Catalysts for the Catalytic Pyrolysis of Biomass

BioBoost Colloquium, Geleen, NL

GRACE

Talent | Technology | Trust™

05.06.2015

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This project has received funding from the European Union’s Seventh Programme
for research, technological development and demonstration under grant agreement No 282873

Grace businesses at a glance

3 Business Segments

Multiple Product Lines

- **GRACE Catalysts Technologies**
  - Refining Technologies
  - Advanced Refining Technologies*
  - Specialty Catalysts and Process Technologies
- **GRACE Materials Technologies**
  - Engineered Materials
  - Darex Packaging Technologies
  - Discovery Sciences
- **GRACE Construction Products**
  - Specialty Construction Chemicals
  - Specialty Building Materials

*Advanced Refining Technologies (ART) is Grace's joint venture with Chevron Products Company

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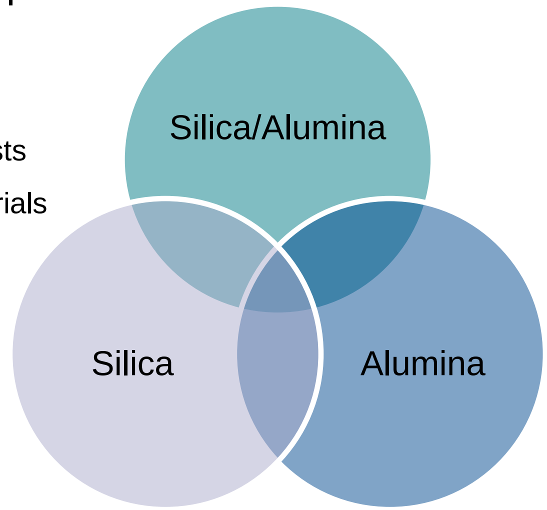
Grace

- Davison Chemical Company (founded 1832), began manufacturing silica gel in 1918 and continued to expand the technology into alumina and silica-alumina (including zeolite), developing new applications
- Davison manufactured the first FCC catalyst in Maryland in 1942
- W. R. Grace acquired Davison in 1954

- Polyolefin Catalysts
- Engineered Materials
- Separation Media



- Zeolite
- FCC Catalysts & Additives
- Chemical Catalysts
- Hydroprocessing Catalysts

Grace Today

- Approximately 6,000 employees
- Operations in over 40 countries
- 2013 worldwide sales of $3.1 billion

Silica, alumina, and silica-alumina are the foundation of Grace technology

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Products and Customers

Proven Materials and Established Relationships

Our Products

- Fluid catalytic cracking (FCC) catalysts and additives
- Hydroprocessing catalysts
- Specialty catalysts
- Silica gels
- Adsorbents
- Packaging sealants and coatings
- Chromatographic media
- Specialty construction chemicals
- Specialty building materials

Our Customers

- Petroleum refiners
- Petrochemical producers
- Digital printers
- Food packagers
- Beverage companies
- Drug manufacturers
- Cement and concrete producers
- Building material companies
- Contractors
- Building material distributors
- Home improvement chains

Though most people don't know it, Grace products are likely all around them

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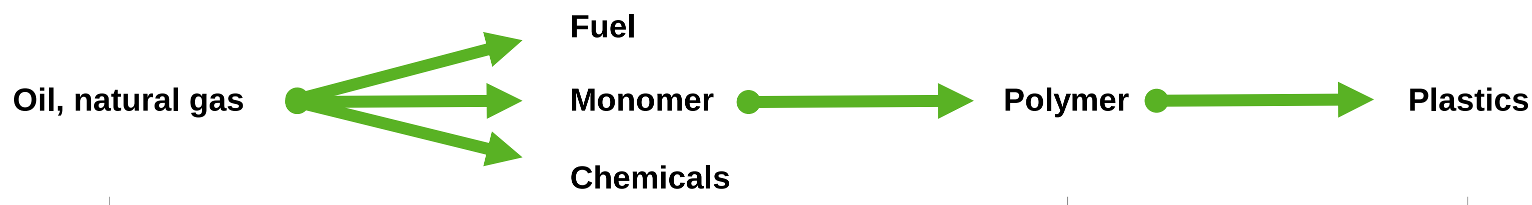
Grace Catalysts Technologies: Product Applications



Refining Technologies:
- FCC catalysts
- FCC additives
- Zeolitic materials
- Feedstock conversion technology
- Hydroprocessing catalysts

Chemical Catalysts:
- Technology for alternative and traditional feedstock production
- RANEY® hydrogenation catalysts
- DAVICAT® catalysts and supports

Polyolefin Catalysts:
- Polyethylene catalysts
- Polypropylene catalysts
- Single site catalysts
- Catalyst supports
- Catalyst components
- UNIPOL® polypropylene process technology

Plastic Additives:
- Silica antiblock
- Combination products:
  - Slip aids
  - Antioxidants
  - Antistatics
  - Other applications

Unique catalyst-based solutions and broad technology portfolio

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Grace Refining Technologies: Focus on FCC

Fluid catalytic cracker or FCCU

- Principle refining conversion unit, versatile, flexible, and very complex
- Replaced thermal cracking processes in 1942, dramatically increasing gasoline yield

Catalyst looks like fine, white sand

- Porous with very high surface area (several hundred square meters per gram)

Zeolite (microporous silica-alumina crystals)

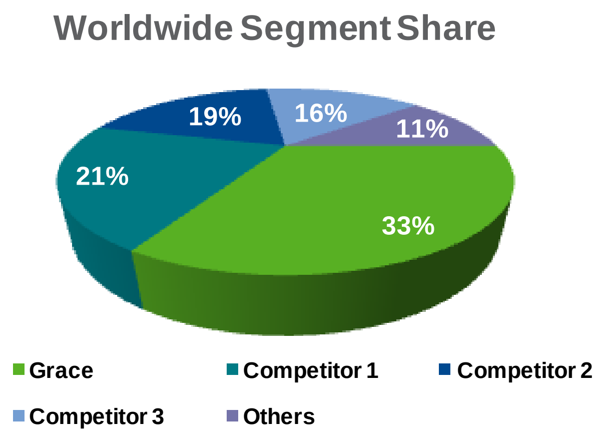
- Primary active ingredient
- Gasoline engine of the catalyst
- Two zeolites are used for cracking
  - Faujasite - in all FCC catalyst
  - ZSM-5 - used to maximize propylene

Specialty aluminas

- Convert the bottom of the barrel

Metals Traps for resid

- Activity and stability in challenging operations



We will innovate state-of-the art products and deliver superior technical service in order to solve our customers' problems and enhance their profitability.

