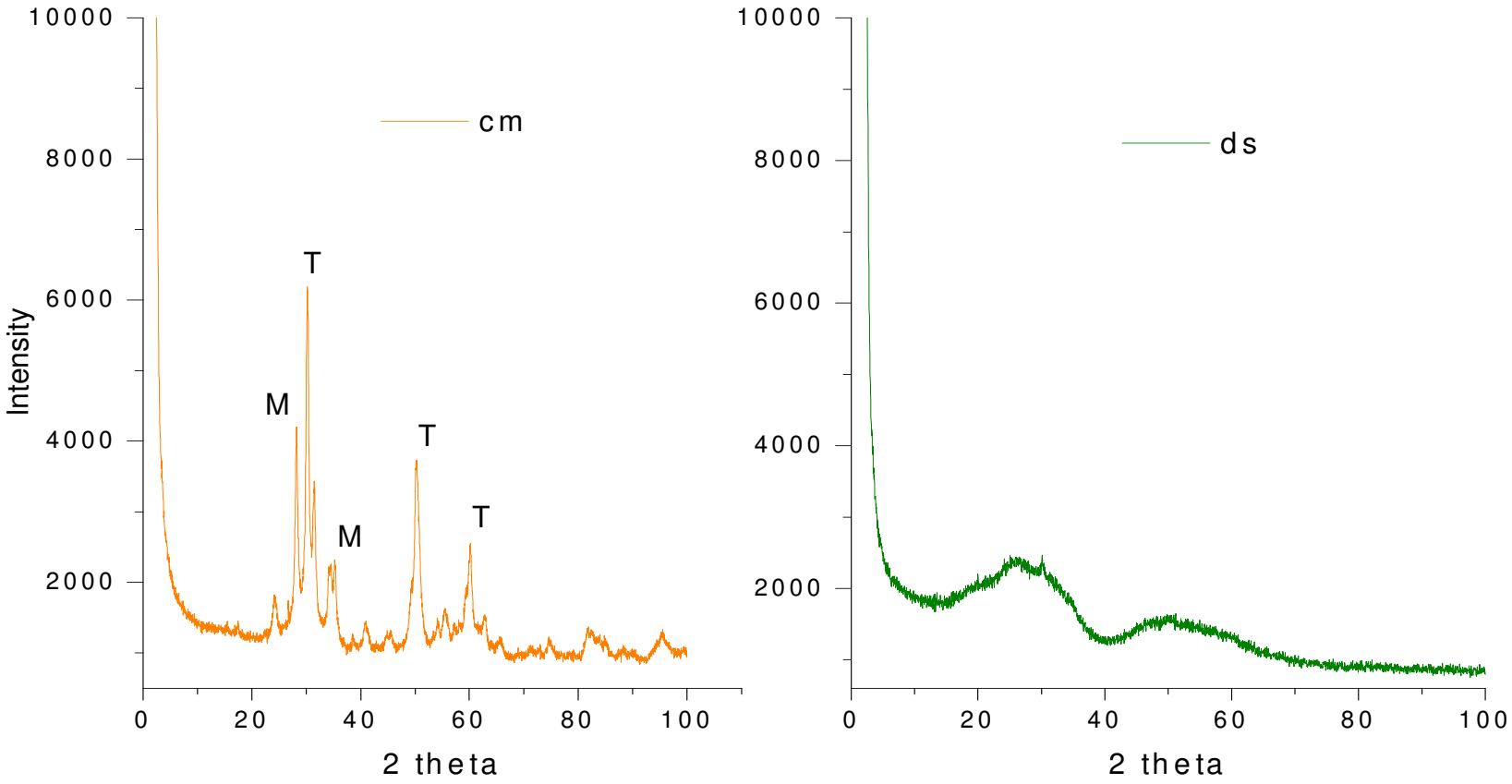
Direct method "ds"



