

Bioenergy - I

Determination of the Blend Level of Mixtures of Biodiesel with Mineral Diesel Fuel Using Near Infrared Spectroscopy

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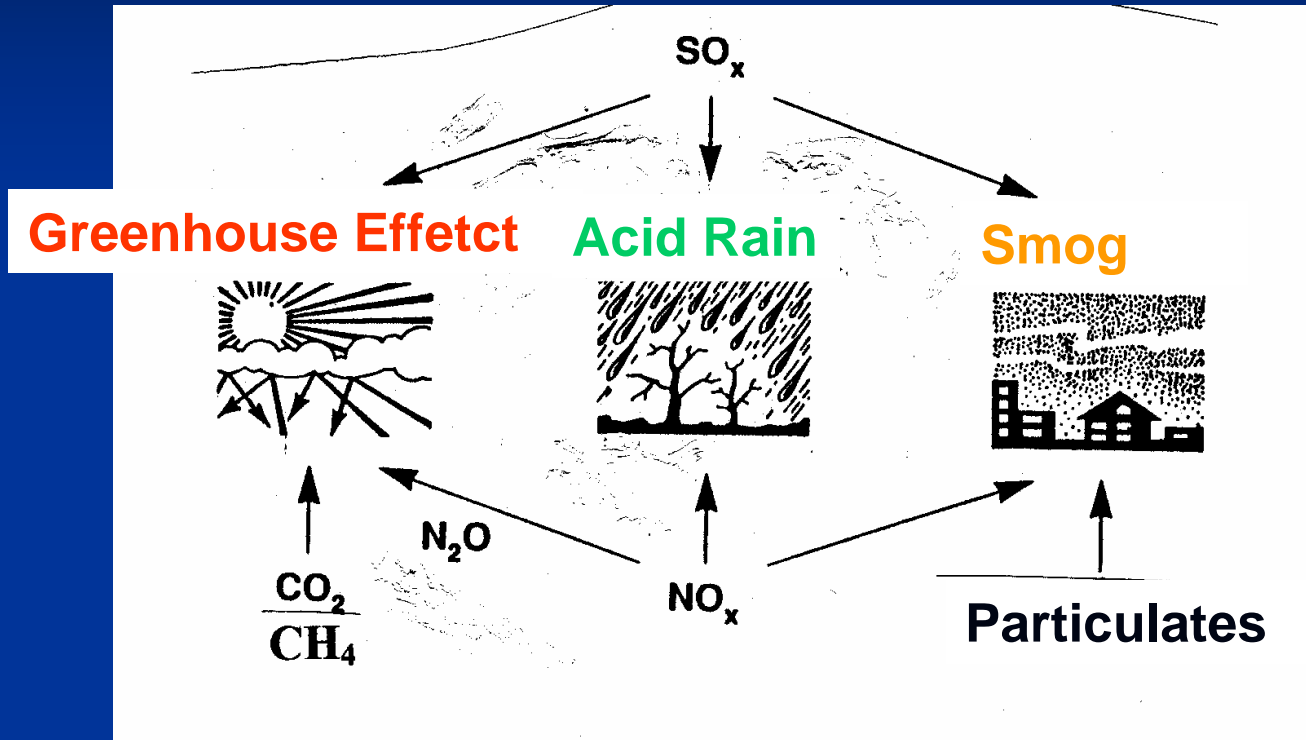
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University of Salvador- Bahia