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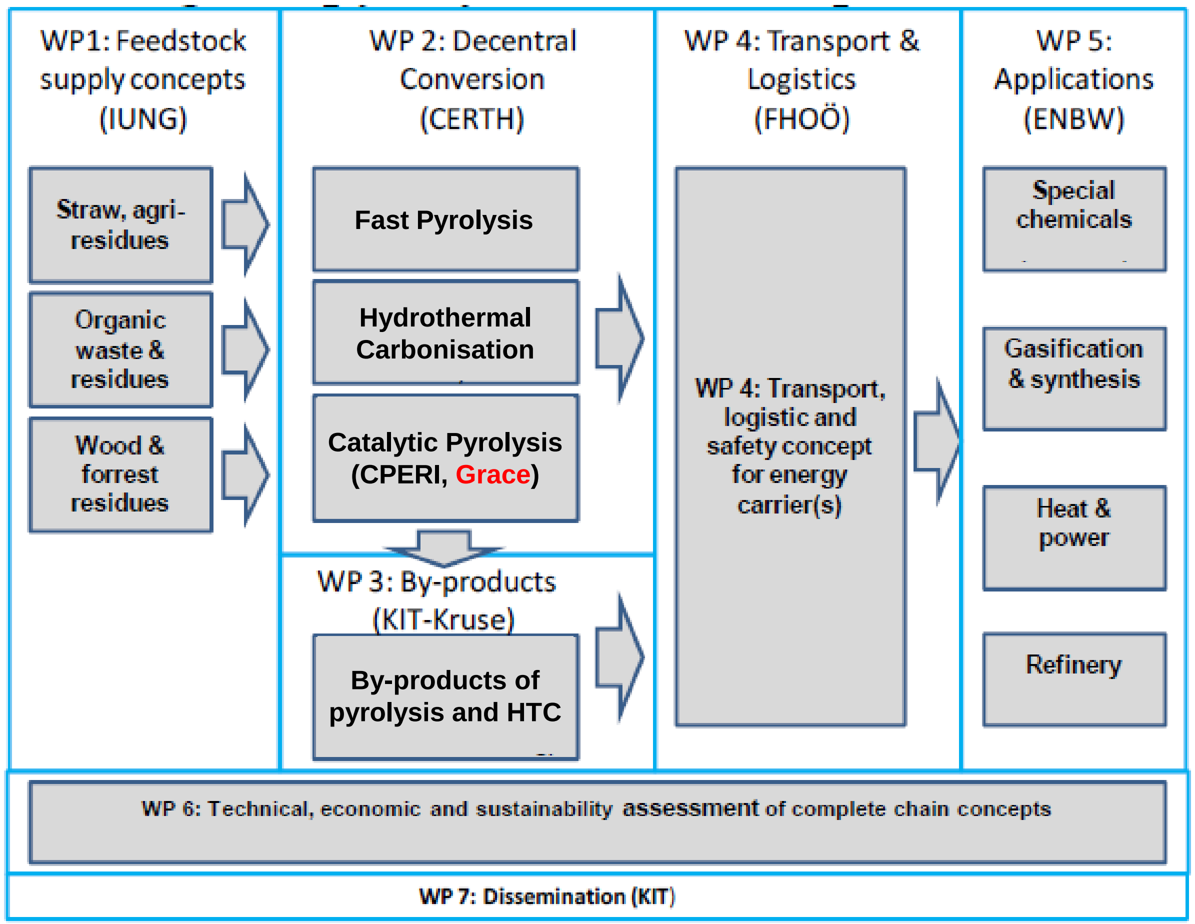
The Role of Grace in the BioBoost Project



GRACE provides the catalysts for the catalytic pyrolysis experiments within WP2

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Catalytic Fast Pyrolysis of Biomass

- Catalytic fast pyrolysis (CFP) of biomass is a thermo-chemical conversion process.
- The biomass is converted by fast pyrolysis to relatively heavy volatiles that contain many oxygenates.
- The quality of these products is characterized by its high oxygen content, high viscosity, high corrosivity, chemical instability, incomplete volatility, solids content, incompatibility with conventional refinery streams and its low heating value.
- In CFP a heterogeneous catalyst is used for the in-situ conversion of the fast pyrolysis products.
- The role of the catalyst is to reduce the oxygen content, to reduce the molecular weight and to alter the chemical structure to supply petrochemical products.

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Catalytic Fast Pyrolysis of Biomass

- Many catalysts have been applied in the CFP.
- The catalysts that generate petrochemical products usually catalyze cracking and deoxygenation reactions.
- The catalysts applied are typically catalyzing carbocation mechanisms, often in combination with hydrodeoxygenation functionality.
- Zeolite catalysts
  - ZSM-5 is the most widely studied zeolite
  - also HY, beta, mordenite, ferrierite
  - metals modified zeolites (Ga, Fe, Zn, Ni, Co etc.)
- Mesoporous catalysts
  - MCM-41, SBA-15
  - Silica alumina
- Metal oxides
  - TiO_2, ZnO, Fe_2O_3, MgO, CaO,
- Basic compouds
  - Na_2CO_3, NaOH

..... etc. etc. .....

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Catalytic Fast Pyrolysis of Biomass

- **ZSM-5 is the most widely studied zeolite.**

ZSM-5 ...