Catalyst application

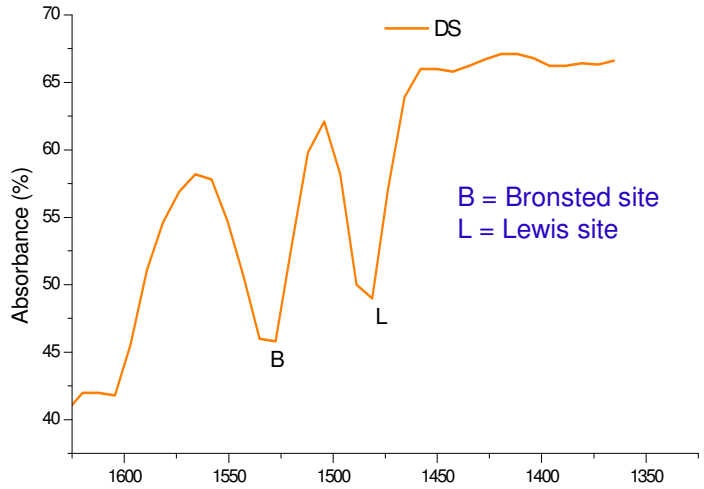


Characterization results

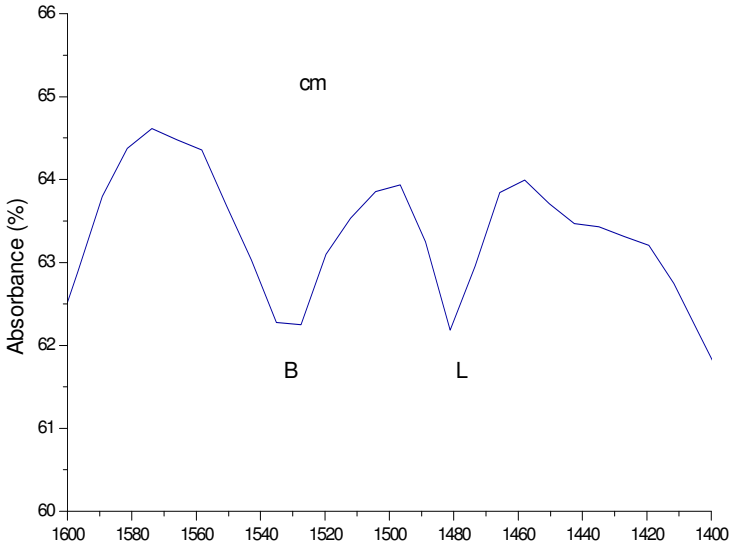


XRD of “cm” and “ds” catalysts

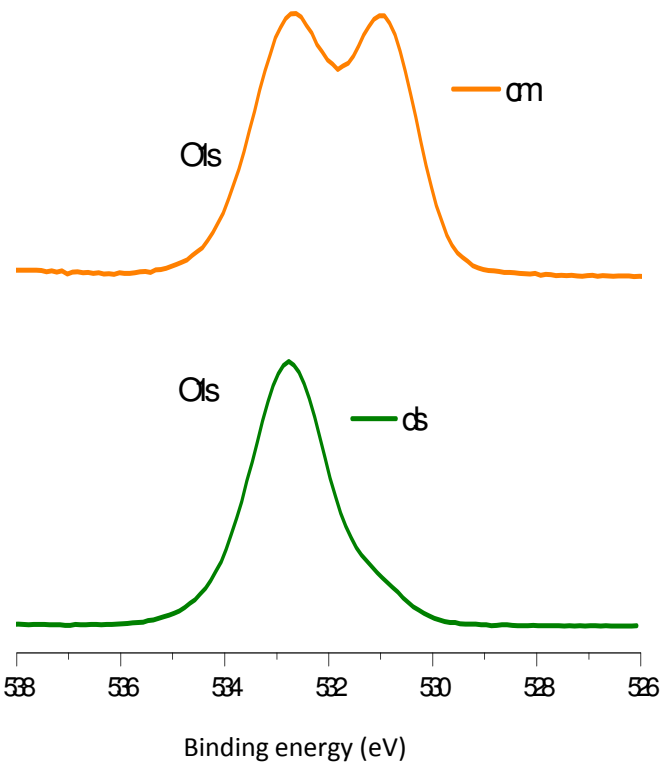
Characterization results



B = Bronsted site
L = Lewis site

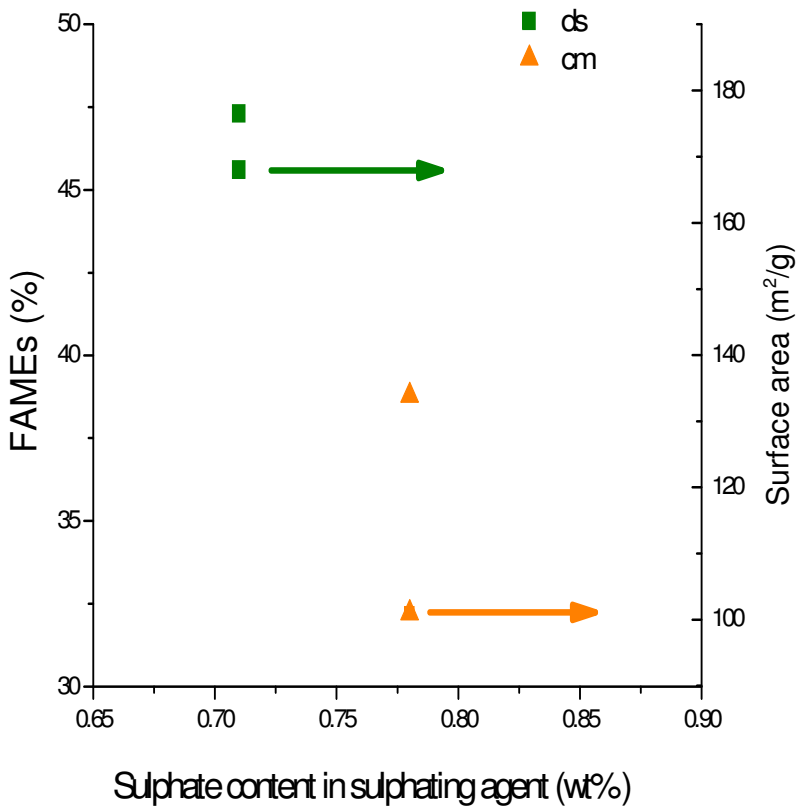


IR spectra of adsorbed pyridine on the catalysts



XPS results for Oxygen on the surface of the catalysts

