QUT Science and Engineering

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Influence of Biodiesel composition on morphology and microstructure of particles emitted from Diesel engines

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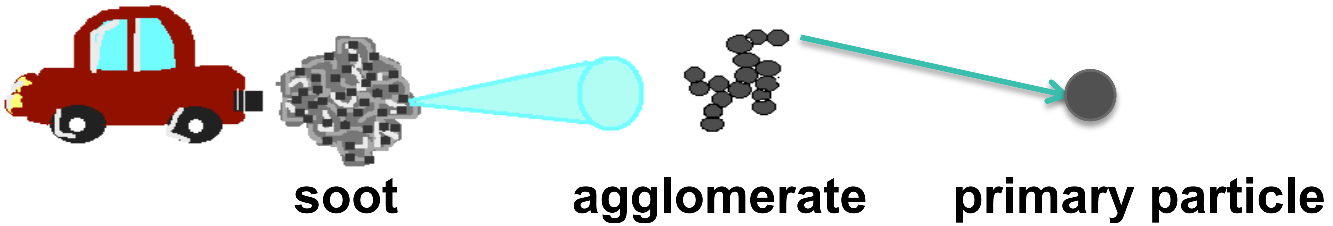
Institute for Meteorology and Climate Research- Atmospheric Aerosol Research, Karlsruhe Institute of Technology, Germany

Introduction

- Particle matter emitted by diesel engines primarily consists of soot.



- Chronic exposure to diesel exhaust particles may lead to cardiovascular, respiratory and pulmonary diseases ➔health effects most likely related to the particles' surface
- Emitted amount of particle matter can be decreased➔by using alternative fuel such as biofuel
- Biodiesel is made of oilseed crops, plants and animal fat and can be used directly in conventional unmodified diesel engines

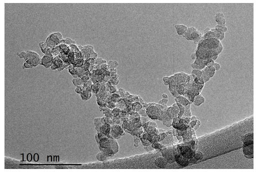
List of contents

Diesel exhaust particle

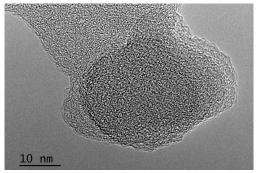
analysed by

Transmission Electron Microscopy (TEM)

Agglomerates

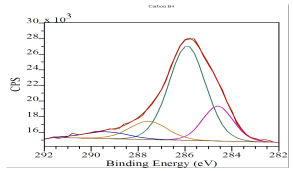


Primary Particles



X-ray Photoelectron Spectroscopy (XPS)

Chemical State Analysis



The Objective

- **Determination of surface properties** of particles from Diesel engines generated with different biofuel content by Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy

- **Expected scientific goals**:

i. Investigation of primary particle size and inner structure
i. Investigation of fractal dimension
ii. Investigation of surface functionalization

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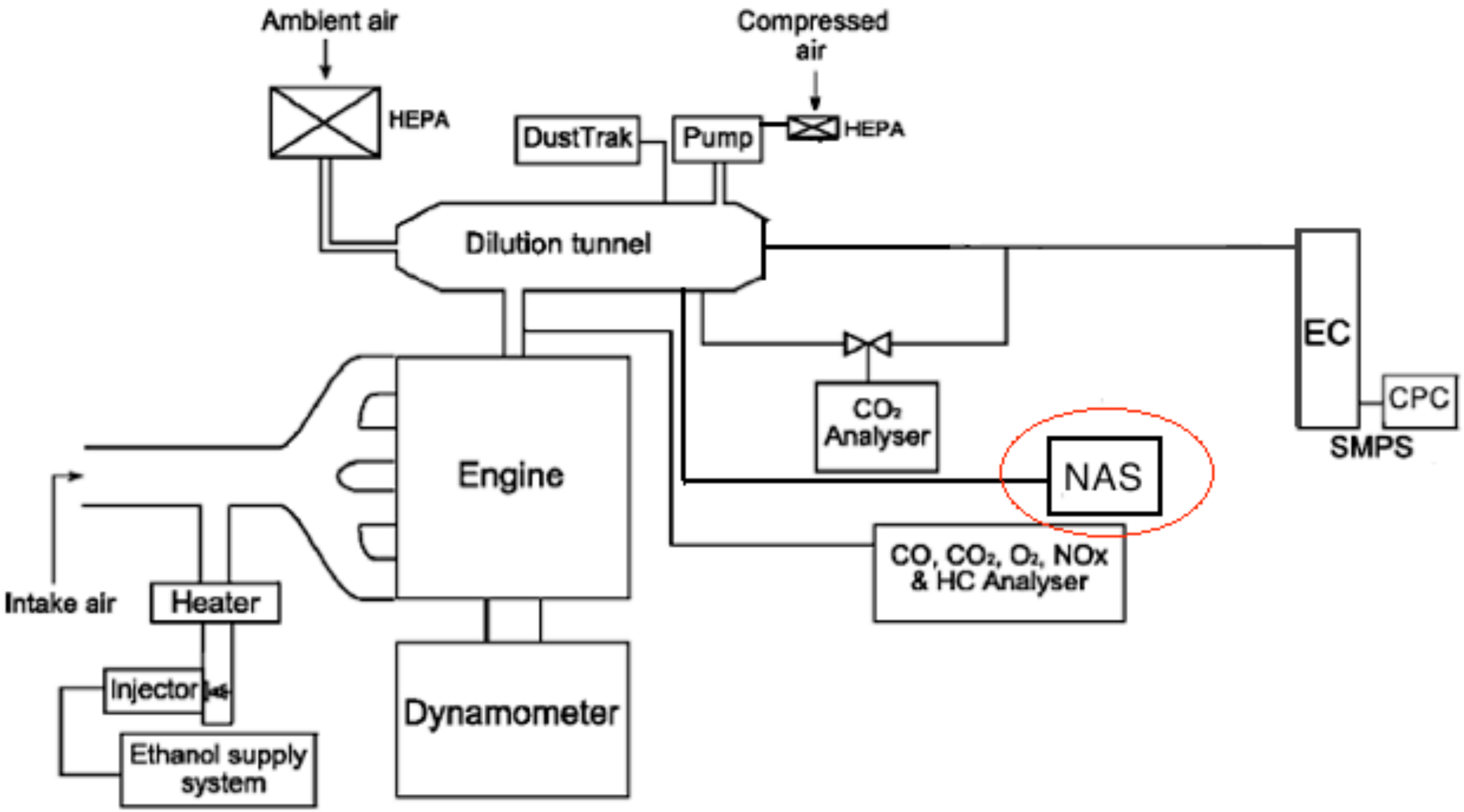
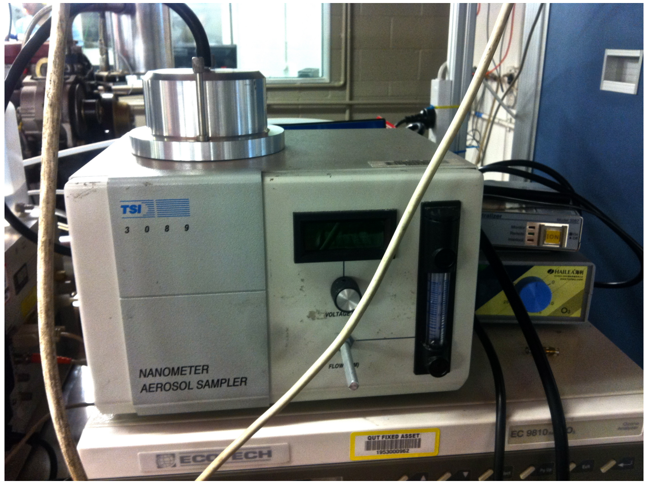
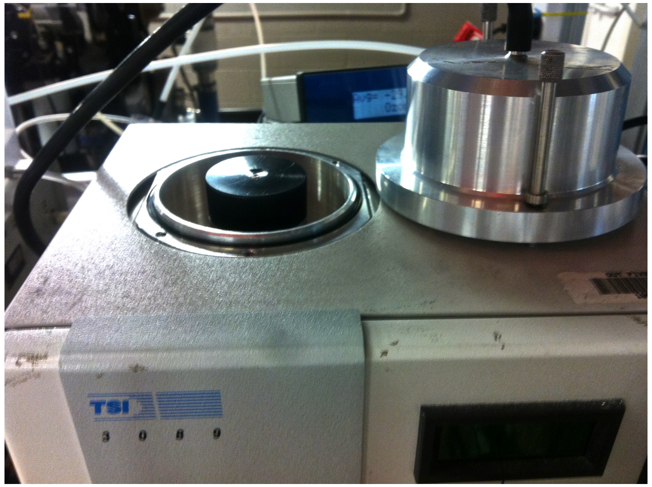
Set-up QUT Campaign

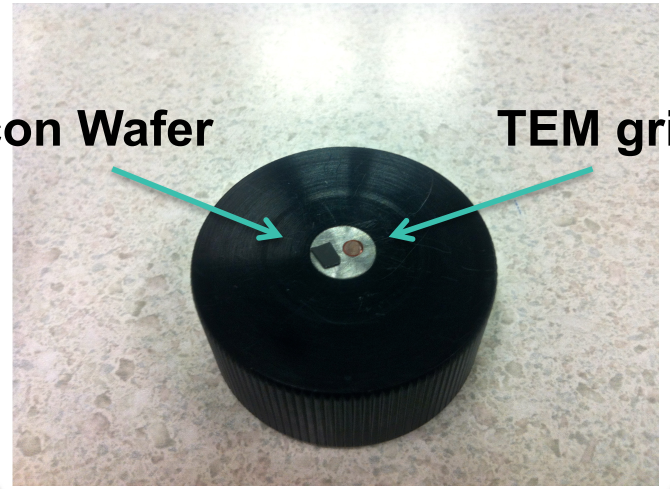


Nanometer Aerosol Sampler

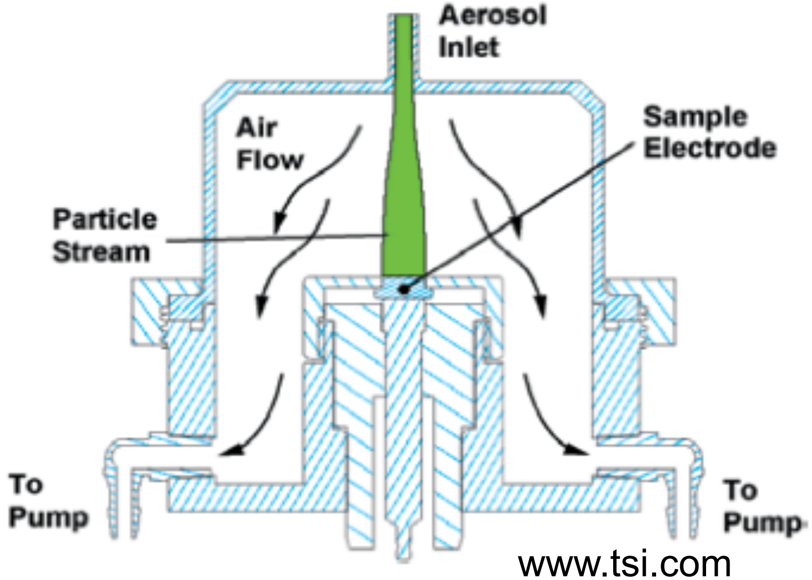




Silicon Wafer **TEM grid**

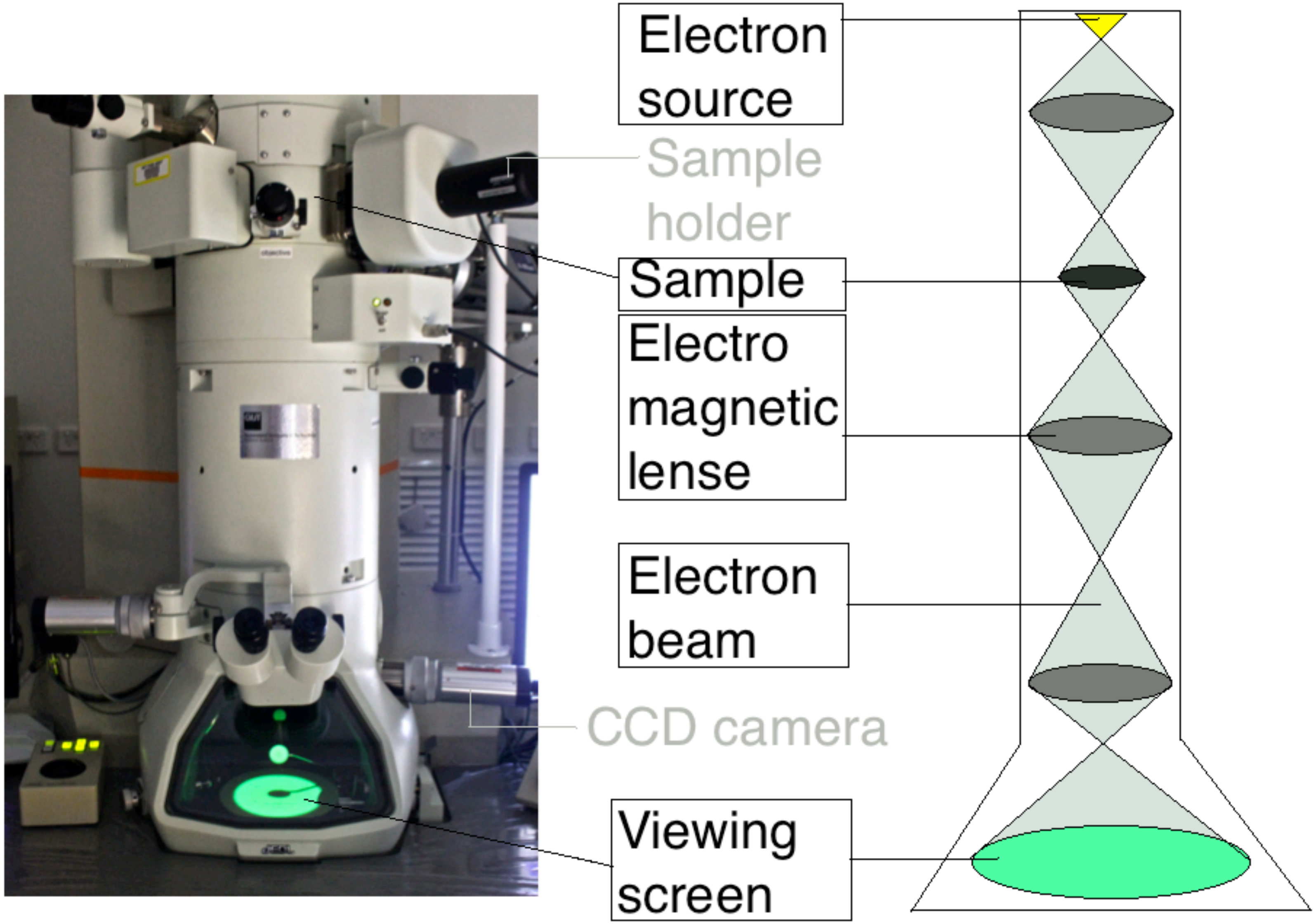


Sample electrode with substrate



www.tsi.com

Transmission Electron Microscope



Diesel and Biodiesel Samples

January Campaign	February Campaign	March Campaign
Diesel	Diesel	Cotton seed oil (CSO)
Palm oil (PO C1214)	Algae	Waste cooking oil (WCO)