- reduces the FP oil yield
- increases the gas, coke and H_2O yields
- is highly active in reducing the molecular weight
- reduces the oxygenated species under CO, CO_2 and H_2O formation
- increases the aromatics content remarkably
- forms phenolic compounds
- is severely deactivated by coke formation
- catalyses these reactions the best at 500-550°C

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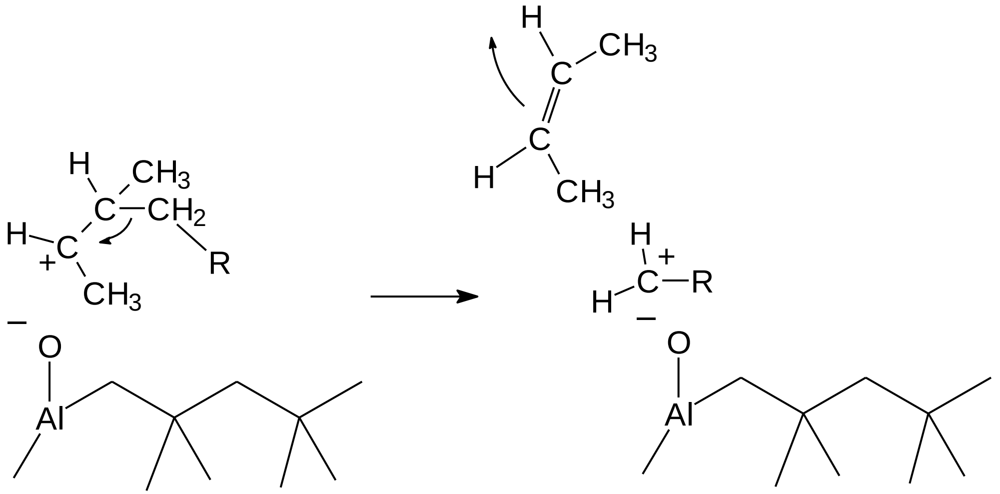
Catalytic Fast Pyrolysis of Biomass

- Typical mechanisms observed with acidic zeolitic catalysts are e.g.
  - Cracking reactions
  - Hydrodeoxygenation
  - Decarbonylation reactions
  - Decarboxylation reactions
  - Hydration
  - Hydrocracking reactions



β-scission

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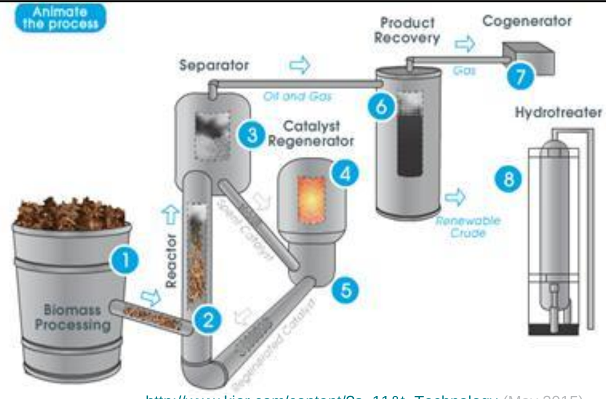
Catalytic Pyrolysis of Biomass

- A technical CFP process can be realized in different ways.
- The challenge is to quickly heat up the biomass to reaction temperatures, to perform the reaction at high catalyst-to-biomass ratios and to facilitate the reaction at low residence times to optimize the yields of liquid products.
- Further challenges are the char formed by the pyrolysis reactions and the rapid deactivation of the applied catalysts by coking and poisoning.
- The FCC process appears to be suited to be retrofitted to the CFP requirements.
- Several processes applying the FCC principles have been and are currently being developed to facilitate the catalytic fast pyrolysis.



http://www.kior.com/content/?s=11&t=Technology (May 2015)

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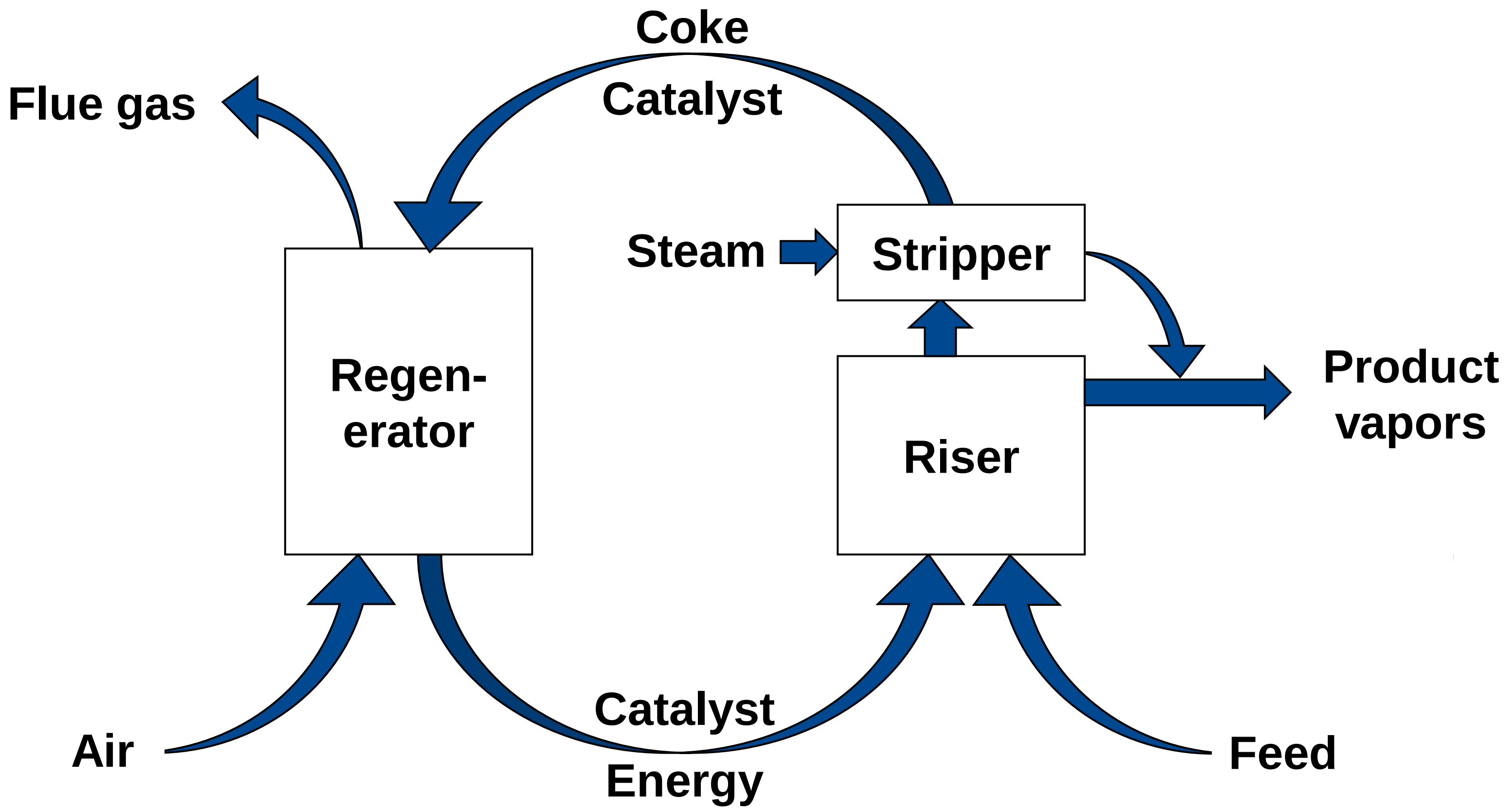
FCC Process