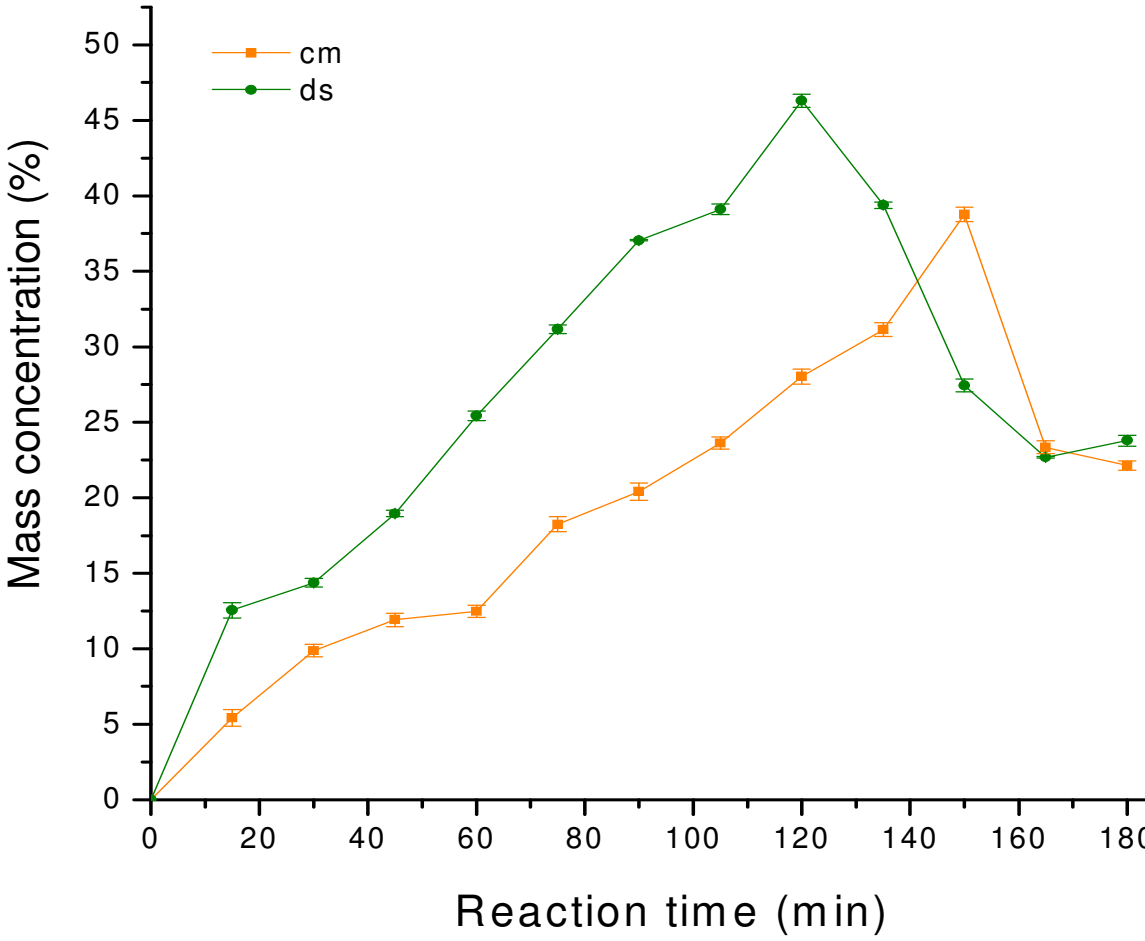
Characterization results

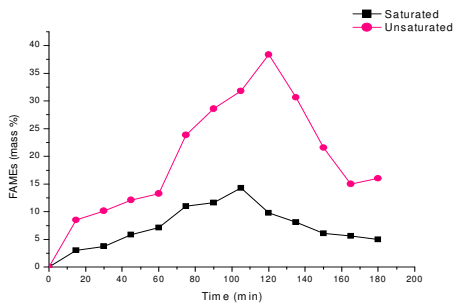


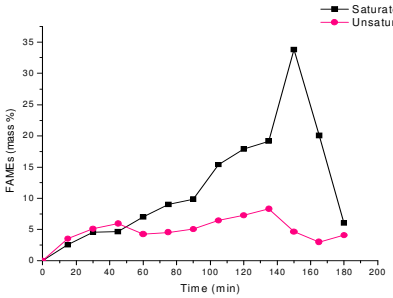
Effect of SA and SO_4^{2-} loading on biodiesel (FAMEs) production

Properties	DS	CM
BET surface area (m^2/g)	168.9	107
Pore size (µm)	0.41	0.32
Particle size (µm)	48.83	25.61
Crystallite size (nm)	-	17.51
Nature of phases	A	T, M