Cruz, R S, Santa Cruz State University - Bahia

FOSSIL FUEL PROBLEMS

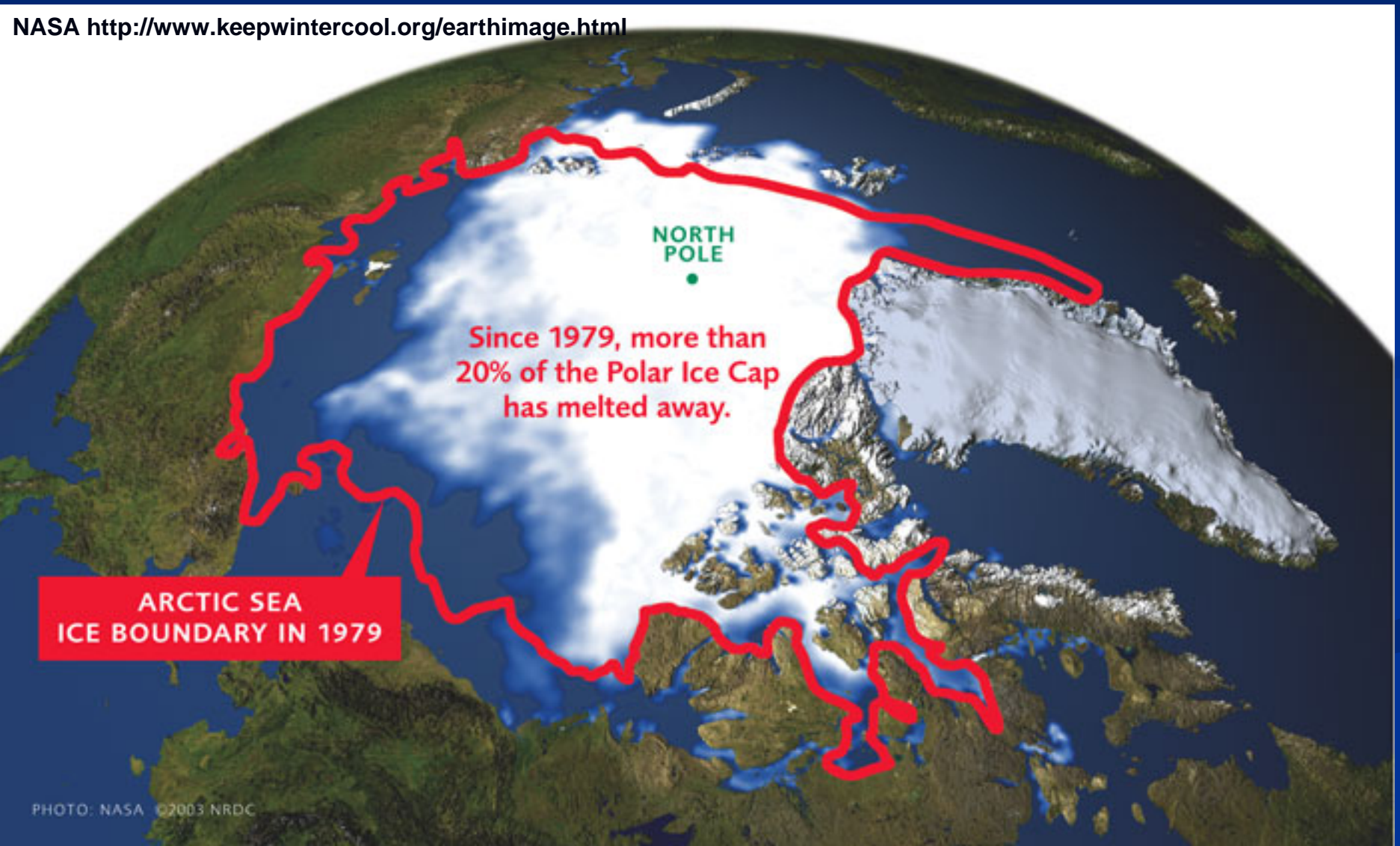


Ref. Smith and Petela, The Chemical Engineering, 1992.