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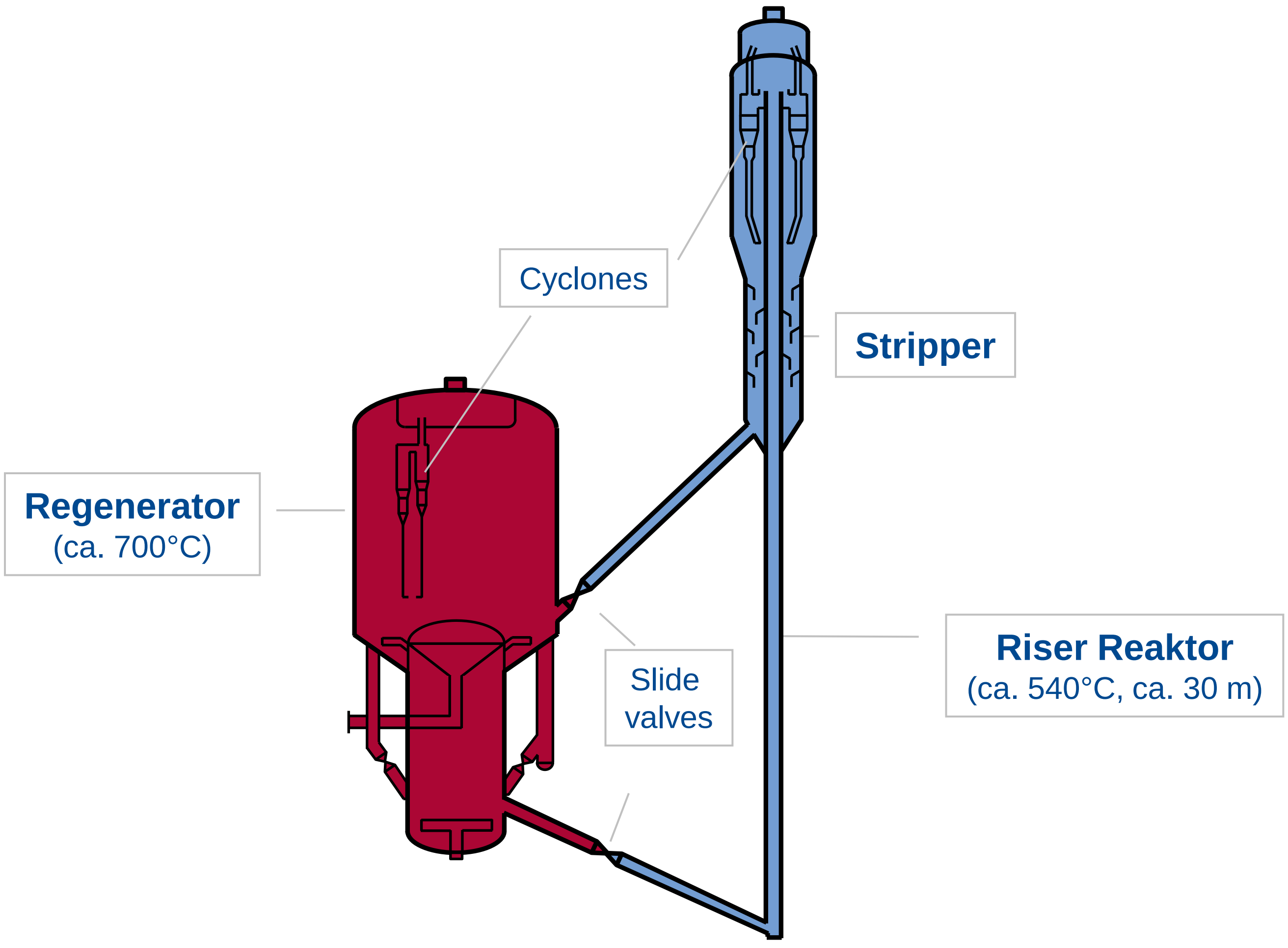
Fluid Catalytic Cracking Process



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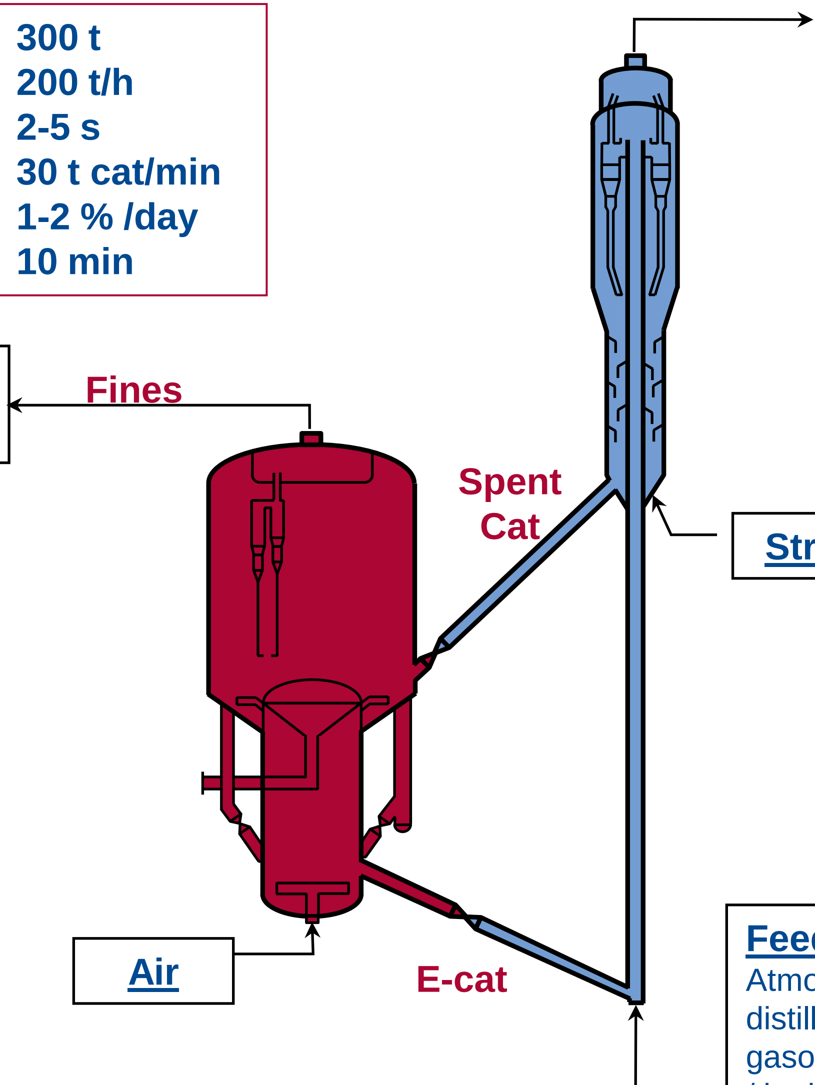
Fluid Catalytic Cracking Process