- All samples were collected at different blends example:

Algae B5

↓

5 % biofuel + 95 % diesel

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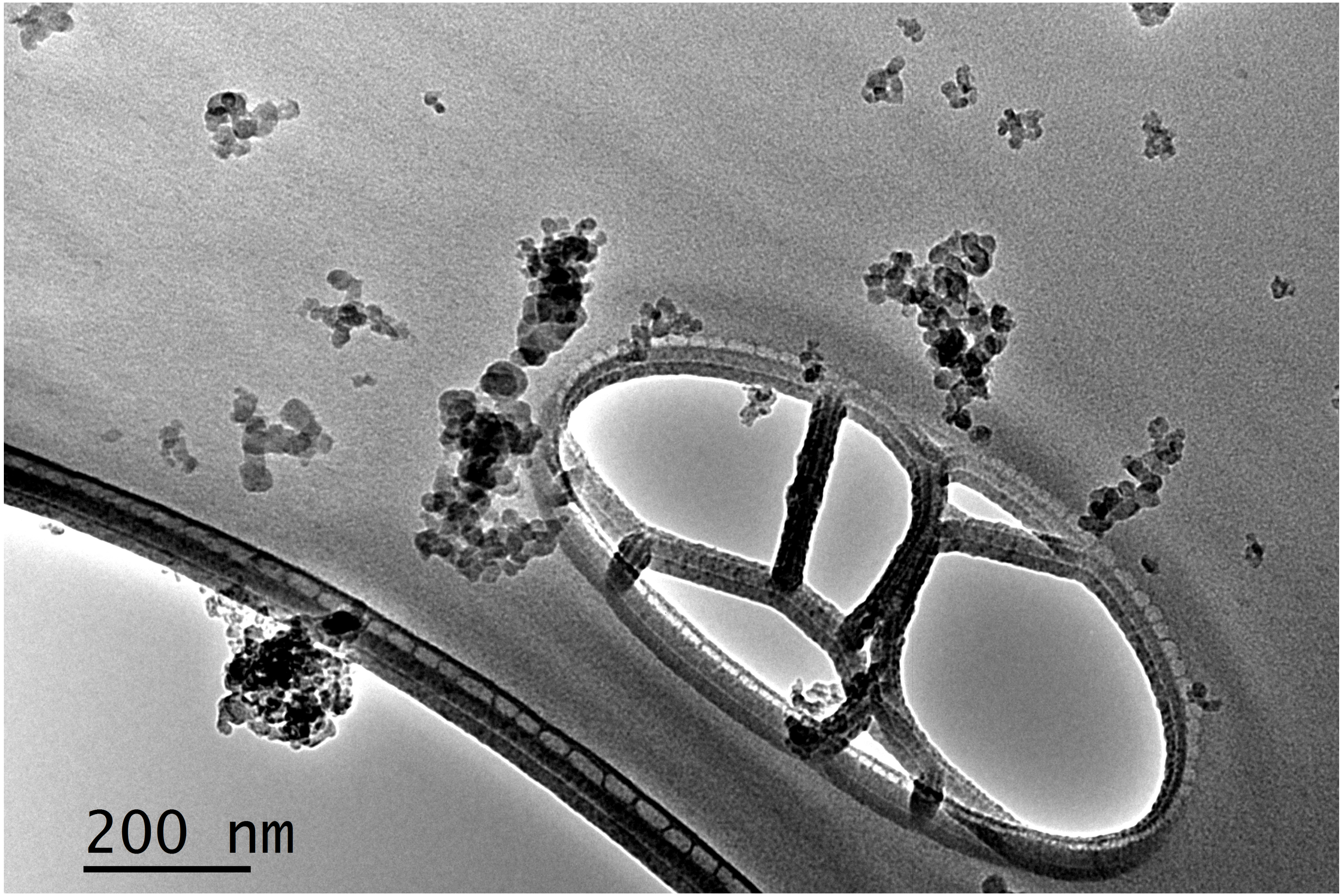
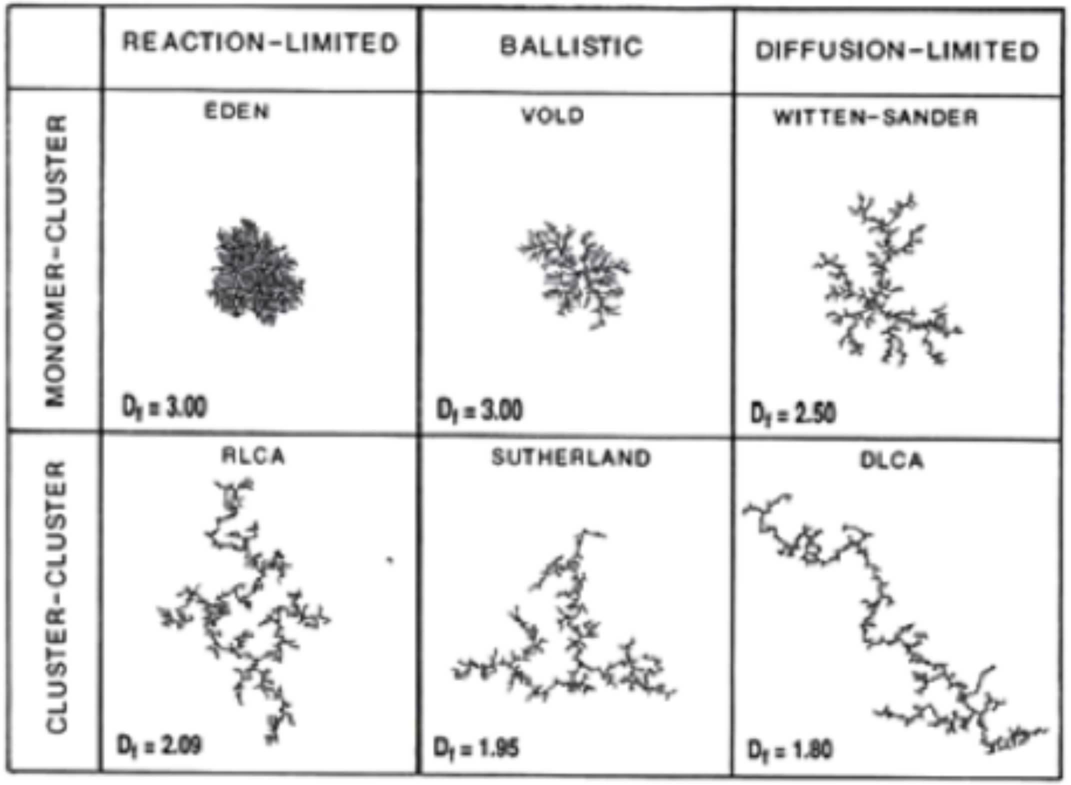
Outer Structure Analysis



Fractal Dimension

Fractal dimension characterizes how compact and spherical a particulate is.

Range of fractal dimension: 1-3 where 3 represents a spherical particle



S. Choi et al.: Review on characterization on nano particle emissions and PM morphology from internal combustion engines: Part 2

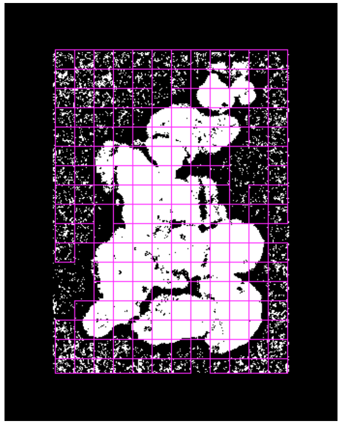
Analysis Fractal Dimension

1. method:

Box counting method: (2-dim)

a.) Draws grids with decreasing box size on the two dimensional image

b.) Curve plotting: log box number vs. log box size



Range: 1 to 2

2. method:

Monte-Carlo simulation: (3-dim)

a.) Conversion from 2 dimensional to 3 dimensional images

b.) Curve plotting log particle number vs. log particle to primary particle ratio

$$N_P = k_L \left(\frac{L}{D_P} \right)^{D_F}$$

Range: 1 to 3

Slope = fractal dimension

Fractal Dimension Result Comparison

Sample	Diesel	Algae, B5	Algae, B50	Algae, B20	CSO, B20	WCO, B20
1. method	1.72±0.09	1.74±0.06	1.80±0.07	1.72±0.06	1.72±0.08	1.73±0.08
2. method	1.74±0.11	1.80±0.10	2.12±0.10	1.85±0.12	1.91±0.08	1.82±0.08
Literature	1.70±0.13			2.00±0.07		

➔ **Marked trend for both derived fractal dimensions to increase for increasing blends**

➔ **2. method was found to exceed the 1. method**

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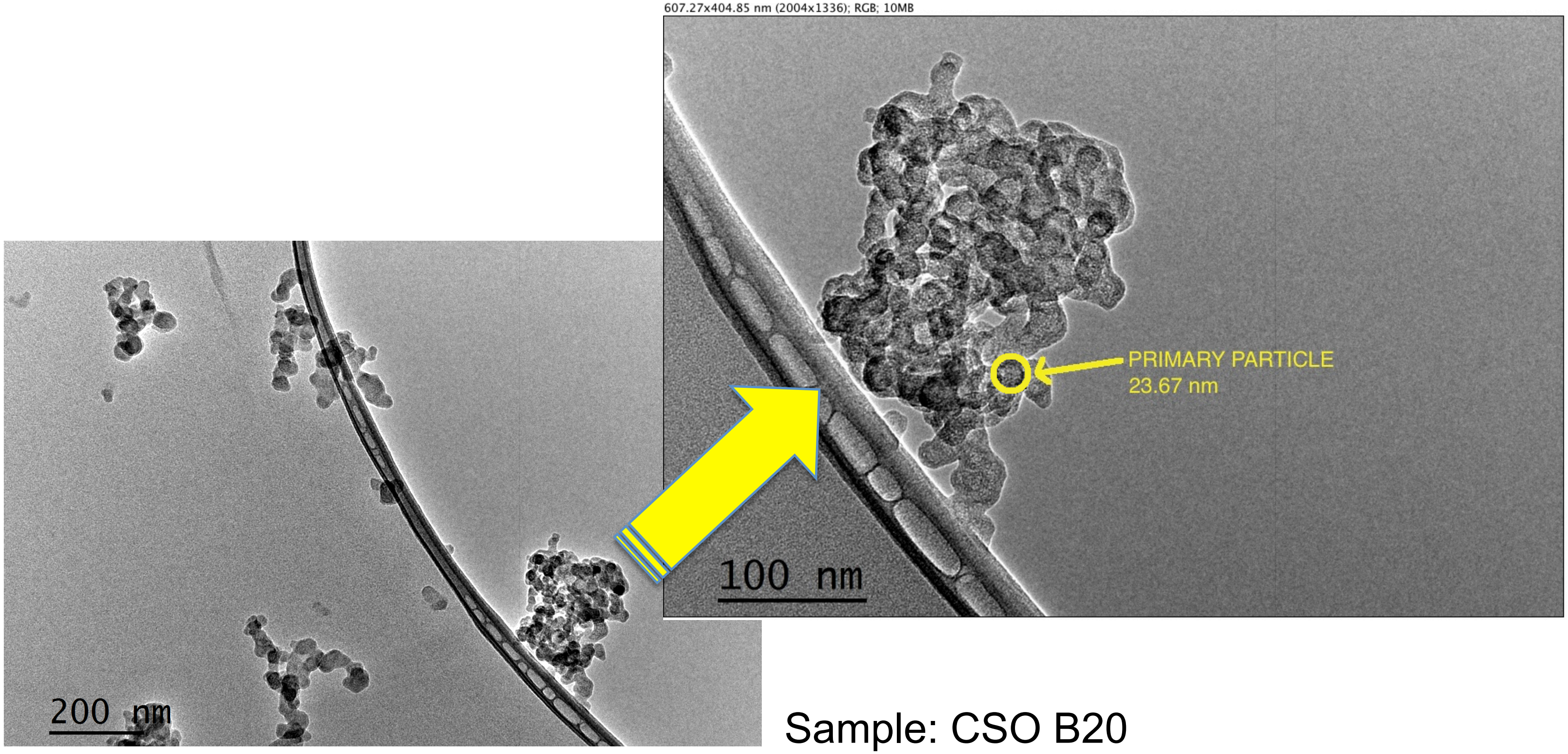
Analysis: Primary Particle Size

