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Synthetic fuels from 3-φ Fischer-Tropsch synthesis using bio-derived gas feed and novel nanometric catalysts

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RÉSEAU BIOFUELNET CANADA

Synthetic fuels from 3-φ Fischer-Tropsch synthesis using bio-derived gas feed and novel nanometric catalysts

<u>James Aluha,</u> Nadi Braidy, Yongfeng Hu, Ajay Dalai and Nicolas Abatzoglou

Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes

Chania (Crete), Greece, Sept. 27 – Oct. 2, 2015

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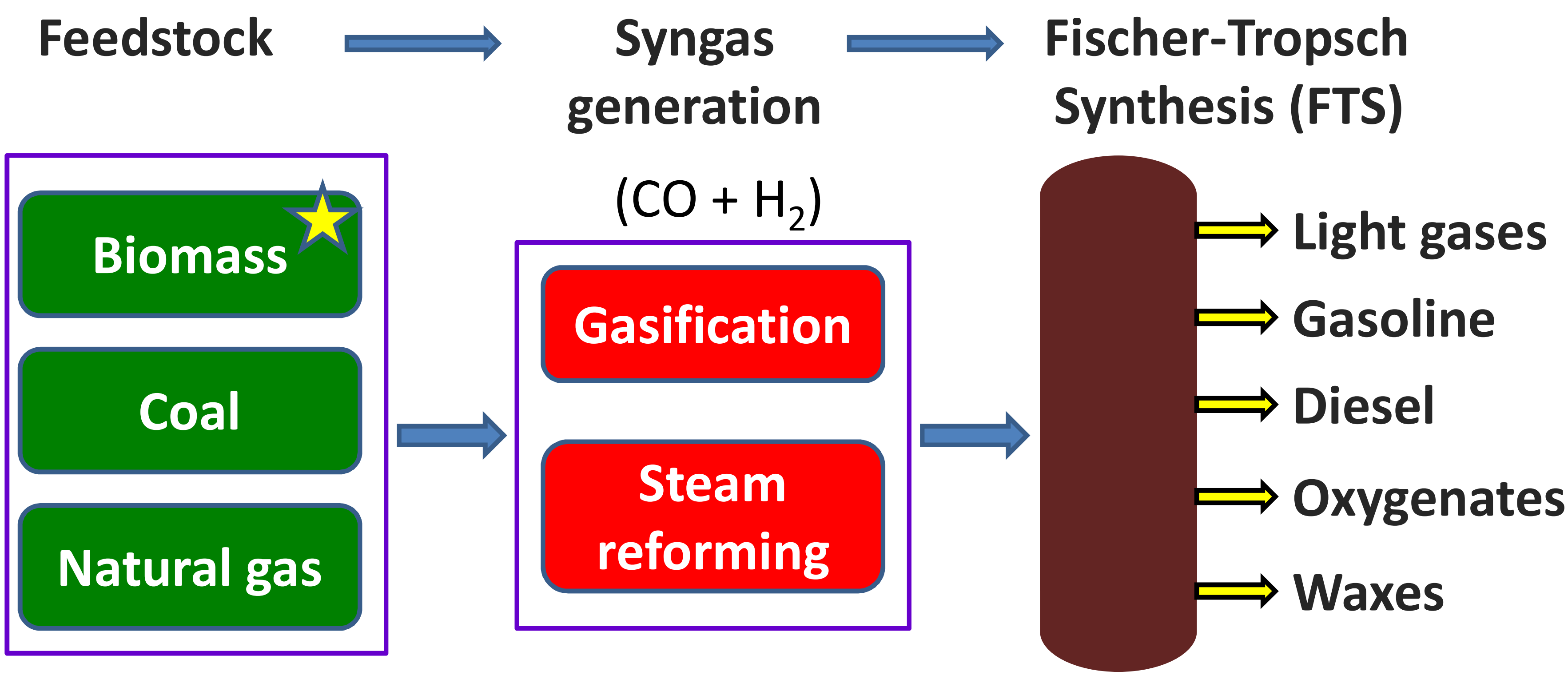
Highlights

1. Introduction
2. Experimental Methods
    a) Catalyst synthesis
    b) Catalyst testing (set up and conditions)
3. Results and Discussion
    a) Catalyst testing
    b) Catalyst characterisation
4. Conclusion

INTRODUCTION

Current industrial fuel production competing with petroleum.



FTS polymerises syngas to gasoline ($C_4 – C_{12}$), diesel ($C_{13} – C_{20}$) and waxes (C_{21+}).

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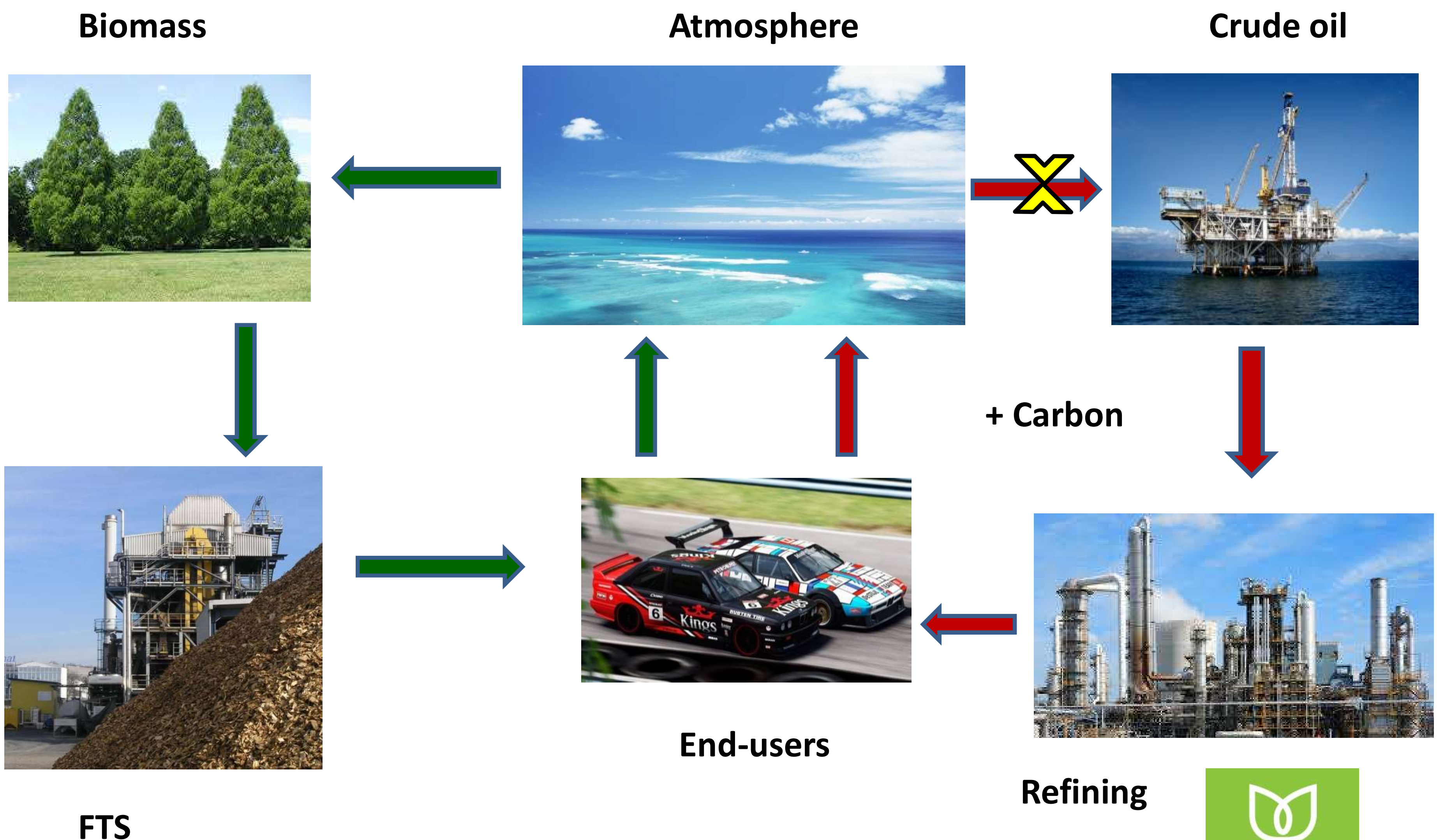
INTRODUCTION



Green process: Advantage of biomass application

INTRODUCTION

Fischer-Tropsch Synthesis (FTS): a targeted technology for biofuel production from renewable resources.

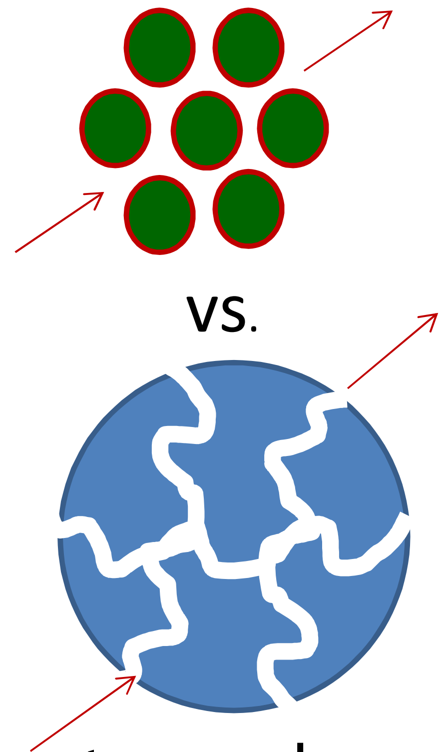
Target	Reaction	Designation
Alkanes	$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$	Eqn. (1)
Alkenes	$2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$	Eqn. (2)
Water-gas shift	$H_2O + CO \rightarrow CO_2 + H_2$	Eqn. (3)
Methane	$3\ H_2 + CO \rightarrow CH_4 + H_2O$	Eqn. (4)
	$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$	Eqn. (5)
Alcohols	$2n\ H_2 + n\ CO \rightarrow C_nH_{(2n+1)}OH + (n-1)\ H_2O$	Eqn. (6)
	$(n+1)\ H_2 + (2n-1)\ CO \rightarrow C_nH_{(2n+1)}OH + (n-1)\ CO_2$	Eqn. (7)

In this project, the target syngas source = Biomass

INTRODUCTION

Properties of a choice catalyst include:

- High surface area; low porosity
- Nanometric = No diffusion limitations
- Inert support = carbon
- Metallic Co or Fe-carbides species



Plasma technology to provide the impetus towards process efficiency in catalyst synthesis because it is a single step process.

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INTRODUCTION

- In previous work, plasma-synthesised Fe/C catalyst performed better than commercially available nano-hematite (Fe-Nanocat®): 24 h activation by CO reduction[a]

Temperature	= 220°C
Pressure	= 31-bar (~ 450 psi)
GHSV	= 2, 575 $ml.g_{cat}^{-1}.h^{-1}$

[a]J. Blanchard, N. Abatzoglou, R. Eslahpazir-Esfandabadi and F. Gitzhofer, *Ind. Eng. Chem. Res.*, 49 (2010) 6948.

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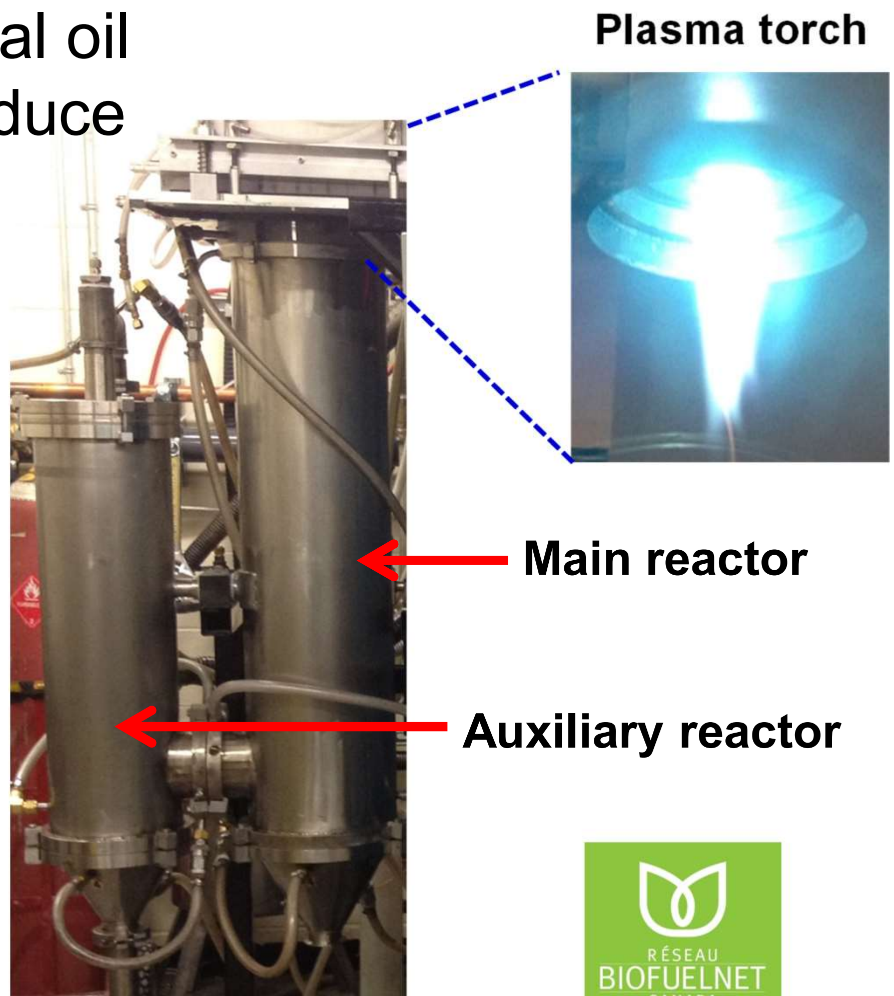
EXPERIMENTAL

Catalyst Synthesis by Plasma:

Suspension of 60 g metal in mineral oil was introduced into plasma to produce various compositions

- Co/C
- Fe/C
- 30%Co-70%Fe/C
- 50%Co-50%Fe/C
- 80%Co-20%Fe/C
- 70%Co-20%Fe-10%Mo/C
- 70%Co-25%Fe-5%Ni/C
- Doped with 5%Au:
  70%Co-25%Fe-5%Ni/C.