Inventory:	**300 t**
Feed oil:	**200 t/h**
Reaction time:	**2-5 s**
Cyclization rate:	**30 t cat/min**
Fresh cat addition:	**1-2 % /day**
Regeneration time:	**10 min**

Flue gas:
$CO_X/NO_X/SO_X/H_2O$



Product yields	wt.. %
H_2	< 1
C_1-C_2	3
C_3	5
C_4	8
Gasoline	50
LCO (216-338°C)	20
HCO (338°C)	7
Coke	6
/ H_2S / Steam	

Stripping steam

Feed oils
Atmospheric tower resid, Vacuum distillates & tower bottoms, Coker gasoil / Lube extracts / var. slopes (raw / hydrotreated / de-asphalted)

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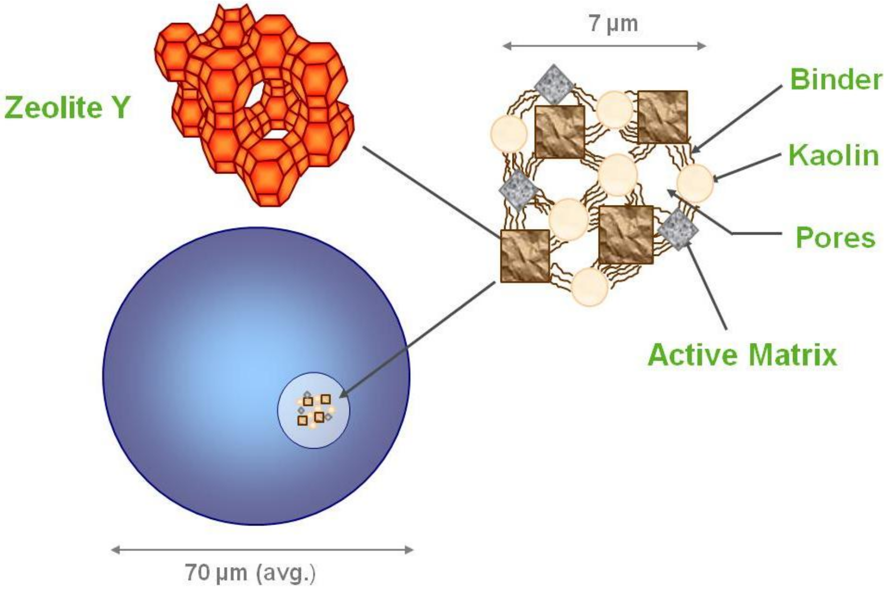
FCC Catalyst Design

- **Activity**
- **Selectivity**
- **Stability**
  - Retention of acid sites
  - Stable porosity
  - Stability against catalyst poisons
  - Mechanical Properties
    - Attrition resistance for catalyst retention
    - Optimum particle size distribution for fluidization
    - Optimum average bulk density for fluidization
    - Specific heat capacity for heat transport



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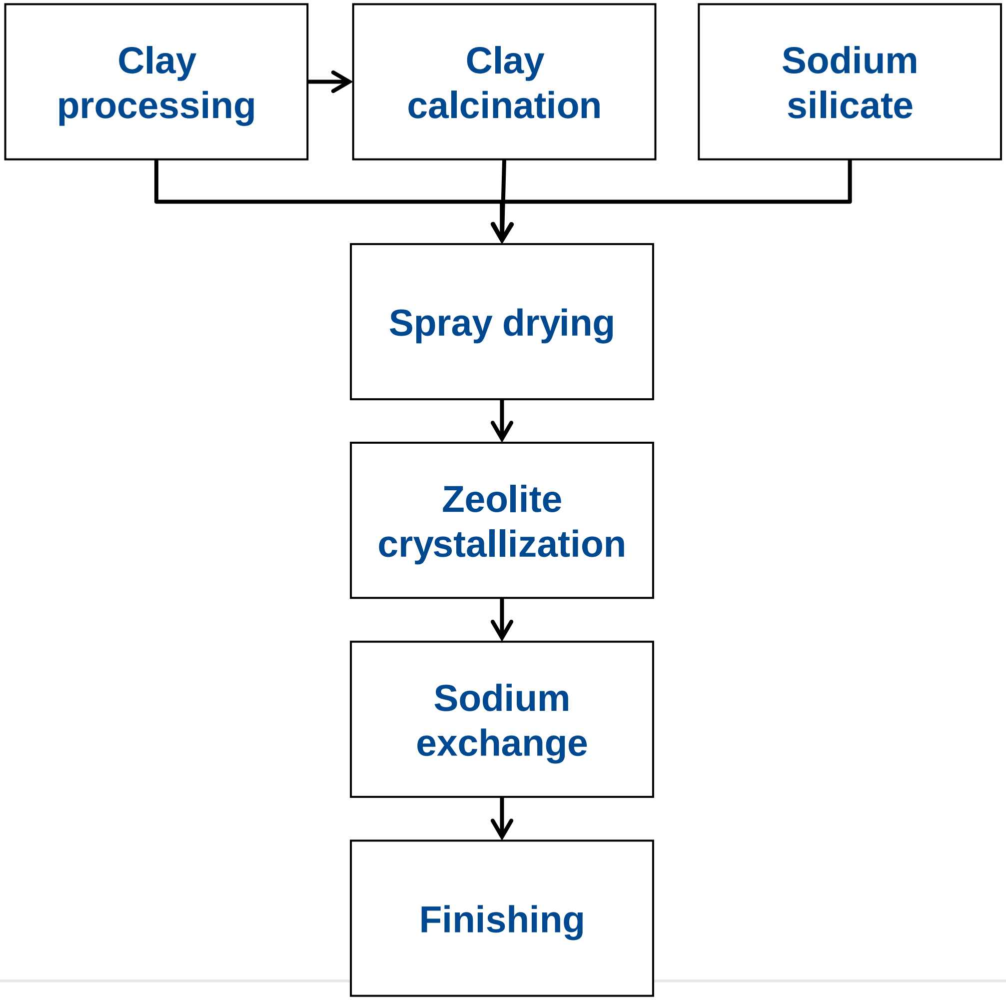
FCC Catalyst Manufacturing