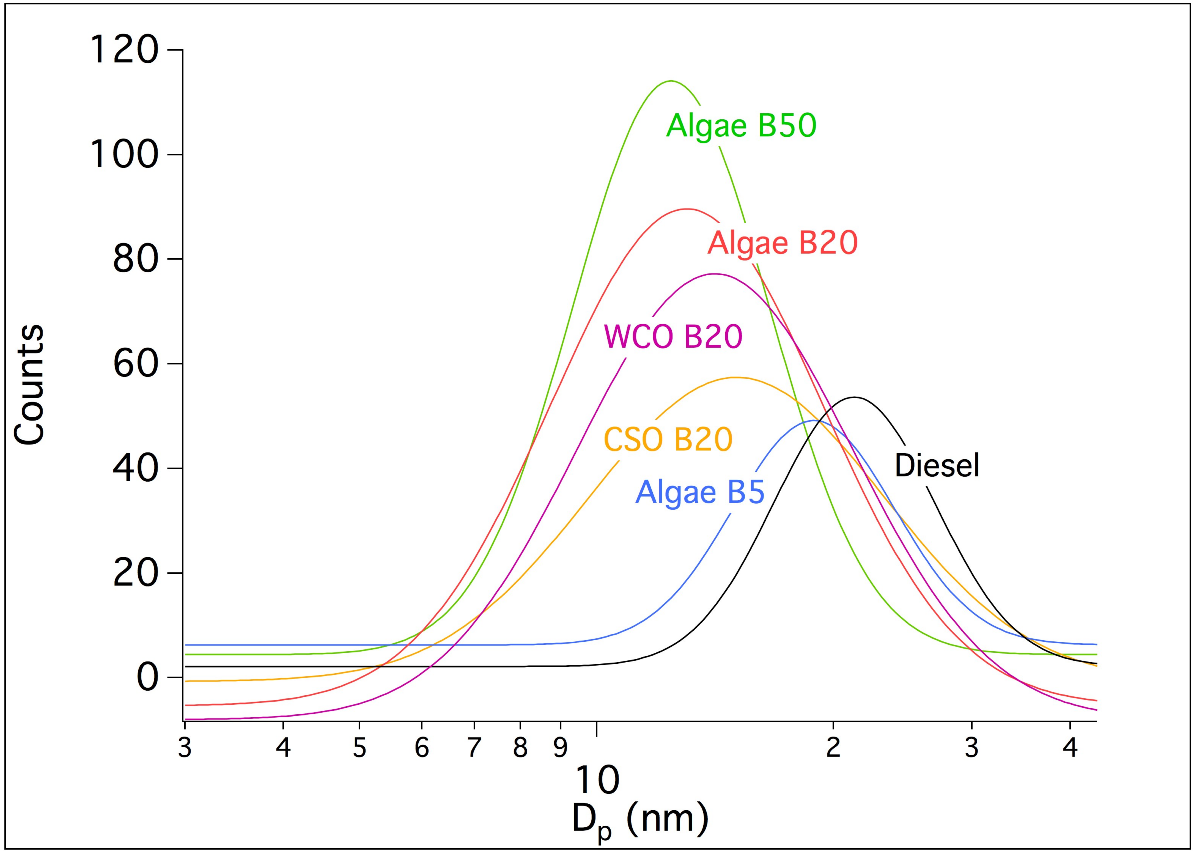
Primary Particle Size Analysis



Sample: CSO B20

Summarized Primary Particle Size

Size Distribution



Algae B50 : 12.4 ± 0.5 nm

Algae B20 : 13.1 ± 0.8 nm
WCO B20 : 14.4 ± 1.0 nm
CSO B20 : 15.1 ± 1.1 nm

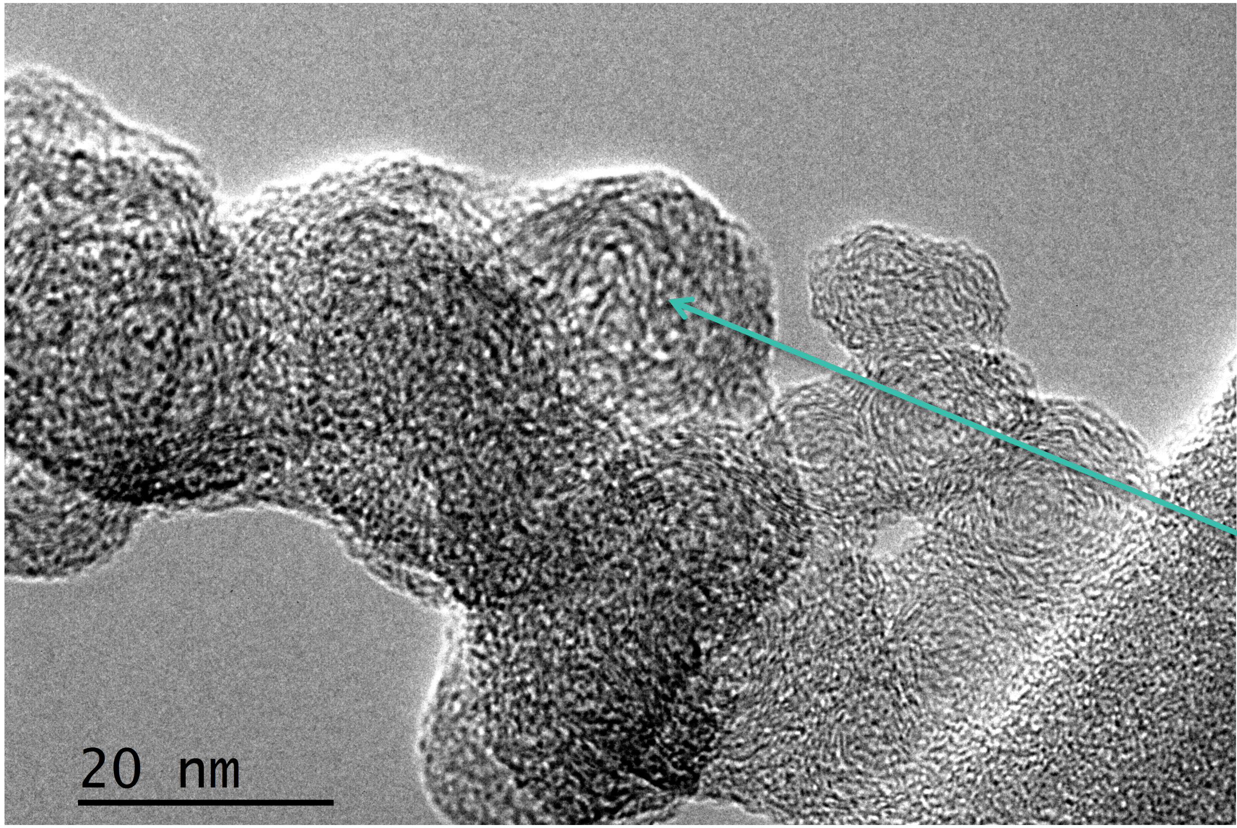
Algae B5 : 18.9 ± 0.5 nm

Diesel : 21.3 ± 1.9 nm

Literatur
Diesel : 23.0 ± 2.3 nm
Biofuel : 18.0 ± 1.8 nm
(Rape oil)

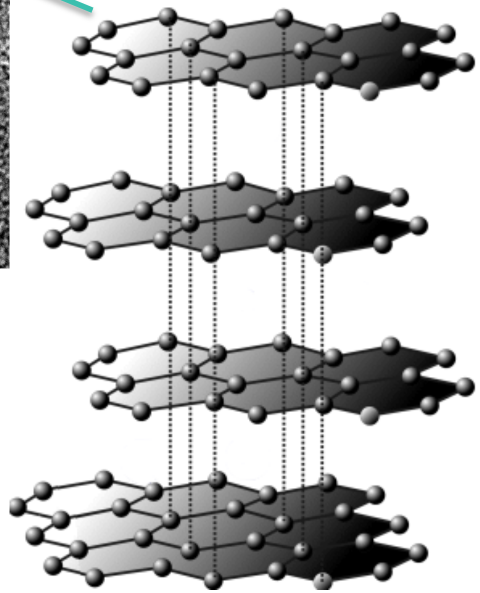
➔ **Higher biofuel content leads to smaller primary particles**

Inner Structure Analysis



Diesel

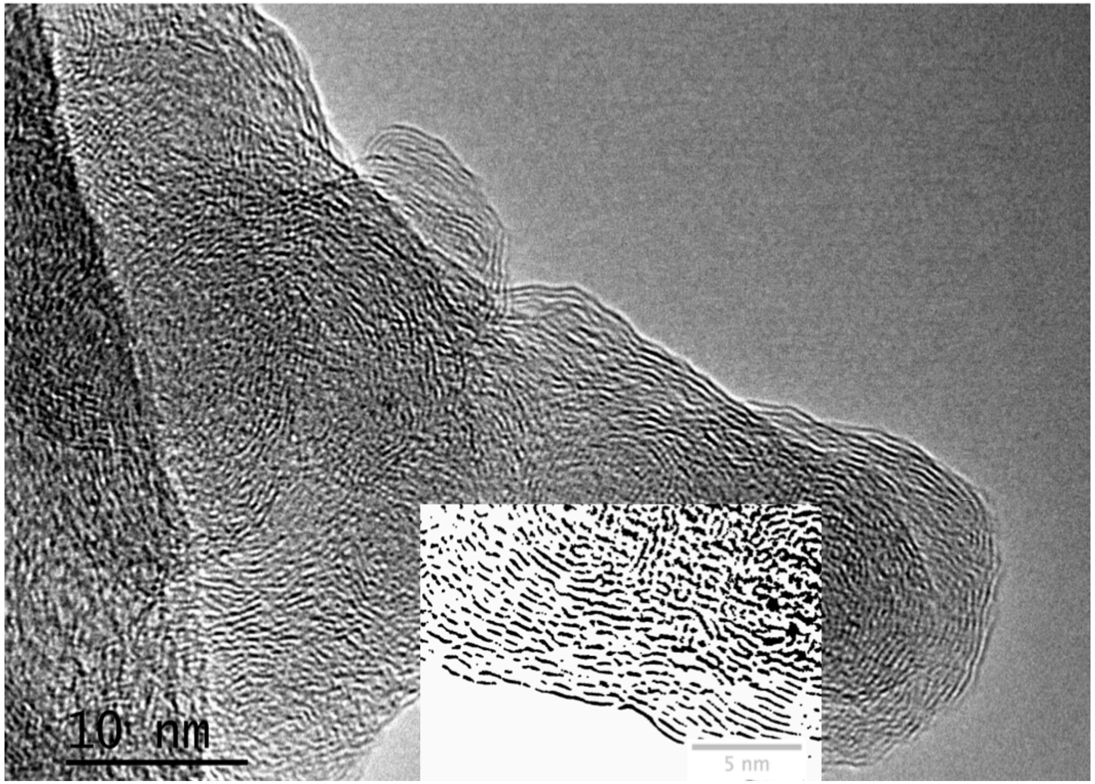
graphene layers of carbon



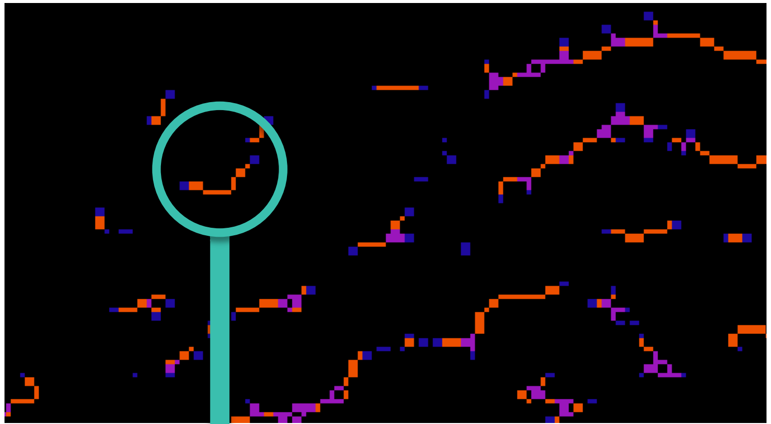
www.chemiereport.at

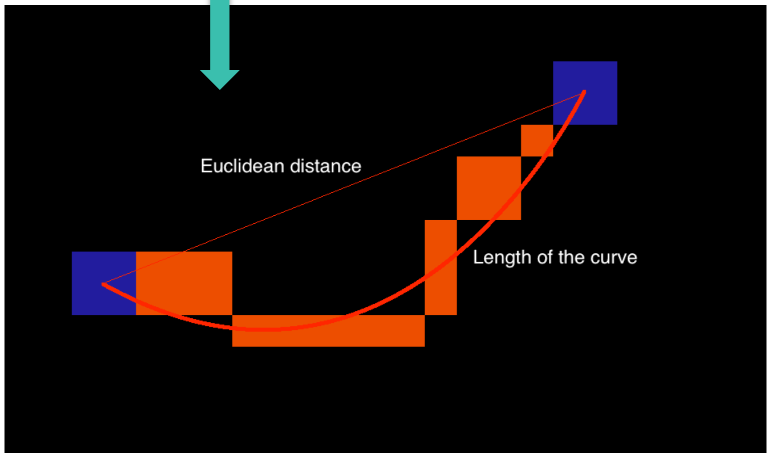
Analysis: Inner Layer Structure

1. Fringe length
2. Degree of curvature (tortuosity)
3. Separation distance



Fringe Analysis





Display of 2 voxels within skeleton image:

1.) voxels → fringe lengths

2.) voxels → fringe end points

→ fringe tortuosity (software supported measurement)

3.) → fringe distance (manual measurement)

Summary Results: Inner Layer Structure

Biofuel is more amorphous and consequently more prone to oxidation

on the basis of:

1. **Smaller fringe length**
2. **Higher fringe curvature**
3. **Larger mean fringe separation distance**

➔ Soot emissions from engines run by biofuel compositions are significantly reduced