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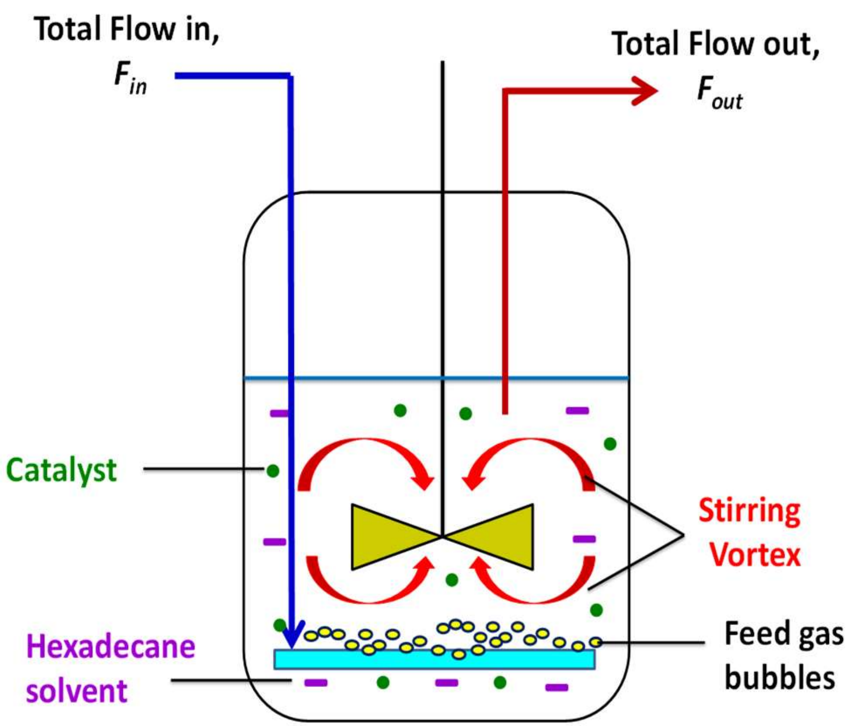
EXPERIMENTAL

Catalyst Testing: Fischer-Tropsch conditions

(i) Reducing conditions:
- 5.0 g Catalyst
- T = 400^oC
- P = 1-2 bar (abs)
- Gas = pure H_2
- Flow rate = 250 ml.min^{-1}
- Time = 24 h

(ii) Add solvent: 150 ml (C_{16})

(iii) Reaction: Regimes to avoid:
1. High CH_4 and H_2O selectivity
2. Mass transfer limitations



EXPERIMENTAL

Catalyst Testing: Slurry CSTR

Reaction conditions:

- Temperature = 220-260°C;
- Pressure = 20-bar
- Stirring rate = 2,000 rpm
- Gas composition = 60%H_2; 30%CO; 10%Ar
- H_2:CO ~ 2:1 ratio
- Flow rate = 300 $ml.min^{-1}$
- GHSV = 3,600 $ml.g_{cat}^{-1}.h^{-1}$
- Test time: = 24 h on stream.

$$Mass\ Balance:\ CO\ conversion\ (\%) = \left[\frac{CO_{in} - CO_{out}}{CO_{in}}\right] x \left[\frac{Ar_{in}}{Ar_{out}}\right] x\ 100$$ [b]

[b] **M.C. Bahome, L.L. Jewell, D. Hildebrandt, D. Glasser, N.J. Coville, *Appl. Catal. A: Gen.*, 287 (2005) 60.**

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RESULTS

Summary I: Unique Catalyst Properties

1. Catalysts are non-porous
2. There is uniform distribution of metal in the carbon matrix
3. No sintering occurs during use in Fischer-Tropsch reaction

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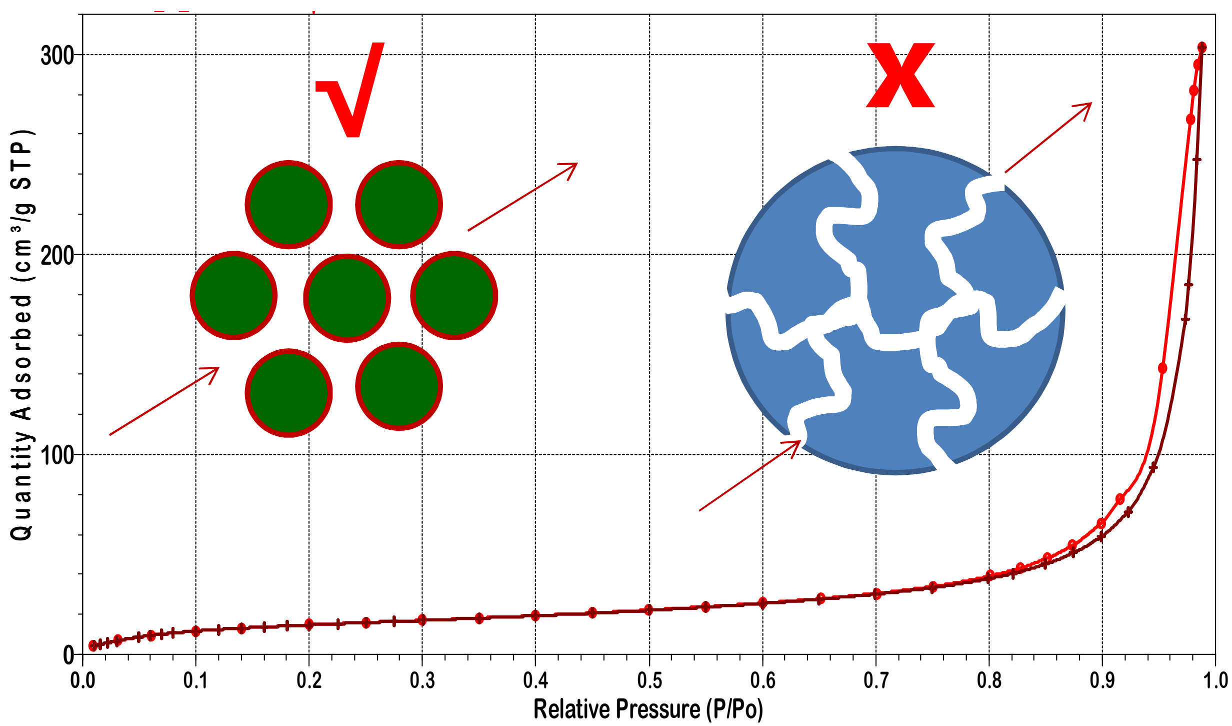
RESULTS

Catalyst Characterisation: BET surface area

- Material = non-porous (no hysteresis)
- Micro-porosity an effect of nano-particles packing



Sample	BET surface area (m^2/g)
100%Fe	72
30%Co-70%Fe	89
50%Co-50%Fe	89
80%Co-20%Fe	65
100%Co	56

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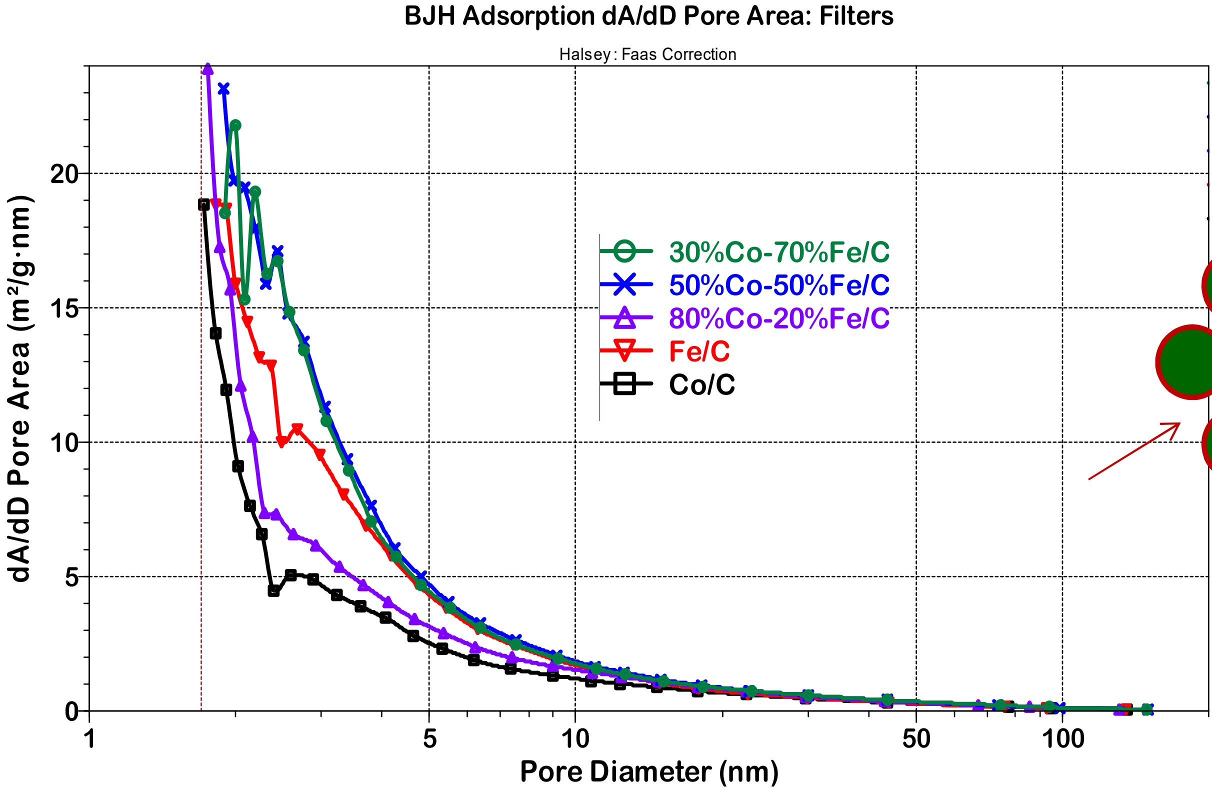
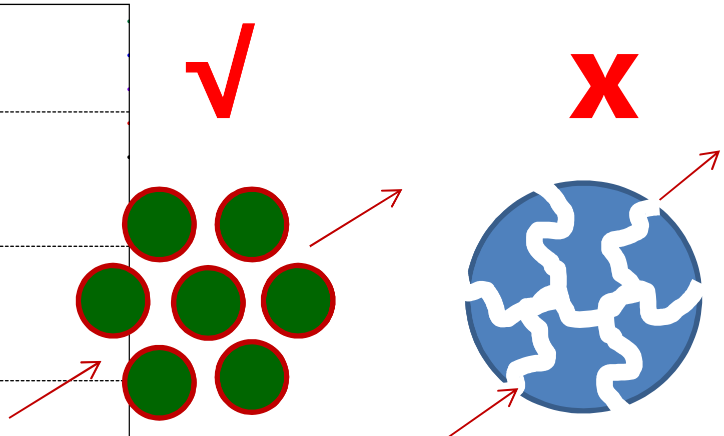
RESULTS

