Center for Research and Technology Hellas (CERTH)
Chemical Process & Energy Resources Institute (CPERI)

BioBoost

BioBoost Colloquium

Boosting Biofuels and Chemicals Production from 2nd Generation Biomass

The biomass catalytic pyrolysis as a technology pathway to produce a high value energy carrier

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SEVENTH FRAMEWORK PROGRAMME

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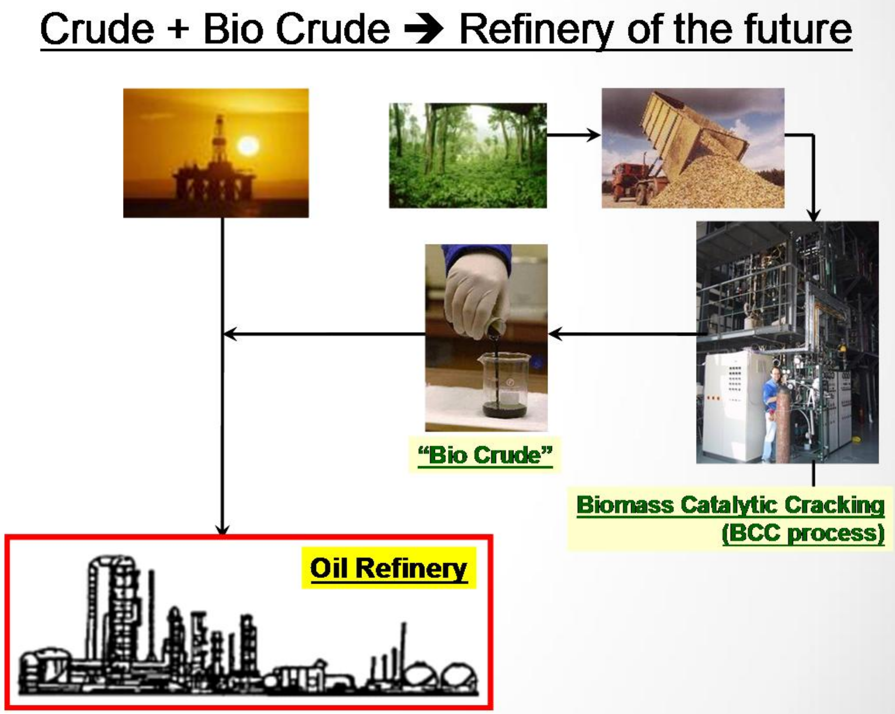
THE BIOBOOST FP7 EU PROJECT

- BioBoost concentrates on dry and wet residual biomass and wastes as feedstock for de-central conversion by Fast Pyrolysis (FP), Catalytic Pyrolysis (CP) and Hydrothermal Carbonisation (HTC) to the intermediate energy carriers (EC) oil, coal and slurry
- A logistic model for feedstock supply and techno/economic and environmental assessment of the value chain supports the optimization of the EC
- Application of EC is investigated for heat and power production, synthetic fuels & chemicals and as bio-crude for refineries

FAST PYROLYSIS (FP) vs. CATALYTIC FAST PYROLYSIS (CFP) OF BIOMASS

- FP: thermo-chemical process for the production of liquids, solids and gaseous products
  - a solid heat carrier is used
- CFP: solid catalyst as heat carrier for in-situ upgrading of pyrolysis products aiming at the production of liquids (bio-oil) with better quality:
  - less O_2
  - improved stability and acidity
  - processing into existing refineries
- CFP oil can be a decentralized energy carrier (bio-crude)



