Center for Research and Technology Hellas (CERTH)/Chemical Process Engineering Research Institute/(CPERI)

Production of Bio-Gasoline using Waxes produced from a Biomass to Liquid (BtL) Process

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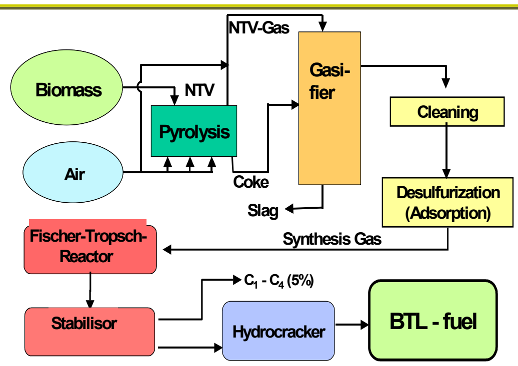
THE F-T BTL PROCESS



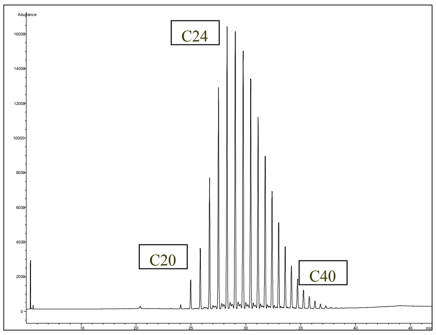
- R&D/Demonstration in EU for Production of final F-T transportation fuels from biomass
- Depending on F-T operation a high amount of Waxes can be produced

Scope of the work: Upgrading the F-T wax to bio-gasoline via catalytic cracking process (FCC) or FCC&Olefin Saturation process

FEEDS OF THE PILOT PLANT STUDY

- A F-T wax feed and a hydrotreated VGO

	Wax	VGO
API	43.10	26.1
s.g	0.810	0.897
S (XRF), ppmw	2.5	2300
Melting point	80°C	
Sim.Dist, 5%	368°C	266°C
Sim.Dist, 95%	474°C	528°C



GC/MS analysis of the F-T wax reveals the highly paraffinic nature

EXPERIMENTAL RESULTS

Upgrading the F-T Wax via Catalytic Cracking

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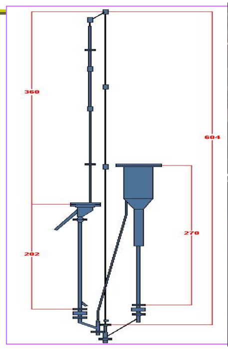
EXPERIMENTAL

Experimental Unit

- **CFB Unit. Solid circulation control by slide valves**
- **Catalyst circulation with continuous regeneration**
- **Riser of 9 meters for full simulation of commercial FCC units**



Catalysts

- **Commercially available (by Albemarle)**
- **A low activity Ecat (FCC-Y) with low metal:**
  - ✓ **TSA=178 m^2/g, ZSA=58 m^2/g, UCS=24.26Å**
- **A ZSM-5 additive (ZOOM) with a high crystal content (steamed)**

Operating conditions

- **Catalyst/Oil ratio (1-12)**
- **Cracking Temperature (460°C, 500°C, 538°C, 565°C)**

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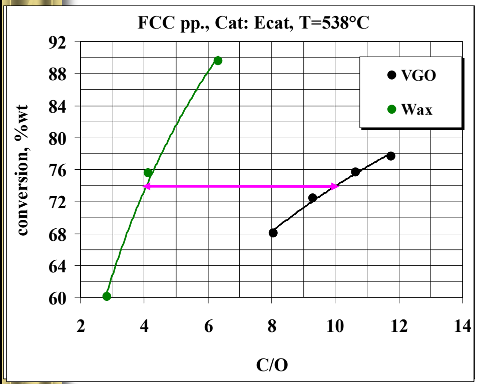
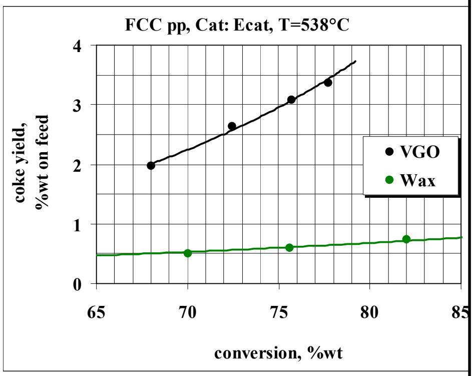
WAX vs VGO CRACKABILITY & COKE





- Wax is much more crackable than VGO due to the highly paraffinic nature of wax molecules
- Wax produces less coke than VGO
- Wax coke: from secondary polymerization reactions of the (rich) olefinic fraction

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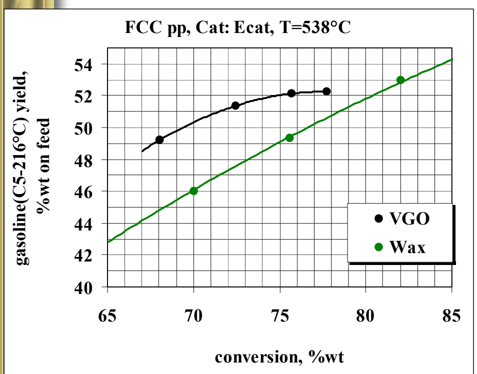
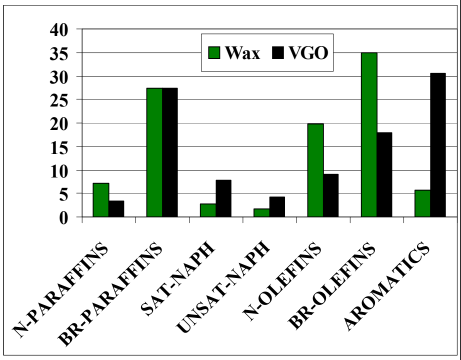
Gasoline of Wax vs VGO Cracking





- Wax-gasoline less than VGO-gasoline due to higher LPG yields
- There is no overcracking in Wax gasoline even at 90% conversion
- Low aromatics in the wax-gasoline (<6%)
- Wax-gasoline contains a lot of olefins
- Small effects of Wax on other HCs

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WAX vs VGO CRACKING AT ISOCONV=75%WT

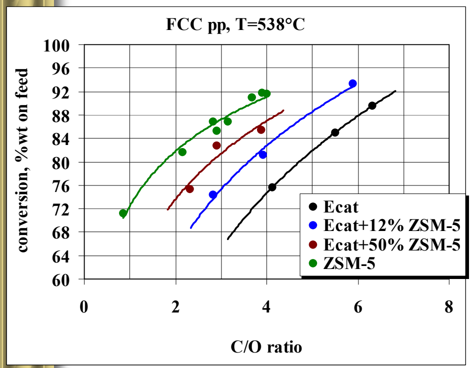
Feed	Wax	VGO
Dry gases	1.23	1.72
C_3H_8	1.57	1.02
C_3H_6	6.51	5.10
n-C_4H_{10}	1.66	0.85
i-C_4H_{10}	3.82	4.1
n-C_4H_8	3.75	2.05
i-C_4H_8	7.5	5.08
LPG	24.82	18.25
CF-216°C	48.51	51.08
HCO	21.25	6.36
Coke	0.60	2.95
RON	90.93	95.24
MON	79.04	83.0

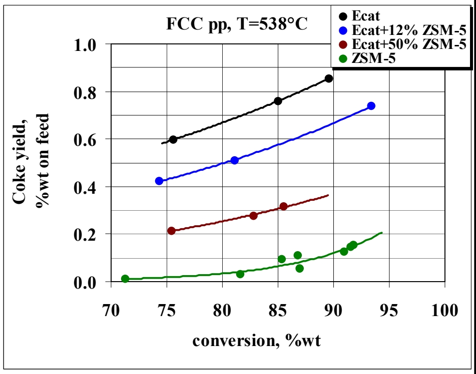
Wax-LCO is very low at all conversions. This is due to high crackability of LCO molecules

EXPERIMENTAL RESULTS

Catalyst and Temperature Effects on Wax Cracking

EFFECT OF ZSM-5 ADDITIVE ON WAX CRACKING

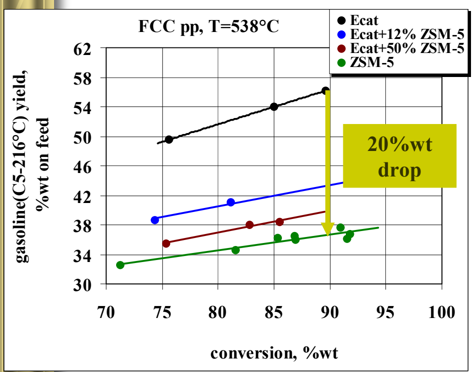


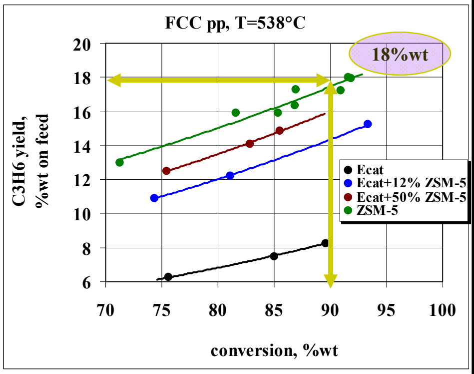


- The presence of ZSM-5 additive makes the Ecat more active
- Linear paraffinic molecules of Wax penetrates easily into the small pores of ZSM-5
- ZSM-5 support may also play an important pre-cracking role

- ZSM-5 additive decreases considerable the coke yield due to lower hydrogen transfer activity

EFFECT OF ZSM-5 ON GASOLINE/LPG YIELD

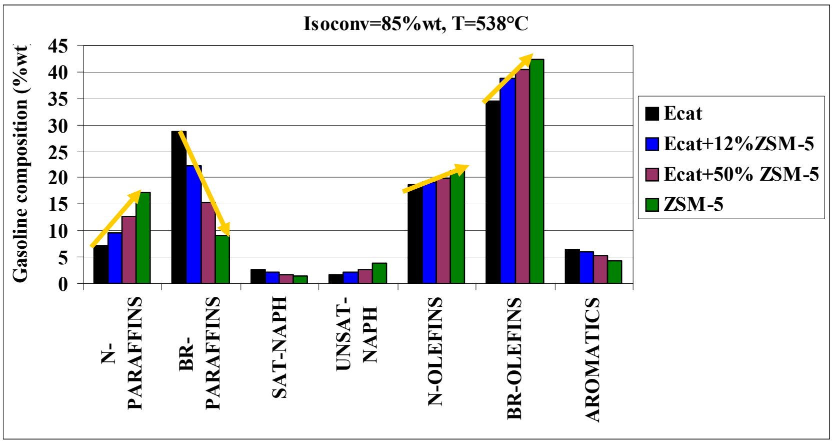




- Strong effect of ZSM-5 on Wax cracking
- Incremental decrease of gasoline very low after 12%wt ZSM-5

- The LPG olefins from ZSM-5 are significantly higher compared to Ecat

EFFECT OF ZSM-5 ON GASOLINE COMPOSITION



- **Gasoline quality with ZSM-5 is significantly different**
- **ZSM-5 affects strongly n- and br-paraffins & n and br-Olefins**

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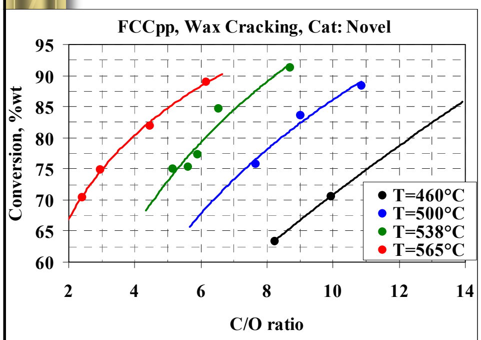
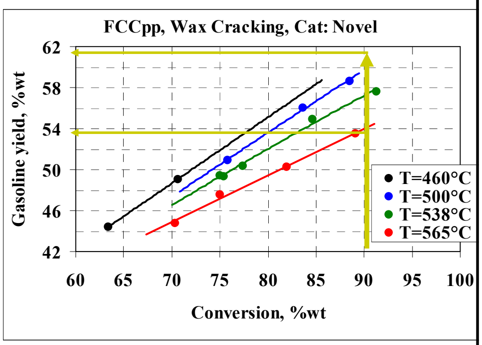
TEMPERATURE EFFECT ON CONVERSION/GASOLINE





- **Temperature has a very strong effect on wax conversion**

- **Gasoline yield is optimized at higher conversions and lower T**
- **Gasoline overcracking is not observed even at 90%wt conversion**
- **At 90%wt conversion, gasoline yield range 54-62 (%wt on feed)**

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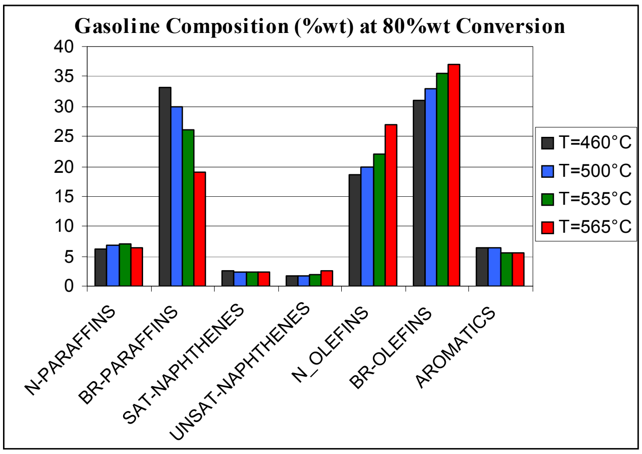
CAT NAPHTHA COMPOSITION VS. TEMPERATURE

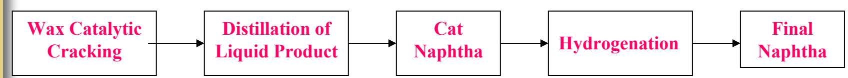


- **Gasoline quality significantly affected by T**
- **Cracking T affects strongly br-paraffins & n and br-Olefins**

NAPHTHA OLEFINS SATURATION

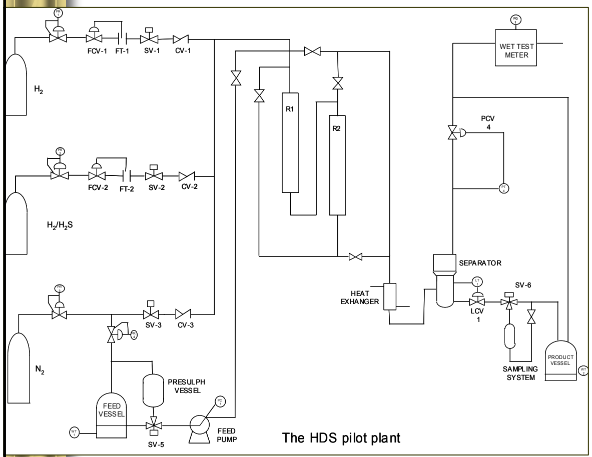
Scope: Upgrading the wax cat naphtha via a hydrogenation step in order to produce a naphtha fraction with more saturated components

Proposed technology:



Naphtha cuts	Naphtha-1	Naphtha-2
Cracking conditions	FCC-Y (T=1000°F)	ZSM-5 (T=1050°F)
Normal Paraffin	7.3	16.7
Iso Paraffin	23.2	9.4
Saturated Naphthene	2.8	2.1
Unsatur. Naphthene	2.5	4.6
Normal Olefins	21.1	19.5
Iso-Olefins	34.5	39.6
Aromatic	5.5	8.0

EXPERIMENTAL



The HDS pilot plant

Experimental Unit

- **Fully automated fixed bed pilot plant**

Catalyst

- **Commercial NiMo Catalyst**

Experimental Conditions

- **LHSV= 1-2 hr-1**
- **T=250-300°C**
- **P=25-40 bar**
- **H2/Nap.=1000-2000 SCFB**

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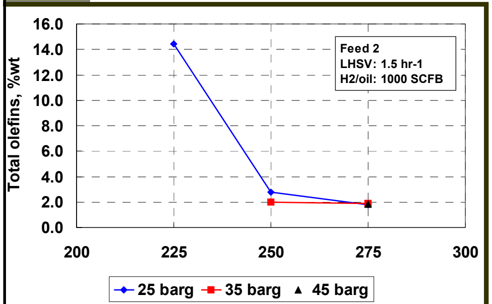
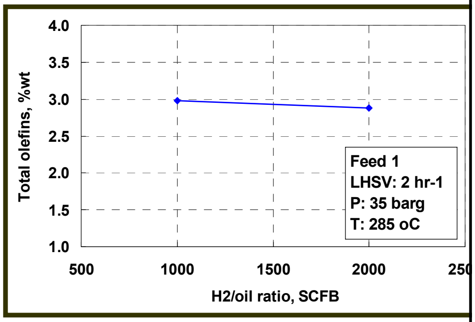
Olefin Saturation Experimental Results





- **For T>250°C no important effect of olefins saturation from P, LHSV, H2/Naphtha**

Naphtha cuts	Naphtha-1 Before	Naphtha-1 After
Normal Paraffin	7.3	26.4
Iso Paraffin	23.2	60.6
Sat. Naphthene	2.8	4.92
Uns. Naphthene	2.5	0.17
Normal Olefins	21.1	0.12
Iso-Olefins	34.5	2.8
Aromatic	5.5	5.0

Naphtha cuts	Naphtha-2 Before	Naphtha-2 After
Normal Paraffin	16.7	32.5
Iso Paraffin	9.4	46.7
Sat. Naphthene	2.1	9.4
Uns. Naphthene	4.6	0.29
Normal Olefins	19.5	0.3
Iso-Olefins	39.6	2.4
Aromatic	8.0	8.40

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CONCLUSIONS

- The catalytic cracking of wax favors gasoline (up to 60%wt) and LPG yield (up to 48%wt) while Diesel is less than 5%wt
- With an optimum selection of process conditions and catalysts the production of different products (gasoline, LPG olefins) can be maximized:
  - Using ZSM-5 additive and wax feed we can produce up to 20% C_3H_6
- Wax-gasoline composition can change dramatically by different cracking temperatures and catalysts (Aromatics< 8%wt in all cases)
- With an olefin saturation step of the Wax cracking naphtha
  - A minimum of T=250°C and P=25 bar is required in order to decrease both olefins (n and br-) at levels <3%wt
  - However, aromatics are not affected
- With a FCC step or an FCC/OS step we can produce from F-T wax different qualities of gasolines/naphthas with a wide range of HC composition
- In the EU project "OPTFUELS" we investigate other options for further upgrading F-T naphthas

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