Catalyst Characterisation: BET surface area

- Material = non-porous
- Micro-porosity an effect of nano-particles packing

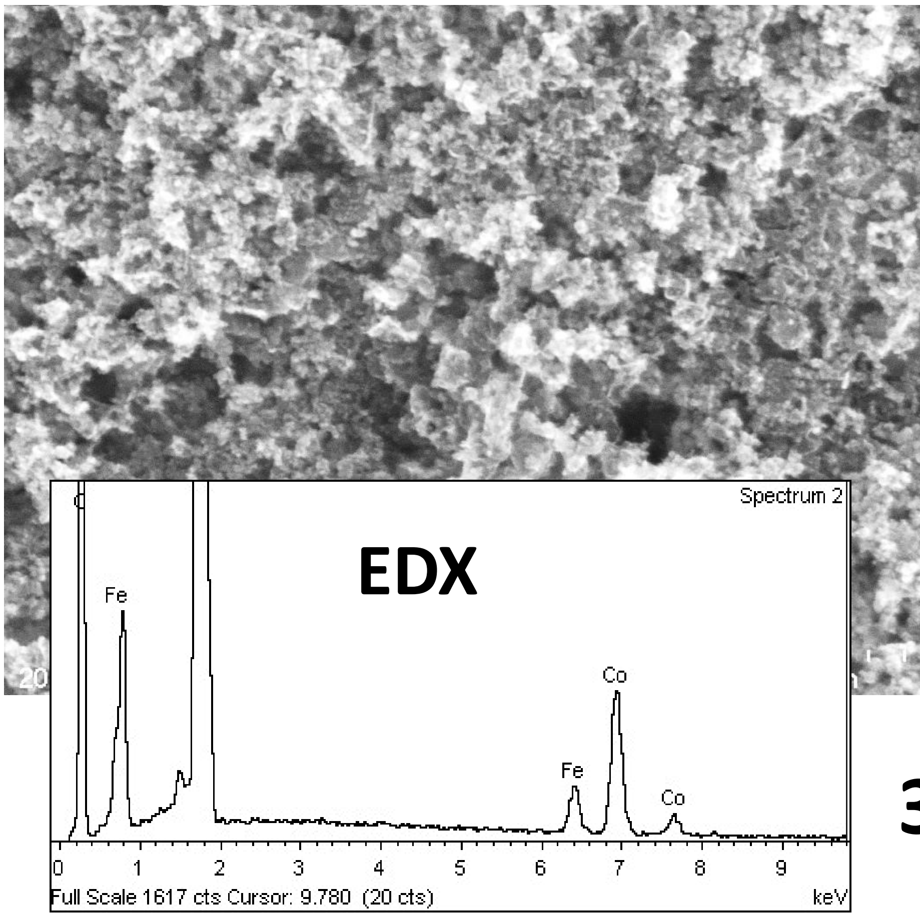




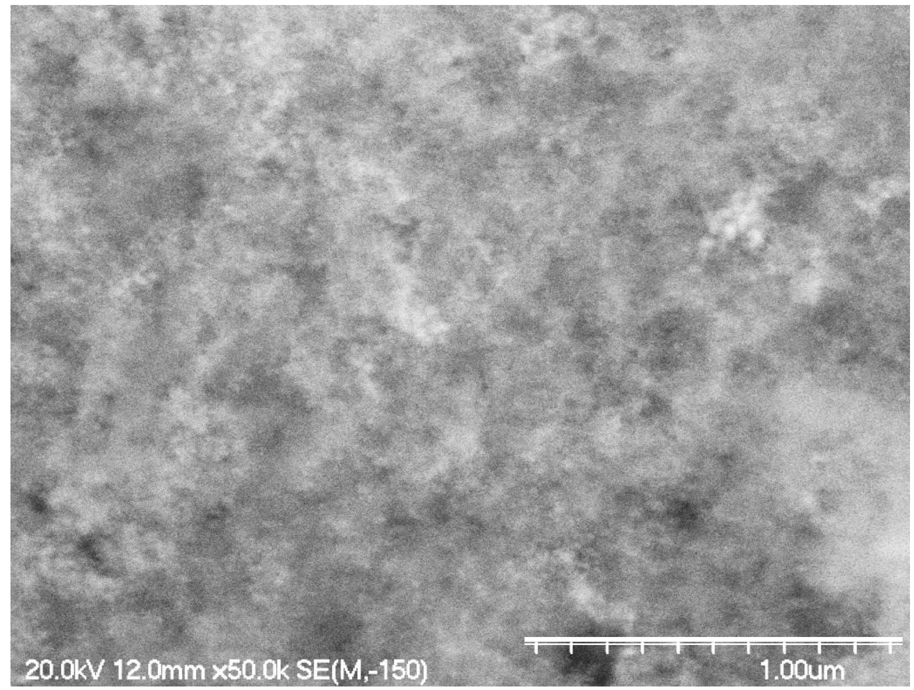
RESULTS

Catalyst Characterisation: SEM imaging

Secondary image



Backscattered image

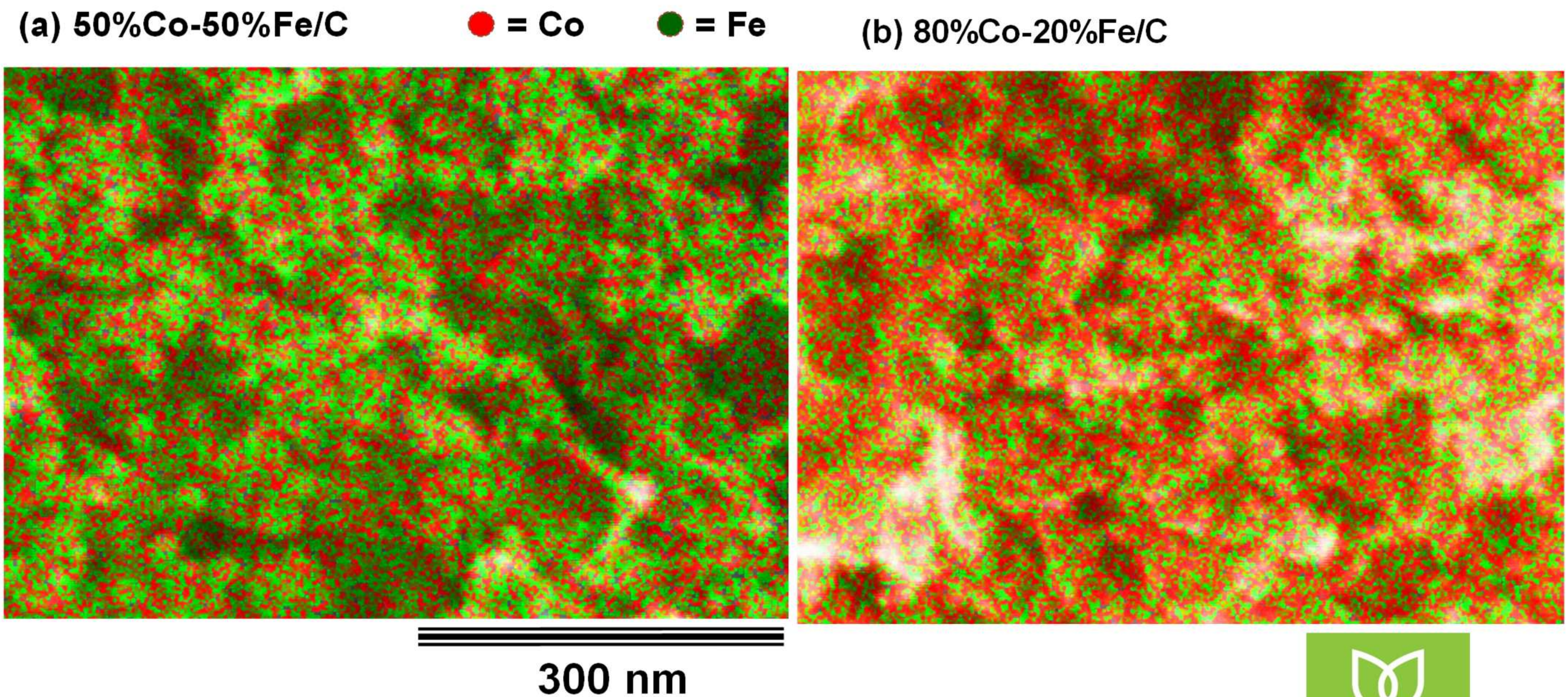


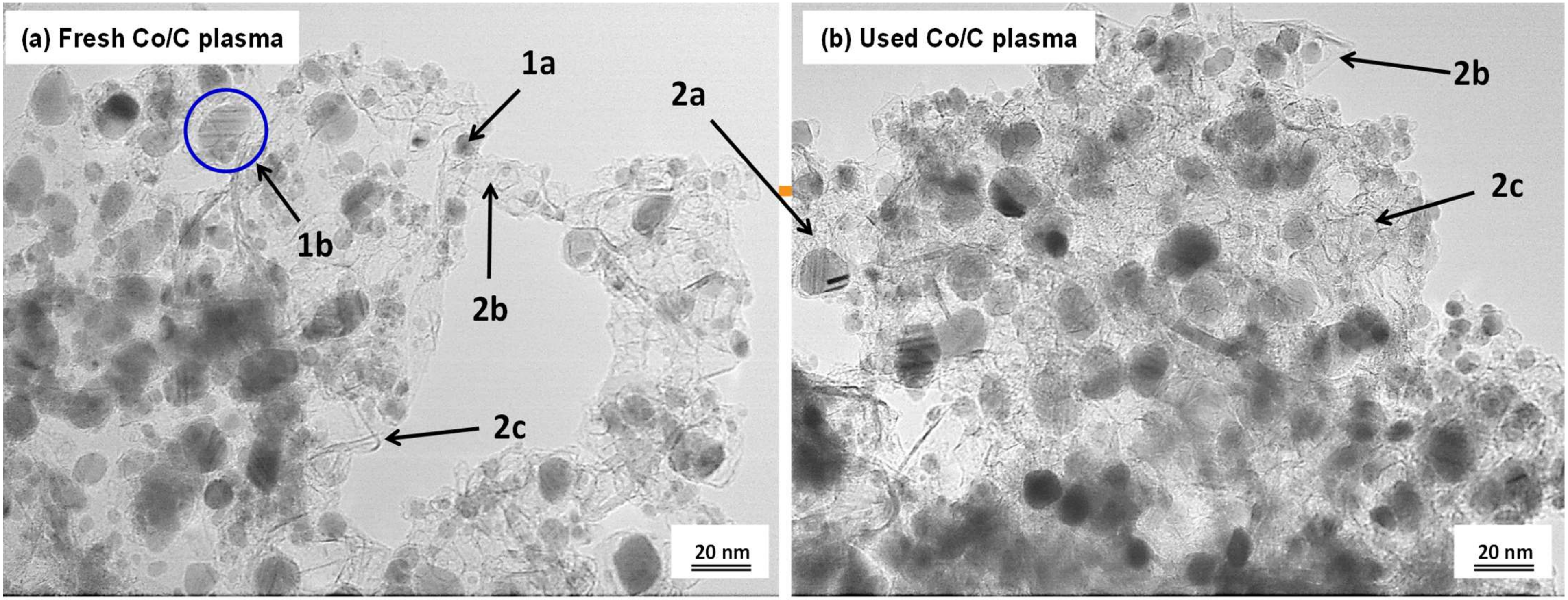
30%Co-70%Fe/C

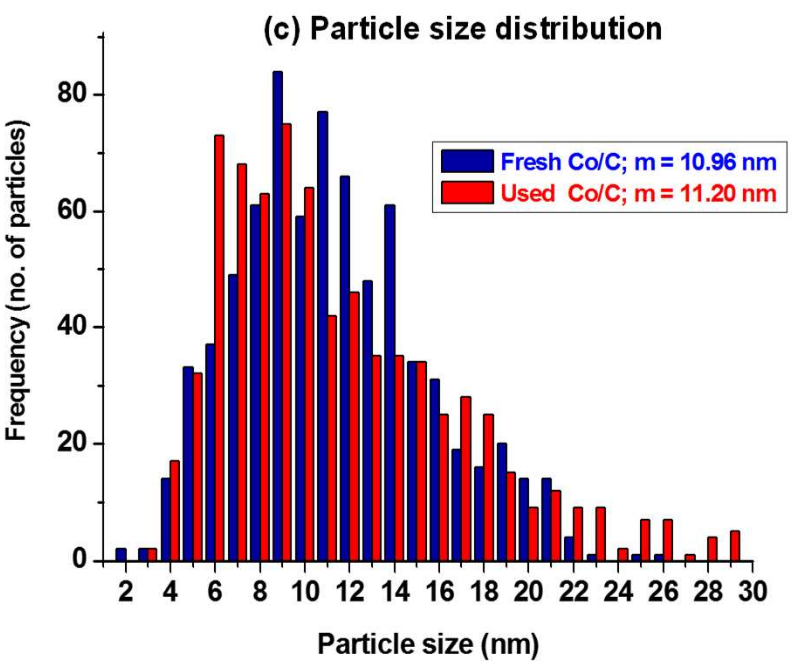
RESULTS

Catalyst Characterisation: SEM

- X-ray imaging: Uniform metal distribution







750 particles measured
Mean ≈ 11 nm

Key:
- **1a = Metal nano-particle**
- **1b = Nano-particle with stacking faults**
- **2a = Carbon matrix (amorphous); disordered**
- **2b = Graphitic sheets**
- **2c = Folded graphitic sheet**