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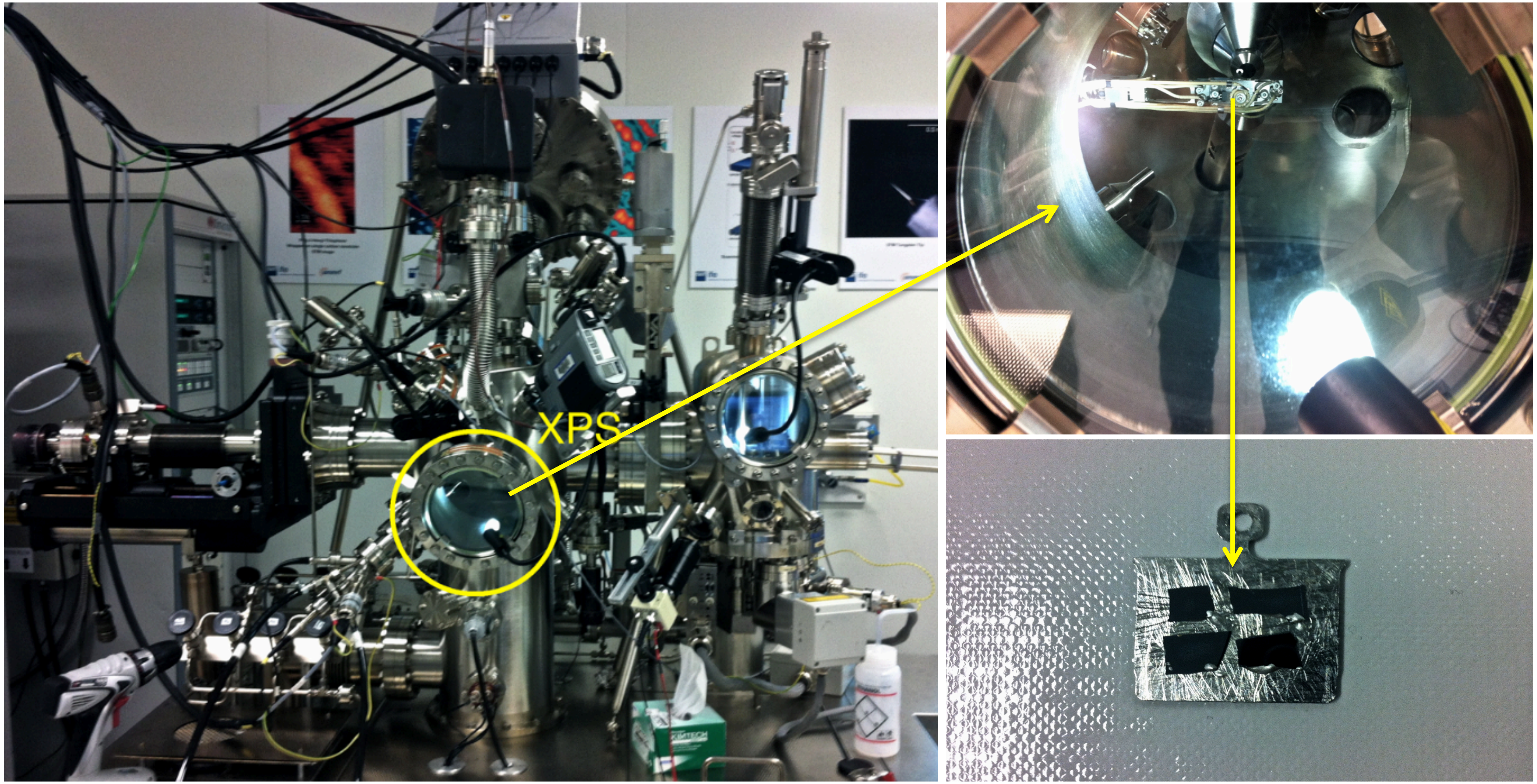
X-ray Photoelectron Spectroscope

X-ray beam- irradiating



Samples-irradiated

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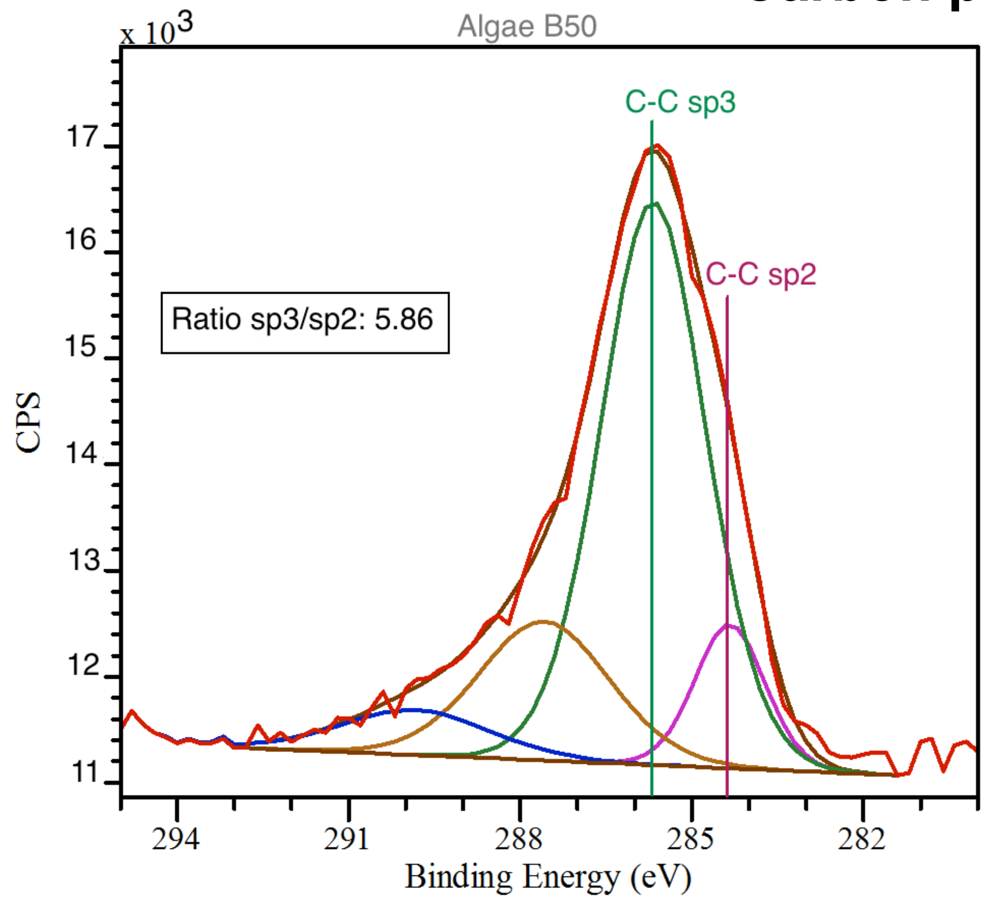
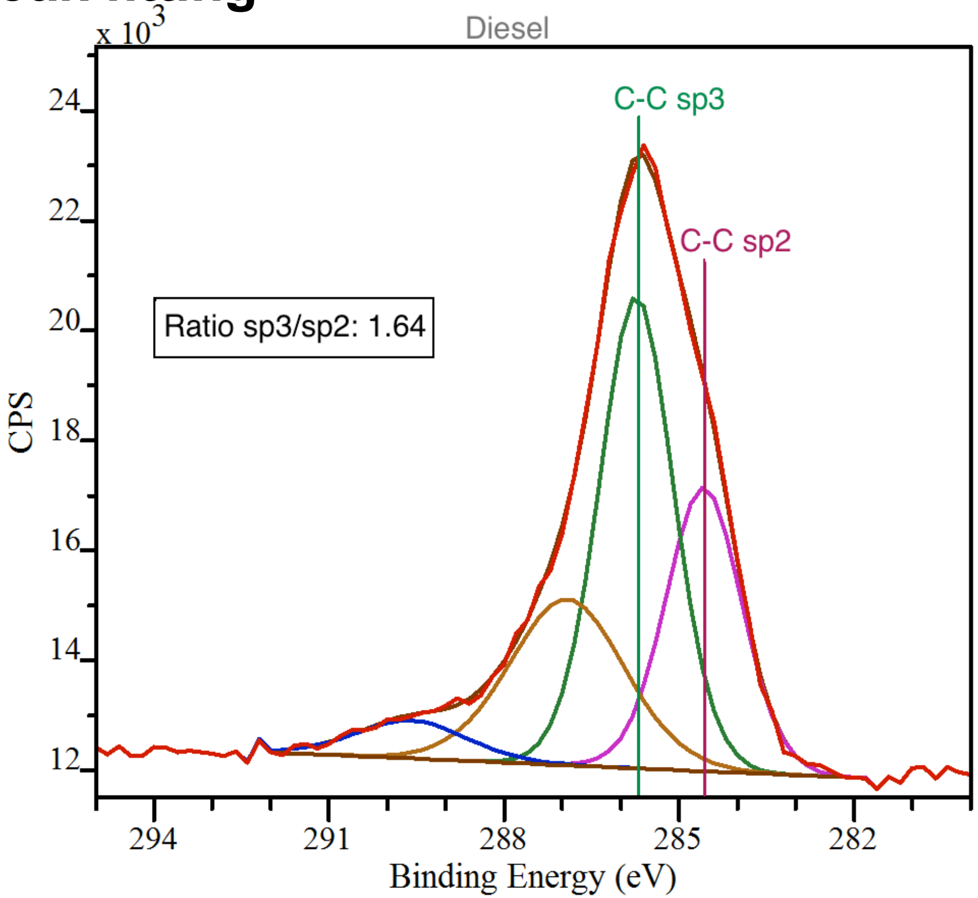
XPS Chemical State Analysis

Carbon peak fitting





sp3/sp2 = organic/elemental carbon:
higher ratio ➔ more amorphous structure

➔ Biodiesel shows more amorphous structure

Summary

- **Investigation of primary particle size of biodiesel and pure diesel samples by TEM**

➔ Biodiesel primary particles appear to be smaller

- **Investigation of the fractal dimension by two methods**

➔ Higher fractal dimension for biofuel

- **Investigation of the primary particle microstructure by TEM**

➔ Biodiesel graphene layers are more likely to be amorphous

- **Chemical state analysis by XPS**

➔ More organic carbon (C-C sp3) in biofuel

No significant distinction in different feedstocks of biofuel

Thank you for your attention!

Literature

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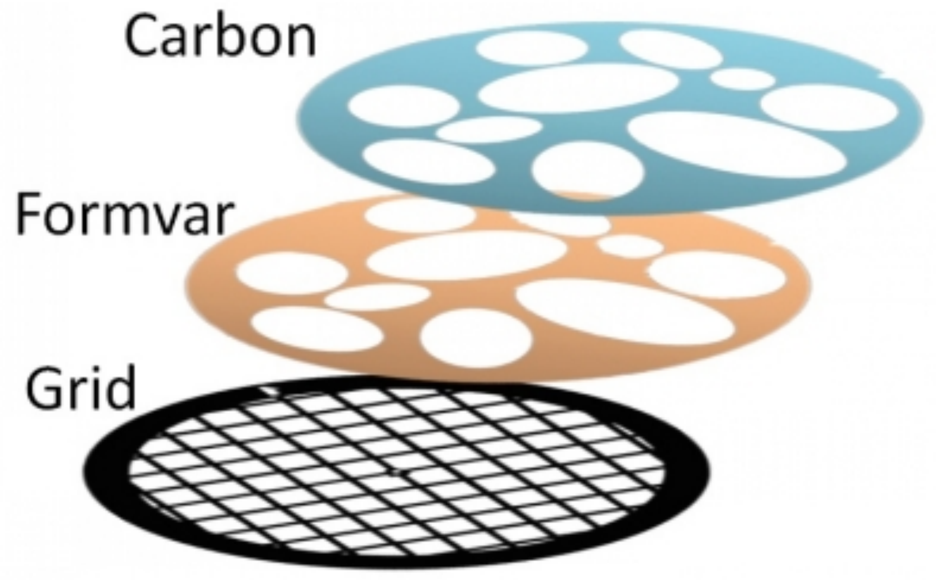
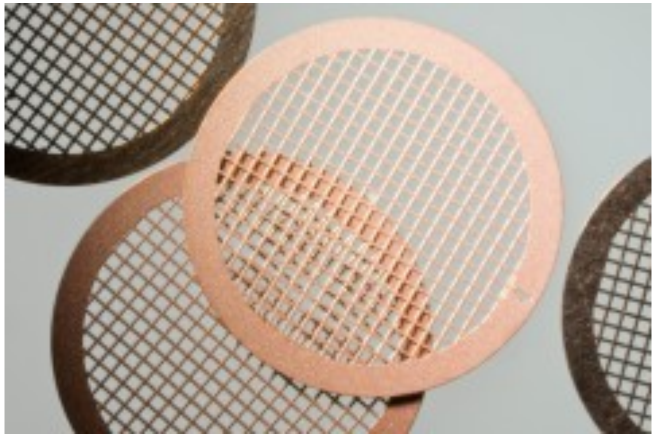
Backup