GREENHOUSE EFFECT

North Pole Cap Melting

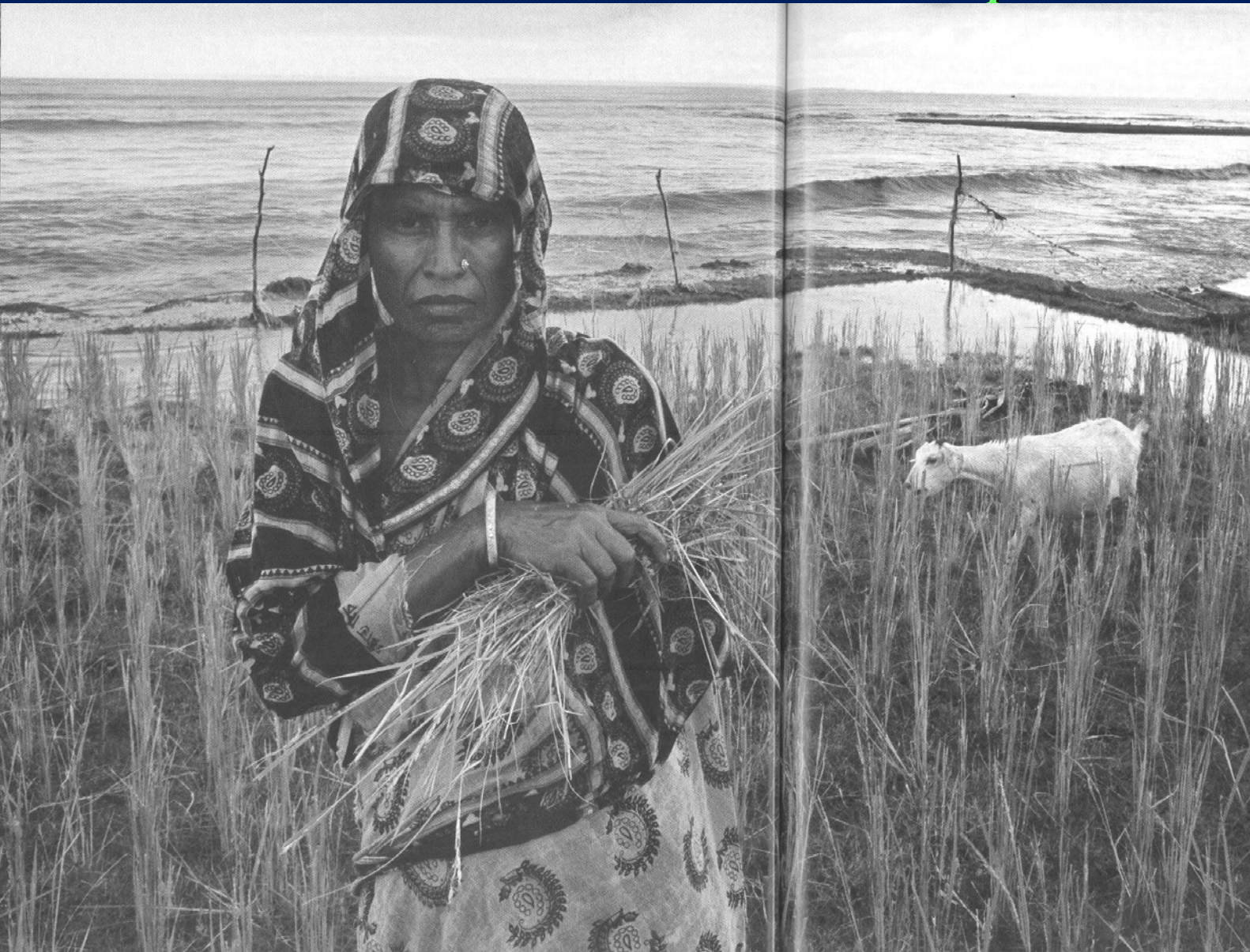
NASA <http://www.keepwintercool.org/earthimage.html>



ARCTIC SEA
ICE BOUNDARY IN 1979

GREENHOUSE EFFECT

Flood Areas and Crops



Petrobras -
Norberto

KATRINA Hurricane



Very Dry Days in Amazon Rain Forests - October 2005



Pescadores entre milhares de peixes mortos no Paraná do Manaquiri (a 150 km de Manaus), um braço de rio agora reduzido a um córrego.

http://www.greenpeace.org.br/amazonia/?conteudo_id=2328&sub_campanha=0



Embora seja uma das regiões onde há mais disponibilidade de água do mundo, na Amazônia, a maior parte da população não tem acesso à água tratada. Foto: Celso Junior/AE