NB: no sintering

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RESULTS

Summary II: Catalyst Performance

1. **Activity**: Highly active for Fischer-Tropsch synthesis;
   - Co/C better than the commercial one

2. **Selectivity**: Favourable towards gasoline and diesel fractions

3. **Low-Temperature Operation**: Single metals catalysts
   High-Temperature Operation: Bimetallics are better

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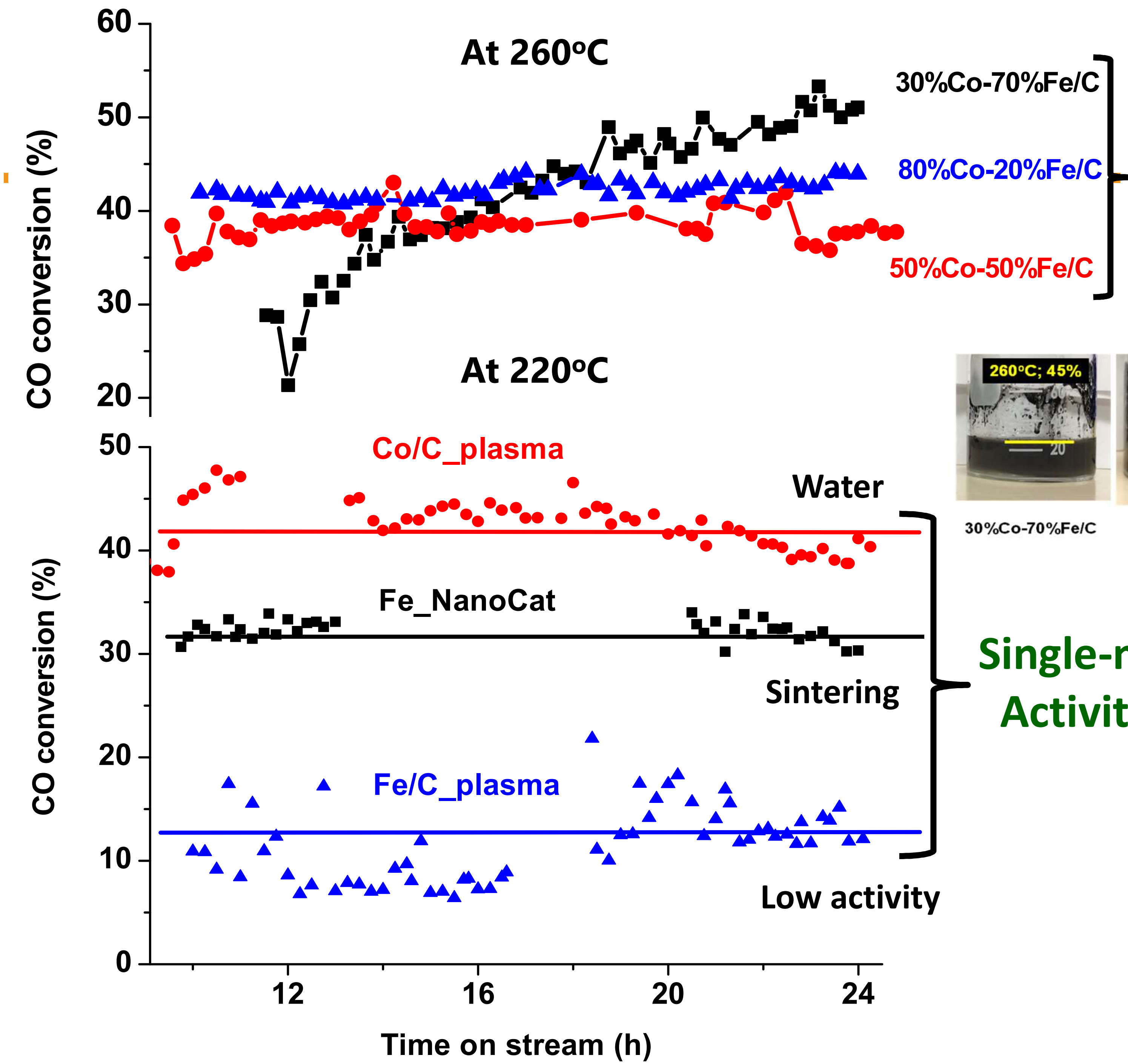
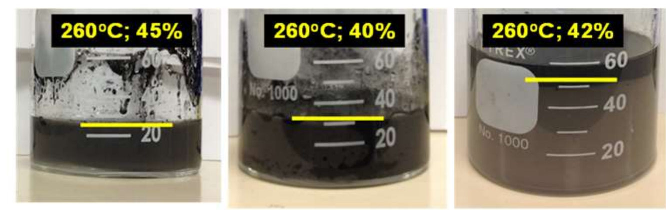


Bimetallic catalysts: No deactivation after 24 h

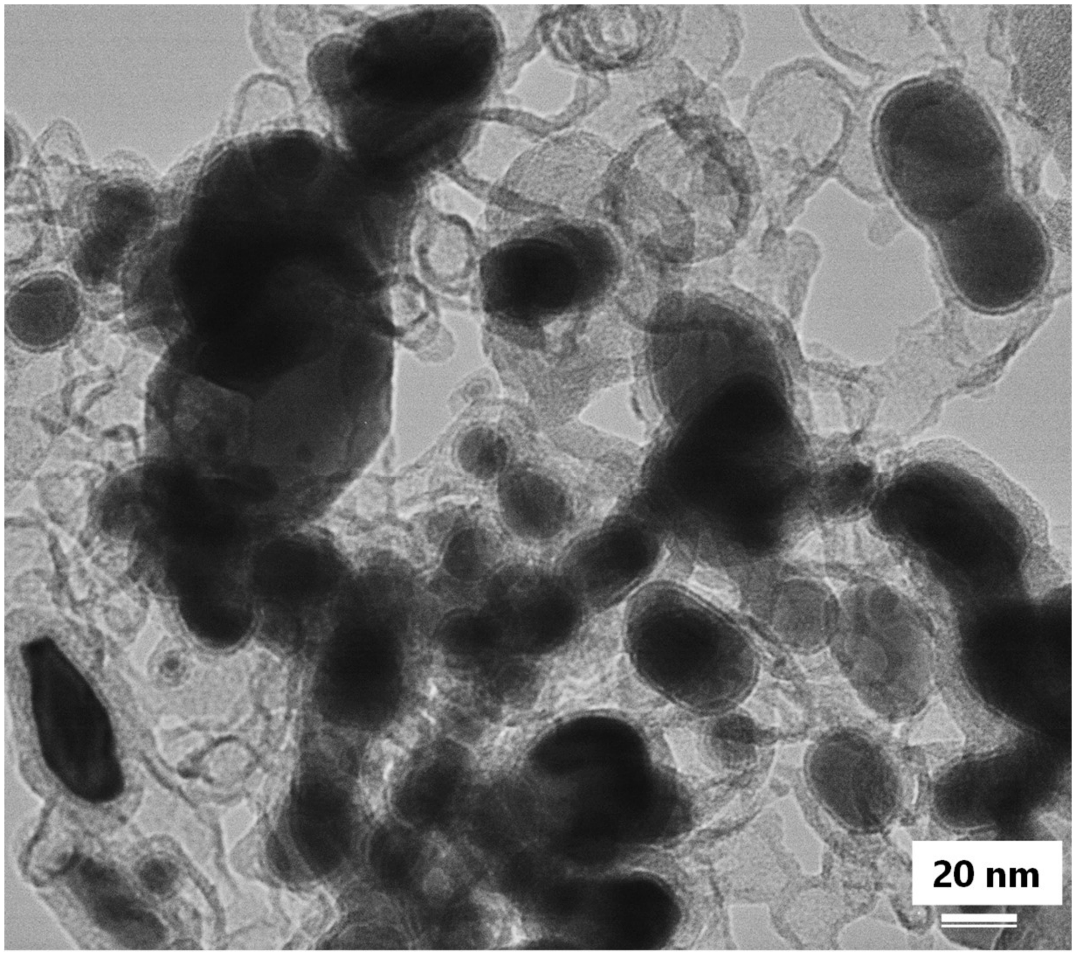


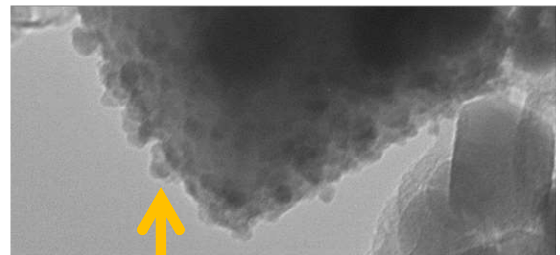
30%Co-70%Fe/C 50%Co-50%Fe/C 80%Co-20%Fe/C

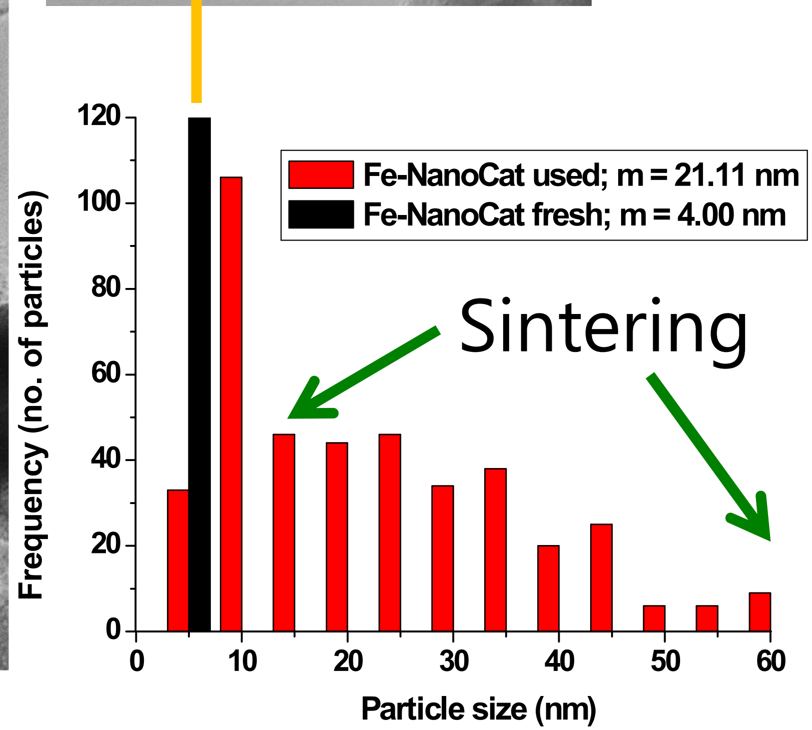
Single-metal catalysts: Activity problems at 24 h

RESULTS

Catalyst Characterisation: TEM (used Fe-NanoCat)