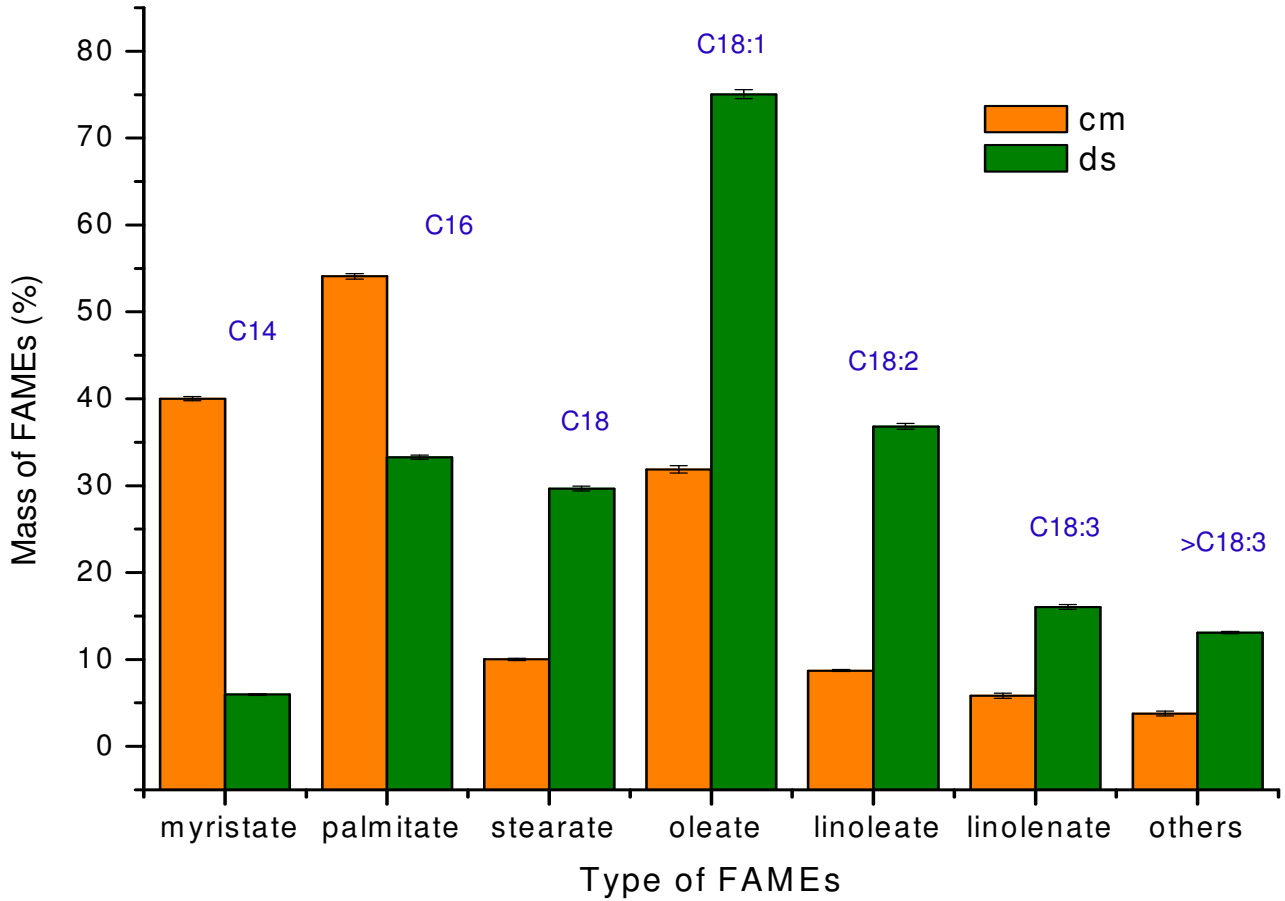
Results


cm
ds
Mass concentration (%)
Reaction time (min)
0
5
10
15
20
25
30
35
40
45
50
0
20
40
60
80
100
120
140
160
180
200


Saturated
Unsaturated
FAMEs (mass %)
Time (min)


Saturated
Unsaturated
FAMEs (mass %)
Time (min)

Results



Selectivity of the catalysts

FAMEs profile showing saturated, mono and poly unsaturated

Summary

Catalyst type	Conversion	BET surface area (m^2/g)	Pore size (µm)	Particle size (µm)	Crystallite size (nm)	Nature of phases	FAMEs (%)	Acid sites (%)	
								B	L
DS	0.70	168.9	0.41	48.83	-	A	47.43	51	49
CM	0.56	101	0.32	25.61	17.51	T, M	38.78	53	47

Conclusions

- Both catalysts were active and contain ``Bronsted sites'' and Lewis sites.
- The morphology of "ds" contributed to it higher activity
- Both catalysts were selective but "ds" exhibited higher selectivity, ~ 50% for FAMEs
- However the cm exhibited a unique selectivity for saturated fatty acid methyl esters

Overall

- The preparation method showed improved physical and chemical properties of the catalysts which influenced their activity observed in the yield of fatty acid methyl ester.
- Biodiesel (FAMEs) can be produced by thermocatalytic cracking of triglycerides using these catalyst from both method of preparation.

Future work

- Further improvement of the catalysts, for optimization of performance and more selectivity.
- The use of non-edible feedstock

Acknowledgements

Thanks to the following for their contributions:

Dr A. P. Harvey

Dr J. G. M. Lee

Karen Wilson; Cardiff University

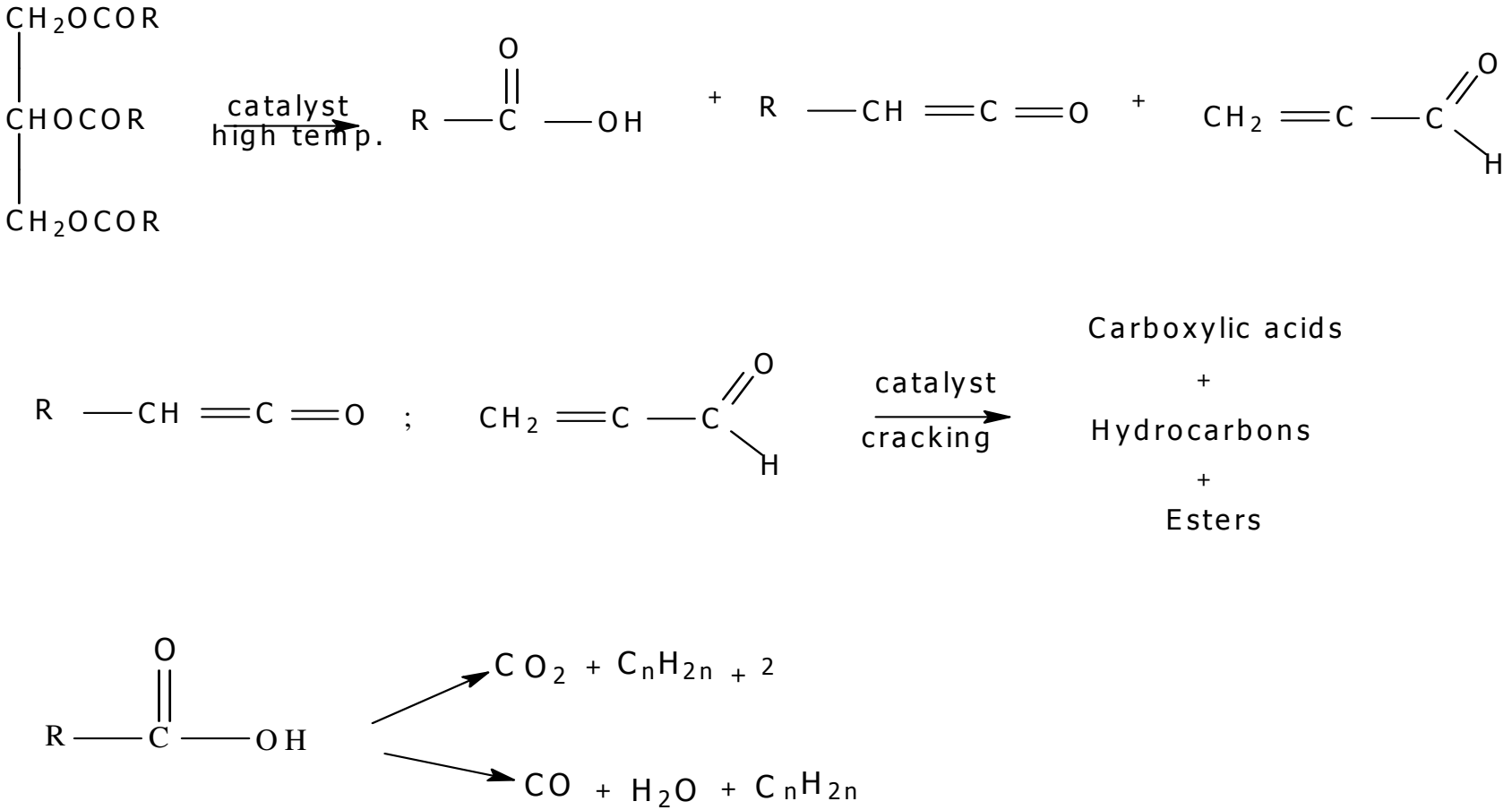
Petroleum Trust Development Fund

THANKS

FOR

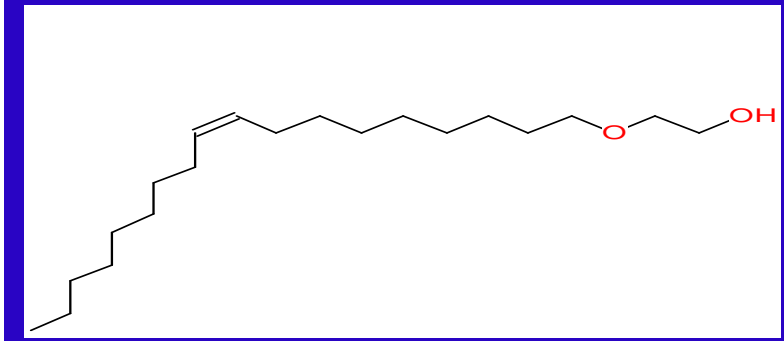
LISTENING

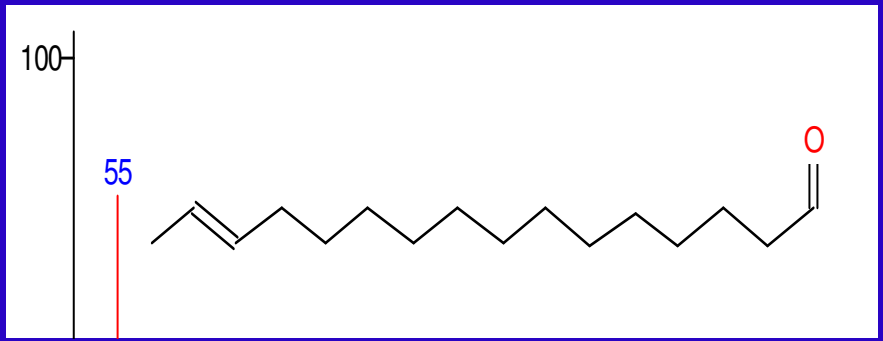
Mechanism



First is deoxygenation by thermal cracking followed by catalytic cracking, oligomerization, alkylation etc of triglycerides

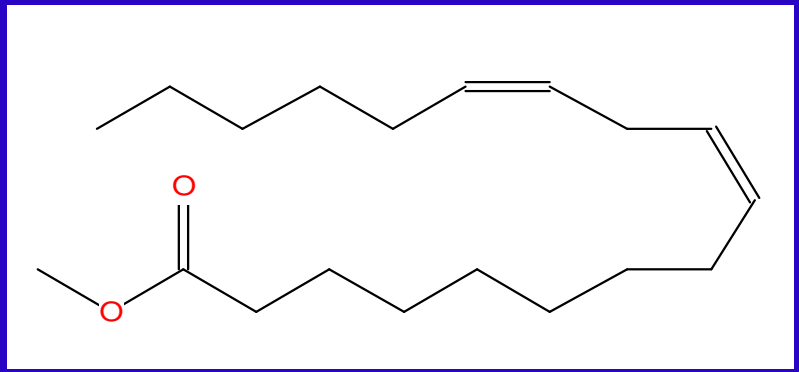
Suarez, P. A. Z. (2006) *thermo- catalytic cracking of triglycerides (www.nist.gov/oiaa/)*