THE CATALYTIC PYROLYSIS PATHWAY

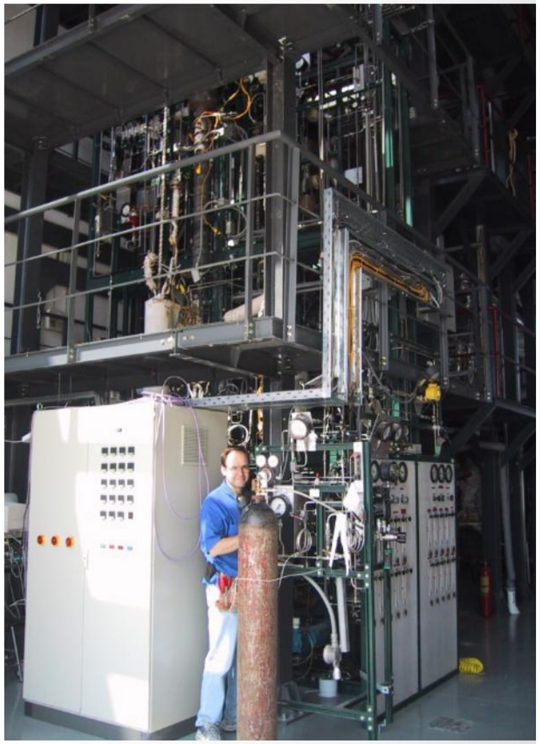
BioBoost

- Bioboost objective: to optimize the biomass catalytic pyrolysis (CP) process using:
  - new more resistant catalysts
  - different types of biomass
  - circulating fluid bed (CFB) technology
  - optimum operating conditions
- The target is to produce the maximum catalytic pyrolysis oil (CPO) yield at the maximum deoxygenation level.

THE CPERI CFB PILOT PLANT UNIT FOR BIOMASS CATALYTIC PYROLYSIS STUDIES

Why CFB for Biomass Catalytic Pyrolysis:

- Continuous catalyst regeneration
- Independent control of pyrolysis temperature
- Independent control and ability to achieve high catalyst / biomass ratios
- Short vapors residence times



CATALYST EFFECTS ON CFP

KEY FACTOR IN CFP: CATALYSIS

Previous work in CPERI: catalyst effects/optimization of CFP catalysts

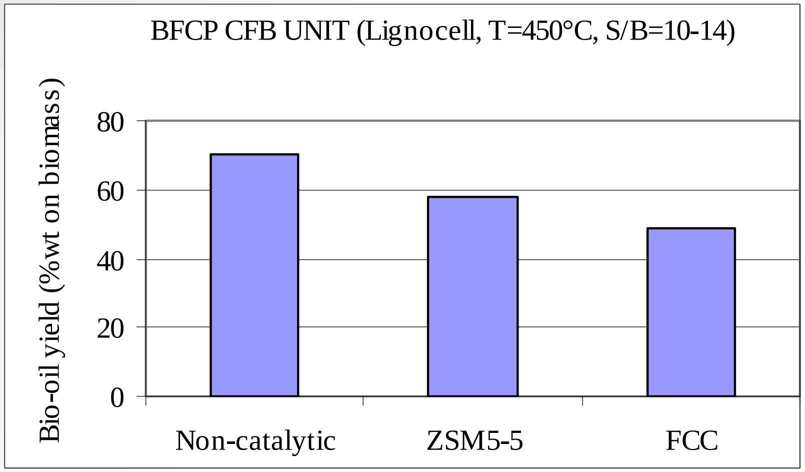
<u>Acidic catalysts:</u>

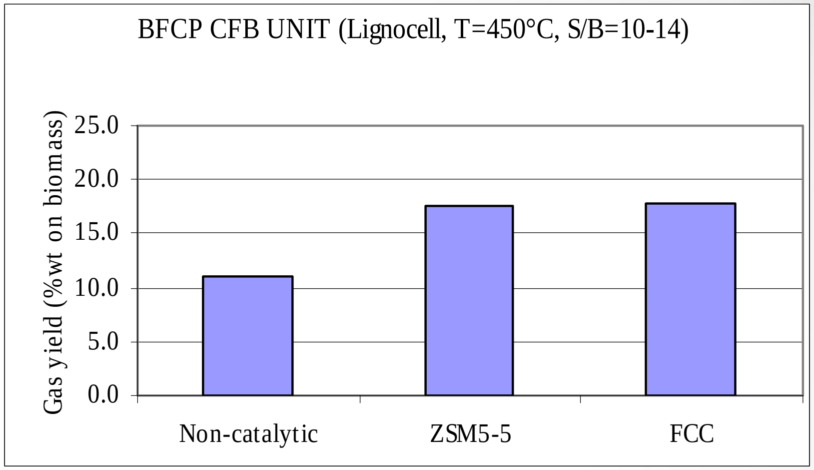
- Effect of microporous crystalline zeolite type:
  - Y vs ZSM-5 vs Beta vs Mordernite vs Silicalite
- Effect of Si to Al ratio (SAR)
- Hybrid zeolites: mesoporous zeolites, etc.
- Metal modified zeolites
- Ordered mesoporous (alumino)silicates: MCM-41, SBA-15,..
- Commercial catalysts: SiO_2-Al_2O_3, γ-Al_2O_3, FCC, etc.