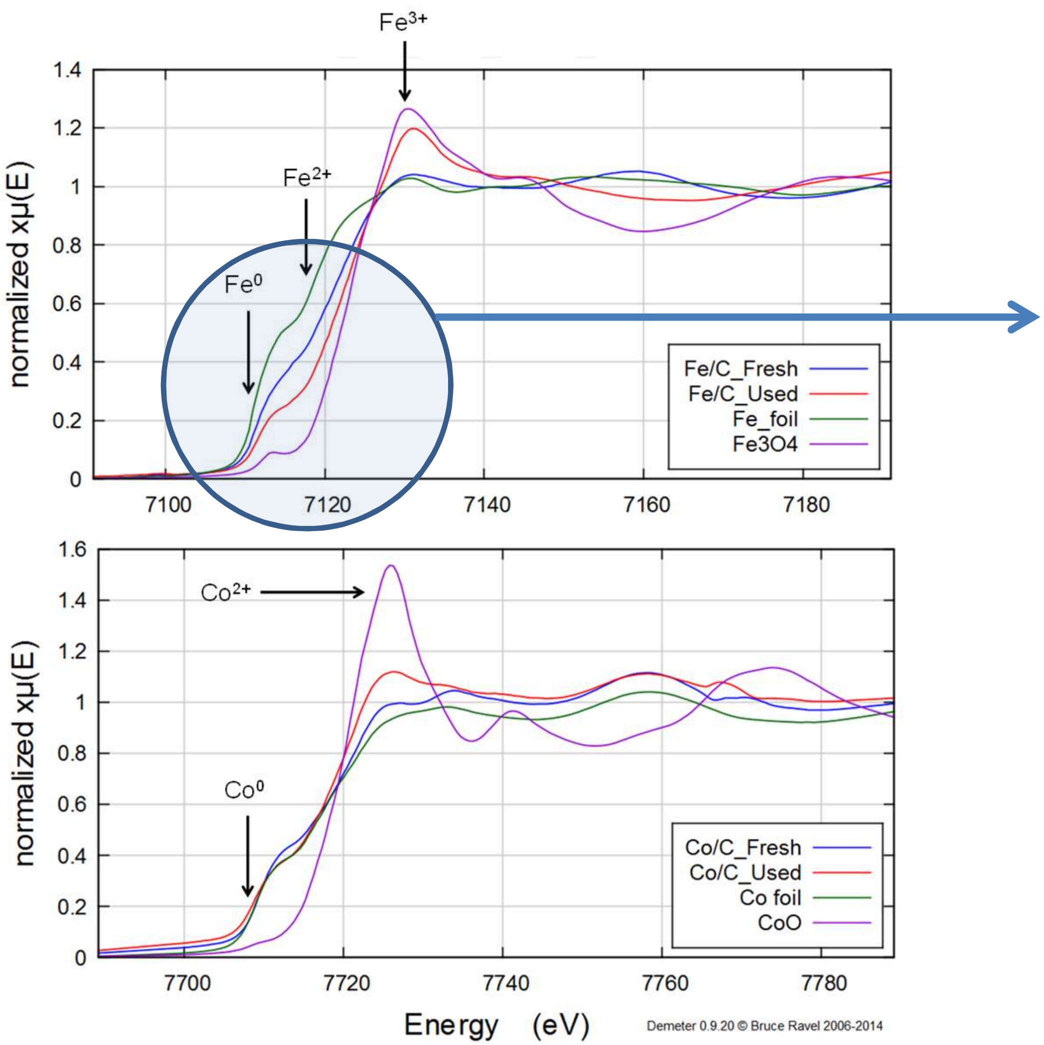


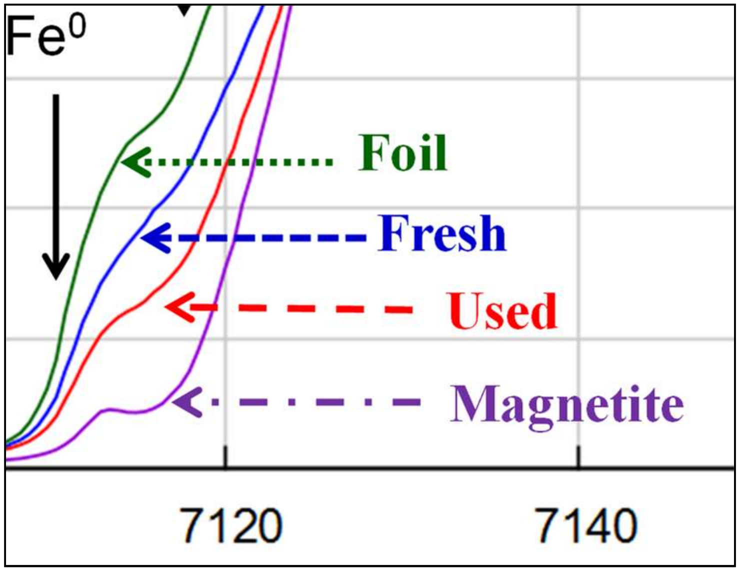




RESULTS

Catalyst Characterisation: XANES

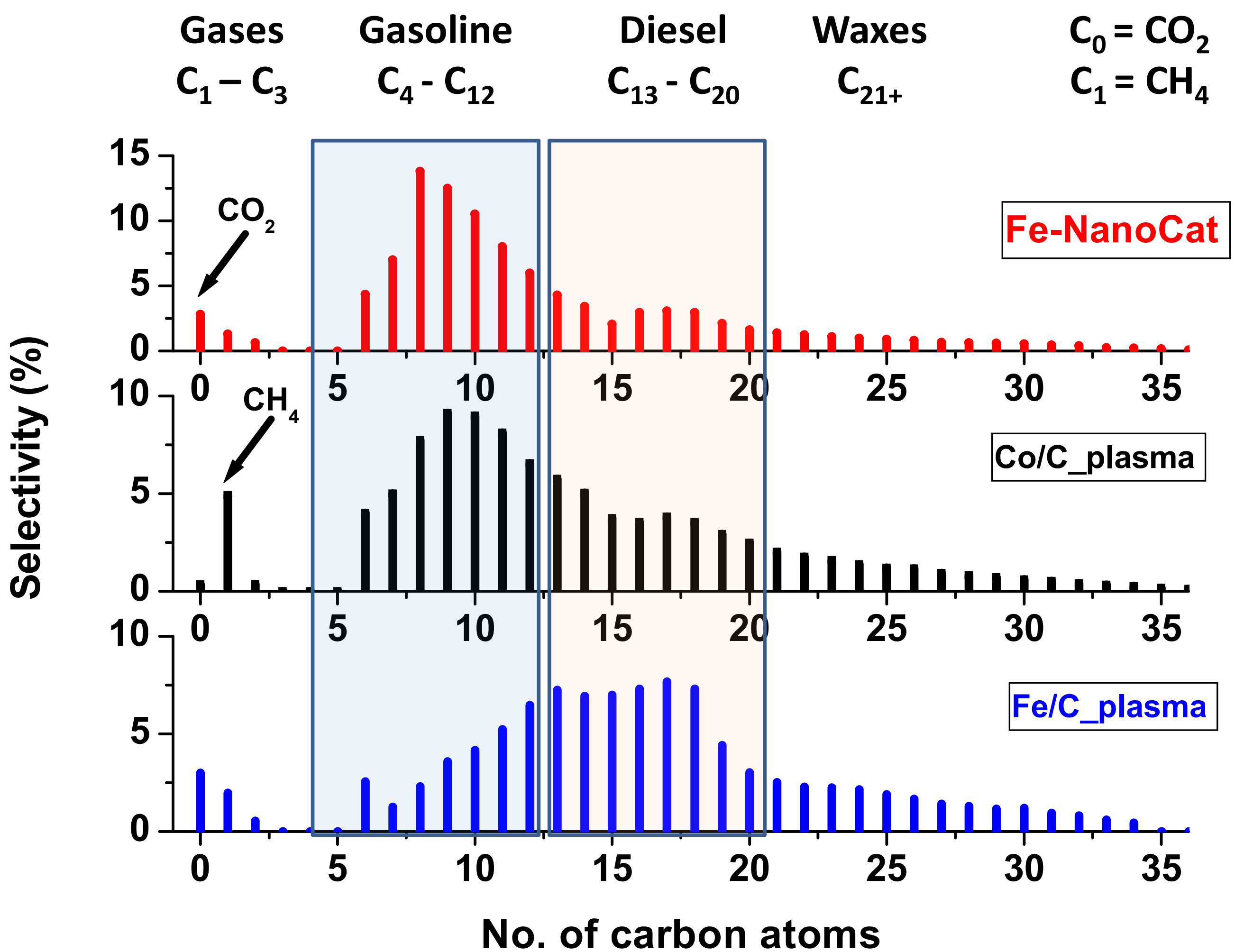




Deactivation in Fe/C: Oxidation in used sample.