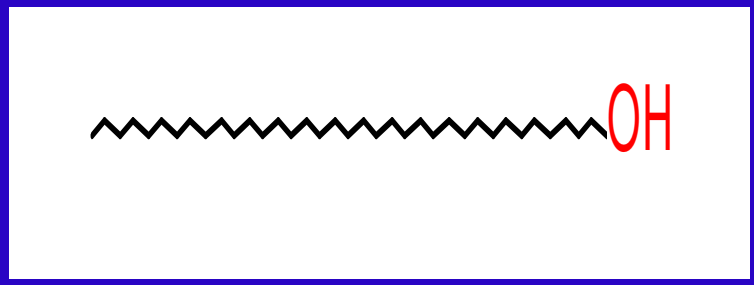




Alcohol
2-cis-9-0ctadecenyloxy
ethanol

E-14-Hexadecenal

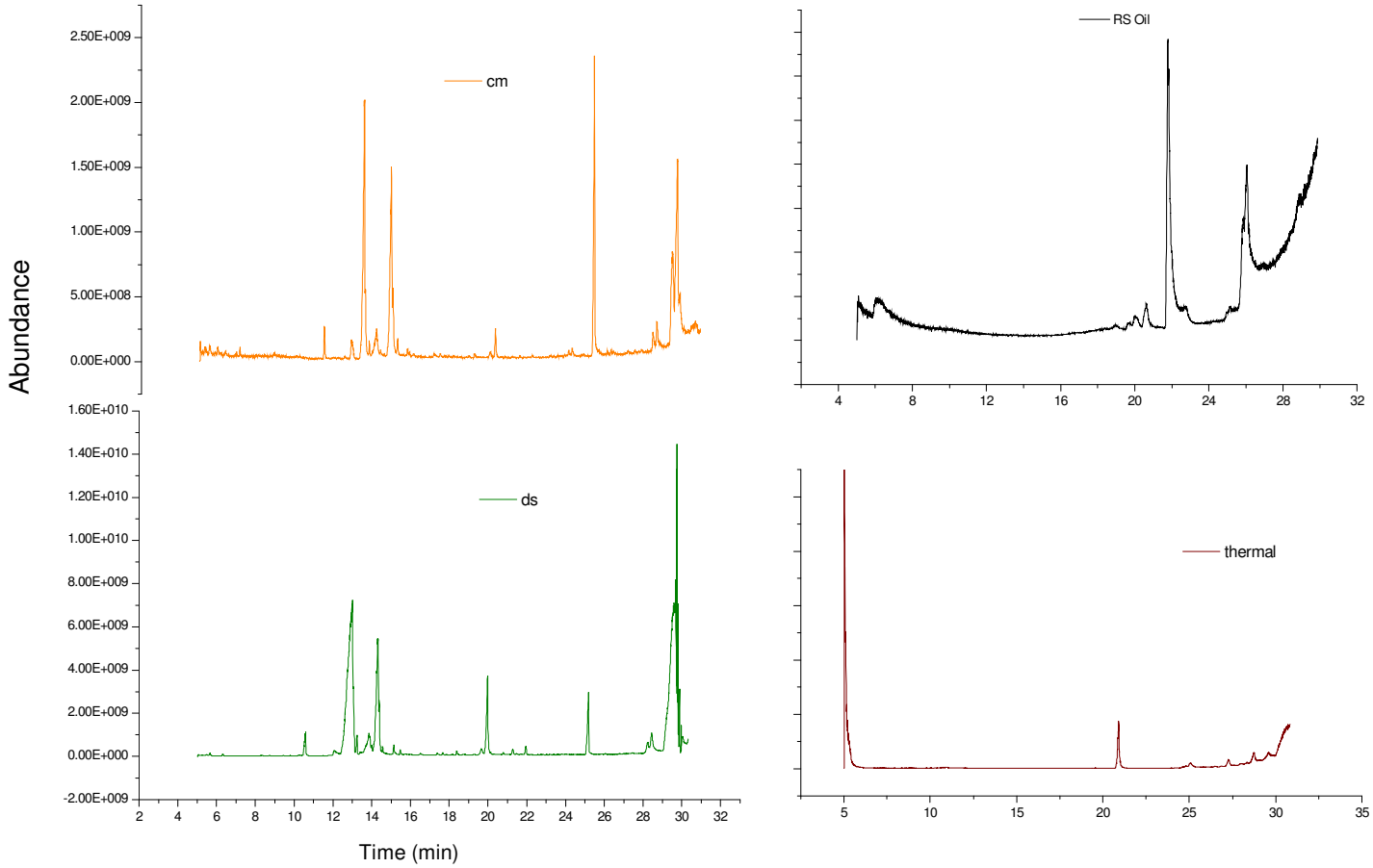




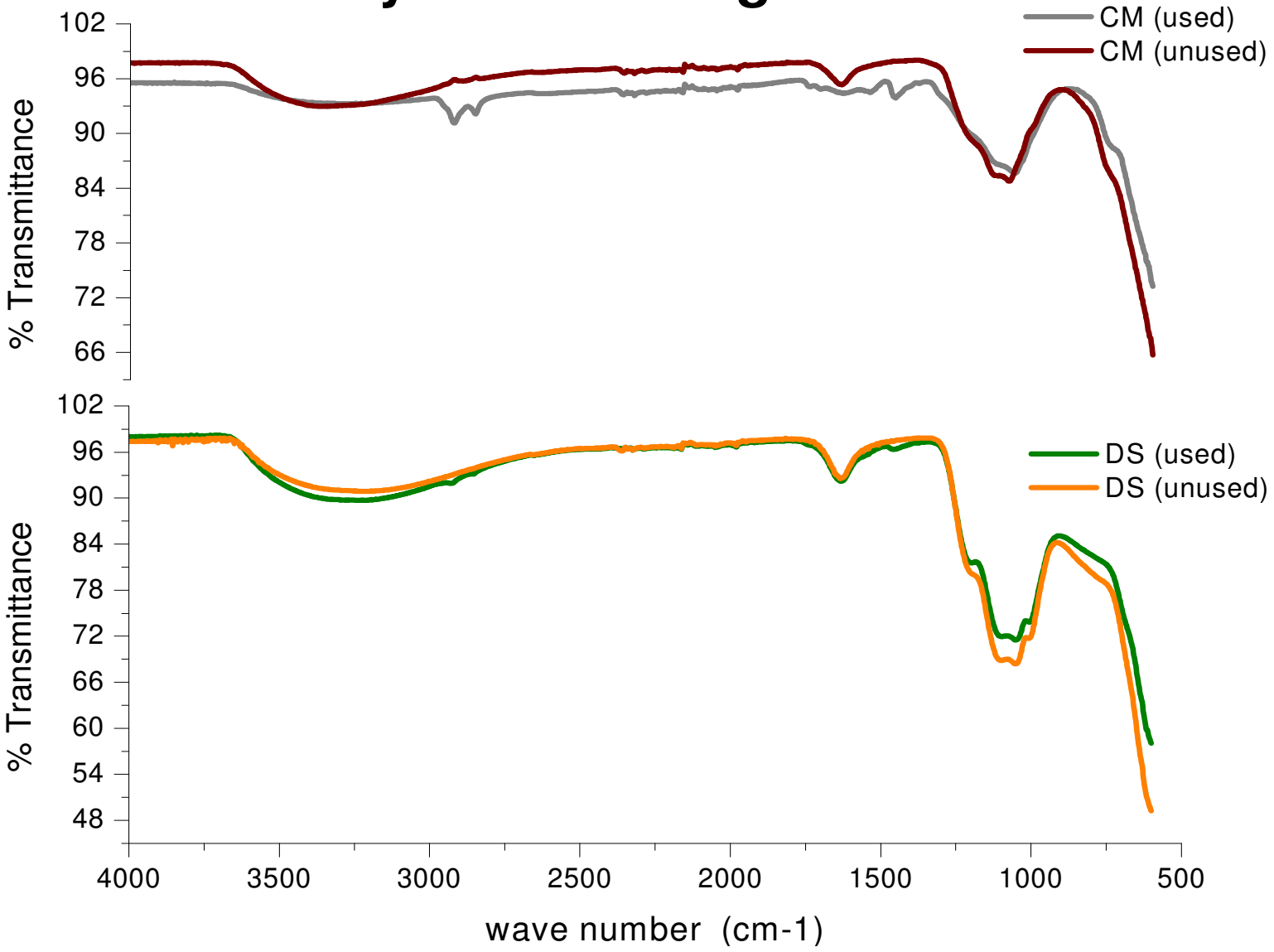
1-Heptatriacotanol

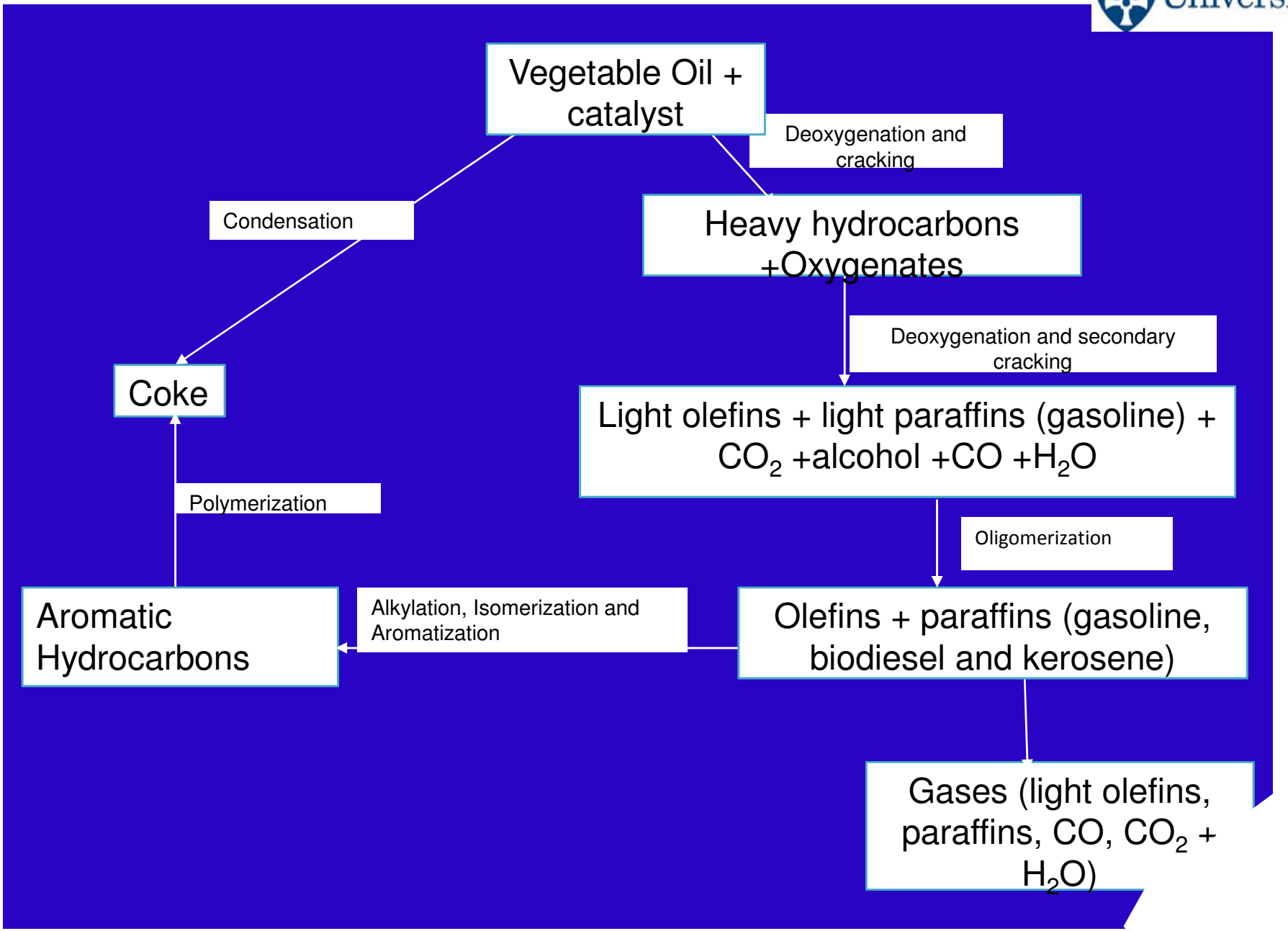
Results

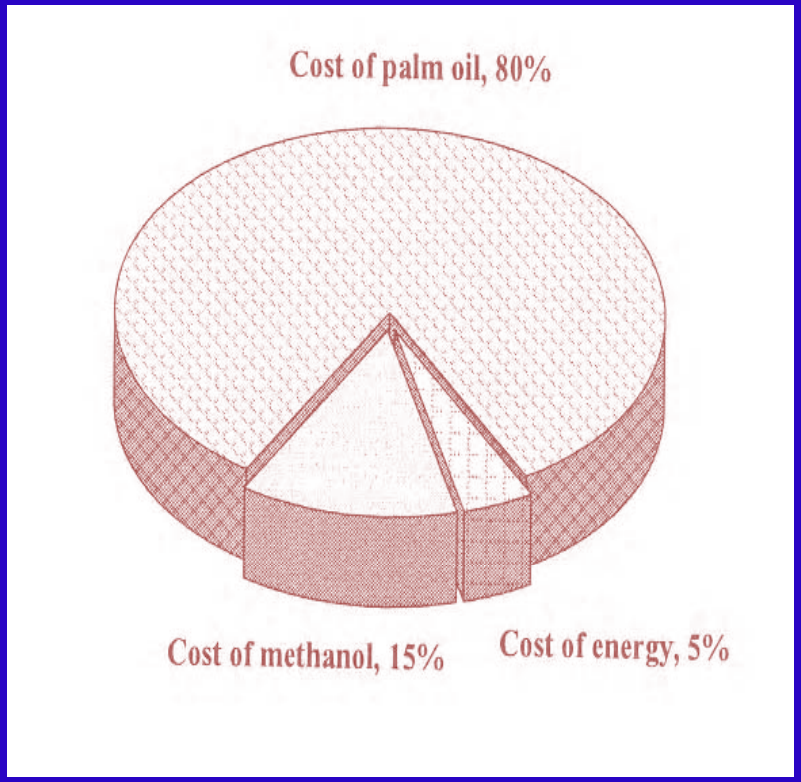