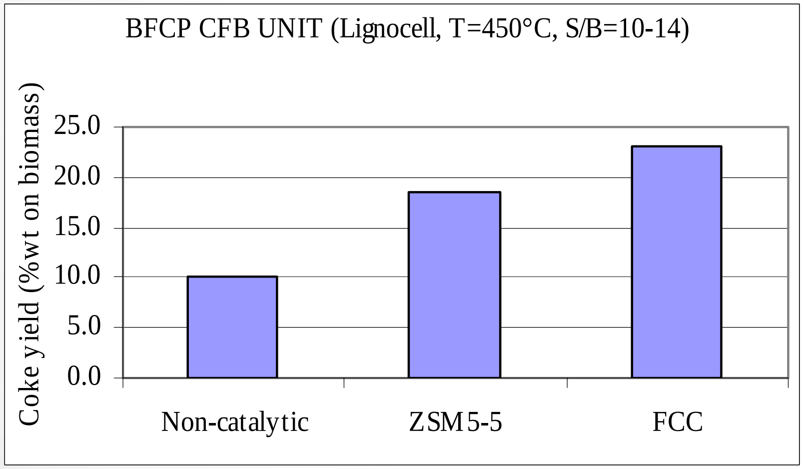
<u>Basic catalysts:</u>

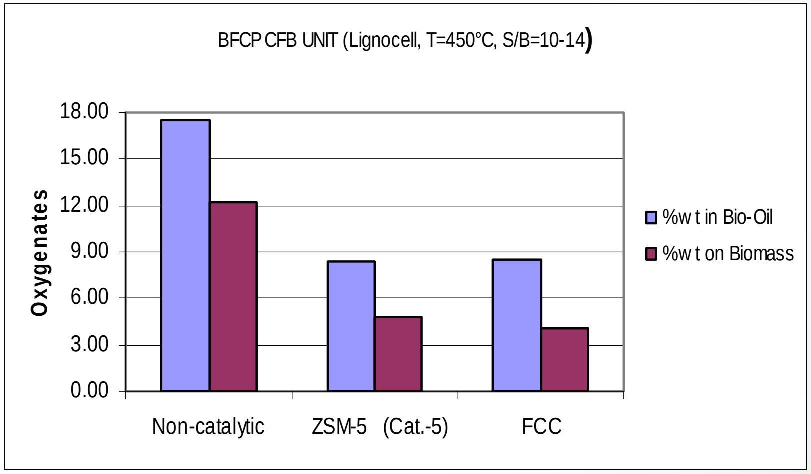
- MgO, CaO, NiO, ZrO_2, ZnO, etc.

EFFECT OF ZEOLITE TYPE: ZSM-5 vs. Y









- The catalysts decrease the production of liquids and increase the water, coke and gas production
  - The presence of catalyst favors the secondary cracking of vapors and the de-oxygenation reactions
- ZSM-5 is a better catalyst that Y