TEM-grids

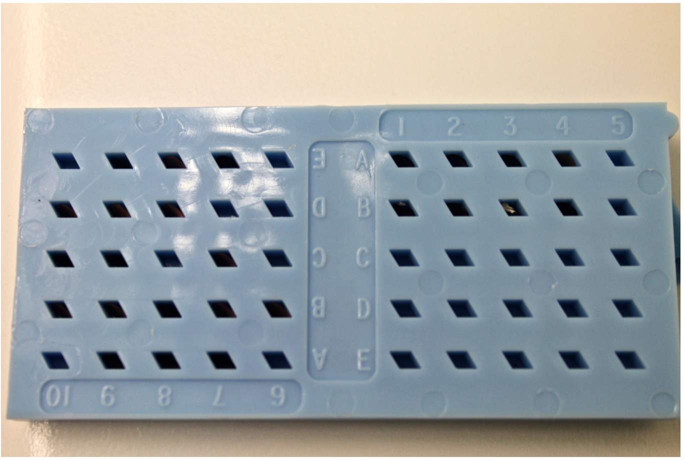
Holey Carbon Grid



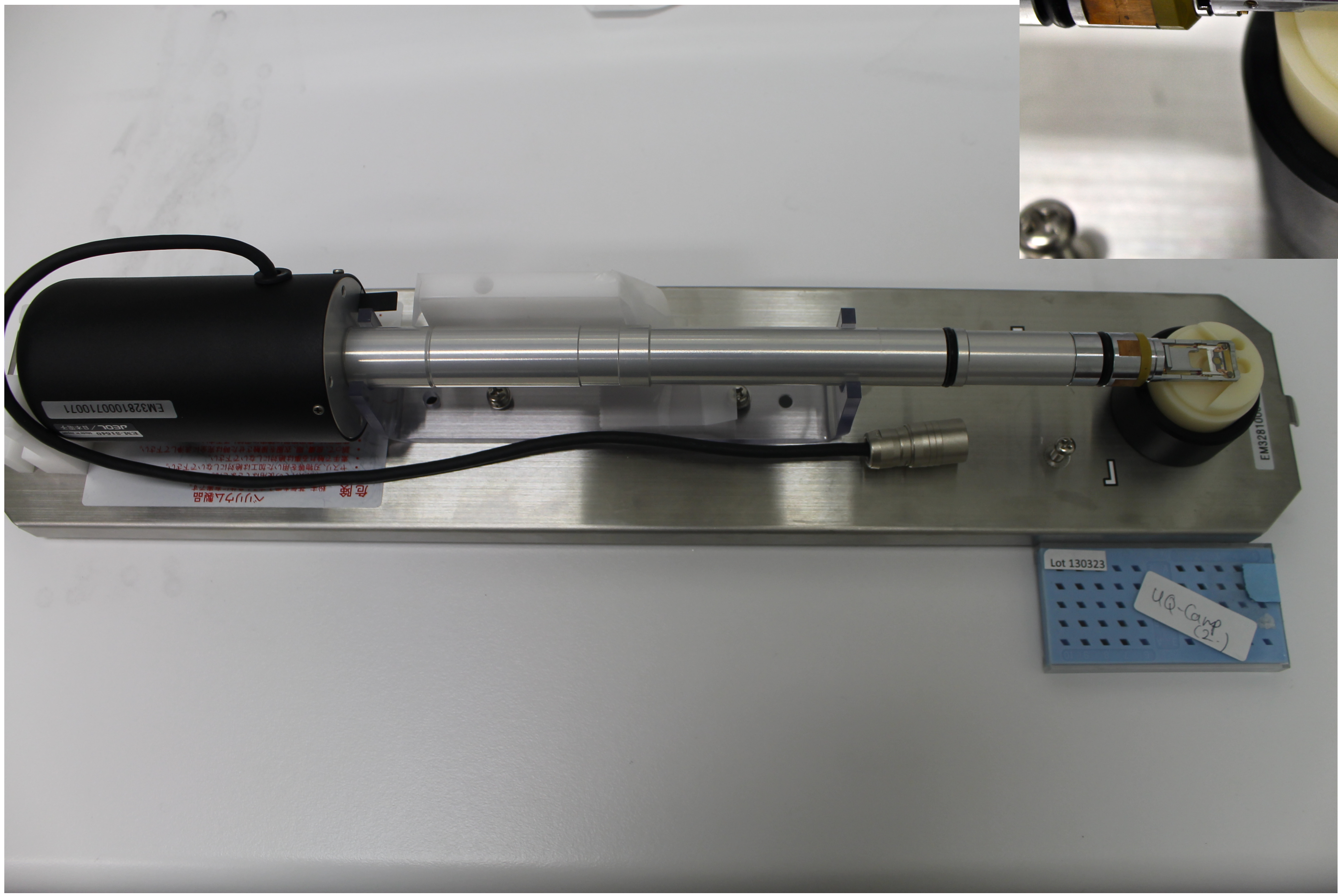
www.latech.com

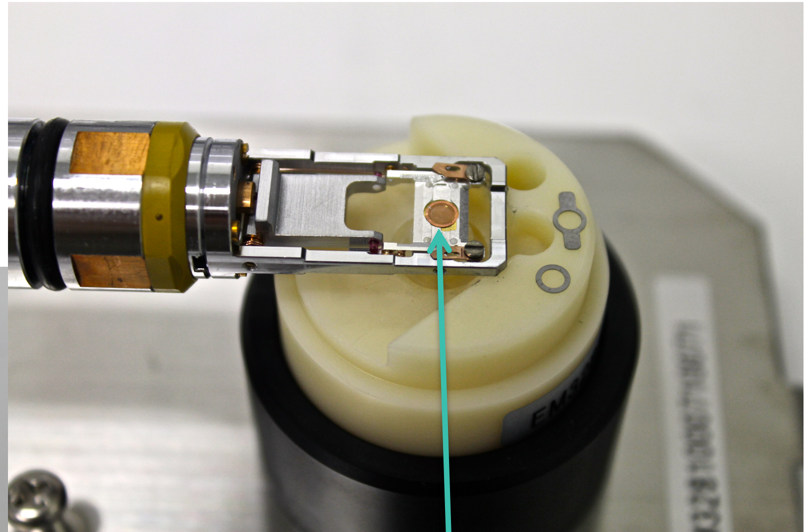


www.scienceservices.de



TEM-Sample Holder



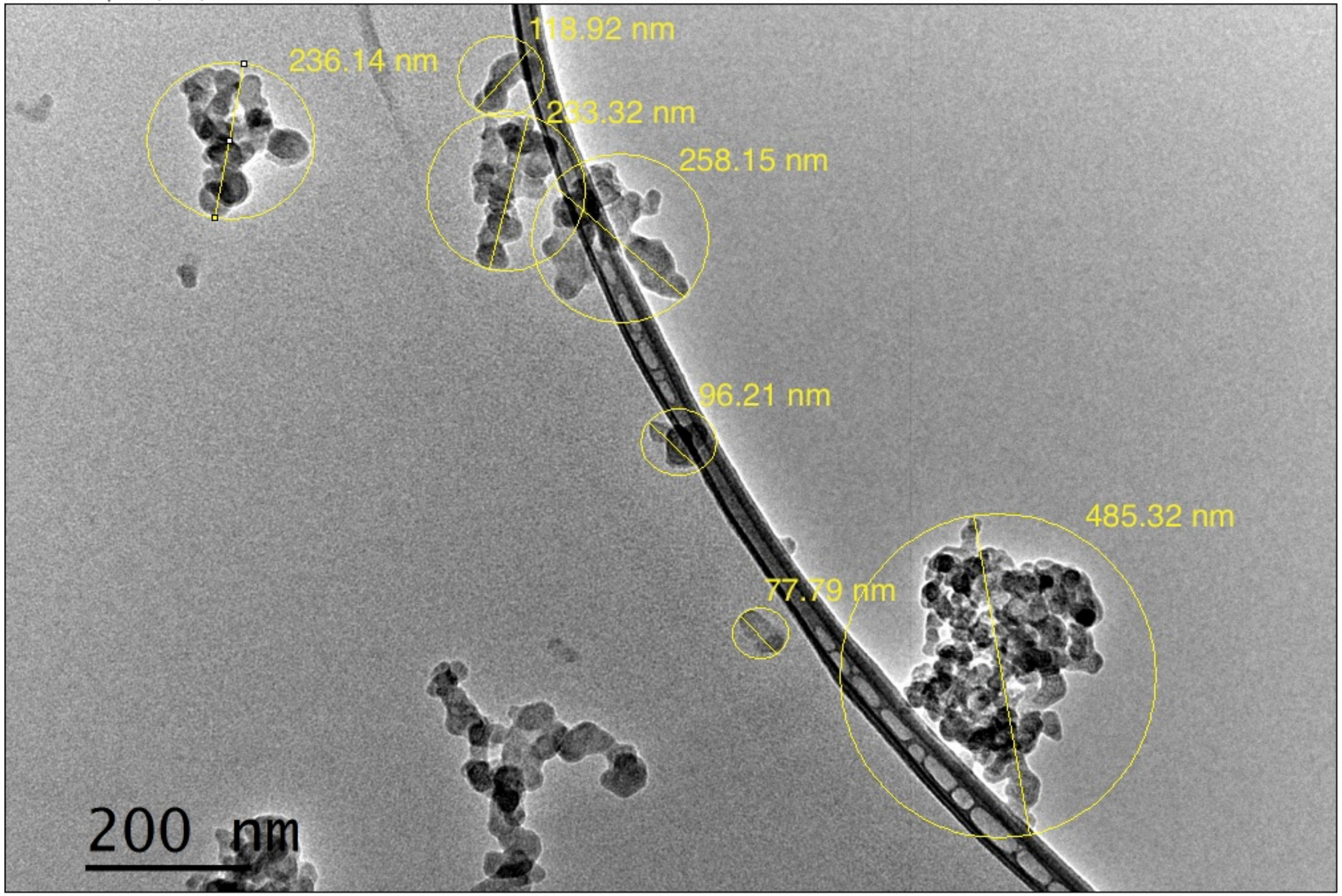


TEM grid, diameter: 3.05 mm

Analysis: Agglomerate Size

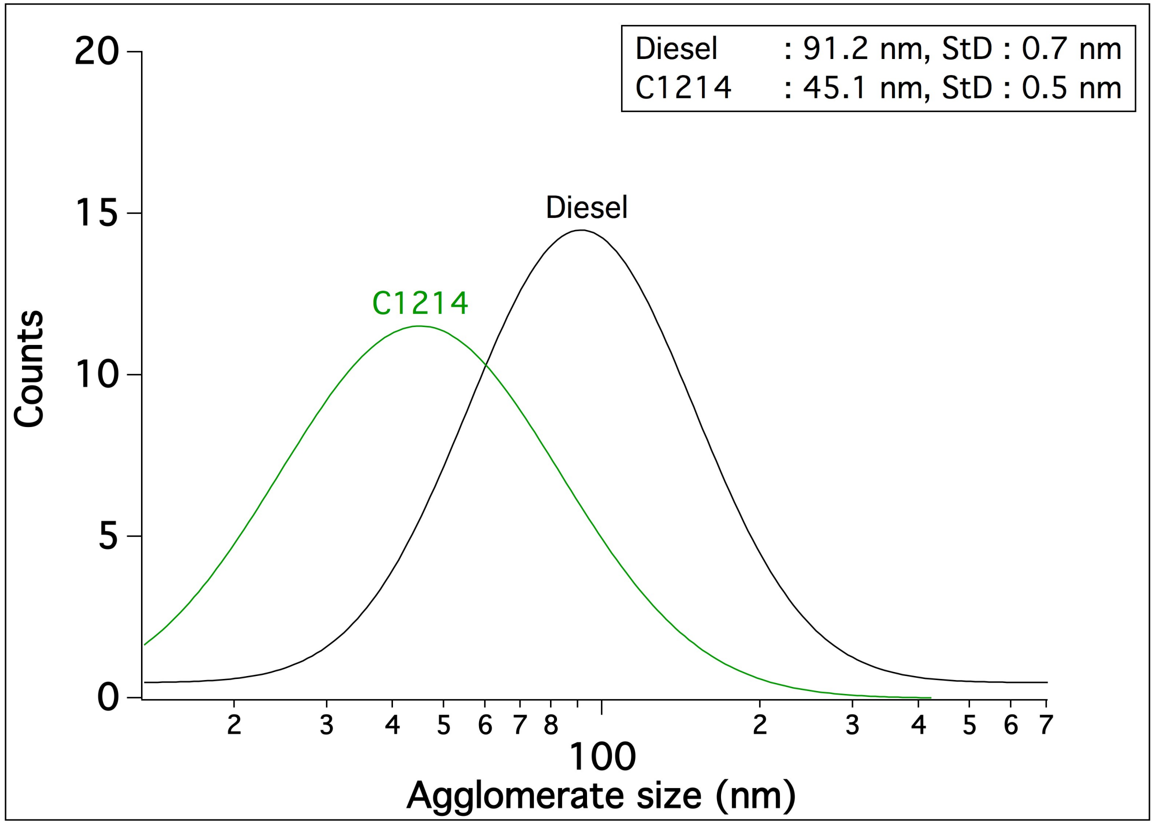
Agglomerate Size Analysis by ImageJ

2004x1336 pixels; RGB; 10MB



Sample: CSO B20, idle

Agglomerate Size Distribution

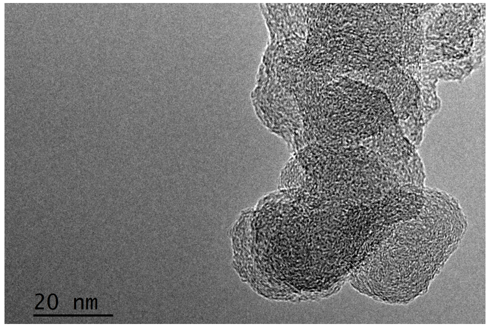


January Campaign : Log normal size distribution of Diesel and palm oil C1214

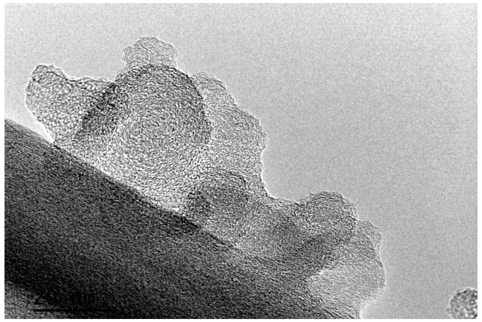
➔ **Pure biodiesel agglomerates are smaller than pure diesel ones**