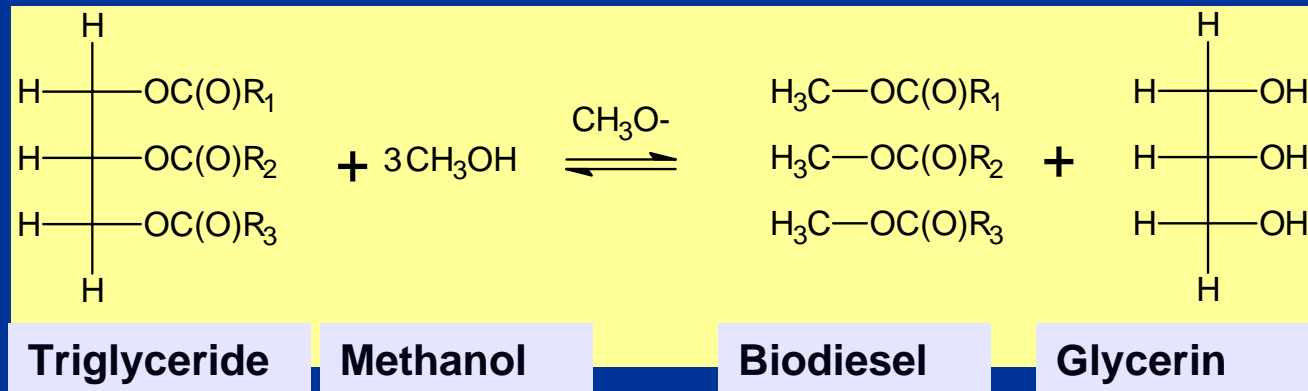
<http://www.estadao.com.br/ext/ciencia/agua/galeria.htm?pg=1>

Biodiesel

Oil Source: Vegetable Oils and Animal Fats

Alcohol Source: Methanol or Ethanol

Transesterification



Renewal Fuel, Biodegradable

Less emission of: Particulates, SO_x, CO₂

Addition of Biodiesel in Mineral Petroleum Diesel

BRASIL

- 2% in 2005 (B2), Mandatory in 2008
- 5% in 2013

PROBLEMS

- Guarantee real 2% or 5% content
- Presence of raw vegetable oil
- High cost of analysis
- Many sources of oils:
 - Soybean oil, used oil, palm oil, castor oil, animal fat

Infrared Spectroscopy

Advantages:

- ✓ **Fast**
- ✓ **Does not need Pre-Treatment**
- ✓ **Non Destructive**
- ✓ **Can be used on line**

MIR - 4.000 - 400 cm^{-1} (MEDIUM INFRARED)

All functional Groups are Detectable

NIR - 10.000 - 4.000 cm^{-1}

1.000 - 2.500 nm

Detect Combinations of compounds

Groups: C-H, O -H, N-H, C=O

Multivariable Modelling

IR



QUIMIOMETRY

To Obtain

Correlation between Infrared and Primary Methods

To Predict Information

Literature Review for Alternative Analysis of Biodiesel

Knothe 2001: $^1\text{H-NMR}$ for BD in petrodiesel

Knothe 1999: content of soybean oil and its biodiesel

Knothe 2001: content 0 to 100% of biodiesel in Petrodiesel

Zagonel 2004: content of soybean biodiesel in a mixture of soybean oil to track reaction conversion

OBJECTIVES

Determine Biodiesel Content in Petrodiesel in the range (2 to 5%)

**Using: MID Infrared or Near Infrared Spectra
Multivariable Calibration**

Determine the presence of raw vegetable oil

Methodology

Sample Preparation

Blends of oils and esters in Mineral Diesel

Factorial Design: 2 factor: ester and oil
0 to 5 vol. %
Central point

Soybean Oil	(Soybean oil) Ester
Castor Oil	(Castor oil) Ester
Used Frying Oil	(Used Frying oil) Ester

26 Blends for Calibration

+ 15 Blends for External Model Validation

Methodology

Apparatus and Calibration

Perkin-Elmer Spectrum One FTIR spectrometer

Sampling ATR for MID (4000 to 600 cm^{-1})

Sampling 1 mm optical length for NIR (780-
2500 nm)

Unscrambler 9.0 (CAMO)

Principal component analysis (PCA)