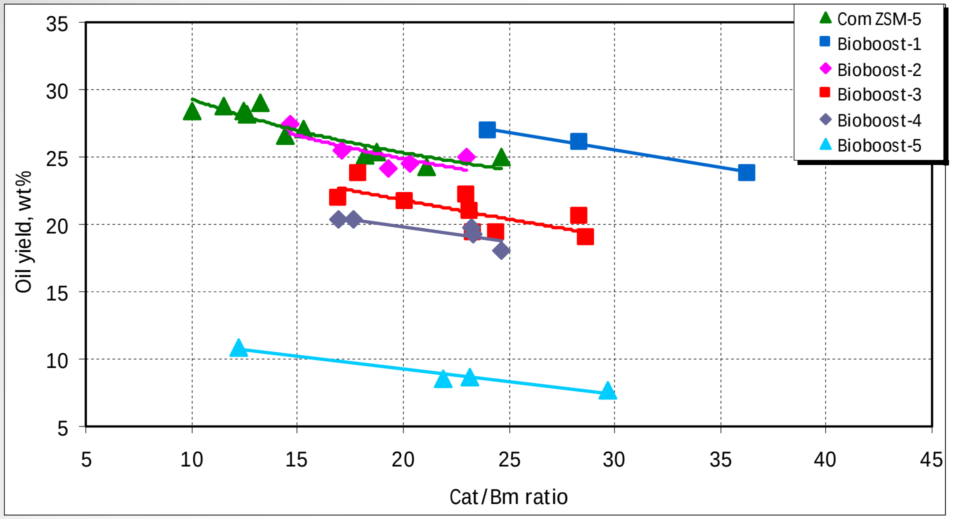
CATALYSTS USED IN BIOBOOST

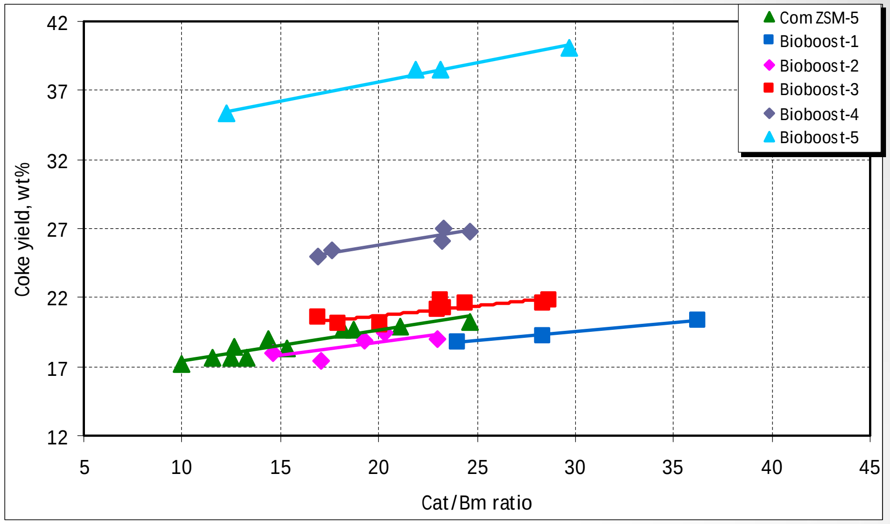
- 15 new catalysts (synthesized by Grace) and 5 commercially available fresh catalysts were pre-screened on a bench scale fixed bed pyrolysis reactor in CERTH.

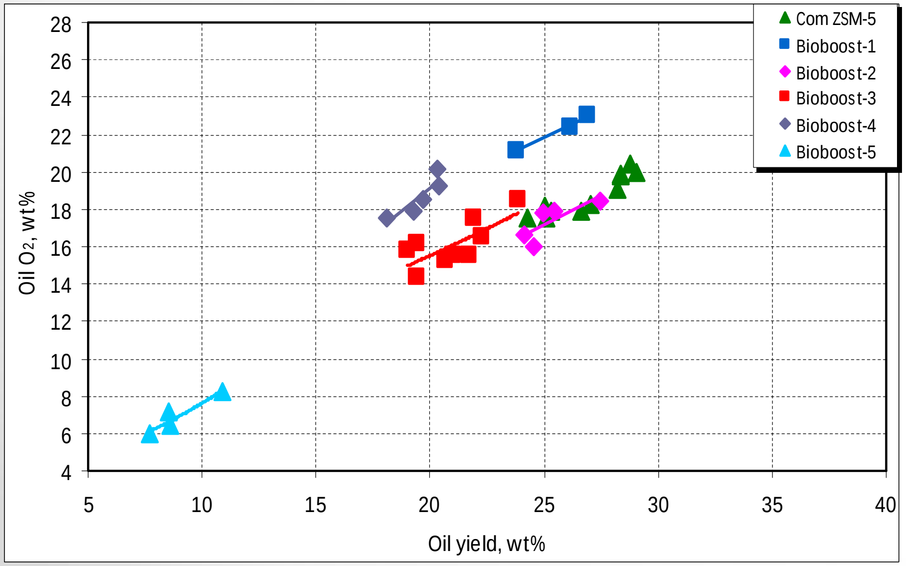
- The five best catalysts were selected and scaled up in Grace at 20 kg level using spray-dried techniques.

- All these five catalysts as well as the best commercial catalyst were tested on pilot scale in CPERI.