Inner Layer Structure

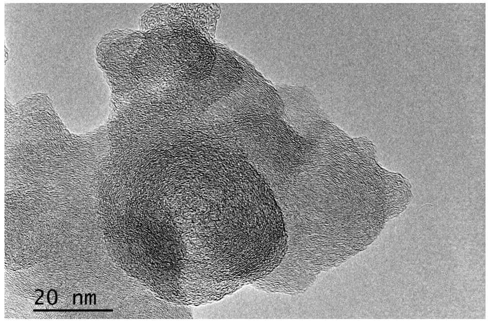
CSO, B20, 50 % Load, UQ II



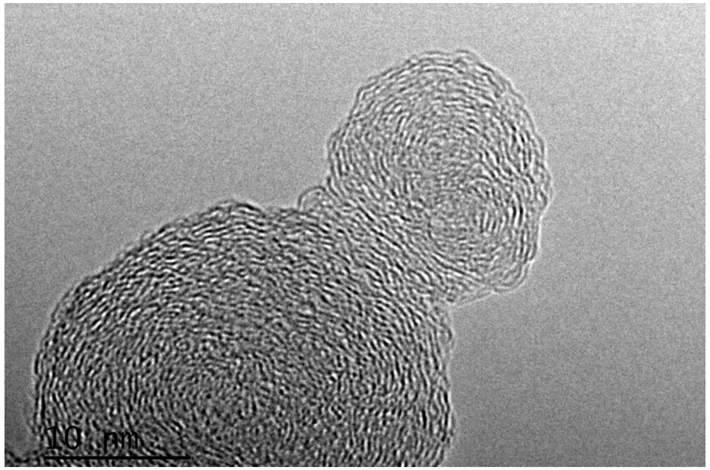
Algae B5, 50 % Load, UQ I

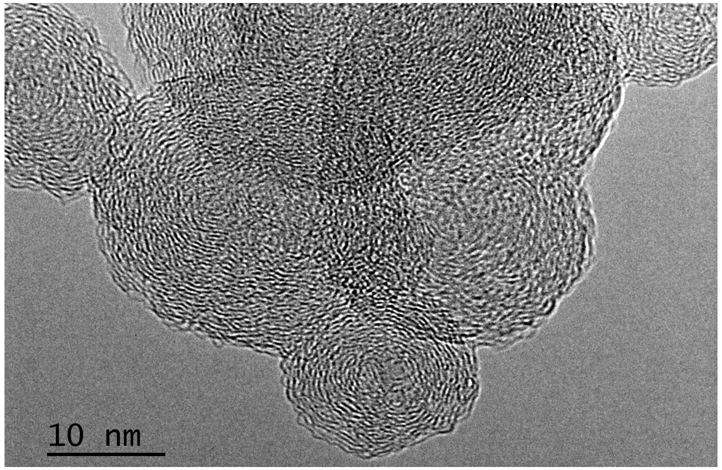


Diesel, 25 % Load, UQ I



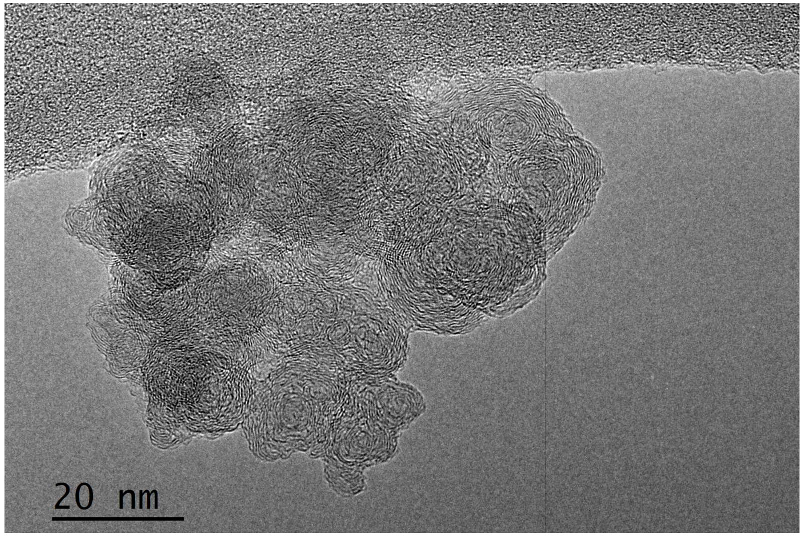
WCO B20, 50 % Load, UQ II





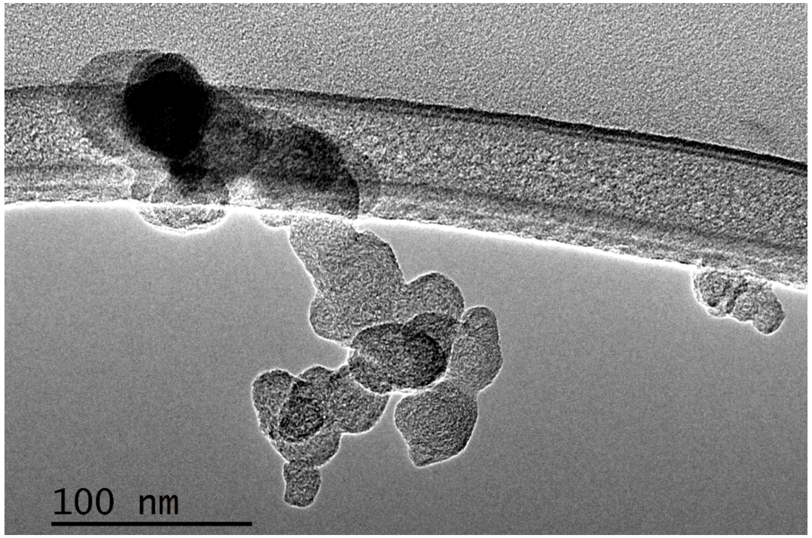
CSO, B20, 50 % Load, UQ II

Examples of Fractal Dimension



a.) WCO B20

FD =1.97 ± 0.04

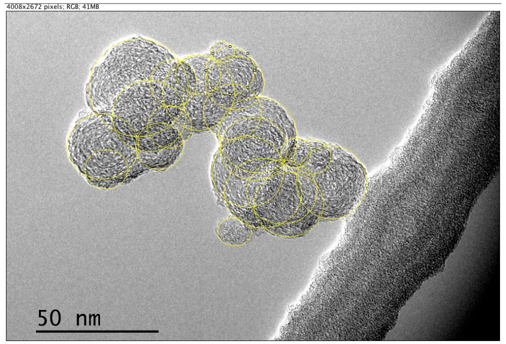


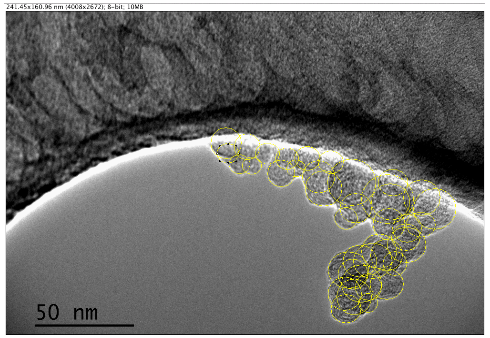
b.) Diesel

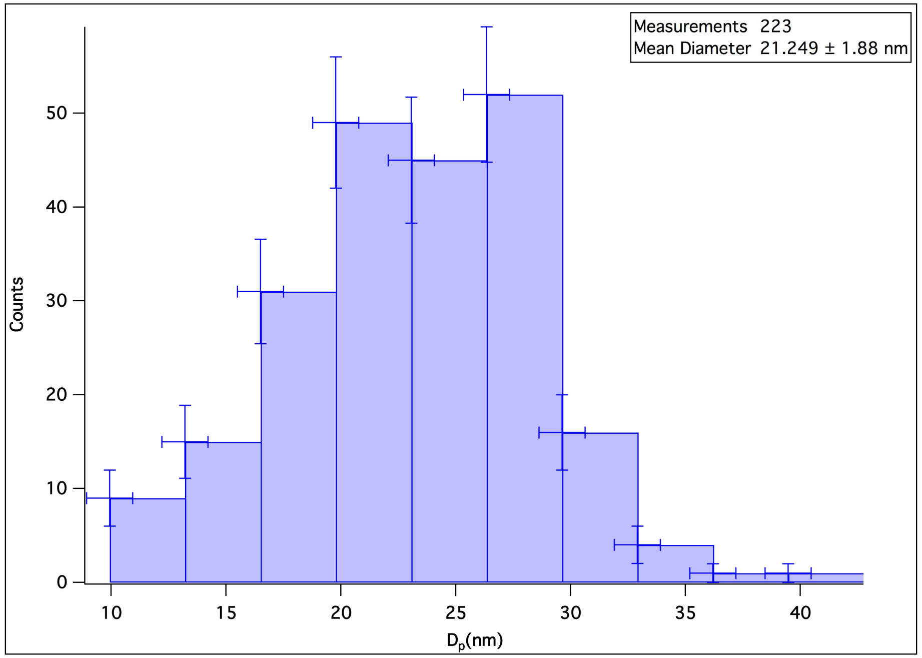
FD = 1.72 ± 0.08

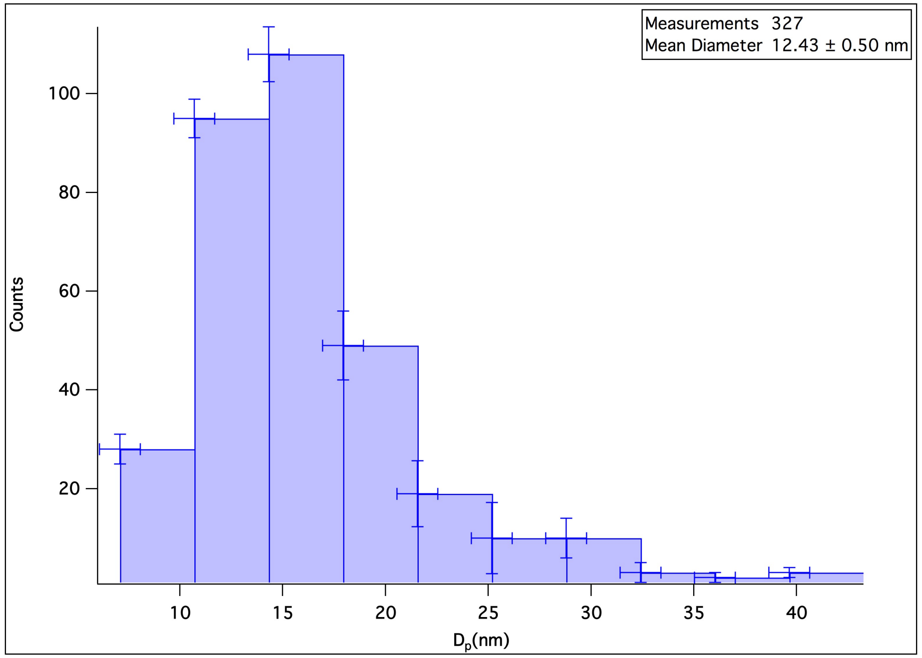
➔ **The smaller, the more spherical, the more compact the agglomerate is, the higher its fractal dimension**

Primary Particle Size Distribution







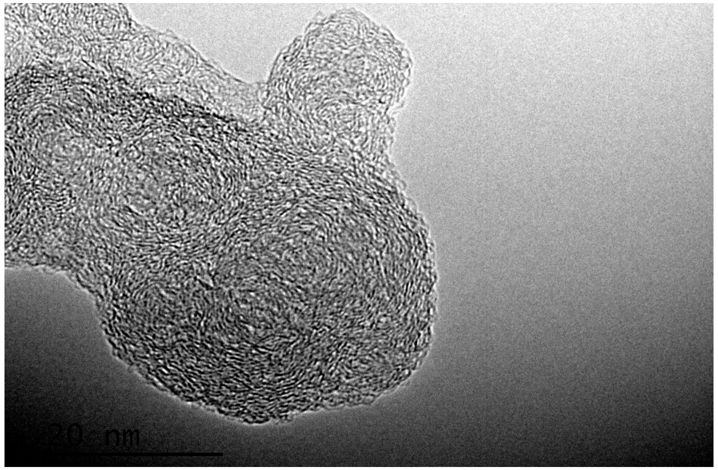


example: Diesel, 50 % Load **example: Algae B50, 50 % Load**

Inner Structure Analysis

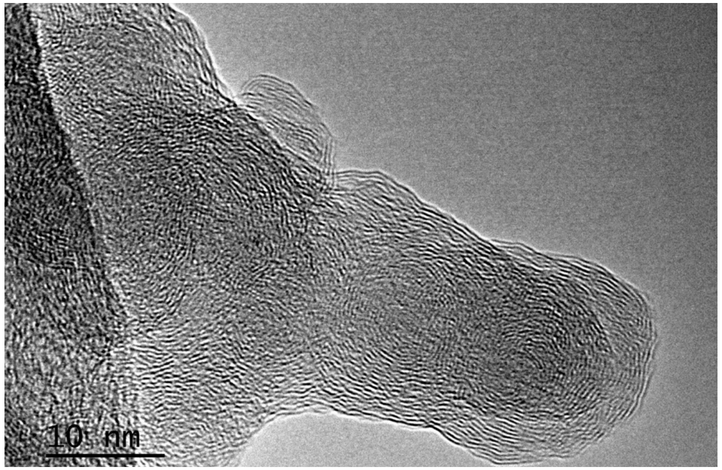
- **Amorphous** structure of graphene layers
  ➔ **disordered** structure

Algae B50



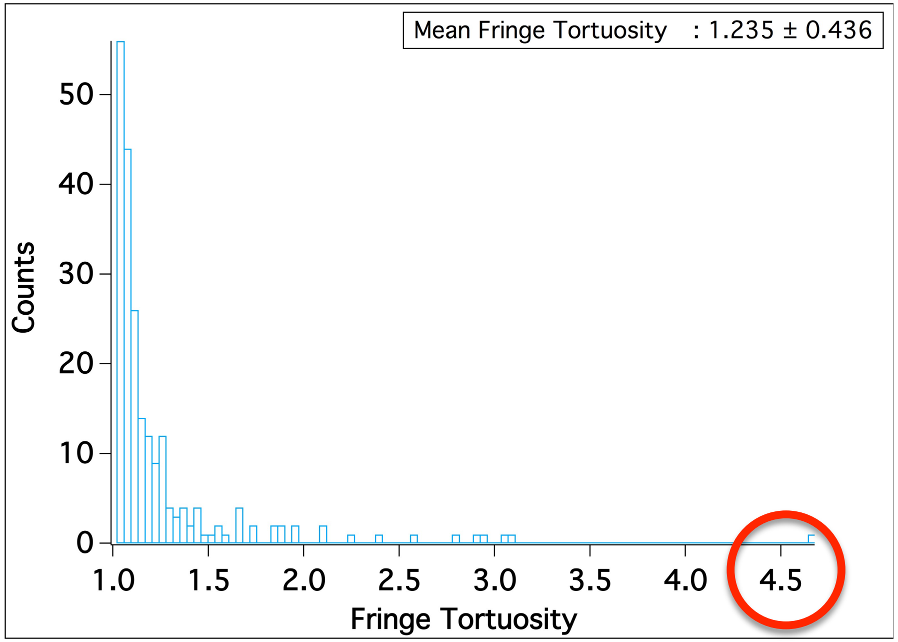
- **Graphitic** structure of graphene layers
  ➔ **ordered** structure