Partial least-squares (PLS) regression

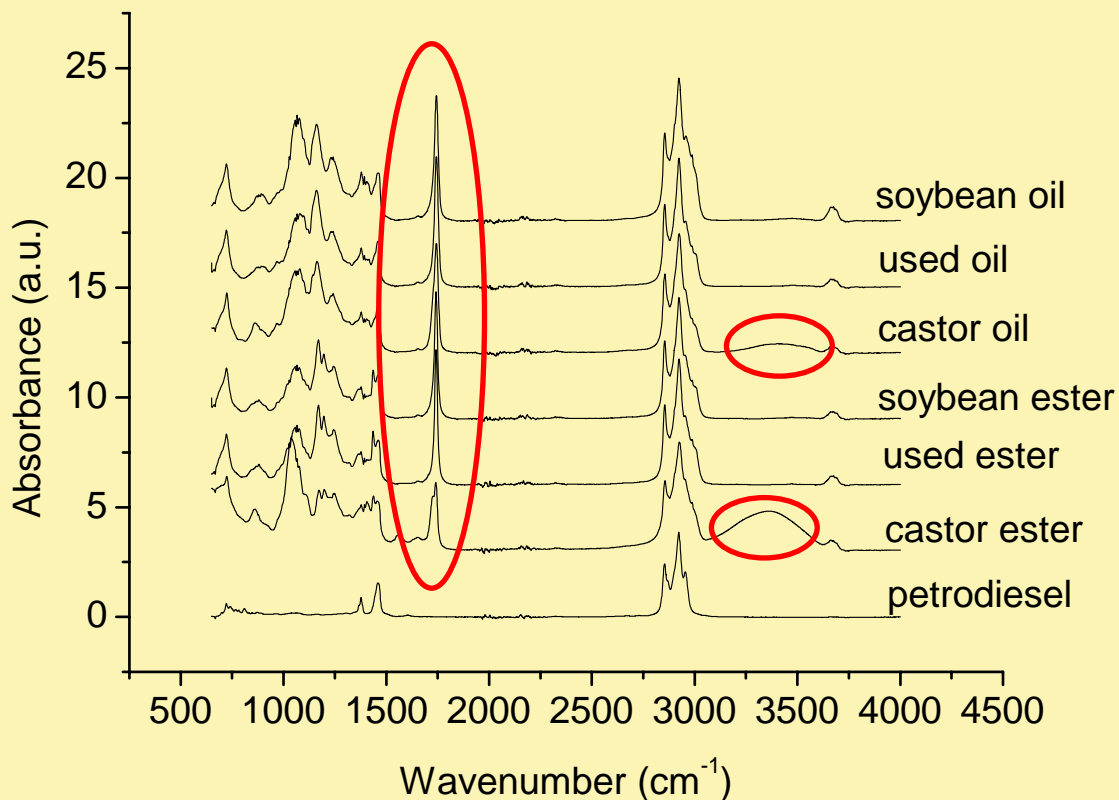
Full cross-validation to define no. of factors

Significant regression coefficients by Martens
Criteria

Results

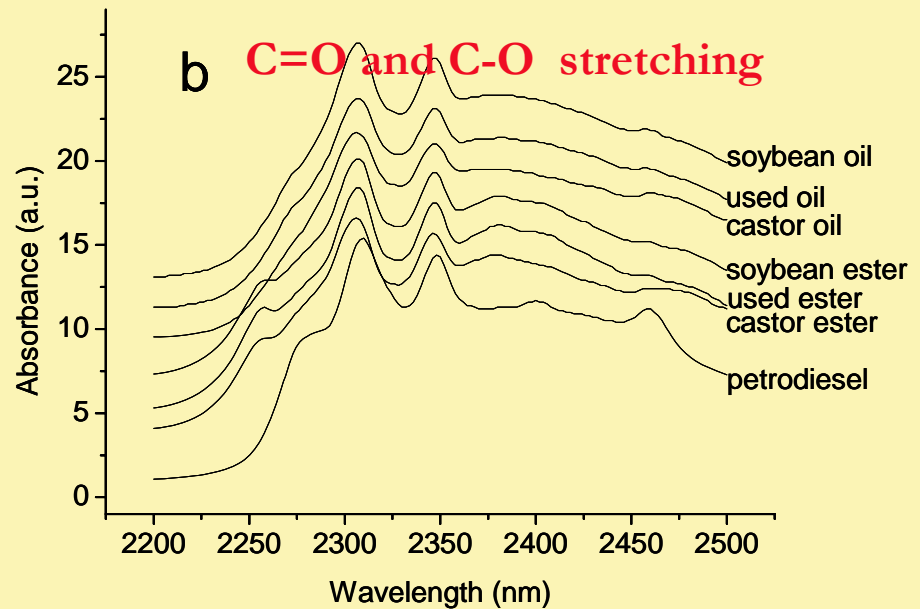
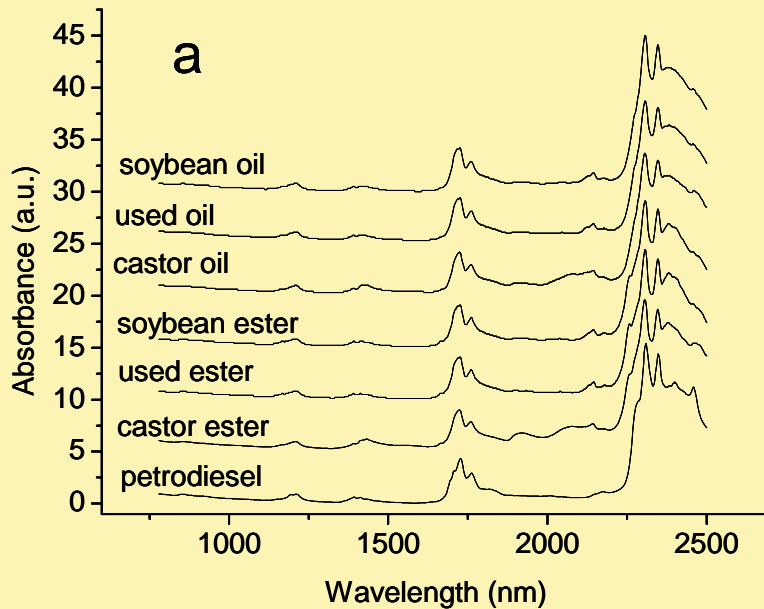
MID spectra: Petrodiesel, oils, esters