Clay-based catalysts



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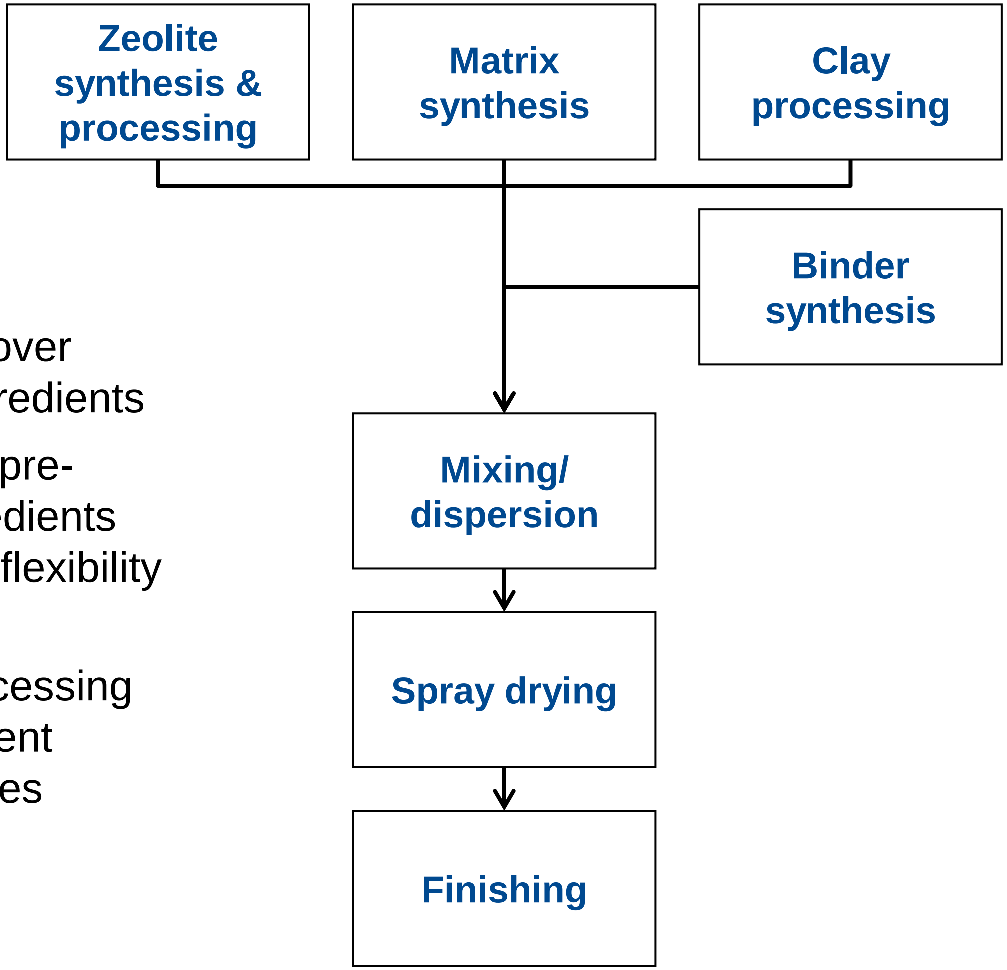
FCC Catalyst Manufacturing

Composite catalysts



- Careful control over quality of all ingredients
- Spray drying of pre-processed ingredients provides a high flexibility in formulation
- Continuous processing enables consistent product properties

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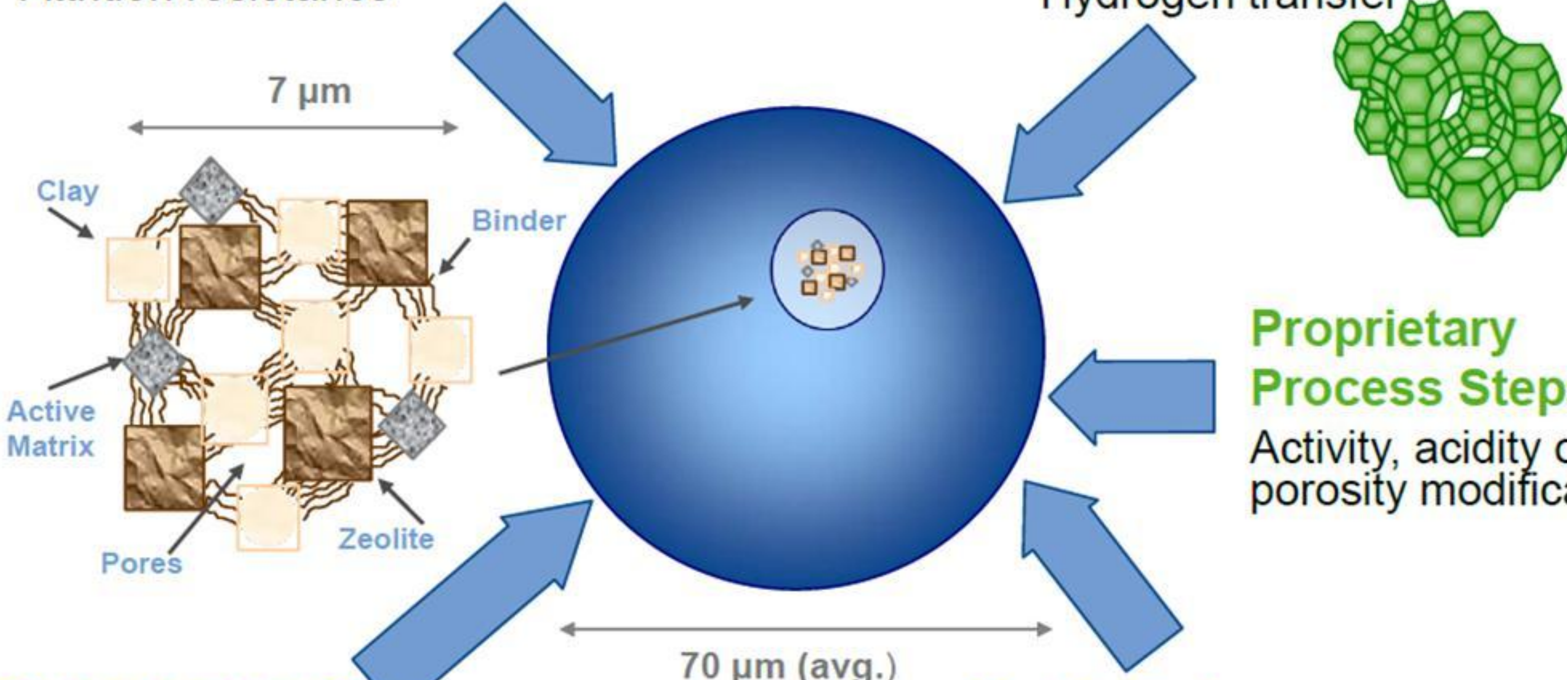
FCC Catalysts