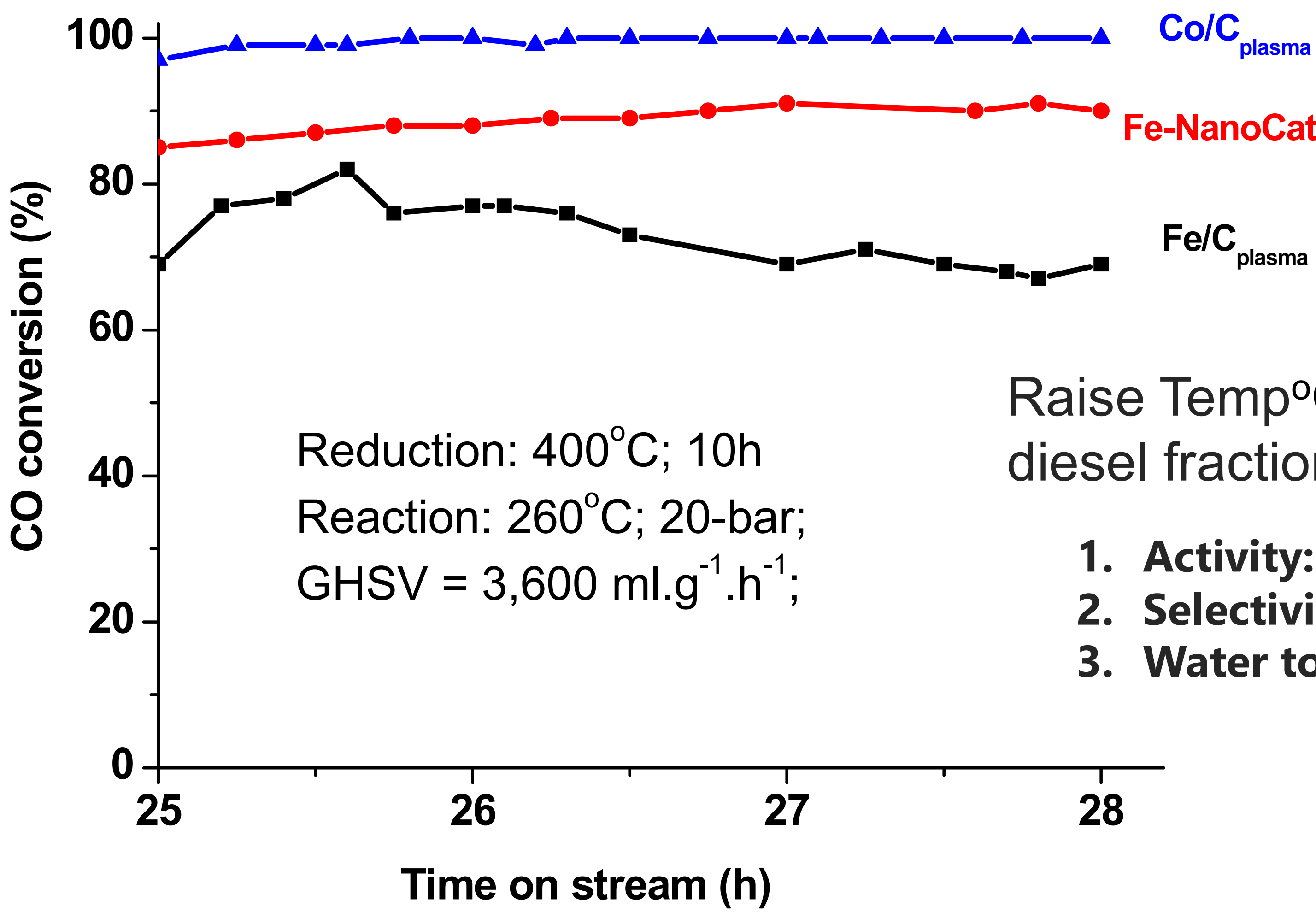
RESULTS

Catalyst Selectivity: Single metals at 220°C



RESULTS

Catalyst Activity: Single metals at 260ºC

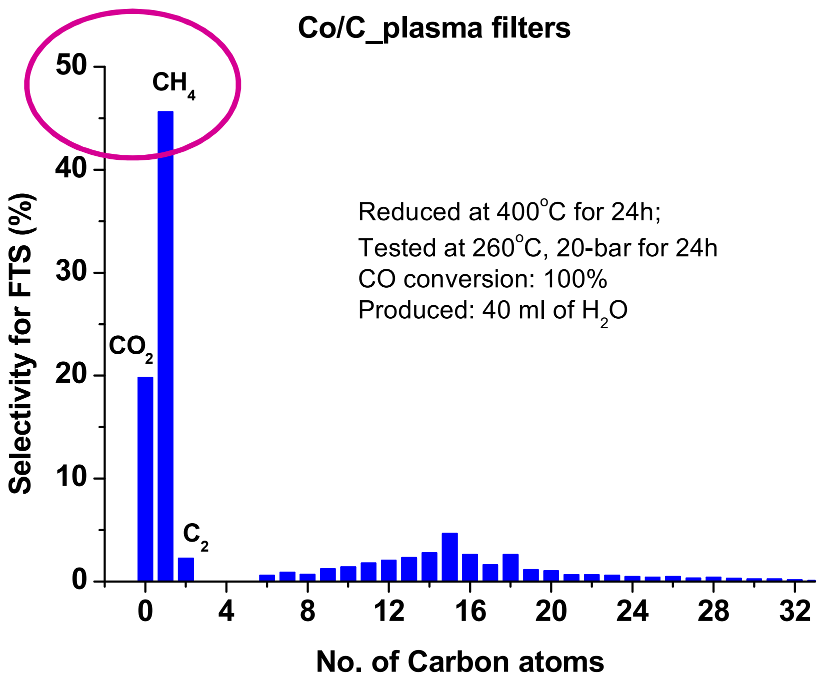


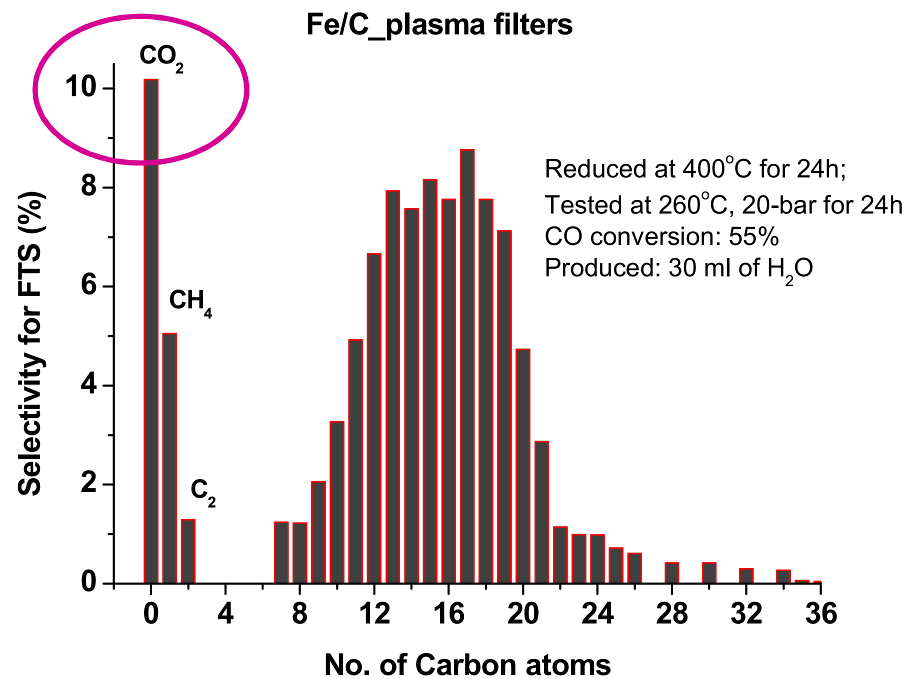
Raise TempºC to enrich diesel fraction:

1. **Activity: High**
2. **Selectivity: Poor**
3. **Water tolerance: Low**

RESULTS

Catalyst Selectivity: Single metals at 260ºC





- **Problem**: Excessive CH_4 and CO_2 formation by single metal catalysts at high temperatures
- **Solution**: Co-Fe/C bimetallics

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RESULTS

Summary III: The Bimetallic Effect

1. **Activity**: Poor reaction (low conversion) at low temperatures

2. **Particle size**: Increases at 50%Co-50%Fe composition due to alloys formation = most of them CoFe crystallites

3. **Water-gas shift**: More Fe (%) means less H_2O production; but more CO_2

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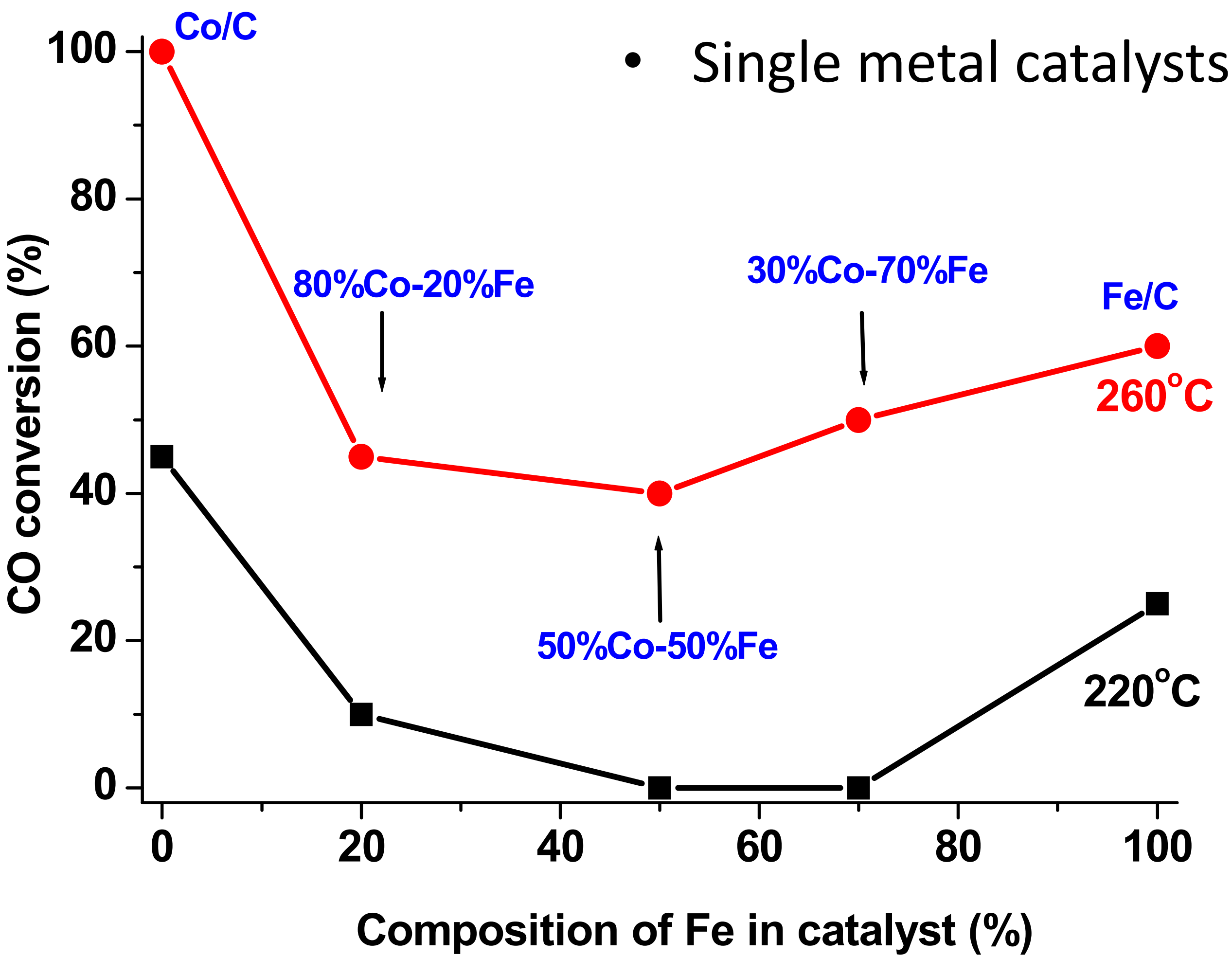
RESULTS

Catalyst Testing: Activity at 220º and 260ºC

- Single metal catalysts: more active

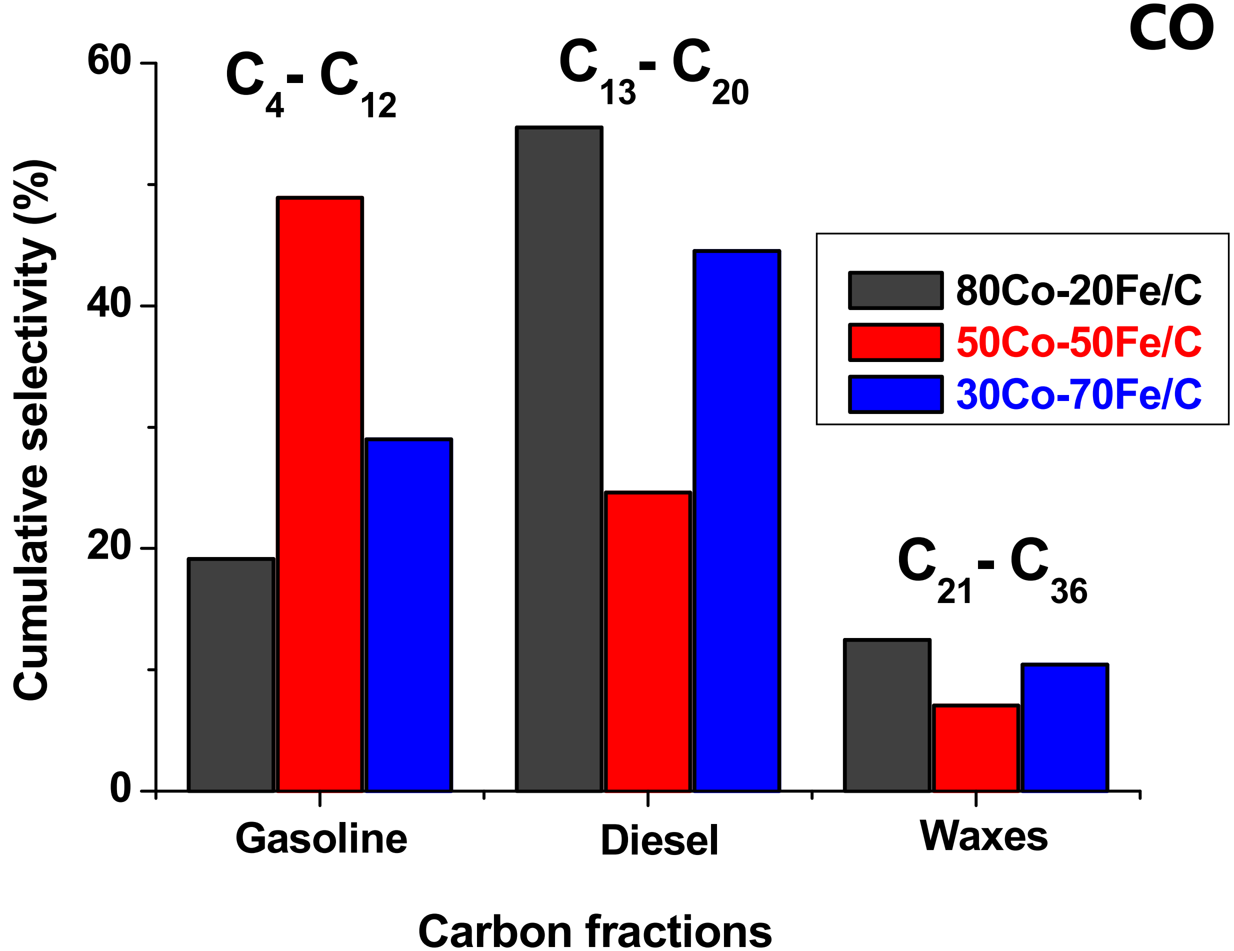


t=24h

RESULTS

Catalyst Selectivity: Overall (at 260°C)