- 1750 cm^{-1} carbonyl bands: overlapped peaks
- Castor Oil and Ester: around 3333 cm^{-1} (deformation of O-H bonds)



Results

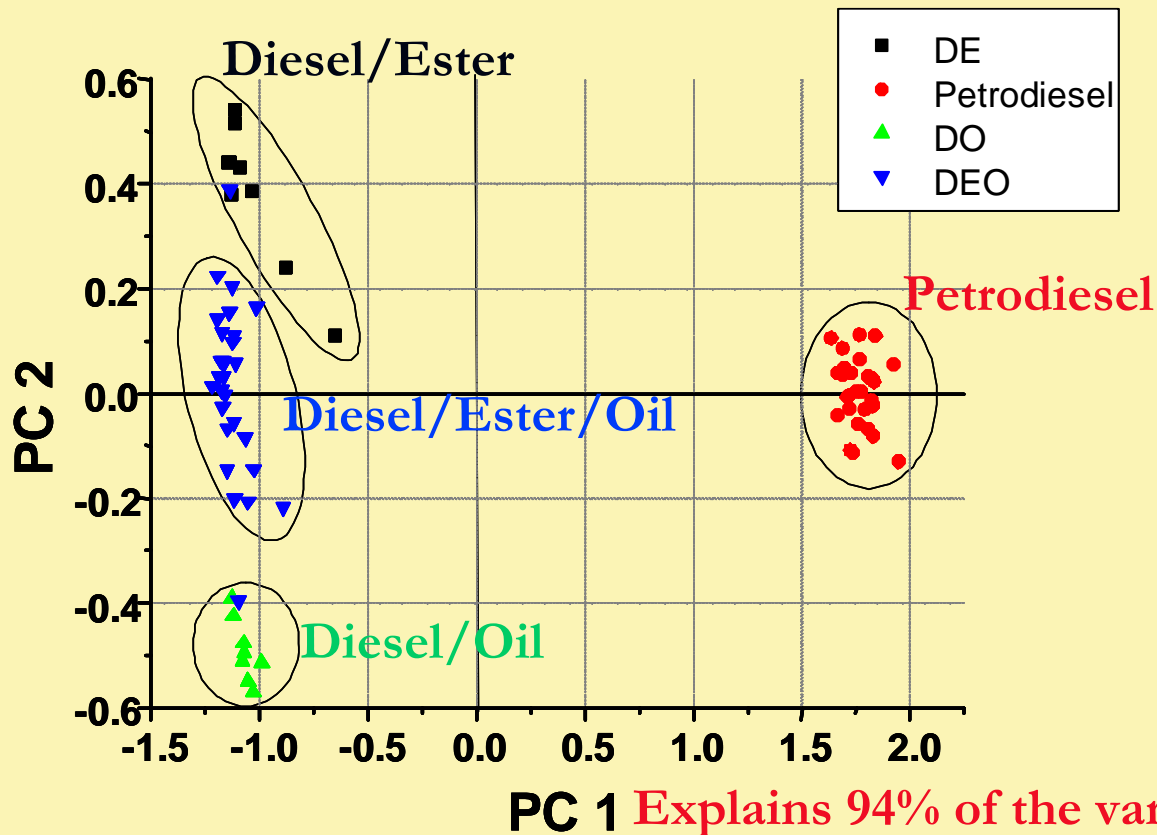
NIR spectra: Petrodiesel, oils, esters



Results

Principal Component Analysis

- 1700-1800 cm^{-1} Carbonyl (first derivative spectra)
- Groups well classified when: Ester/Oil ratio < 5
Oil/Ester ratio < 5



Results

Partial Least Squares (PLS) Models