BIOBOOST Catalyst Evaluation on Pilot Scale with Woody Biomass

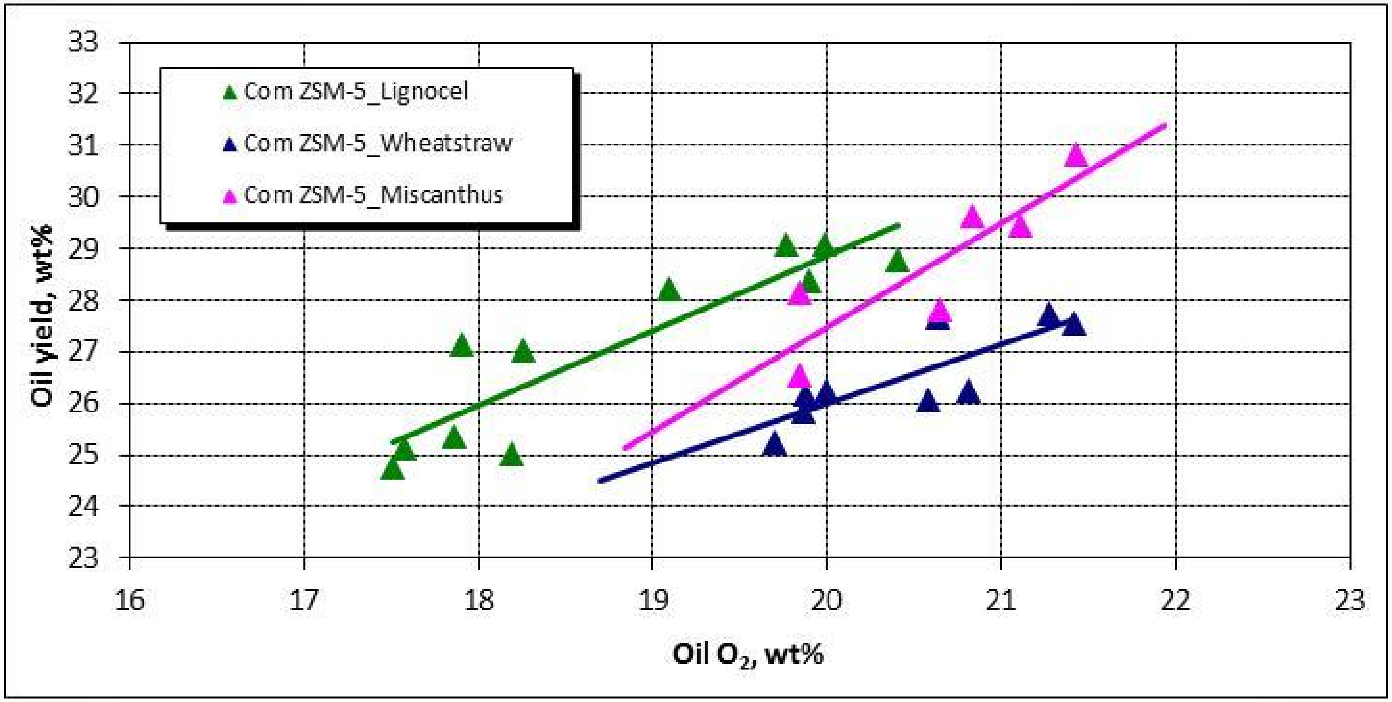






- Higher C/B ratios accelerate cracking reactions resulting in a lower oil yield
- Catalyst activities differ significantly
- Coke selectivity is crucial in CFP
- Cat-2 is the best catalyst and at the same Oil yield gives 1% less O2 compared with the state of the art commercial ZSM-5 catalyst

BIOBOOST Feed Effects: O_2 and Oil



- The woody biomass produces the highest oil yield with the same O_2 content followed by miscanthus and straw