Alumina Catalyst Platform
Formulation flexibility
Matrix activity and porosity
Attrition resistance

Advanced Zeolites
Y or USY based
Activity, Stability, Octane, Coke
Hydrogen transfer



Proprietary Process Steps
Activity, acidity or
porosity modifications,

Selective Matrix
Acidity, Porosity,
Processing heavy molecules,
Coke, Bottoms upgrading

Metals Tolerance
Integral metals traps enhance
stability and preserve activity

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Contribution to BioBoost

Provision of catalyst for bench- and pilot-scale testing at CPERI

- **15 lab-scale preps for bench-scale screening**
- **Five commercial catalysts were provided for pilot plant screening**
- **Five catalysts were scaled-up to allow for pilot plant screening**

✓ The results achieved with those catalysts have been provided by Angelos Lappas in the previous presentation

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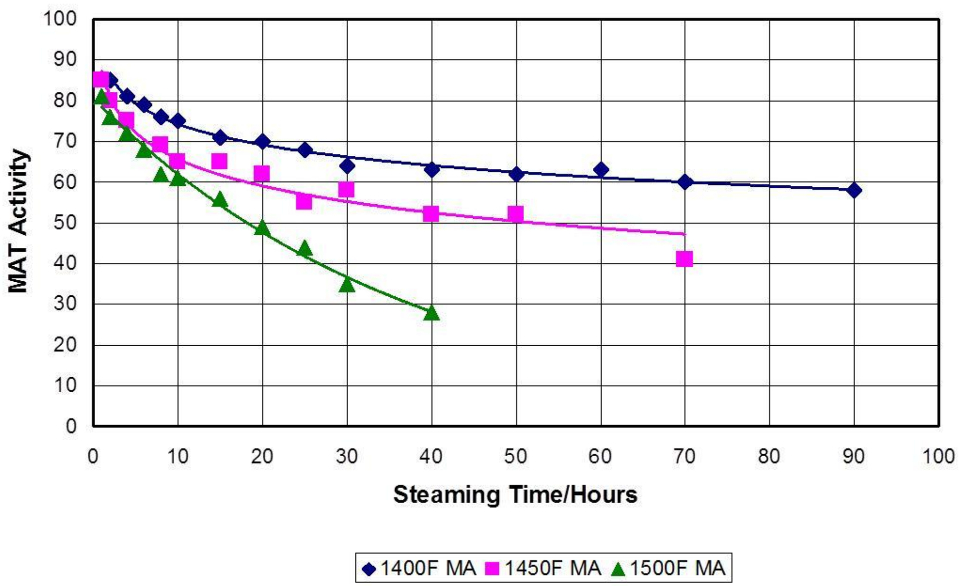
Catalyst Deactivation

Reviewing the literature about CFP we recognized that the catalyst stability is not in the focus of most groups.

FCC catalyst deactivation is key to understand catalyst performance. Therefore it is key to test properly lab- and pilot-scale deactivated catalysts.

The main deactivation mechanisms are:

- Hydrothermal deactivation
- Metals deactivation



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Catalyst Deactivation

Key Yields
Coke, dry gas, LPG, gasoline, gasoline composition, bottoms. conversion, C/O

Testing Strategies

Laboratory Deactivation

Fresh Catalyst

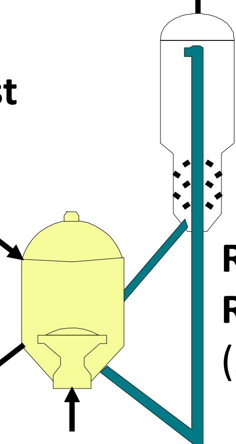
↓

Metals Deposition
Steaming
50-100% Steam
2-50 h, 750-800°C

↓

Simulated E-cat

Commercial Unit



Yields

Fresh Catalyst Make-Up

Regenerator
(~50 d/700°C
~12% steam)

Riser Reactor
(540°C, 2-5 s)

Air

Equilibrium Catalyst

Feedstock
Ni, V, Fe, Na

Catalyst Testing

Yields

E-cat or Sim E-cat → DCR / ACE / MAT

Feedstock

Key Properties
ZSA, MSA, UCS
Ni, V, Fe, Sb, Metals Distribution
Oxidation State, Age Distribution

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Contribution to BioBoost

Deactivation Study

- Determination of typical metals contamination.

  Based on the metals content of CPERI catalyst after two days on stream;

  (300 ppm Na_2O, 2600 ppm K_2O, 1300 ppm CaO, 500 ppm MgO, and 200 ppm P_2O_5)

➢ Preliminary experiments with two grades of commercial ZSM-5 additive

- Spray Impregnation of a 'metals ladder'

  Extrapolation of contaminant levels to extremely high contamination

- Steam deactivation applying the AM-1500 and the CPS-3 protocols

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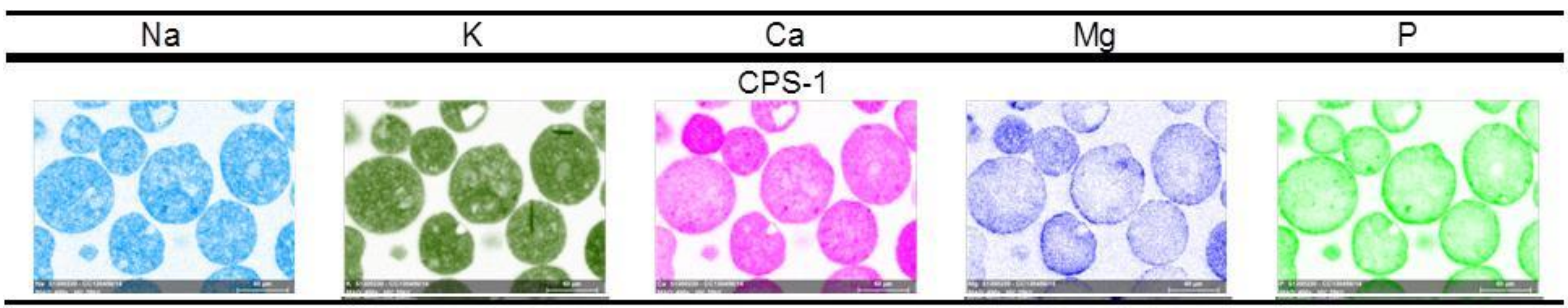
Contribution to BioBoost

Deactivation of commercial ZSM-5 Additives

TOS(*)	Days	2	10	20	30	40	50	Ratio
Na_2O	ppm	300	1500	3000	4500	6000	7500	6
K_2O	ppm	2600	13000	26000	39000	52000	65000	53
CaO	ppm	1300	6500	13000	19500	26000	32500	27
MgO	ppm	500	2500	5000	7500	10000	12500	10
P_2O_5	ppm	200	1000	2000	3000	4000	5000	4
Sum	ppm	4900	24500	49000	73500	98000	122500	

SEM/EDX Elements mapping of the TOS 40 d sample

- Homogeneous distribution for Na, K & Ca and egg shell distribution for Mg & P.



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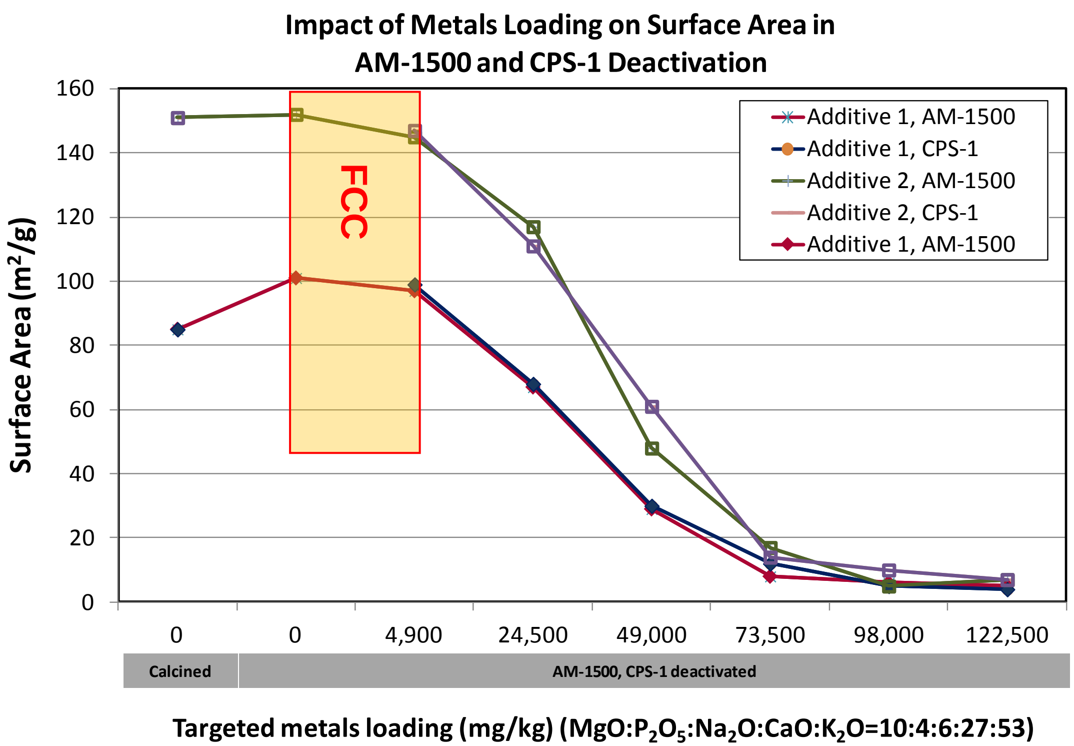
Contribution to BioBoost

Deactivation of commercial ZSM-5 Additives



- Significant collapse of the structure at contaminant metals levels above 2.5wt.%
- AM-1500 and CPS-1 result in similar surface areas.

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Contribution to BioBoost

Deactivation of commercial ZSM-5 Additives

- The deactivation experiments show that ZSM-5 catalysts withstand a certain amount of contaminant metals.
- The catalysts broke down beyond a threshold of about 2.5 wt.% contaminant metals.
  - Alkali and alkaline earth silicate formation
- The ash deposition on the catalyst during the real process has still to be investigated.
  - Possibly the contaminant metals ends up in the flue gas rather than on the catalyst.
- The deactivation severity under steady state conditions is unknown to us.
  - Long time runs have been performed in the CPERI pilot riser.

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Outlook

- Catalytic Fast Pyrolysis is a promising pathway to integrate Biocrude into the current refining environment.
- Several approaches are currently on promising pathways to commercialization (e.g. Anellotech with Axens or the International Research Triangle Institute, RTI)
- High manufacturing cost is a major threat when entering the highly competitive refining environment .
  The KiOR company which was running an industrial CFP plant based on FCC principles has already failed based on the discrepancy between the production cost of $6.72 per gallon and the selling price of $ 2.76 per gallon[1]
- The BioBoost approach to evaluate the complete value chain will allow for a proper assessment of the economic chances of such a process in the EU. The results of the BioBoost project will provide an indication in how far the process will have to be improved to make economically sense.

Biomass → CFP → mild Hydro-processing → Hydropro-cessing → Biofuel

[1] http://www.bloomberg.com/news/articles/2014-11-10/kior-inc-biofuel-company-files-bankruptcy-plans-sale **(Nov. 2010)**

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