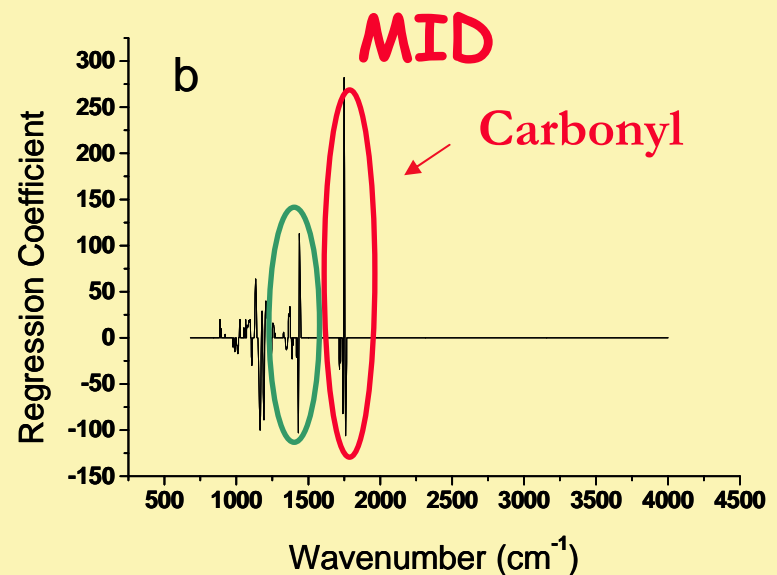
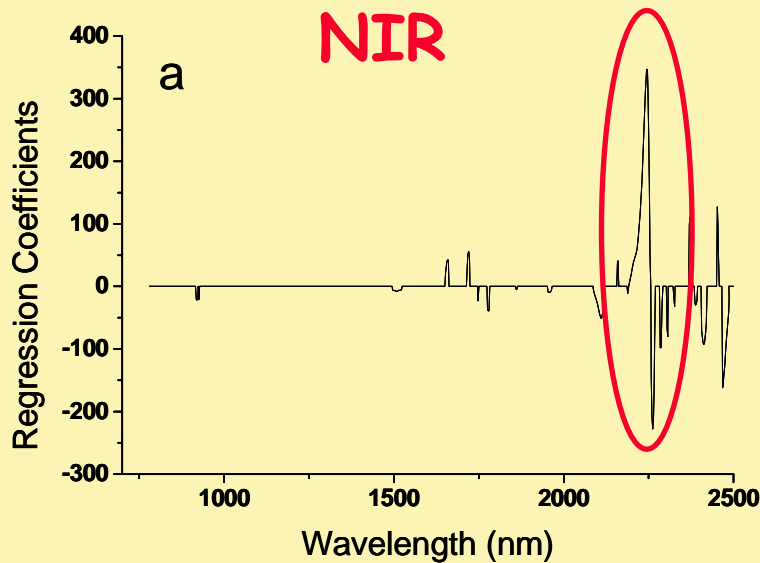
➤ Predict the Content of Biodiesel in Petrodiesel

Calibration (26 Blends)			
Spectral Region	RMSECV (% v/v)	R	Number of factors
MID	0.28	0.990	3
NIR	0.27	0.990	6
Prediction by independent set of data (15 Blends)			
Spectral Region	RMSEP (% v/v)	R	Relative average errors (%)
MID	0.25	0.986	10.2
NIR	0.18	0.994	6.7