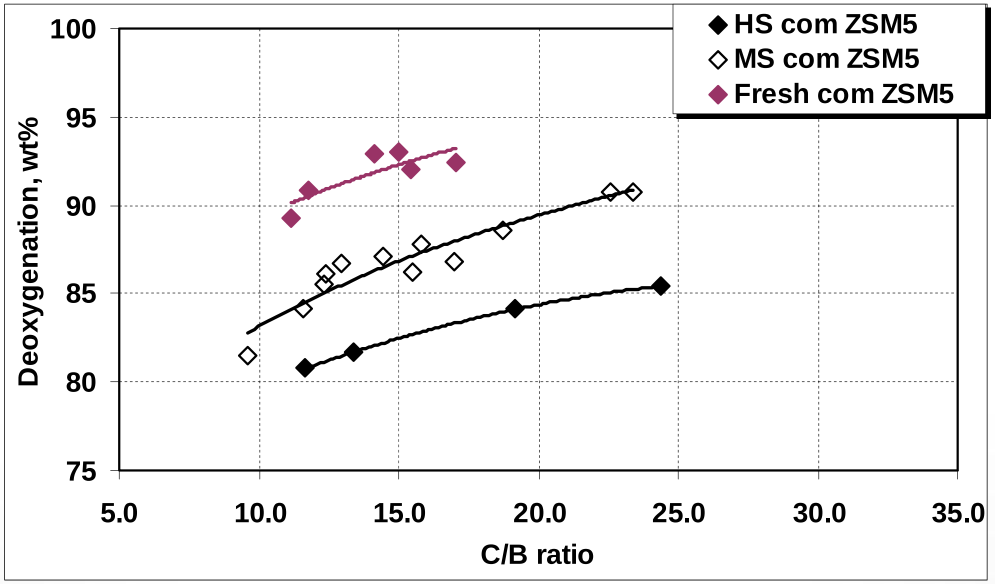
CFP CATALYST DEACTIVATION

- Hydrothermal deactivation due to severe conditions during regeneration
- Biomass ash metals poisoning: K, Na, Ca, Mg
  - Ash-metals deposition rate
  - Ash-metals nature
  - Metals effects on catalysts activities / selectivities

HYDROTHERMAL DEACTIVATION OF CFP CATALYSTS

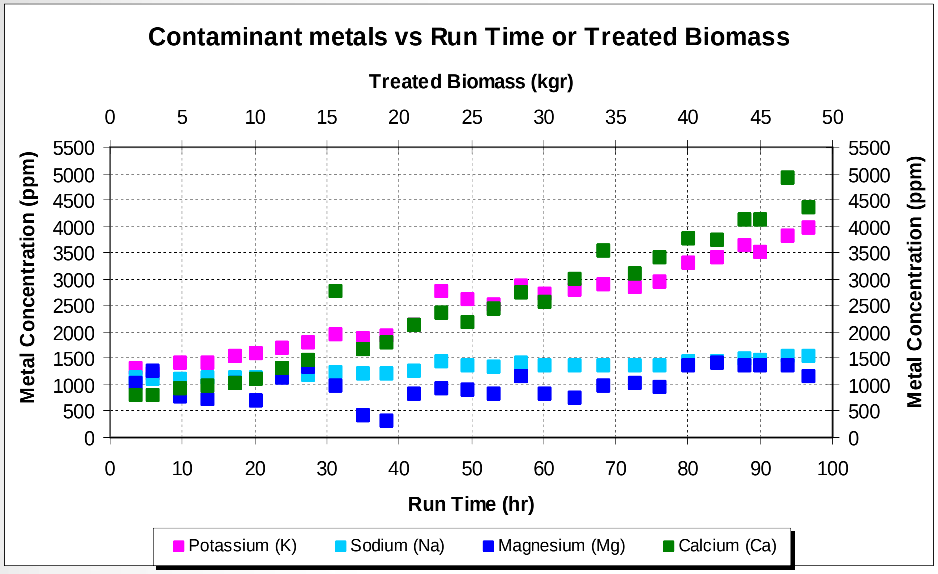
Testing: Fresh vs medium severity (MS) vs high severity (HS) steamed samples