Diesel

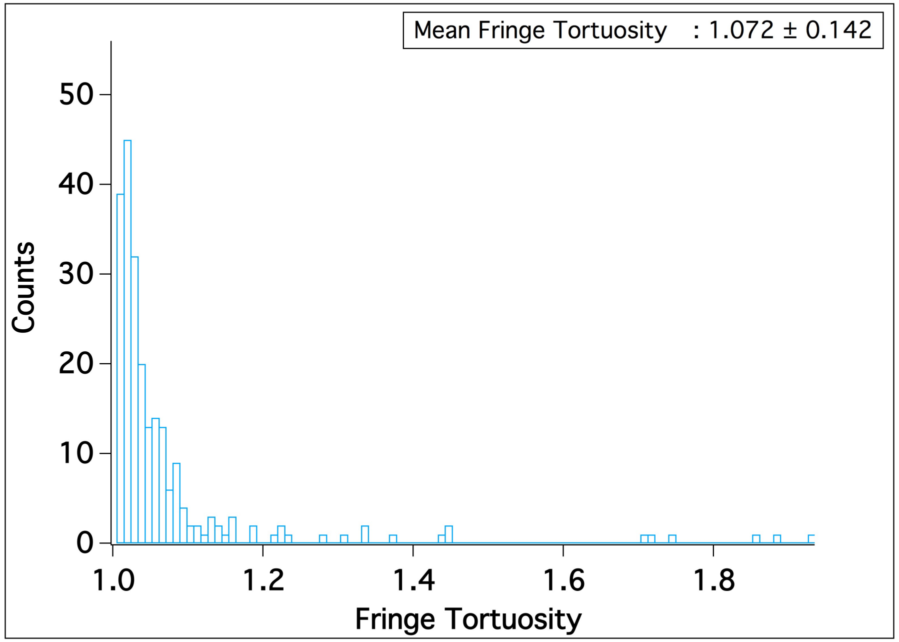


➔Biofuel is more likely to be amorphous

Fringe Characterization Results: Tortuosity



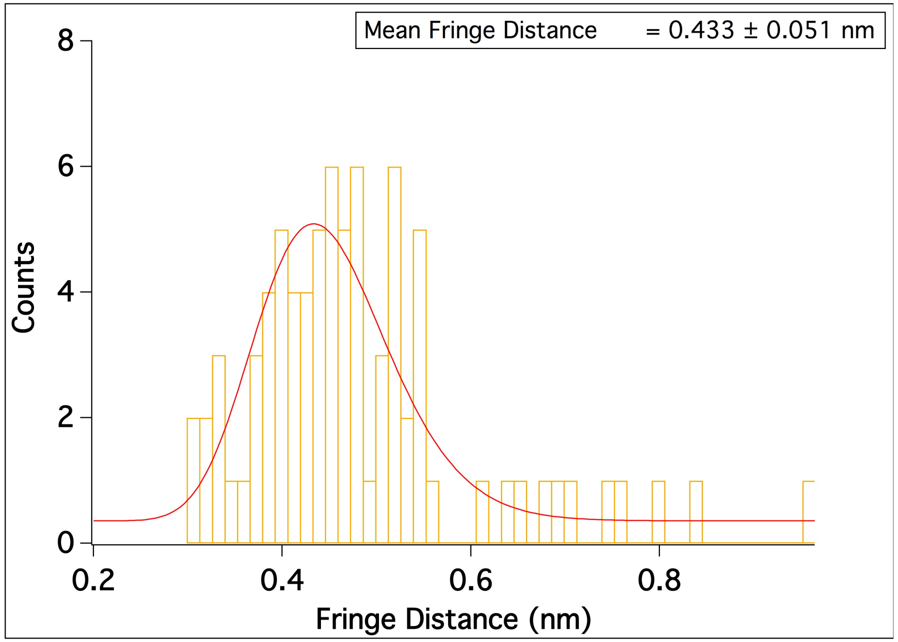
a.) example: Algae B50, 50 % Load



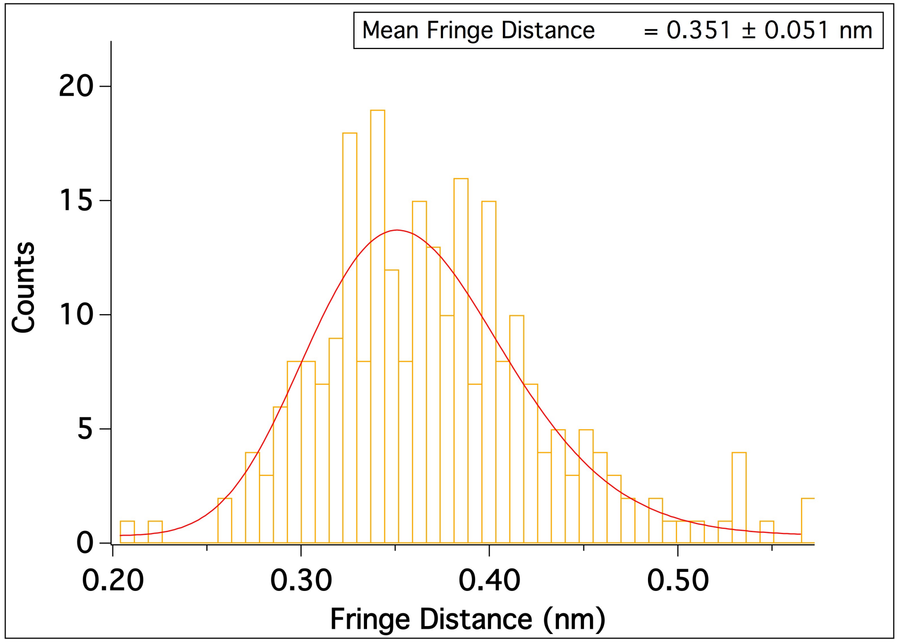
b.) example: Diesel, 50 % Load

➔ Biodiesel fringes are more likely to be curved

Fringe Characterization Results: Distance



a.) example: Algae B50, 50 % Load



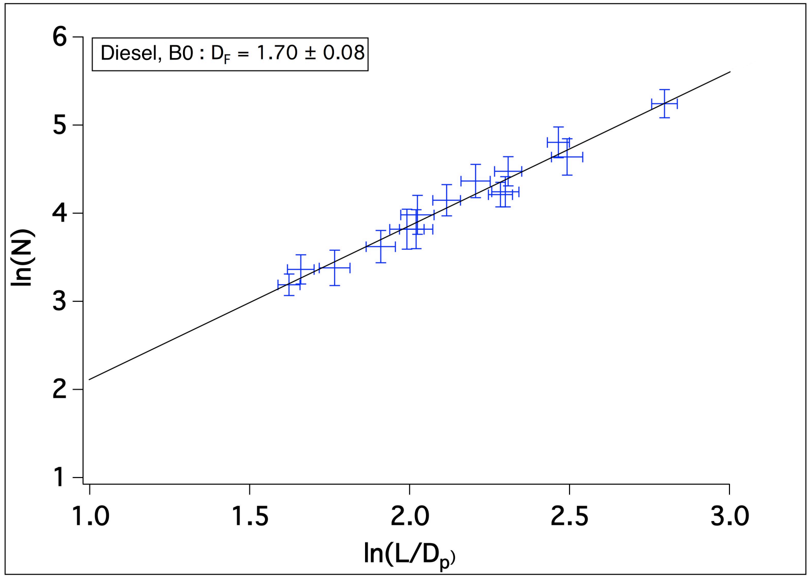
b.) example: Diesel, 50 % Load

Fringe distances <0.2 nm were discarded as artifacts

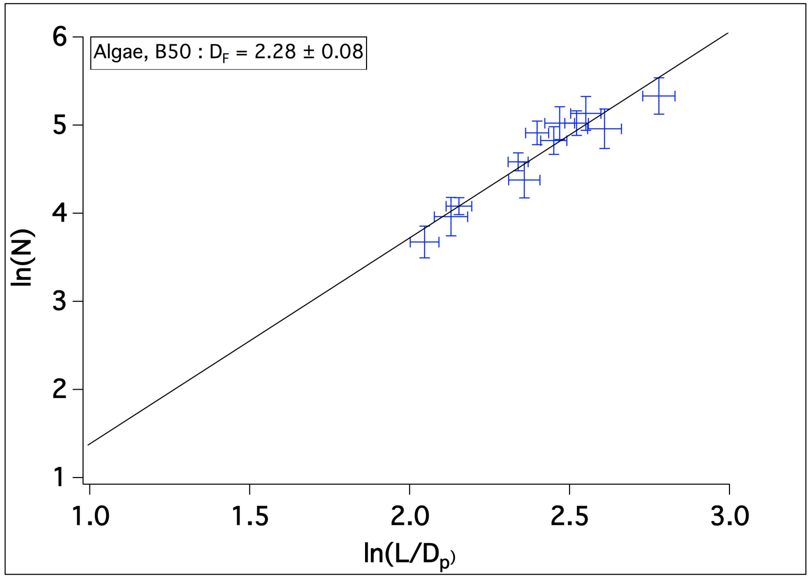
➔ Diesel shows the closest value to the graphene layer distance of graphite (0.335 nm)

➔ Fringe separation distances of biofuel appear to be larger

Analysis: Fractal Dimension by Equation



a.) example: Diesel, all loads

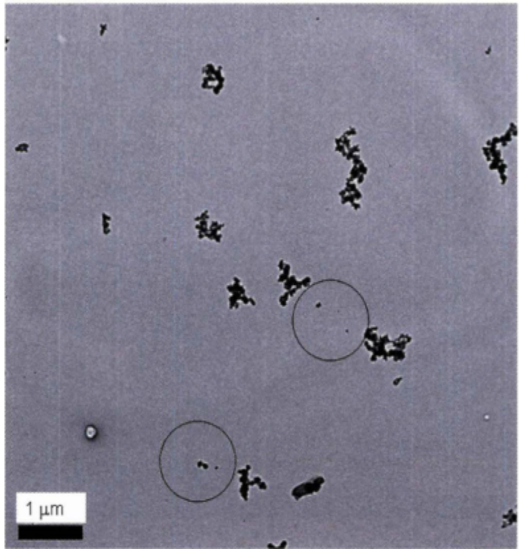


b.) example: Algae B50, all loads

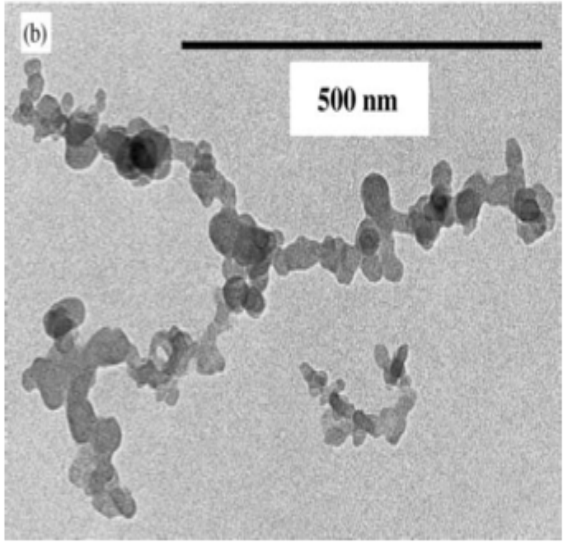
➔ The Fractal dimension $\mathbf{D_F}$ is derived from the slope

Introduction

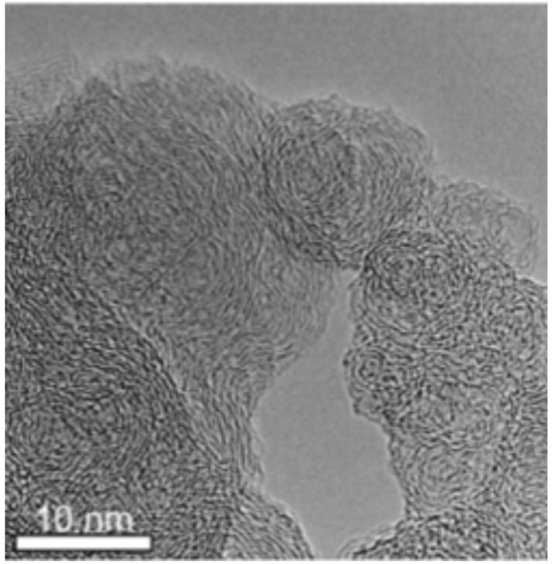
- Previous research has been done on investigating the particle structure of diesel and biofuels by transmission electron microscopy



Kihong Park et al.: Structural Properties of Diesel Exhaust Particles Measured by Transmission Electron Microscopy: Relationships to Particle Mass and Mobility