Results

Partial Least Squares (PLS) Models

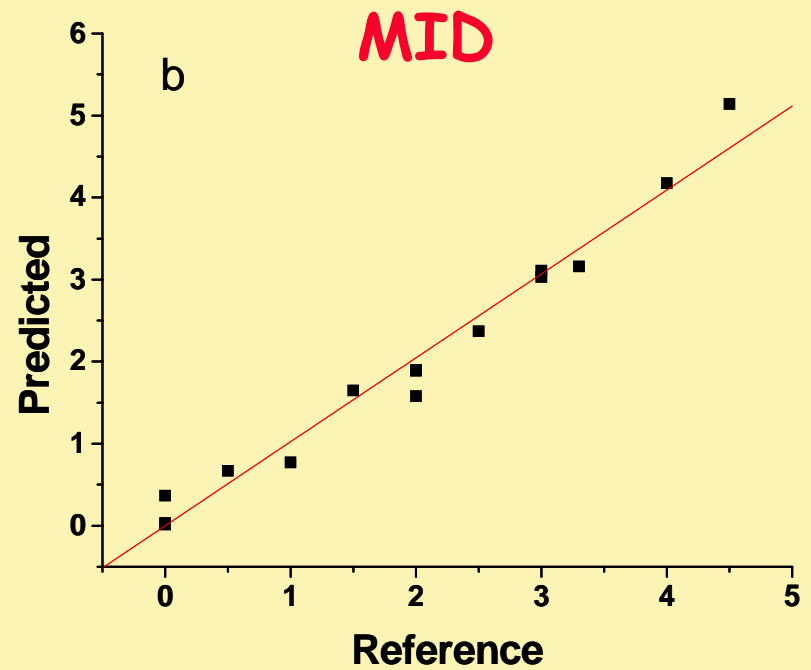
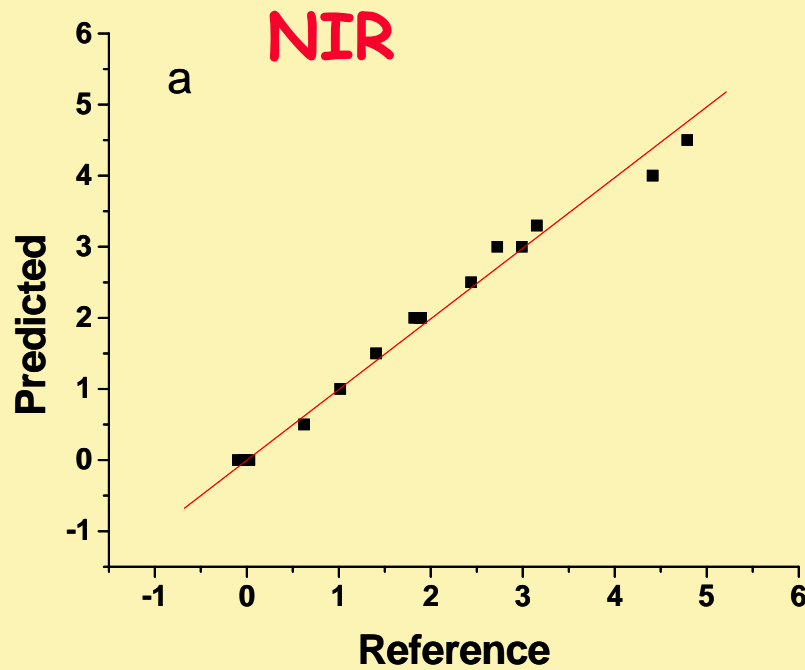
- Significant Regression Coefficients chosen by Marten's Criteria



Results

Partial Least Squares (PLS) Models

- Good Correlations for Predicted vs. Reference values



Conclusions

PSL Model based on MID and NIR spectra

Can Predict Biodiesel content in Conventional diesel blends (0 to 5 vol. %)

Rapid and low Cost Method for Monitoring Quality of Biodiesel Blends

Biodiesel from different origins: soybean oil, castor oil, used frying oil

PCA of MID ($1700-1800\text{cm}^{-1}$) was suitable to identify

- Petrodiesel from Blends of Biodiesel
- Presence of Raw oil in Biodiesel Blends

Authors's Universities