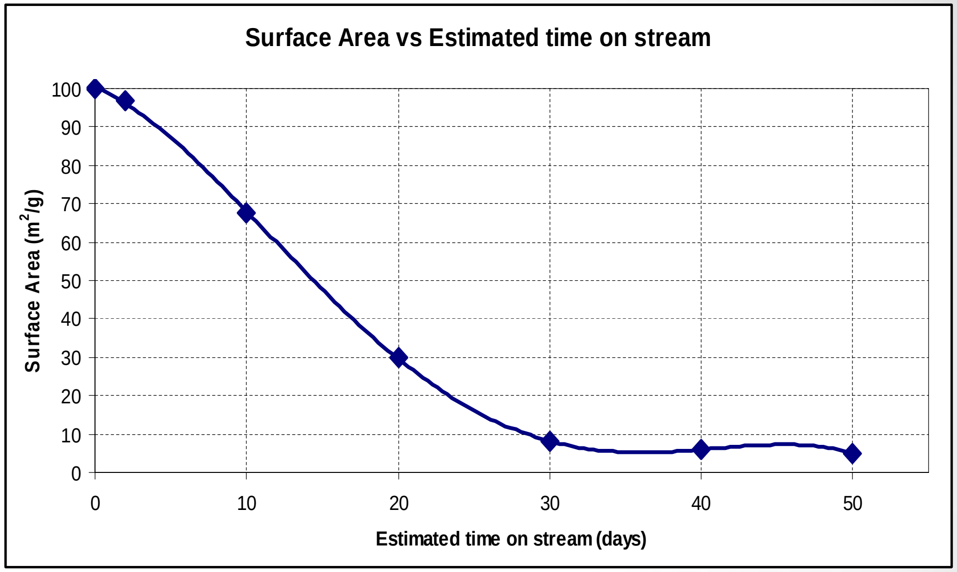
	Br. Acidity (µmol/g)	Lewis Acidity (µmol/g)
Fresh	36	20
MS Steamed	10	11
HS Steamed	8.0	8.5



- Hydrothermal deactivation plays a significant role in CFP catalyst performance

CATALYST DEACTIVATION BY CONTAMINANT METALS





- Long experiment in CERTH showed that the biomass metals are deposited on the catalyst with a deposition rate of at least 55%. After 4 days of operation there is a drop of about 3 %wt in deoxygenation of the derived biooil
- An ash metals spray-impregnated/steamed study in GRACE showed that CFP catalyst is stable up to about 10-20 days time on stream. Then zeolite is largely destroyed.

Characterization of CPO from BIOBOOST

BioBoost CP bio-oils analyses produced by different catalysts and Beechwood

Catalyst	Commercial ZSM-5	BioBoost Cat-1	BioBoost Cat-2	BioBoost Cat-3	BioBoost Cat-4	BioBoost Cat-5
Water	6.51	7.49	4.70	5.48	5.46	1.44
C	74.30	72.44	77.74	78.29	75.35	85.44
H	7.38	5.19	6.38	6.13	5.86	6.61
O (by dif.)	18.33	22.38	15.88	15.58	18.79	7.95
Density	1.09	1.10	1.09	1.10		
Calorific value (HHV, MJ/kg)	29.5	30.8	31.83	31.79	29.69	35.08
TAN	38.09	47.89	25.00	29.24	41.59	0.95
MCRT	17.79	20.84	14.15	12.82		