M. Wentzel et al: Transmission Electron Microscopical and Aerosol Dynamic Characterization of Soot Aerosols



Matti Happonen et al.: The Comparison of Particle Oxidation and Surface Structure of Diesel Soot Particles between Fossil Fuel and Novel Renewable Diesel Fuel

outer structure

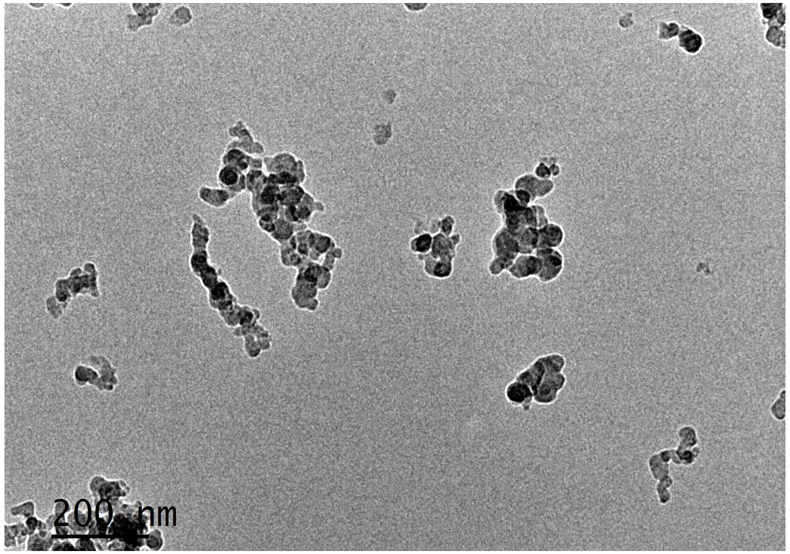
inner structure

Introduction

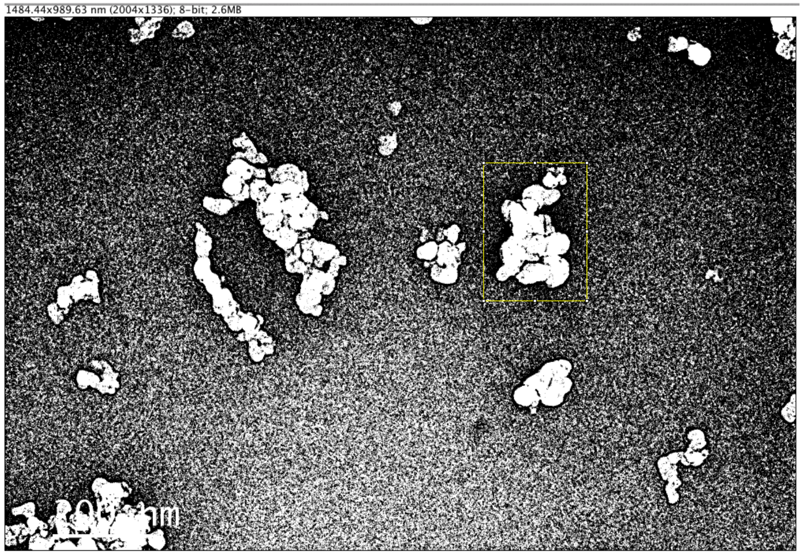
- Only a small number of research has been done on the analysis of the inner AND the outer structure of diesel AND biodiesel by means of transmission electron microscopy
- None research has been done on the morphology of algal biofuel
- The physical properties of diesel particles and of biofuel particles of different feedstocks including algae will be investigated

Analysis: Fractal Dimension by ImageJ

a.)



b.)



Example Diesel, UQ I: a.) TEM-image, b.) converted into binary image

Fractal Dimension Results

Sample	Diesel, B0	Algae, B5	Algae, B50	Algae, B20	CSO, B20	WCO, B20
FD Image J	1.72±0.09	1.74±0.06	1.80±0.07	1.72±0.06	1.72±0.08	1.73±0.08

- → **Higher values for the fractal dimensions for biodiesel**
- → **Increase of fractal dimension for increasing blends**

Analysis: Fractal Dimension by Equation

$$N_P = k_L\left(\frac{L}{D_P}\right)^{D_F}$$

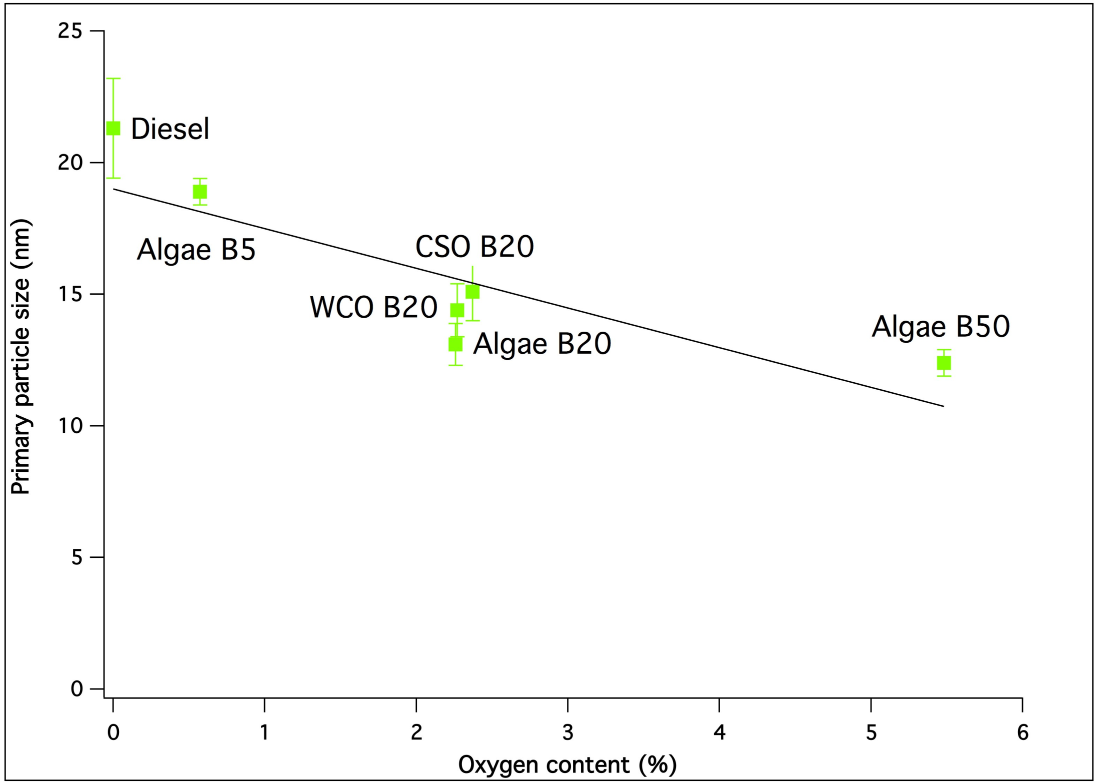
Approach of Brasil to determined Fractal Dimension

$$N_P = k_\alpha\left(\frac{A_\alpha}{A_P}\right)^{\alpha}$$

Empirical correlation to obtain N_P

where $\mathbf{D_F}$ is the fractal dimension, $\mathbf{N_P}$ is the number of primary particles in the aggregate, **L** the maximum length of the aggregate, $\mathbf{D_P}$ the diameter of the primary particles

Oxygen Content in Biofuel



Primary particle size vs Oxygen content for all fuel compositions and blends at half load

➔ **More oxygen produces smaller primary particles**

➔ **Smaller particles being oxidised more easily (Liati et al.)**

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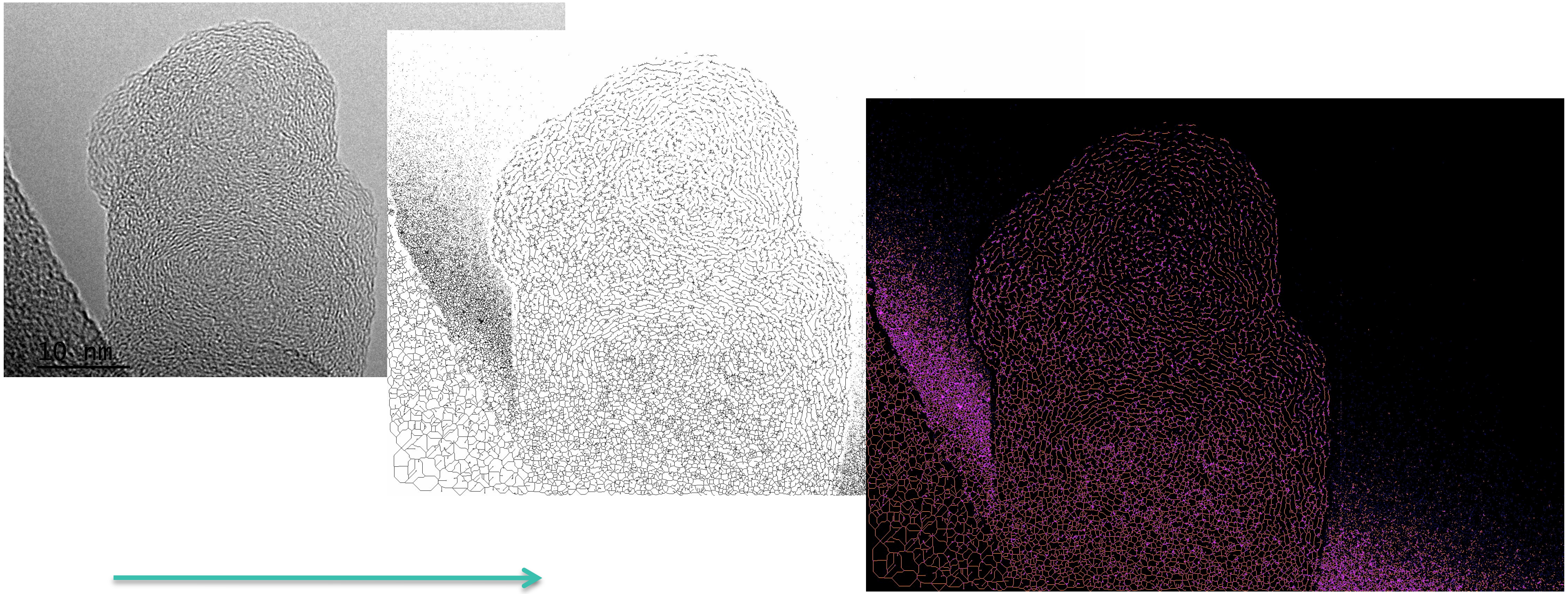
Hypothesis Project Proposal

- 1.) More oxygen in the fuel will produce smaller primary particles ✔

Hypotheses Project Proposal

- 2.) Biodiesel produces amorphous primary particles and as a results more prone to oxidation ✔

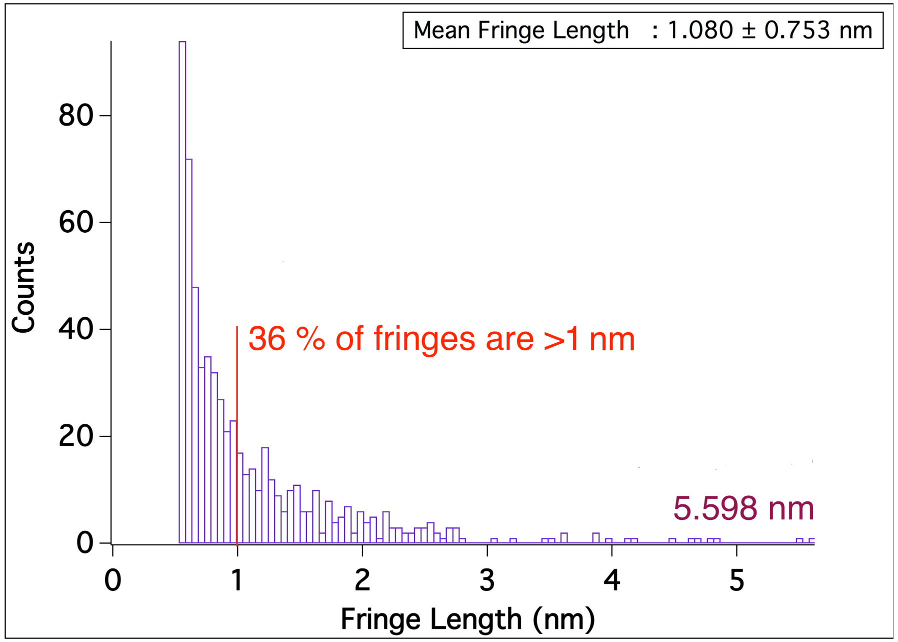
Fringe Analysis



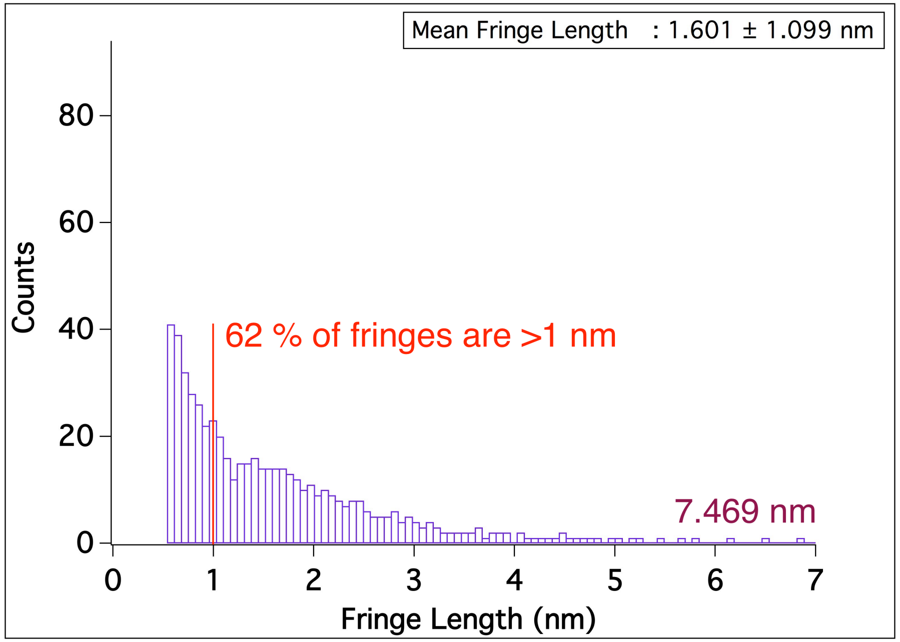
skeletonization

tagged skeletonization

Fringe Characterization Results: Length



a.) example: Algae B50, 50 % Load



b.) example: Diesel, 50 % Load

Fringes shorter than 0.5 nm were sorted out as noisy structure

➔ Biodiesel shows shorter fringes

XPS Elemental Analysis

Spectral analysis of biodiesel and diesel showed:

- → **Elements within fuels: Mainly oxygen and carbon**
- → **Higher oxygen to carbon ratio for biofuel**