CO conversion > 40%



More Biodiesel:
80%Co-20%Fe/C
30%Co-70%Fe/C

More Gasoline:
50%Co-50%Fe/C

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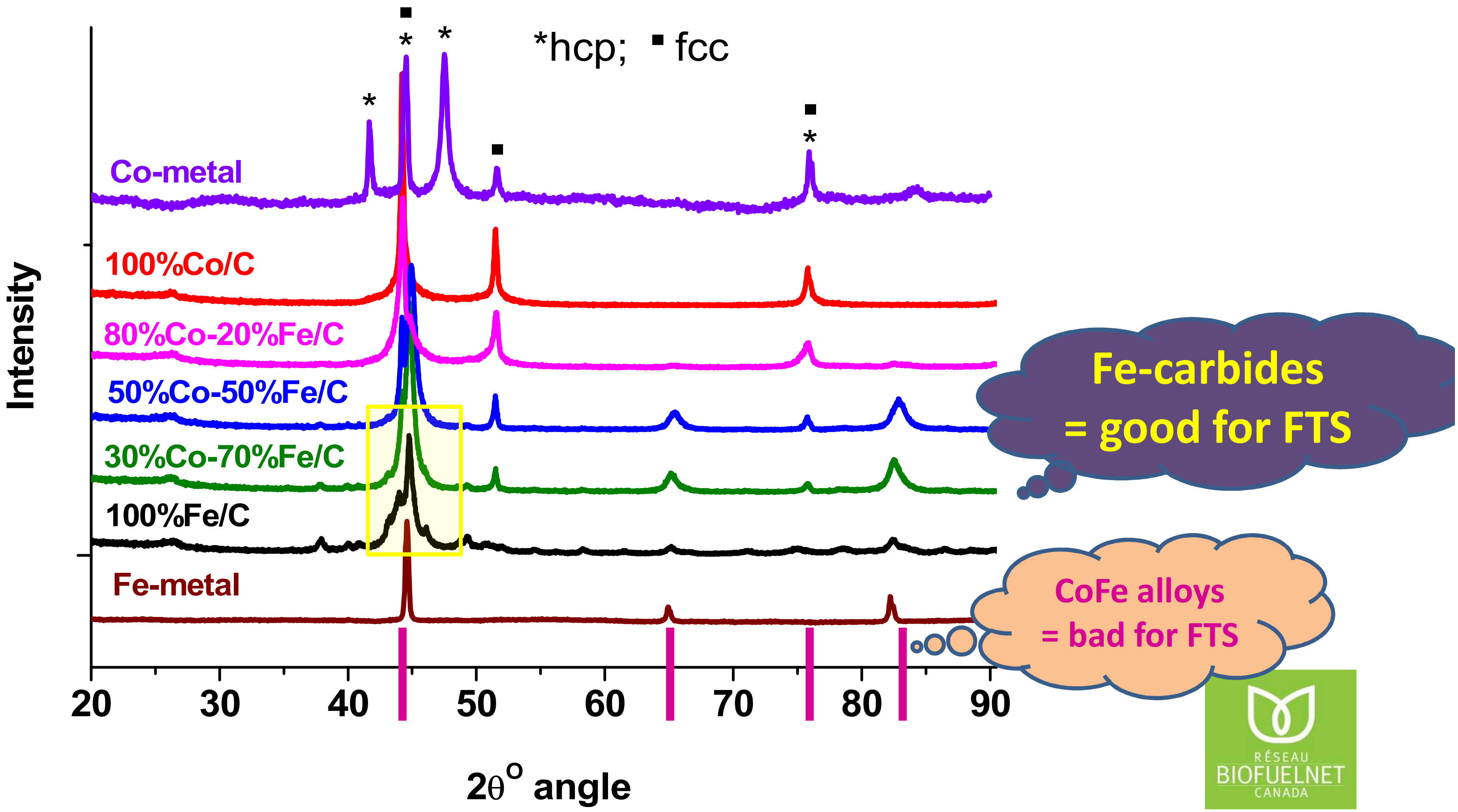
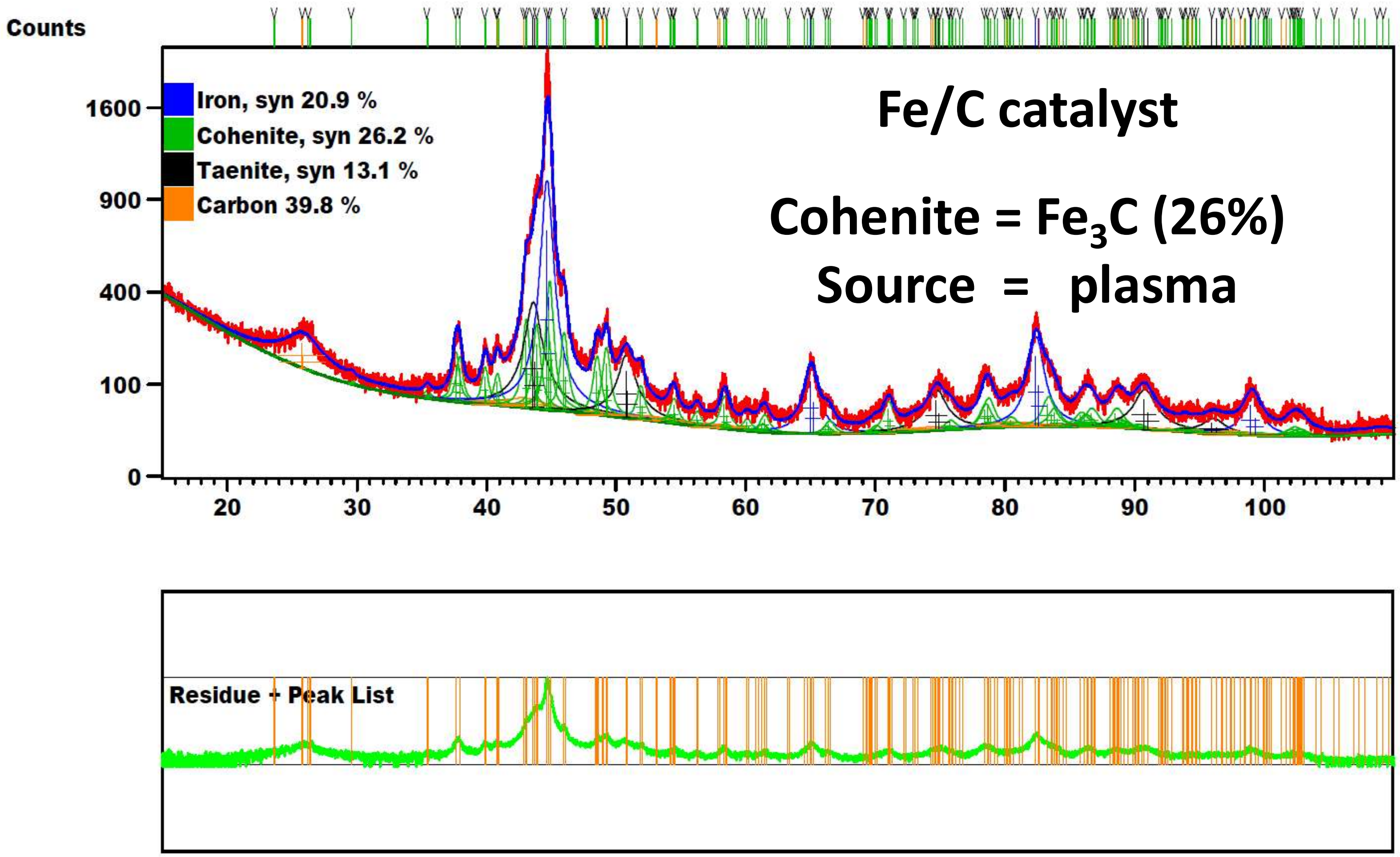
RESULTS

Catalyst Characterisation: XRD



RESULTS

XRD by Rietveld Quantitative Analysis (RQA)



RESULTS

Summary IV: Promotion with Mo & Au

1. **Effect of Au**: Lowers FTS activity; we expected Au-Ni-Fe to enhance water gas shift reaction[c]

2. **Effect of Mo**: Surface acidity (+Mo) improves selectivity towards diesel fraction, low CO conversions (activity)

[c] A. Venugopal, J. Aluha, M.S. Scurrell, *Catal. Lett.*, 90 (Issue 1 – 2) (2003) 1.

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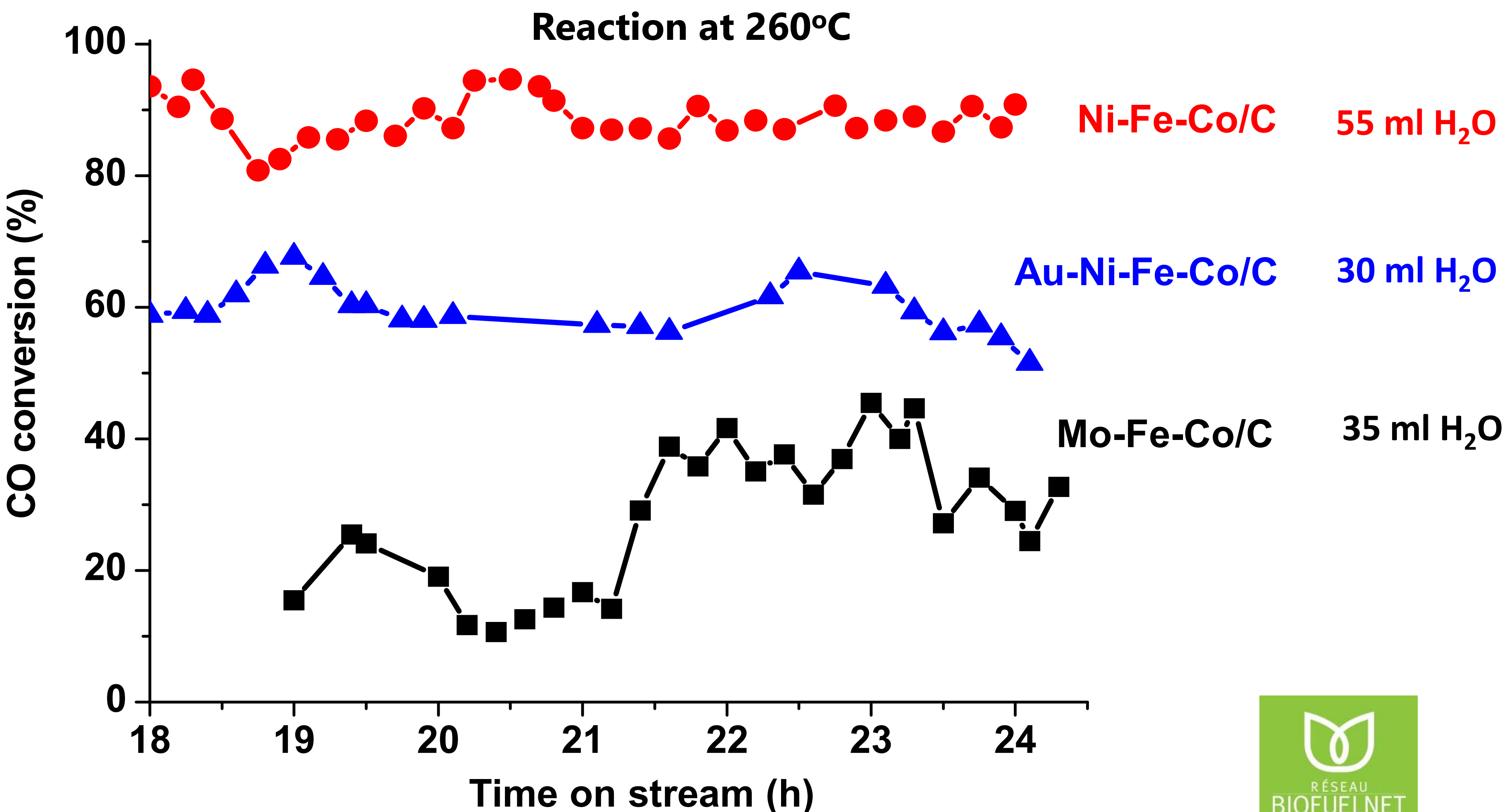
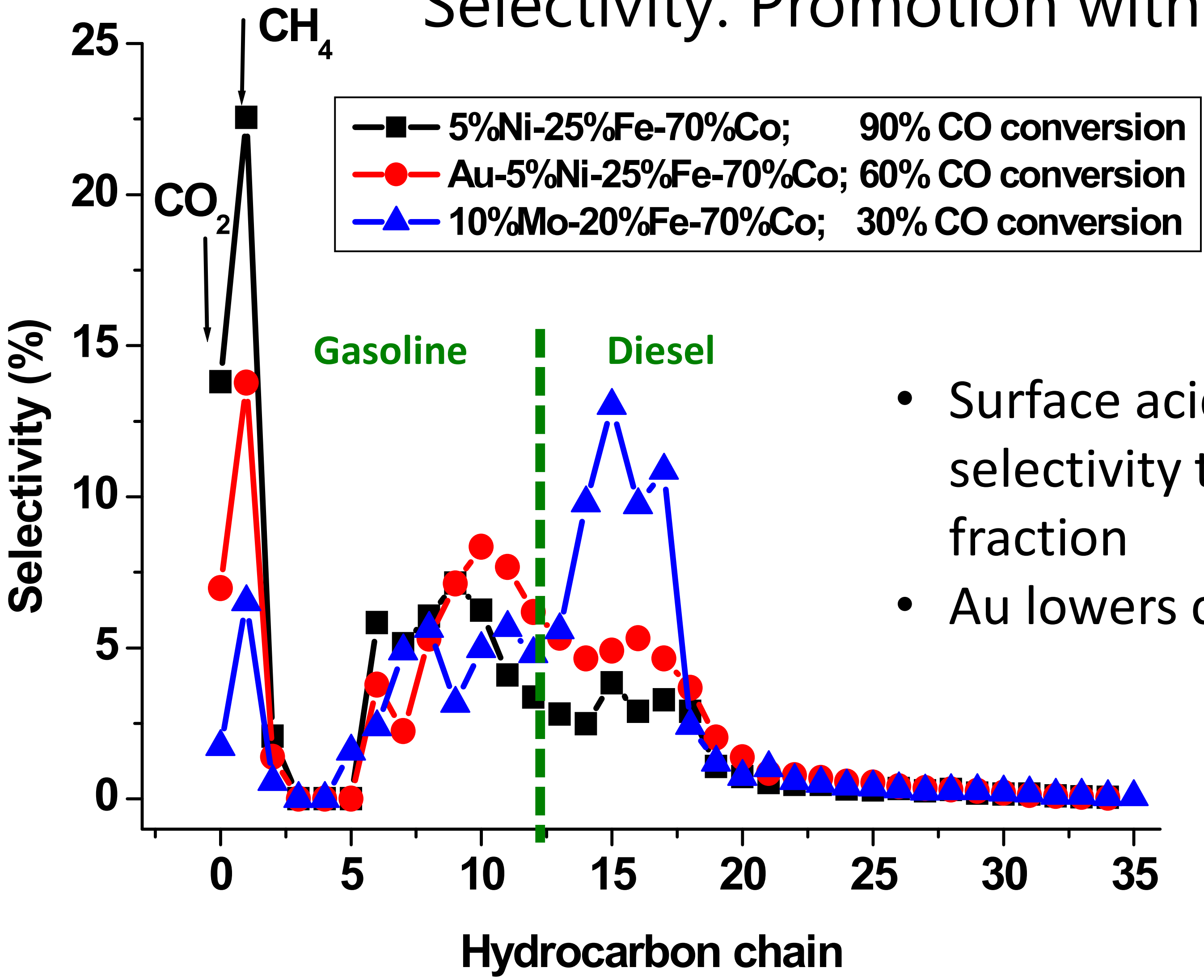
RESULTS

- Au depresses catalyst activity: less products formed.