Characterization, handling and storage of CPO in CERTH

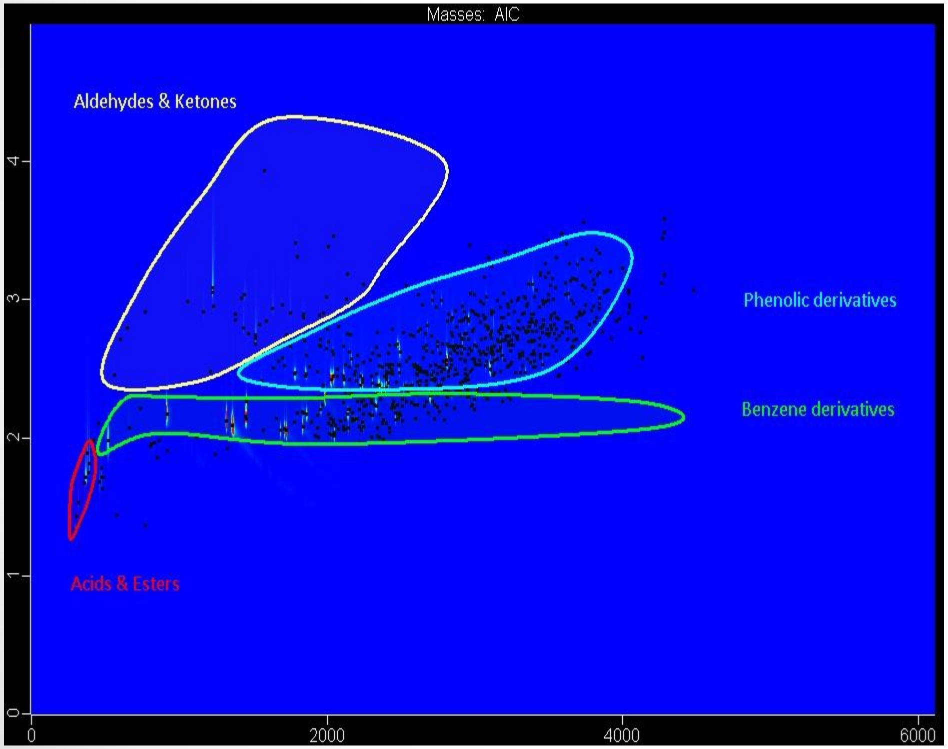
BioBoost

Storability of CP bio-oil

	0 months	stored in a cool room at 4°C, in dark for 6 months	stored in a cool room at 4°C, in dark for 12 months	stored in a cool room at 4°C, in dark for 18 months	stored in a cool room at 4°C, in dark for 22 months	stored in a cool room at 4°C, in dark for 27 months	accelerated ageing at 40°C for 7 days	accelerated ageing at 80°C for 24 hrs
C %	69.66	68.68	68.07	69.27	67.88	68.85	68.19	68.66
H %	7.8	7.17	7.27	5.7	6.12	7.53	7.00	7.04
O %	22.54	24.13	24.65	25.01	25.98	23.61	24.79	24.28
S (ppmwt)	n.a.	157	145.3	154.2	157.2	146.8	155.5	150.3
Density (g/mL)	1.1206	1.1237	1.1280	1.1317	1.1297	1.1308	1.1283	1.1269
Viscosity, 50°C (cSt)	13.6913	16.2569	-	25.8866	25.787	28.1242	23.9342	20.3159
HHV (MJ/kg)	29.5161	29.2492	29.6627	29.3934	29.3636	29.1754	29.5210	29.2832
TAN (mgKOH/g)	40.4036	41.5490	39.1287	40.9398	40.5965	41.0389	44.1220	41.4673
H_2O (%wt)	6.5	6.4308	6.1026	5.8399	7.8162	7.5	6.8924	7.0882
Copper Corrosion	n.a.	1A	1A	1A	1A	1A	1A	1A

Excellent stability and storability of CPO

ORGANIC PHASE QUANTIFICATION OF CPO WITH 2DGC-TOFMS



Compound	% w/w	Group	Total %w/w
Benzene, 1,3-dimethyl-	4.77	AR	16.35
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2.77	ALI	0.20
Phenol	2.47	PH	20.55
Toluene	2.11	FUR	2.07
Naphthalene, 2-methyl-	2.09	AC	0.00
Vanillin	2.08	EST	0.01
Phenol, 3-methyl-	1.93	AL	0.10
Phenol, 2,5-dimethyl-	1.80	ETH	0.08
Phenol, 2-methyl-	1.56	ALD	5.39
2-Cyclopenten-1-one	1.55	KET	5.18
Benzene, 1,2,3-trimethyl-	1.30	PAH	4.34
1,2-Benzenediol	1.22		
2-Propenal, 3-phenyl-	1.13		
Ethylbenzene	1.11		
Benzene, 1-ethyl-4-methyl-	1.10		
Benzaldehyde	1.02		
2-Methylindene	0.94		
Naphthalene, 1,7-dimethyl-	0.94		
2-Methylindene	0.89		
Indane	0.85		
Total $_{\text{Top 20 compounds}}$ (% w/w)	33.60		
Determined % w/w of total biooil	54.53		

- Absence of levoglucosan
- Lower Acids concentration
- Increased peak number in the aromatic hydrocarbons area

STATE OF THE ART ON CPO WITH ZSM-5

	CPO (BIOBOOST PROJECT)	TPO
H_2O content, %wt	5.0	25
C, %wt (dry basis)	77.5	53.0
H, %wt (dry basis)	6.5	7.5
O, %wt (dry basis)	16.0	39
TAN, mgKOH/g	25	80
HHV, MJ/Kg	31.5	20
Density, gr/cm^3	1.09	1.2
Stability	very good	medium

CFP CONCLUSIONS

- CFB technology can be applied for CFP
- With new catalysts developed in Bioboost we can achieve state of the art CPO properties with 18%O2 at 25%wt yield
- Catalyst deactivation in CFP is a challenge
- Woody biomass is the best for catalytic pyrolysis following by the energy crop (Mischanthus) and the agricultural residue (wheat straw)
- CPO is a very promising bioenergy carrier
  - low O_2, high C, less TAN, good stability
  - source of useful chemicals like phenols