Evidence of catalytic cracking

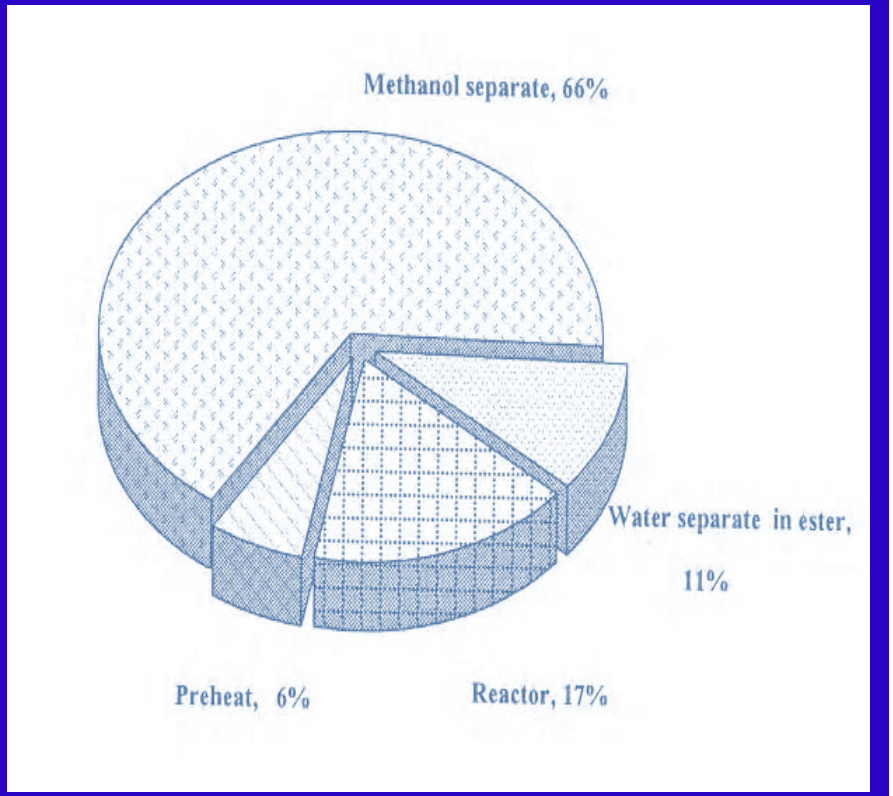


Catalysts leaching




Vegetable Oil + catalyst
Deoxygenation and cracking
Condensation
Heavy hydrocarbons +Oxygenates
Deoxygenation and secondary cracking
Coke
Light olefins + light paraffins (gasoline) + CO_2 +alcohol +CO +H_2O
Polymerization
Oligomerization
Aromatic Hydrocarbons
Alkylation, Isomerization and Aromatization
Olefins + paraffins (gasoline, biodiesel and kerosene)
Gases (light olefins, paraffins, CO, CO_2 + H_2O)





Kapilakarn and Peugtong (2007)
International Energy Journal