RESULTS

Selectivity: Promotion with Mo & Au



- Surface acidity (Mo) improves selectivity towards the diesel fraction
- Au lowers catalyst activity

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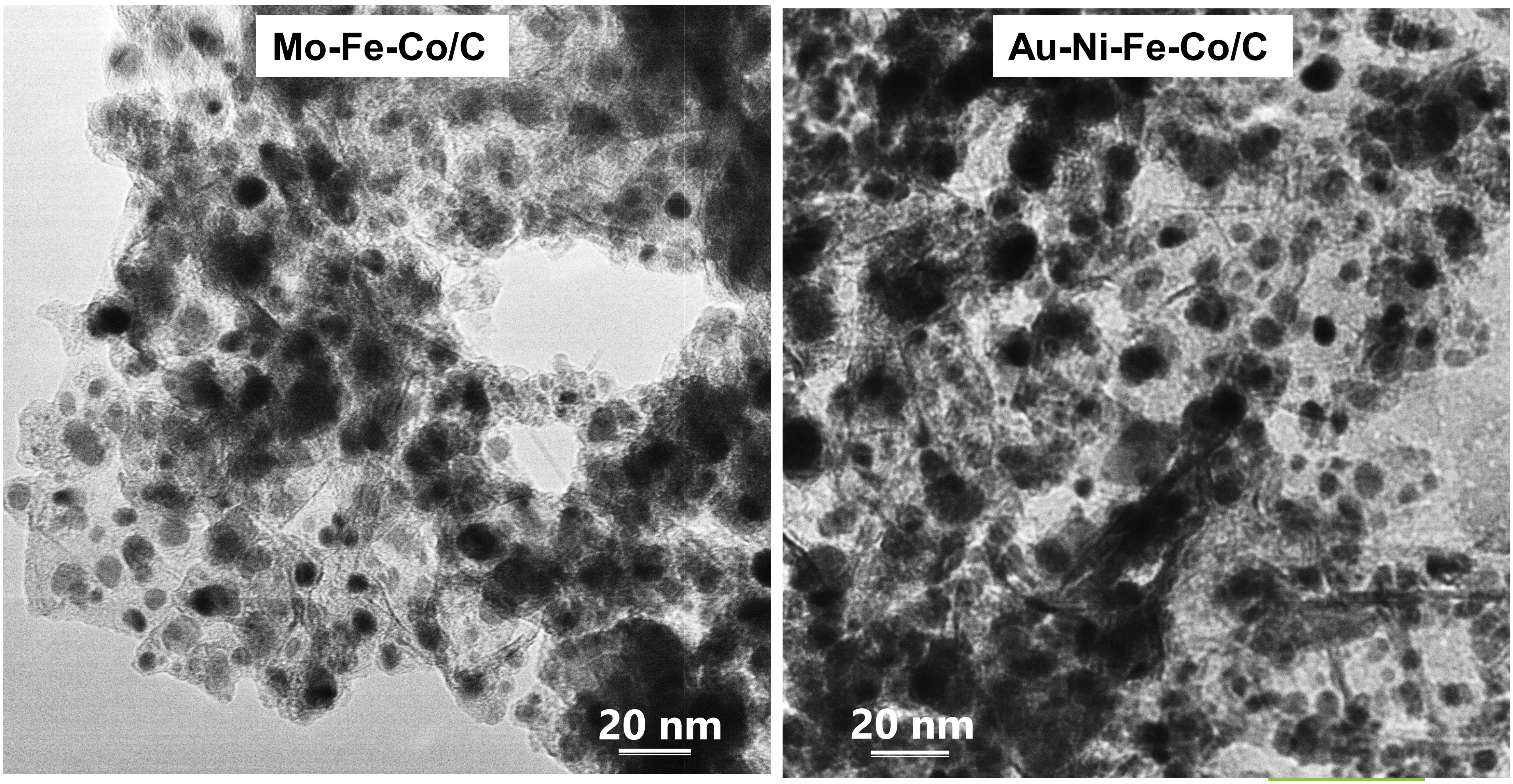
RESULTS

Characterisation: TEM (used catalysts)



CONCLUSION

1. All catalysts have capacity to produce both gasoline and diesel fractions depending on composition and reaction conditions.
2. Catalysts have uniform distribution of metal in the carbon matrix.
3. Non-porous catalysts are excellent in dealing with mass transfer limitations.
4. No sintering occurs during use in Fischer-Tropsch reaction.
5. Plasma synthesis produces significant amounts of Fe-carbides (Fe_3C, Fe_5C_2) responsible for FTS catalysis.

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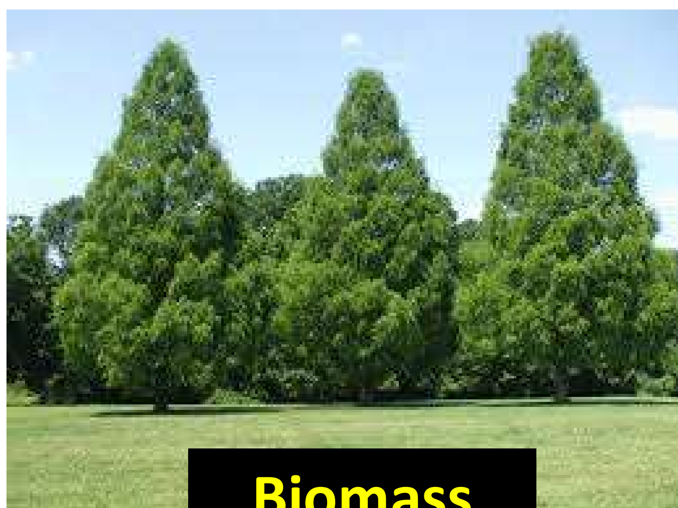
CONCLUSION

Sustainable Technology

Plasma Technology

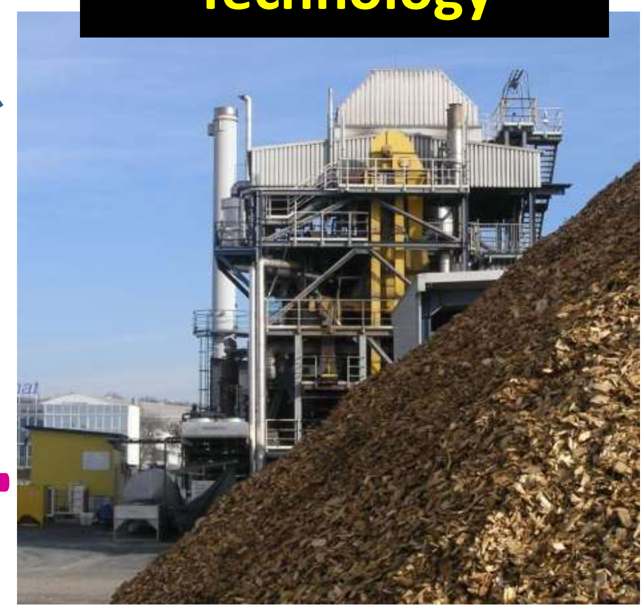
+



Biomass

+

Fischer-Tropsch Technology



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GRATITUDE

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BioFuelNet is a member of the Networks of Centres of Excellence of Canada program. Website: www.biofuelnet.ca

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Thank you!

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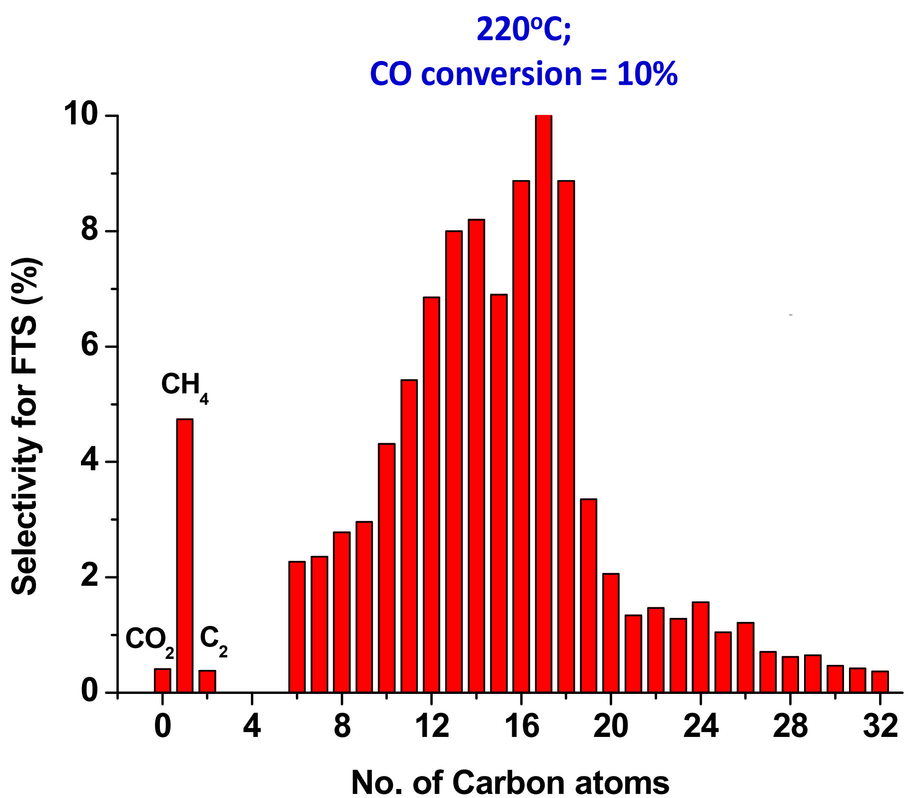
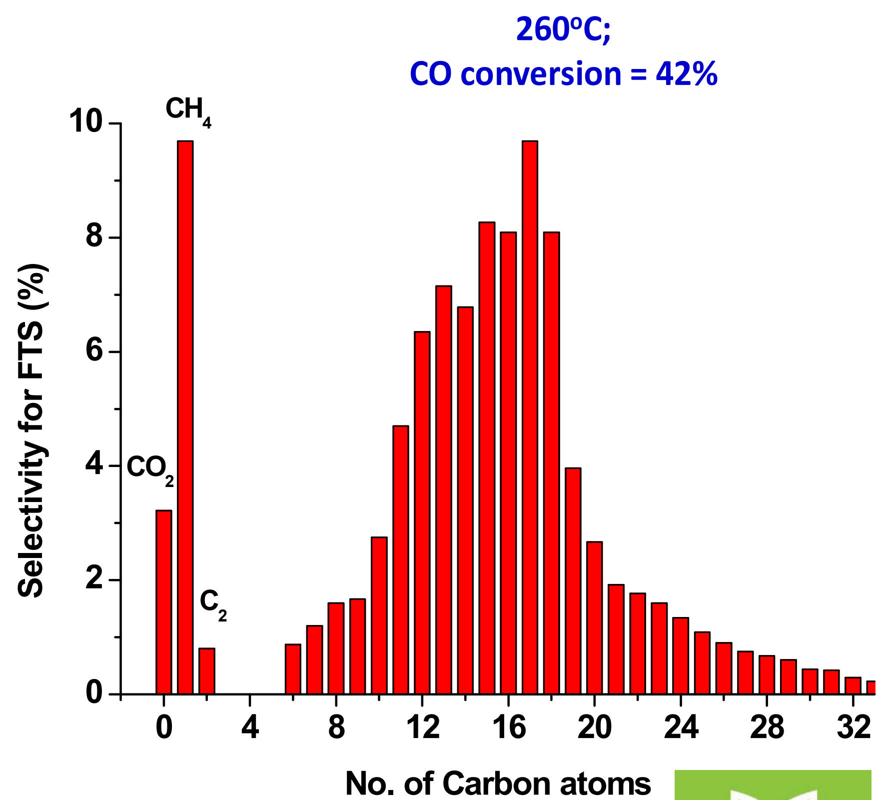
RESULTS

Catalyst Selectivity: Only the 80%Co-20%Fe/C was active at both temperatures





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RESULTS

Metal particle size distribution: