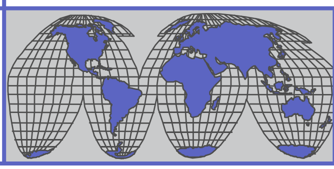
Development of a Solid Acid Catalyst Alkylation Process



AlkyClean®
Solid Acid Alkylation

October 6, 2006

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AlkyClean® solid acid alkylation

Presentation Outline

- Introduction
- Process Development
- Demonstration Unit
- Economic Benchmarking
- Summary

AlkyClean process for gasoline alkylate

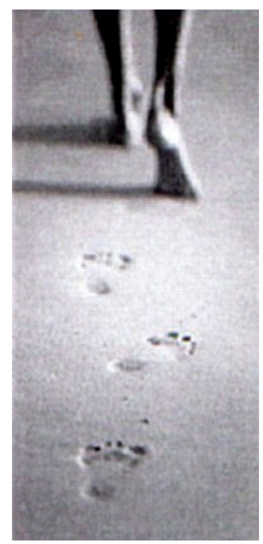
- Mandate: Cleaner fuels and "Greener" refining processes
- Answer: Alkylate = Clean Gasoline High RON & MON, virtually no olefins, aromatics or sulfur, low RVP
- Problem: Safety, environmental and reliability issues associated with current liquid acid technologies
- Challenge: Develop and demonstrate an environmentally friendly and competitive Solid Acid Catalyst (SAC) technology to replace HF and H_2SO_4 technologies

Alkylation processes

H_2SO_4 (Sulfuric acid)	HF (Hydrogen fluoride)	*AlkyClean* (Solid acid)

Liquid
80 kg/ton alkylate

Gas
4000 gram/ton alkylate



Solid
<400 gram/ton alkylate

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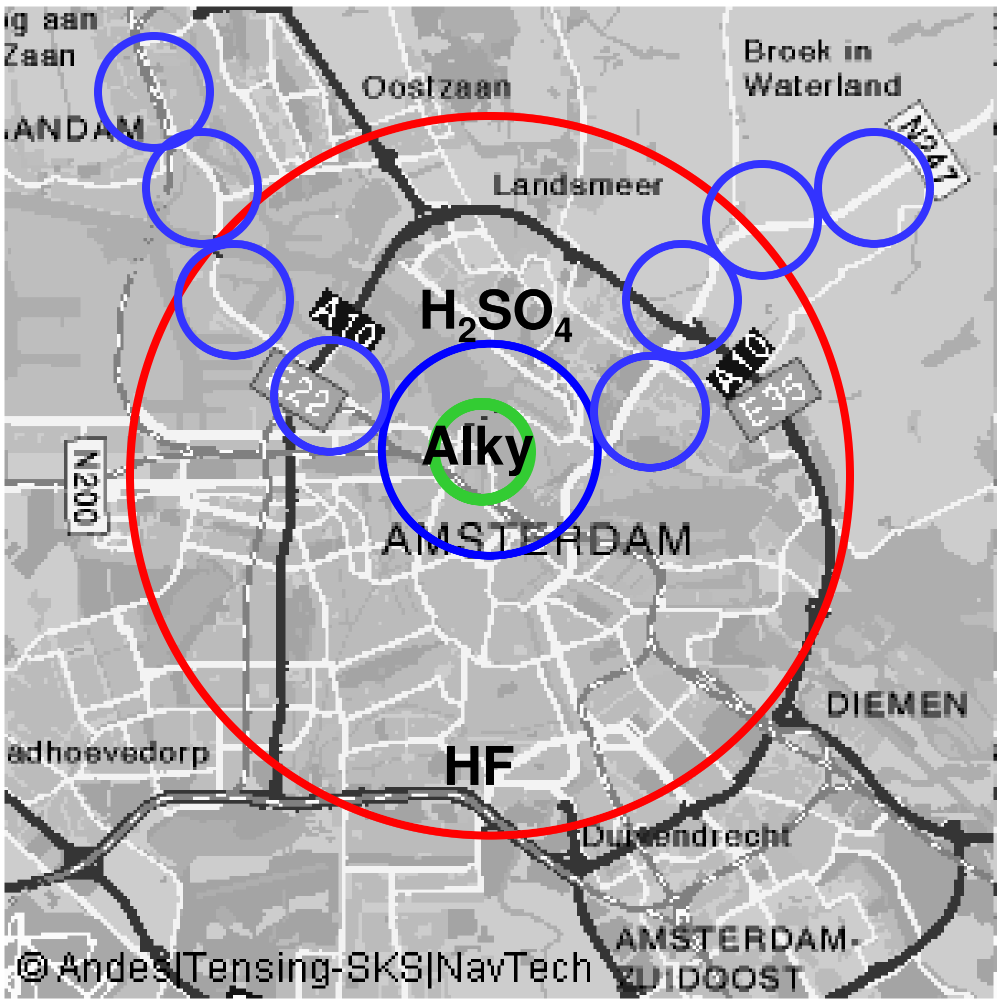
Localized risk during use

- Measured by risk analyses (experimental data and individual risk measurement)



Alkylation market drivers

- Economic driver – increases quantity of gasoline
- Environmental driver – high quality RFG blend stock
  - No olefins, aromatics, or S
  - Low volatility (“RVP”)
  - High octane, RON & MON
  - MTBE replacement

Gasoline alkylation

Butene + isobutane

(Often mixed olefin feeds)

↓

iso-octane

Gasoline alkylation chemistry

- Reaction of C_3-C_5 olefins with isobutane to produce primarily gasoline boiling range C_7-C_9 isoparaffins

- Primary reaction: $IC_4 + C_4= \rightarrow$ TMPs — Preferred– High Octane

- Secondary reactions yield: DMHs, C_5 - C_7s, C_9+ } Undesirable - Low Octane, High RVP or High B.P.

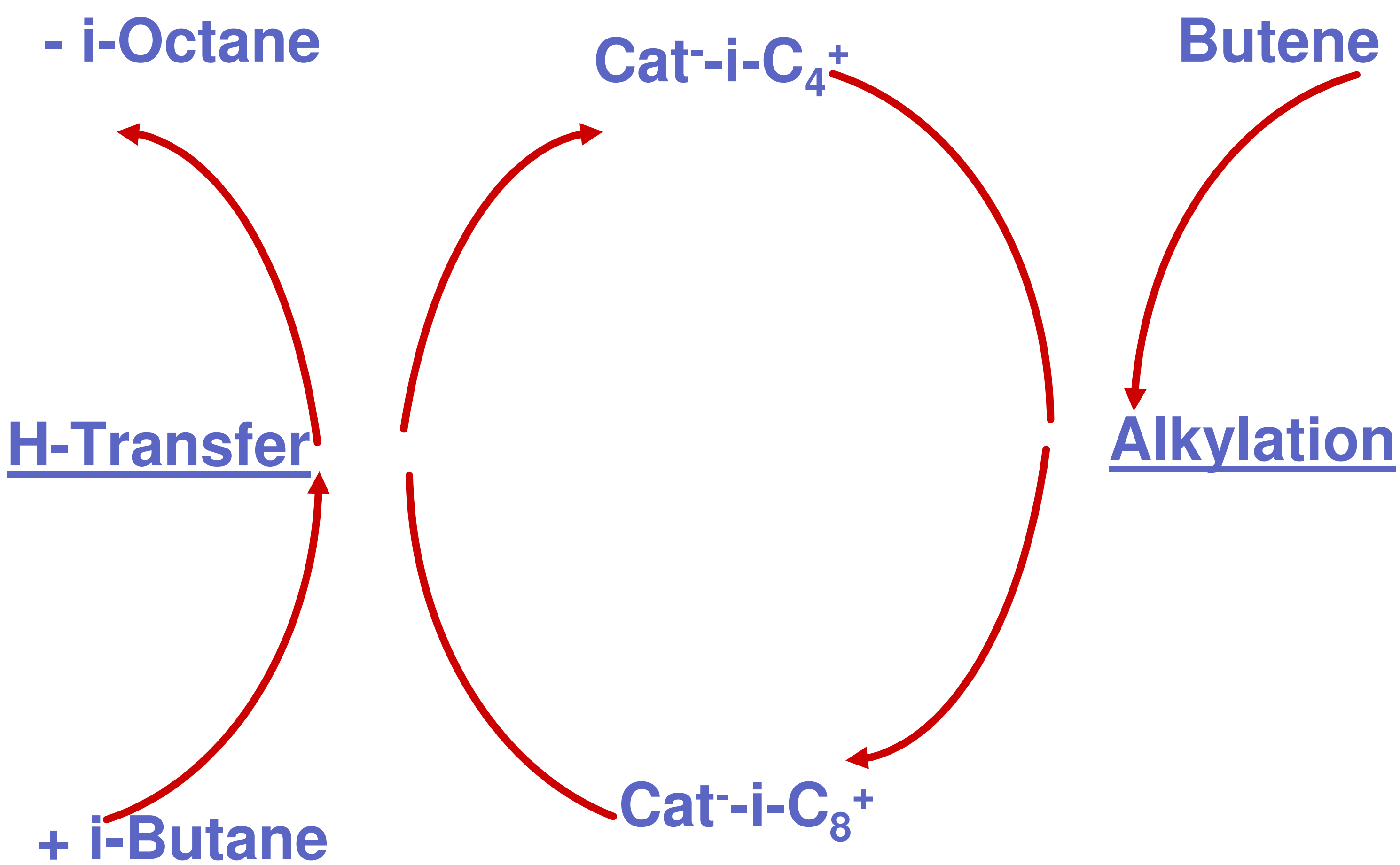
Selectivity to TMPs favored by:

- Higher isobutane/olefin (I/O) ratio at catalytic sites
- Higher hydrogen transfer rates (catalyst function)
- Lower reactor operating temperature

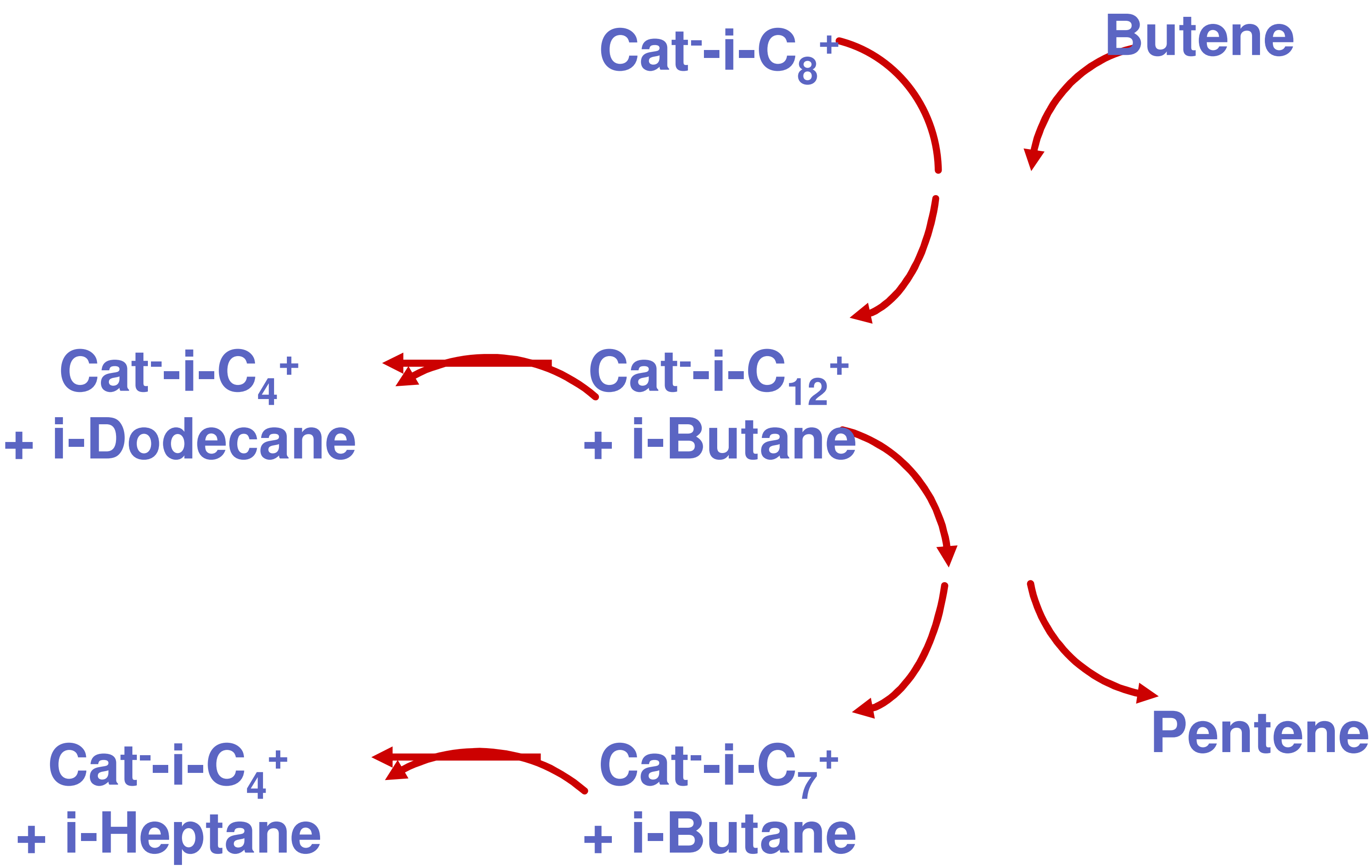
C_5+ alkylate from C_4 olefins:

- RON: 95-96 , MON: 92-94 , RVP: 4-5 psia

Alkylation cycle



Side reactions



Alkylates' role in clean gasoline

	Alky	FCC	Reformate	Poly
Aromatics	0	29	63	0
Olefins	0	29	1	95
Sulfur	~0	756	~0	~0
MON	92-94	81	87	82
RON	94-98	92	98	94

Octane yield comparison

Process	Yield Vol/Prod/Vol Olefin Used	RON Volume per Volume of Olefin Used	MON Volume per Volume of Olefin Used
Alkylation C_4=	1.7	163	158
Alkylation C_5=	1.8	163	160
MTBE	1.25	144	121
Dimerization	0.85	83	79
Cat. Poly.	0.8	78	66

AlkyClean catalyst

Features

- True solid acid: no halogens or volatile components
- Properties tailored to yield high quality alkylate, with maximized activity and stability
- Robust: low sensitivity towards feedstock composition variation and common impurities

Successful commercial scale-up

- Successful commercial trial production of the original catalyst in 2002 and of a new optimized version in 2004

Joint venture development progression

- ABB Lummus Global
  - Initiated R&D effort 1994
- ABB Lummus Global and Albemarle Catalysts
  - Cooperation since 1996
- Neste Oil
  - Joined the team in 2001 for technology demonstration

Development and demonstration status

- Bench scale development work completed
- *AlkyClean* catalyst manufactured at commercial scale
- Demonstration unit constructed and initially operated during 2002-2003, proving key technology aspects and process operability
- Further bench scale effort focused on improvement of catalyst/ process performance and resulting economics
- Successfully completed demonstration of these catalyst and processing improvements in 2004
- Technology offered for license beginning 2005
- Bench-scale work continues to expand data base and support next generation catalyst

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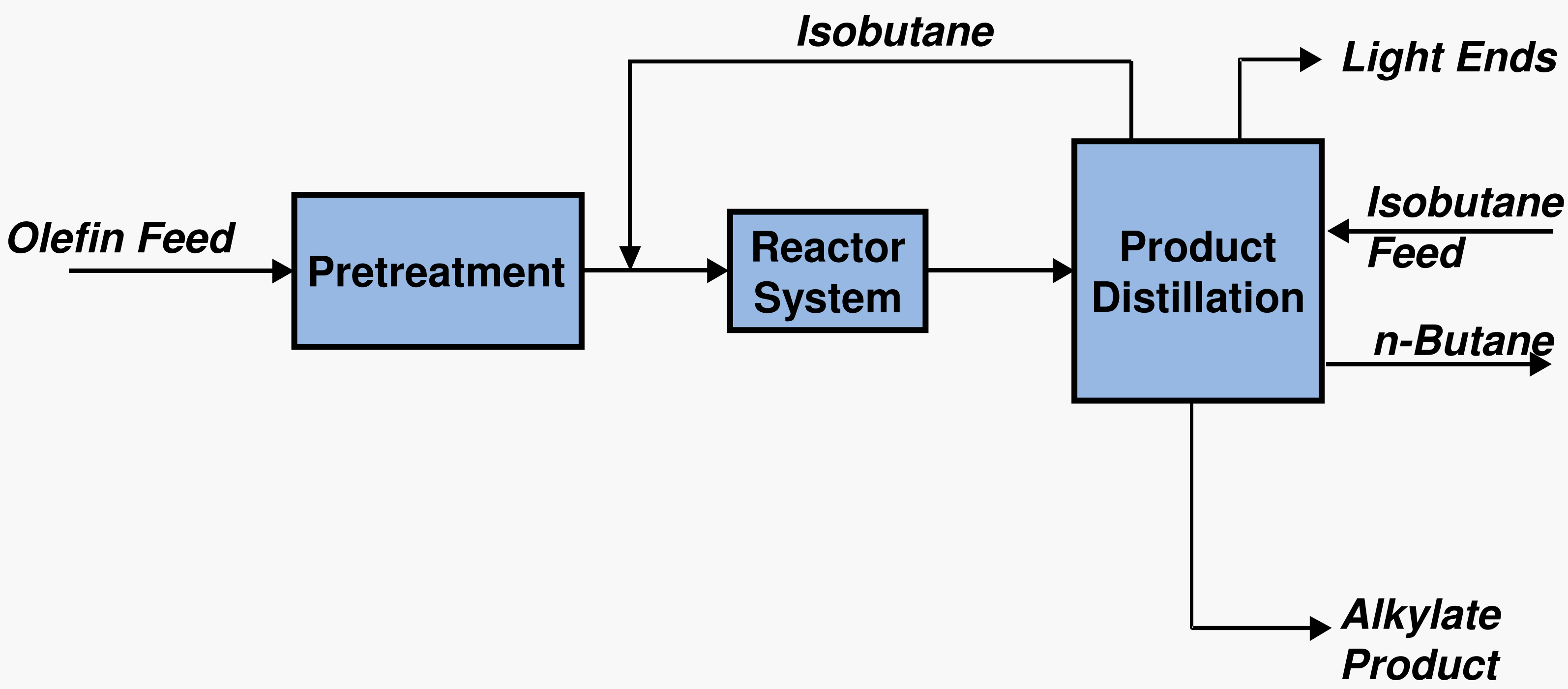
Simplified block flow diagram



Process Development

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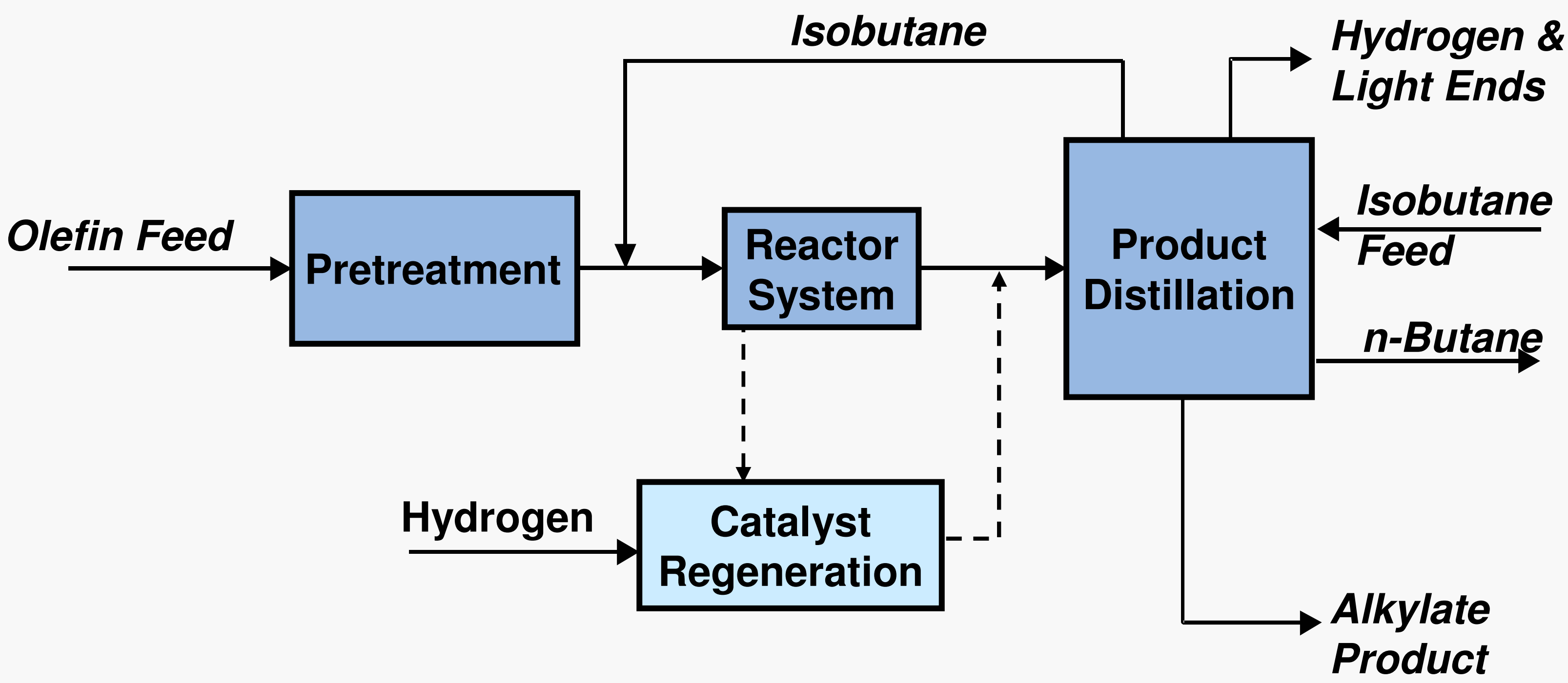

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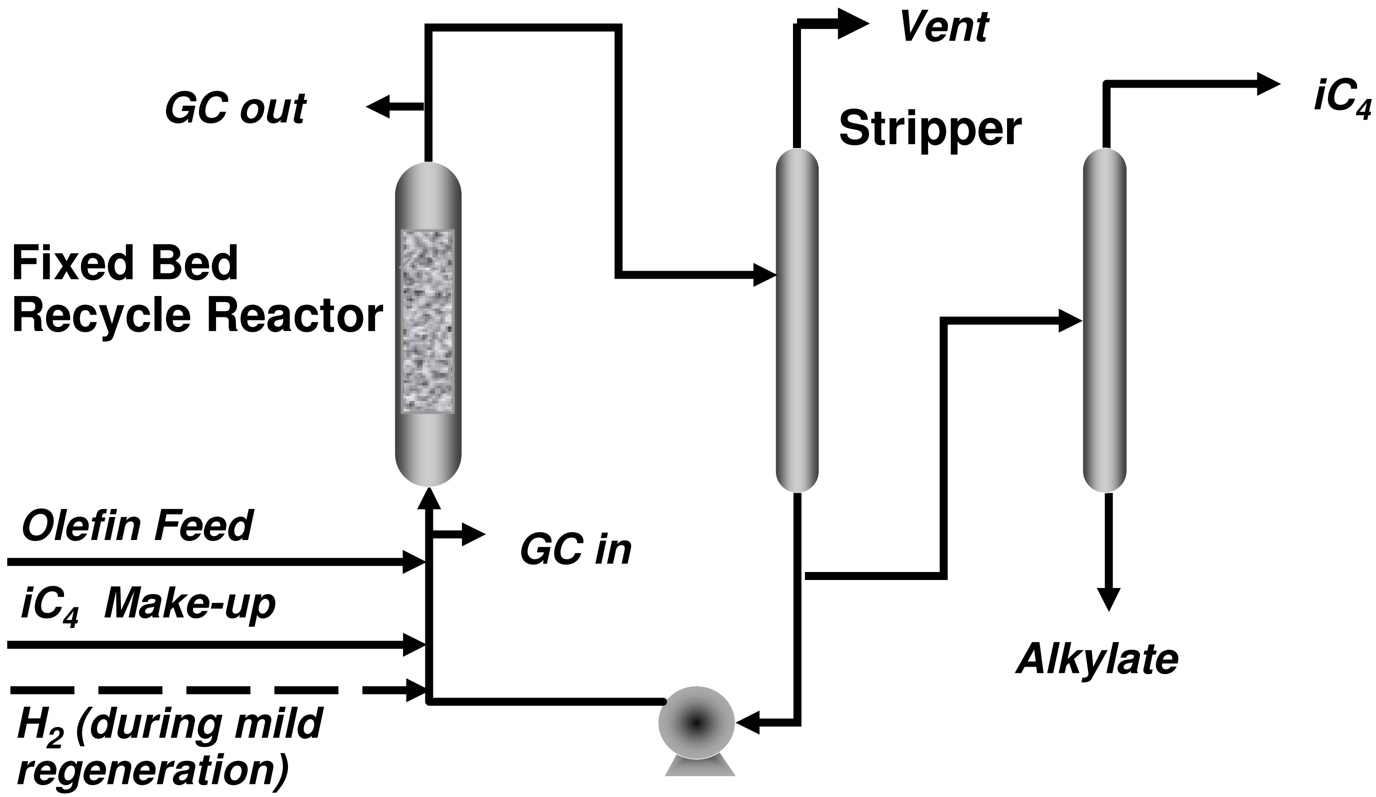
Bench scale development unit



Typical: External I/O of feed 5 to 30
At reactor inlet (internal I/O) 250 and higher
Liquid phase @ 21 barg, 50°C - 90° C

Process Development

Cyclic pilot unit in Amsterdam

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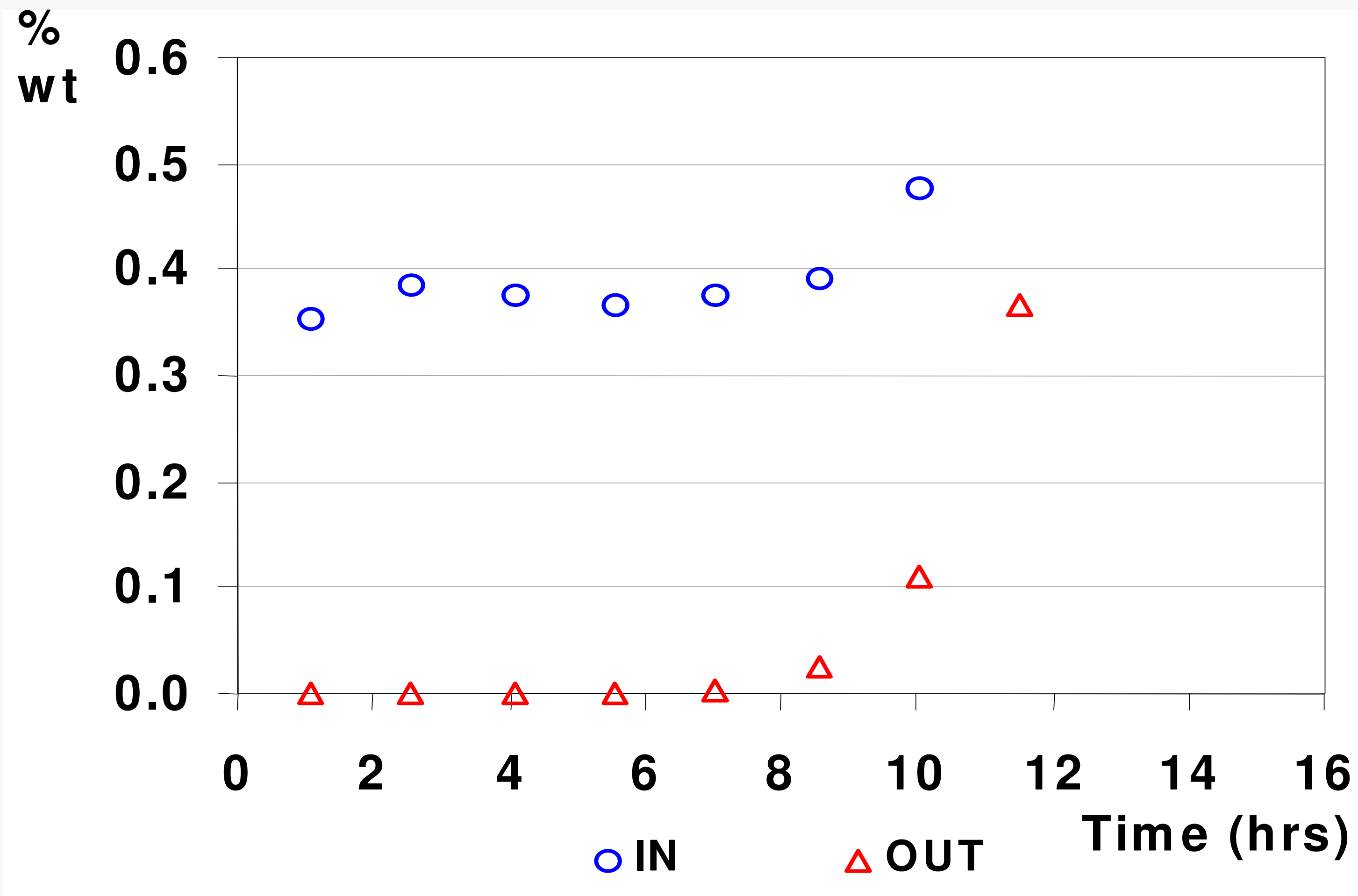
Process Development

Olefin concentration versus time



Process Development

Effect of regeneration procedure

Exp.	*Regenerant*	*T (°C)*	*P (bar)*	*Time (hr)*	*Cat. Life (hr)*
0	Fresh catalyst				10
1	H_2 gas	250	21	1	10
1a	H_2 gas	250	21	1	10
1b	H_2 gas	250	21	1	10
2	i-C_4 liquid with dissolved H_2	90	21	66	6.5
3	iC_4 liquid with dissolved H_2	115	30	18	4

NEW TITLE

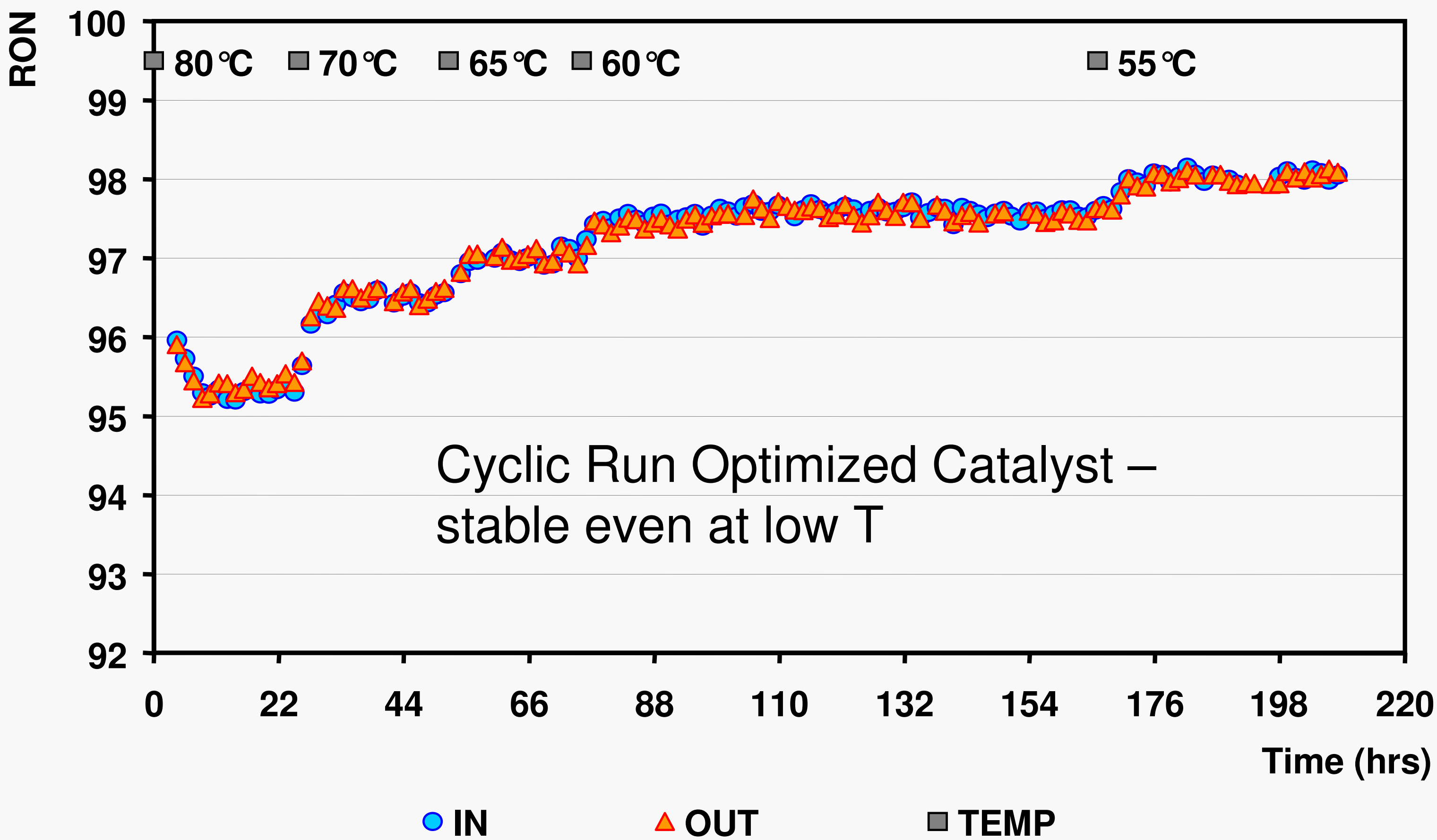
Conclusions – Regeneration after olefin breakthrough

- Regeneration at 250℃ in H_2 (gas phase) completely recovers activity and selectivity
- Regeneration with i-C_4 and dissolved H_2 (liquid phase) not successful

Next – Investigated short cycle mild regeneration

- Alternating periods of alkylation and liquid phase regeneration with i-C_4 and dissolved H_2
- Regeneration occurs prior to significant olefin breakthrough

RON versus temperature



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Process Development

Process key – cyclic reactor operation

Short cycle alkylation / mild regeneration

- Alternating periods of alkylation and liquid phase mild regeneration with i-C_4 and dissolved H_2
  - Seamless – no change in operating conditions; hydrogen injection substituted for olefin feed
  - Mild regeneration is pre-emptive – occurs prior to excessive deactivation and formation of ‘hard’ coke
  - Allows for continuous operation and maintenance of product quality
  - First patent granted in 1999 – US 5,986,158

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Process Development

High temperature regeneration (HTR)

- Gradual catalyst deactivation, over time under cyclic operation, necessitates off-line HTR
- HTR: hot hydrogen strip at 250°C – completely recovers activity and selectivity
  - HTR undertaken before formation of hardest coke species (e.g. high MW condensed cyclics), which would require oxidative 'burn-off'
- Required HTR frequency 4-30 days depending on operating severity
- Effectiveness of HTR to fully restore activity proven over > 6 months of operation

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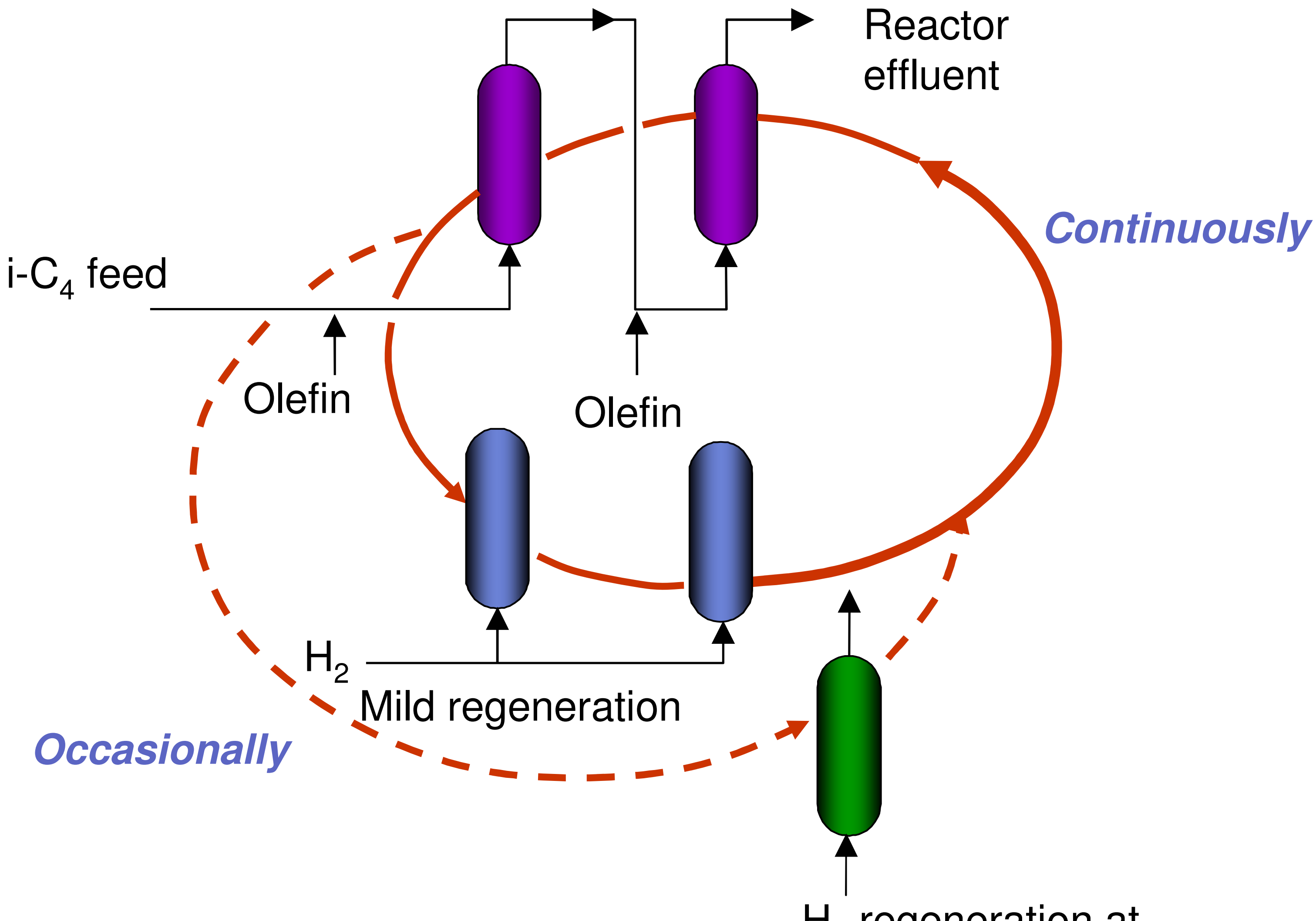
Process Development

AlkyClean reactor scheme



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Operating conditions comparison

	AlkyClean	***H_2SO_4***	***HF***
Operating Temp.	50-90°C	4-10°C	32-38°C
Feed I/O (External)	8-15/1	8-10/1	12-15/1

Process Development

Olefin variation sensitivity

Octane debit relative to 100% 2-butene

	AlkyClean	*H_2SO_4*	*HF*
1-butene	-	-	Up to - 4.0 RON
Isobutene (25 vol%)	- 0.5 RON	- 1.0 RON	- 0.5 RON
Propylene (30 vol %)	- 1.0 RON	- 1.5 RON	- 1.0 RON

Results of feedstock impurity testing

- Water saturated feed gave the same results as dry feed
- After spiking total reactor feed with:
  600 ppmw DME,
  200 ppmw CH_3SH,
  1200 ppmw H_2S
  1800 ppmw butadiene
  (each separately)
- Any activity loss could be recovered by high temperature regeneration with H_2 at 250℃

Process Development

Catalyst testing results

- Sensitivity to olefin composition (C_3=, n-C_4=, i-C_4=) variation is relatively low compared to HF/H_2SO_4
- Exposure to high levels of typical feed impurities (H_2O, oxygenates, sulfur compounds, butadiene) does not cause irreversible deactivation
- Commercial feeds can be converted with good activity, selectivity and stability, yielding high quality product with no co-production of an ASO (heavy hydrocarbon bleed stream) without “clean up” facilities

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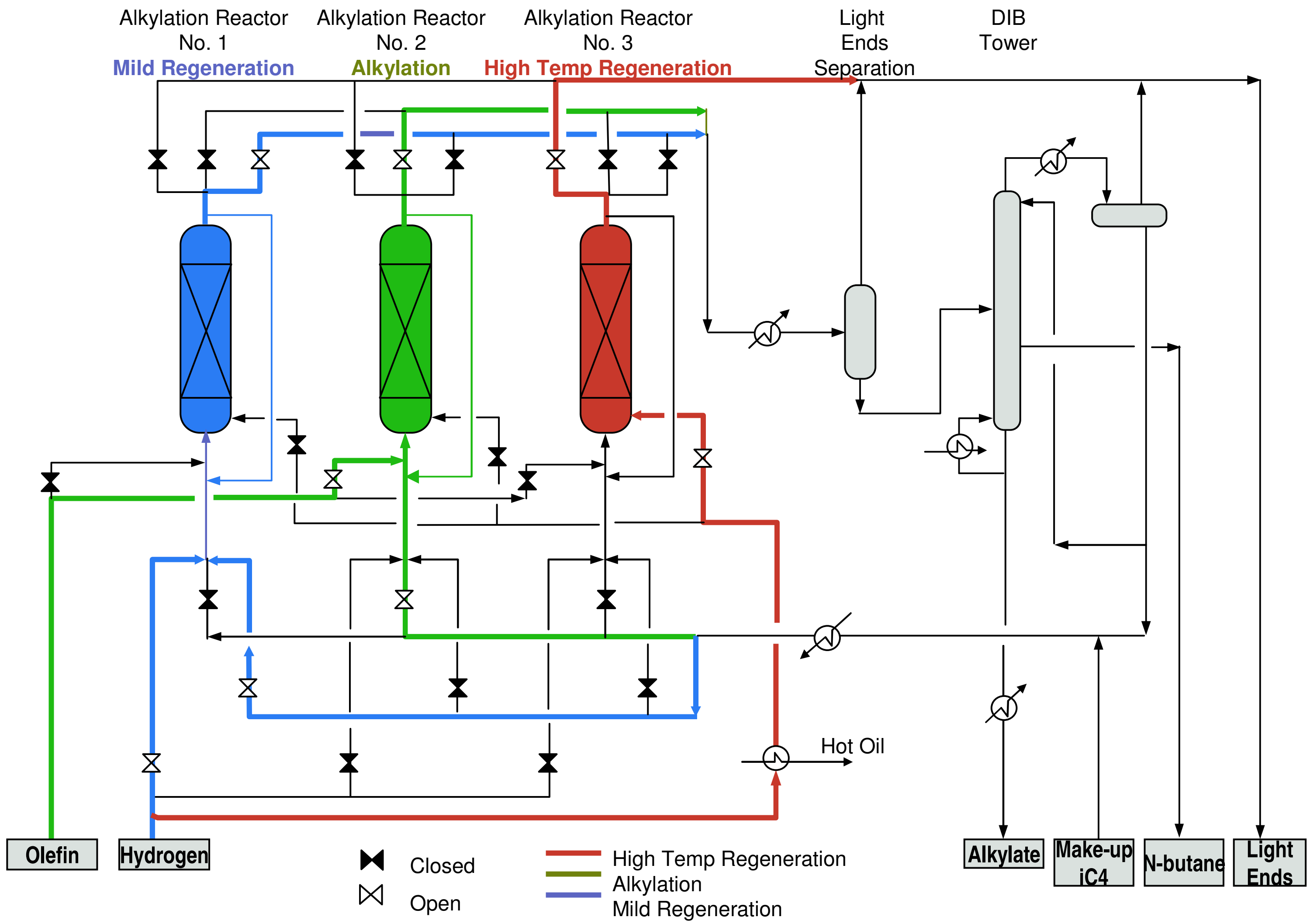
Demonstration Unit

AlkyClean demonstration unit

- Neste Oil joined team in early 2001 for technology demonstration
- ABB Lummus Global's basic engineering completed 2001
- Demonstration unit construction completed in 2002; operates at Neste facilities in Porvoo, Finland with actual refinery feed streams; 10 BPD production capacity
- Contains all key elements and is analogous to commercial design
- Allows for proving operability, confirmation of design parameters and reliable scale-up

Flow schematic



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Demonstration Unit

Outside view

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Reactor section

Reactor lower section

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Demonstration Unit

AlkyClean demonstration unit

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Demonstration Unit

Operation summary

- Unit reliably operated for over two years utilizing refinery slipstreams, both C_4 and C_3/C_4 mixed olefins
- Alkylate quality comparable to Porvoo HF unit
- Key technology aspects proven
  - Operated continuously with multiple high temperature regenerations
  - Catalyst activity recovered consistently
- Performance data obtained over a wide range of conditions
  - Support correlations/modeling effort and economic benchmarking
  - Some surprises, leading to insights and opportunities for catalyst/process optimization
- Absolutely no fouling, plugging, corrosion, erosion or degradation to the plant over the years of operation

Demonstration Unit

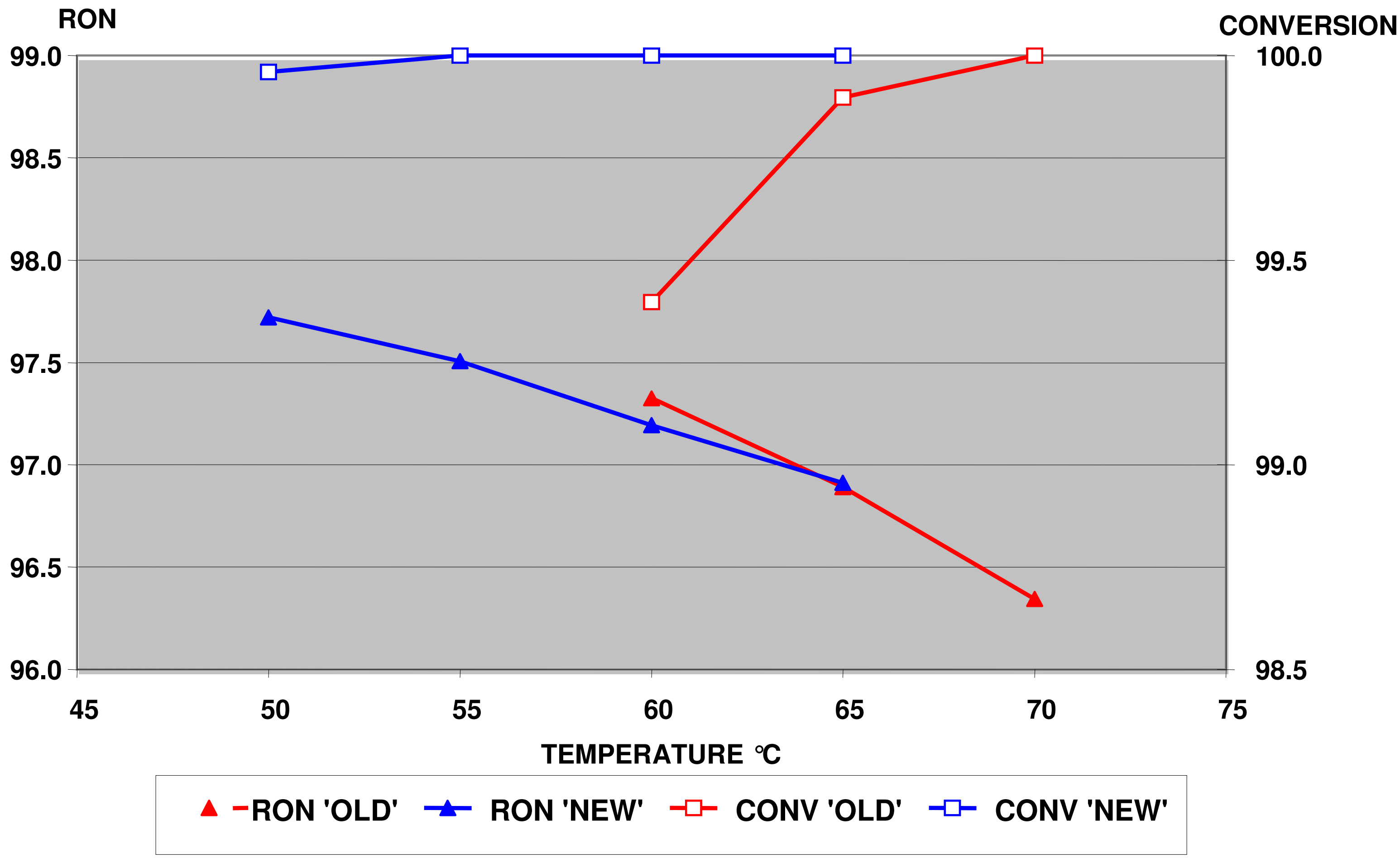
Recent operations

- In April 2004 second generation of catalyst tested:
  - Successful bench scale catalyst / processing optimization effort
  - As with the first generation, commercial trial manufacture of the new improved catalyst
  - Demo unit modifications incorporated operational improvements
- Demonstration operated successfully for another six months
  - Benefits of operational improvements confirmed
  - Improved catalyst activity and stability confirmed
- Established excellent correlation between this unit and the bench scale unit
- Demonstration unit available for client feedstock testing
- Bench scale unit continues to operate for parametric optimization

Demonstration Unit

Catalyst – second generation

Performance of “old" and “new" commercial-plant-produced catalyst



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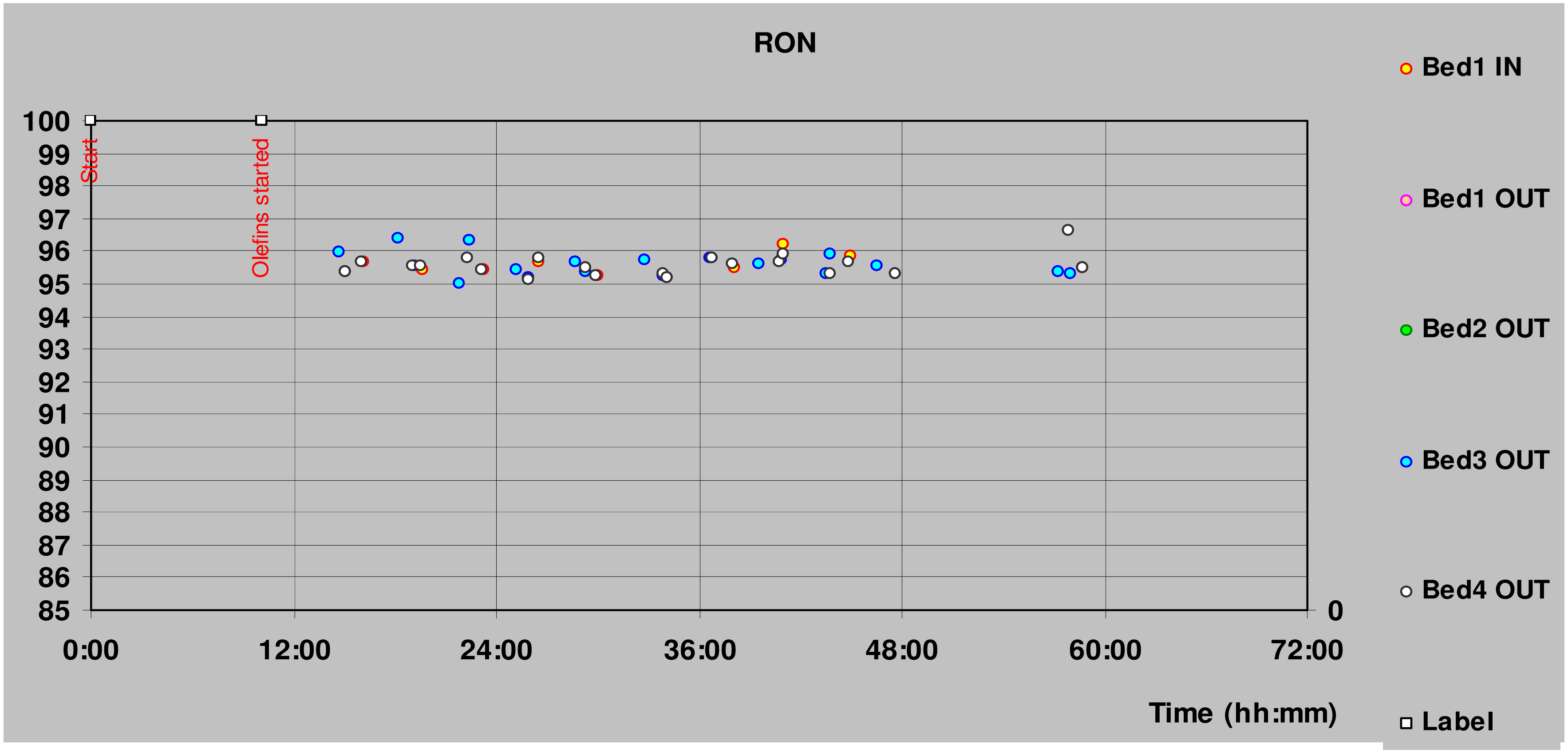
Demonstration Unit

Performance processing refinery C_4 olefins



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Demonstration Unit

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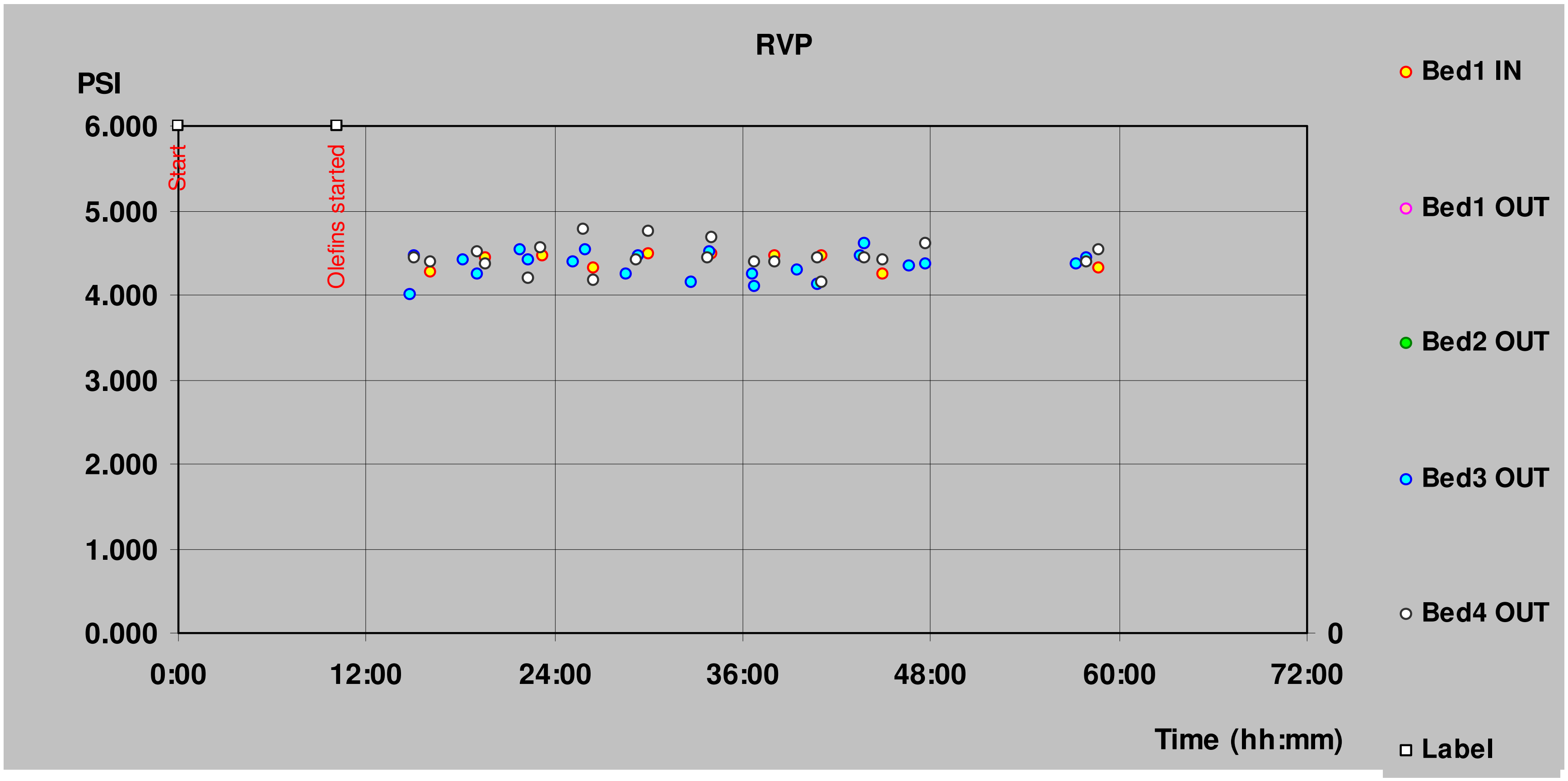

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Demonstration Unit

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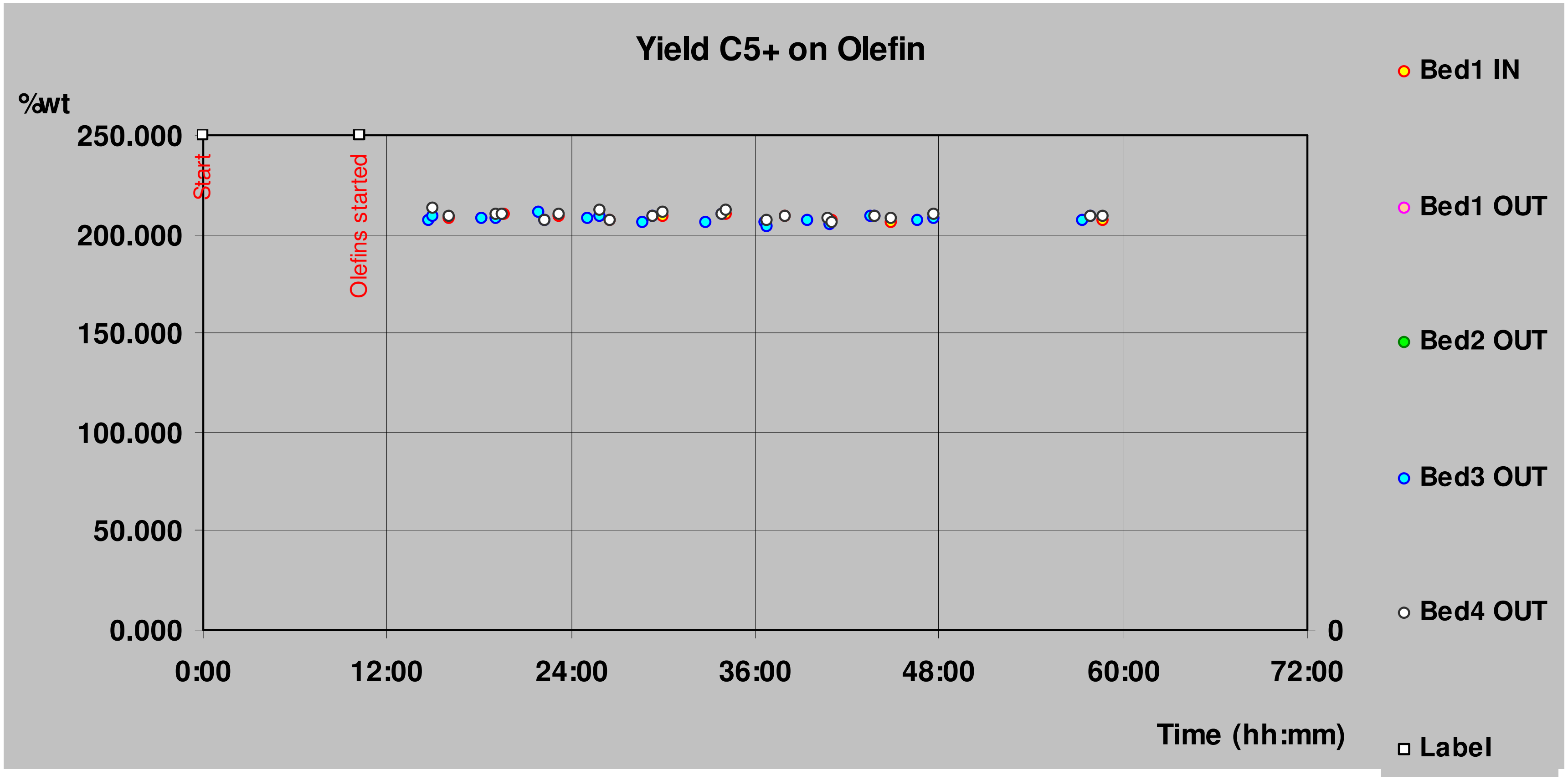

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Design feed composition

FCC C_4s

Component	wt %
Propane	1.09
Propylene	0.52
Isobutane	33.08
n-Butane	10.65
i-Butene	15.32
1-Butene	11.66
2-Butene	27.08
Butadiene	0.10
Pentanes	0.38
Amylenes	0.12
Total	100.00

Comparative economics

	AlkyClean	H_2SO_4
Alkylate Capacity, BPSD	10,000	10,000
Alkylate RON	95.0 - 96.0	95.0 - 96.0
Estimated ISBL TIC, U.S $ M	31.0	36.5
Production Costs, $/Bbl		
Variable Costs (Feeds – by-products + Cat./Chem. + Utilities)	21.74 - 22.24	20.82
Fixed Costs (Labor+Maintenance+Ovhd. +Insurance+Misc. Indirects)	1.90	2.05
Capital Costs (Depreciation+Return on Capital)	4.85	5.71
Total Production Cost	28.49 - 28.99	28.58

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Summary

Benefits of the *AlkyClean* process

- True solid acid catalyst eliminates the hazards associated with liquid acids
- Low emissions / environmental impact
- No production of acid soluble oil (ASO)
- No product post treatment needed
- No refrigeration or alloy construction; common refinery equipment, non-corrosive/erosive
- Reduced maintenance and manpower
- Lower sensitivity towards olefin feed composition
- Robust with respect to key impurities
- Competitive economics with comparable alkylate quality

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Summary

In conclusion

The AlkyClean process

- Offers significant environmental and operational benefits relative to existing liquid acid technologies at a competitive cost

- FYI… Wall Street Journal Europe Innovation Award 2002

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