1-Octene from Butadiene

New Technology Based on Heterogeneous Catalysis

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Outline

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- **Current technology options**
- **Background**
- **Results**
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  - **Hydrogenation**
  - **Cracking**
  - **Process scheme**
- **Conclusions**

Why?

- **Low flexibility of LAO technologies**
- **Tight 1-hexene/1-octene comonomers market. Annual growth 5+%**
- **Develop an on-purpose C8-1 technology**
- **Add value to C4 streams from steam crackers**

Current 1-Octene Manufacturing Options

- **LAO by ethylene oligomerization**
  - BP, CPC, Shell, Axens, Idemitsu, Sabic
- **Fischer-Tropsch synthesis** (Sasol)
- **On-purpose technologies**
  - Commercial – CPC (C2= to 1-hexene)
  - Pre-commercial
    - BP, Sasol – (C2= to 1-octene)
    - Dow, Oxeno, Kuraray, Shell – (BD to 1-octene)
    - ABB (C4s= to 1-hexene)

On-purpose 1-Octene, BD Route

1. Telomerization
Butadiene + Methanol
→ Octadienyl ether

C-O-C-C=C-C-C-C-C=C

2. Hydrogenation
Octadienyl ether + H2→
Octyl ether

C-O-C-C-C-C-C-C-C-C

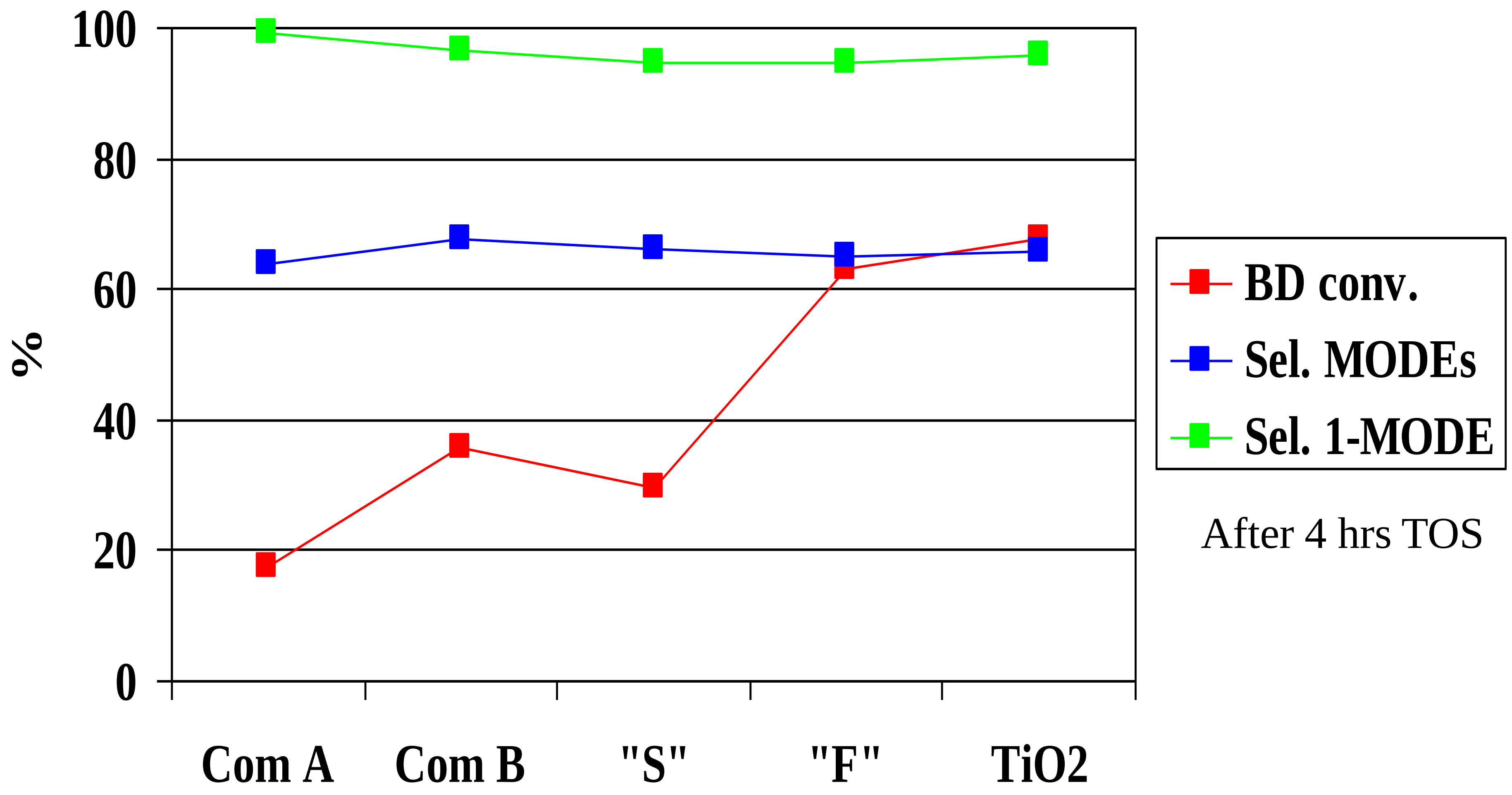
3. Cracking
Octyl ether →
1-octene + methanol

C=C-C-C-C-C-C-C + CH3OH

Challenges

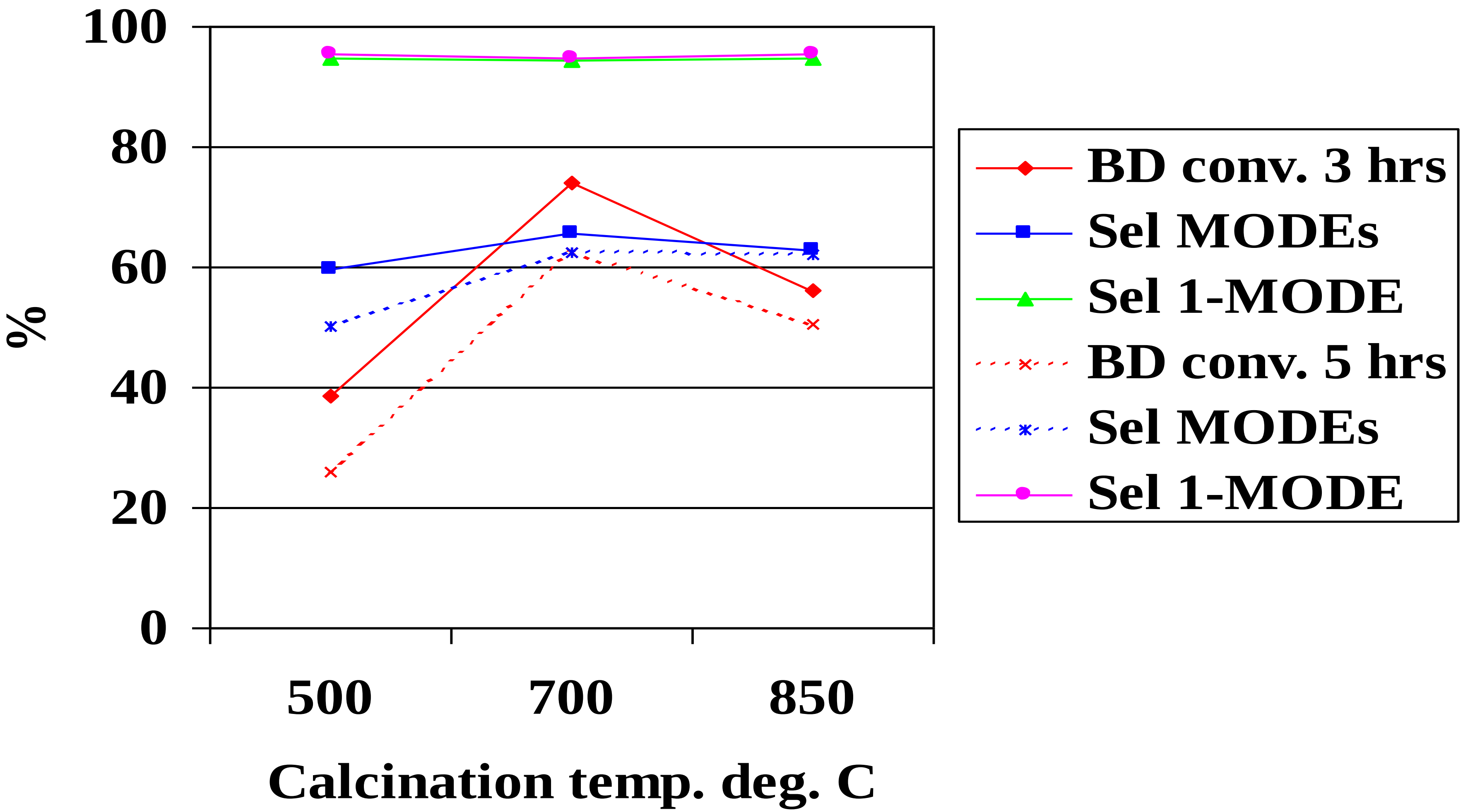
- **Process economics**
  - **Simplicity**
  - **No solvents, minimum recycling**
- **Catalyst development for each process step**
  - **Selectivity**
  - **Life-time**
- **Process integration**

Telomerization
Effect of Support

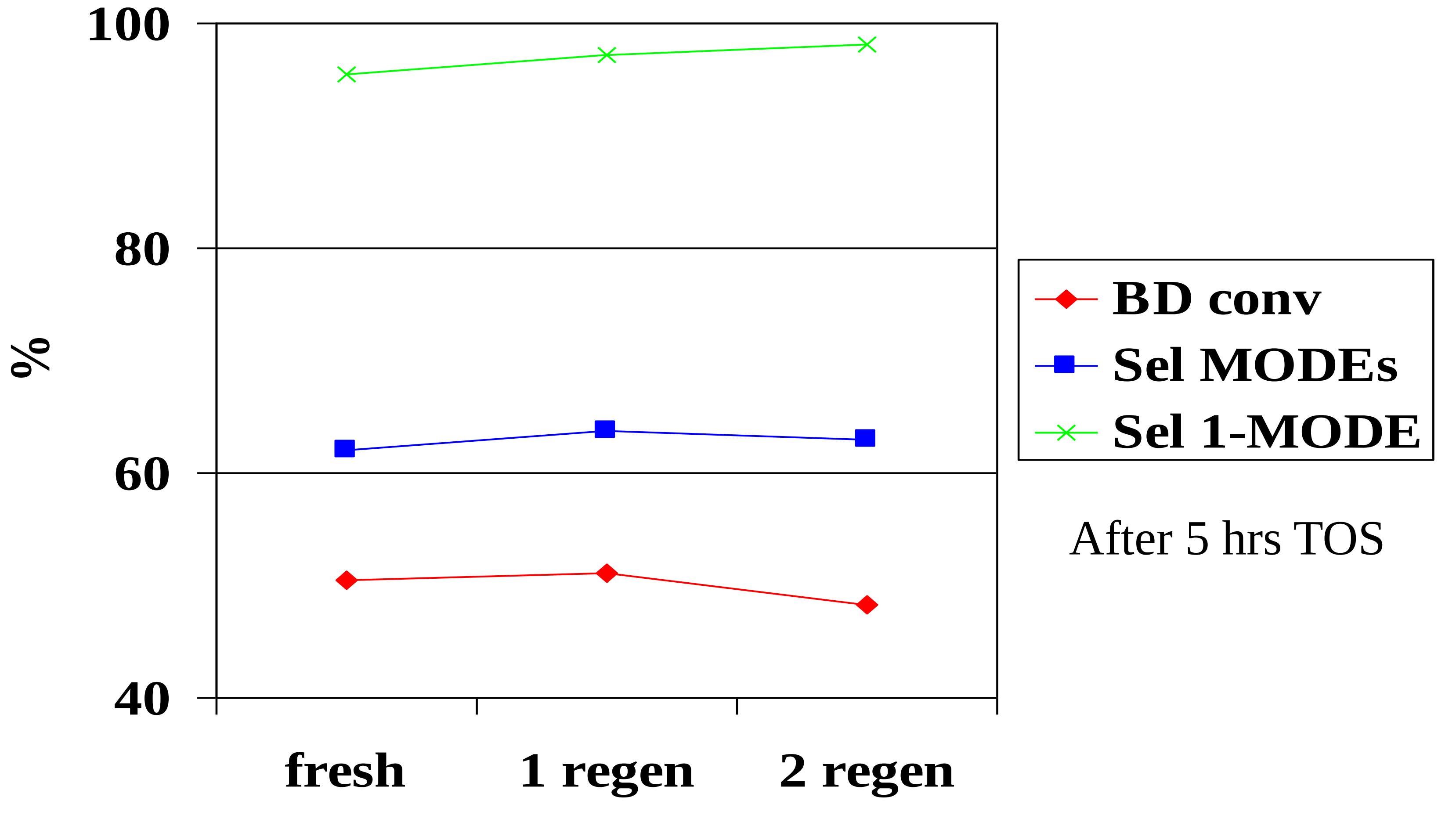


After 4 hrs TOS

Telomerization
Effect of Catalyst Calcination

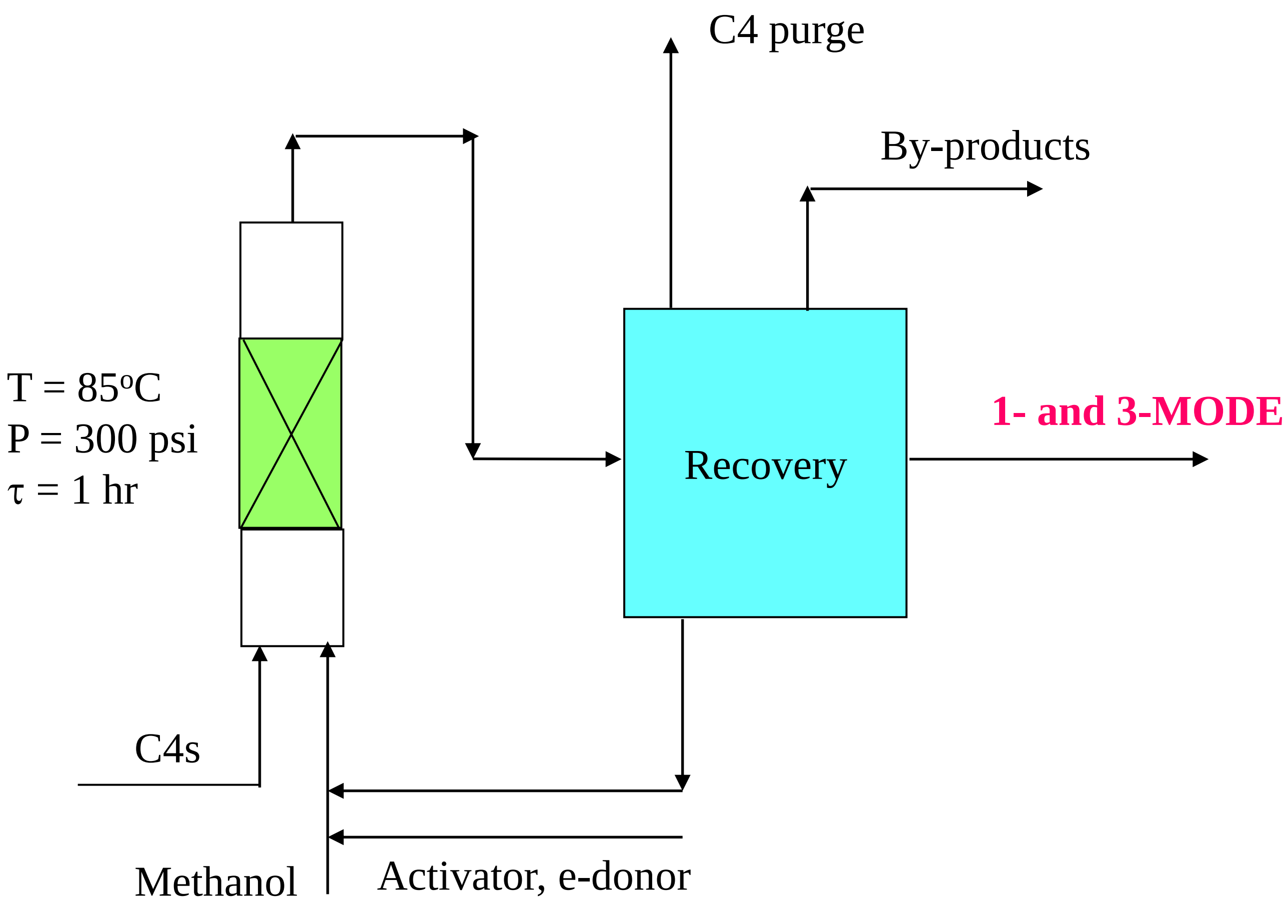


Telomerization
Effect of Catalyst Regeneration



After 5 hrs TOS

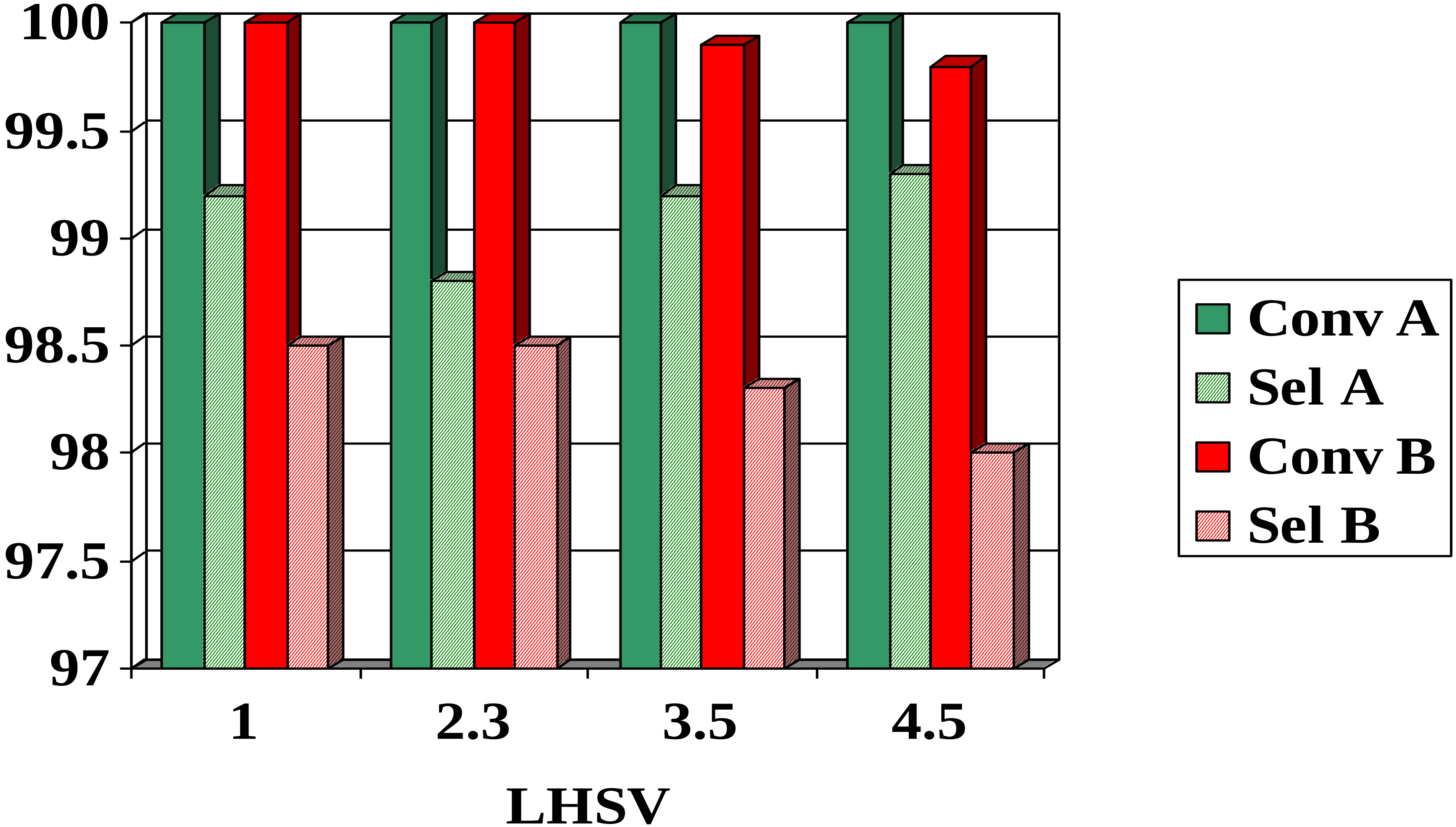
Telomerization



Telomerization - Conclusions

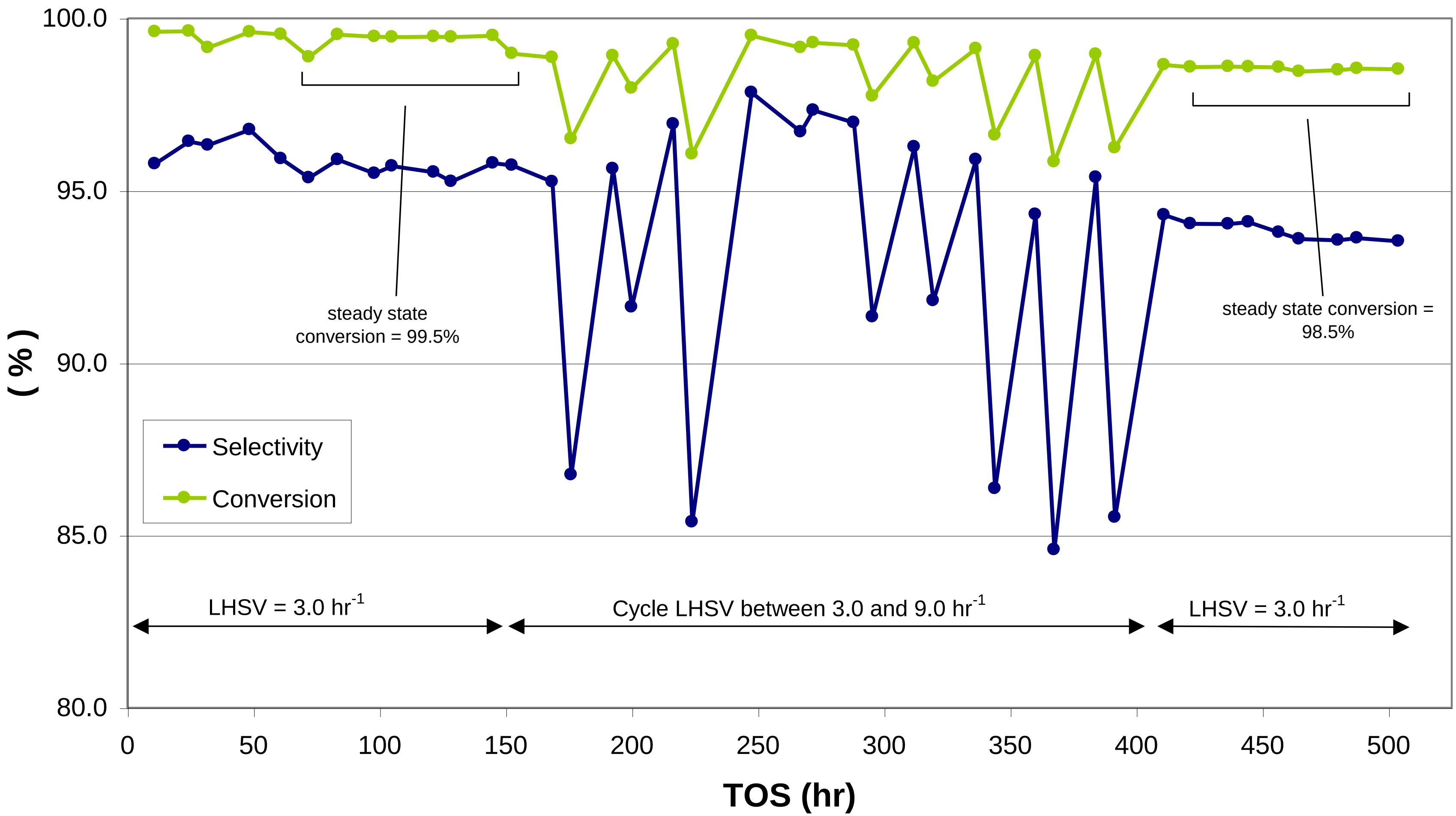
- **Telomerization of butadiene with methanol is possible over solid catalysts containing Palladium in ionic state**
- **Catalysts are stable and could be regenerated**
- **Large catalyst surface area and the exposure of Pd ions allow to achieve high butadiene conversion in relatively short residence time**
- **Product spectrum is similar to the products from a homogeneous reaction systems**
- **Commercial catalysts containing Pd in reduced form are not active in the telomerization**

Hydrogenation
Selection of Ni Based Catalyst



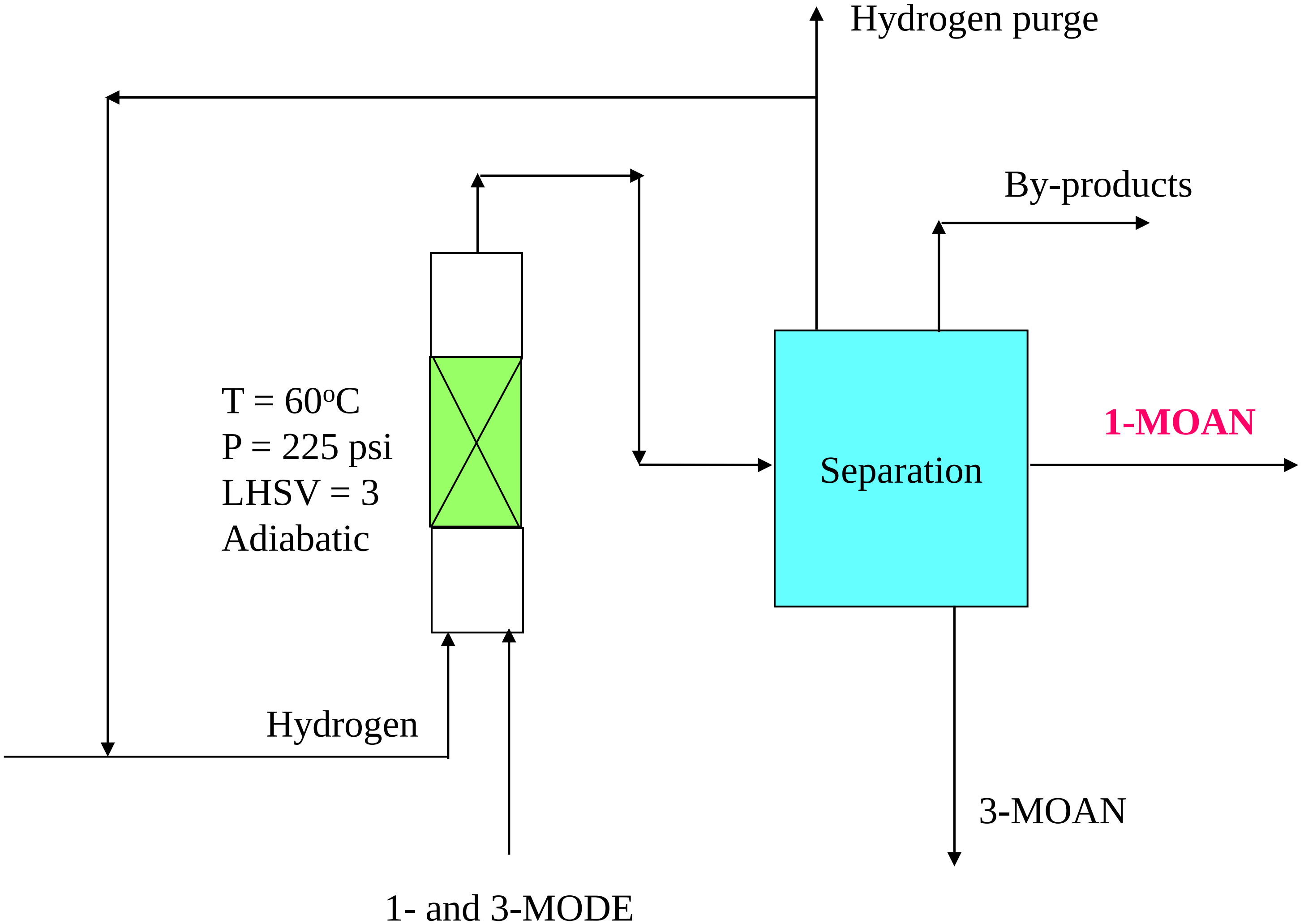
(Adiabatic reactor, CHX – diluent, T = 60^{o}C, p = 225 psi)

Ni Catalyst Accelerated Ageing



(Adiabatic reactor, MOAN – diluent, T = 60°C, p = 225 psi)

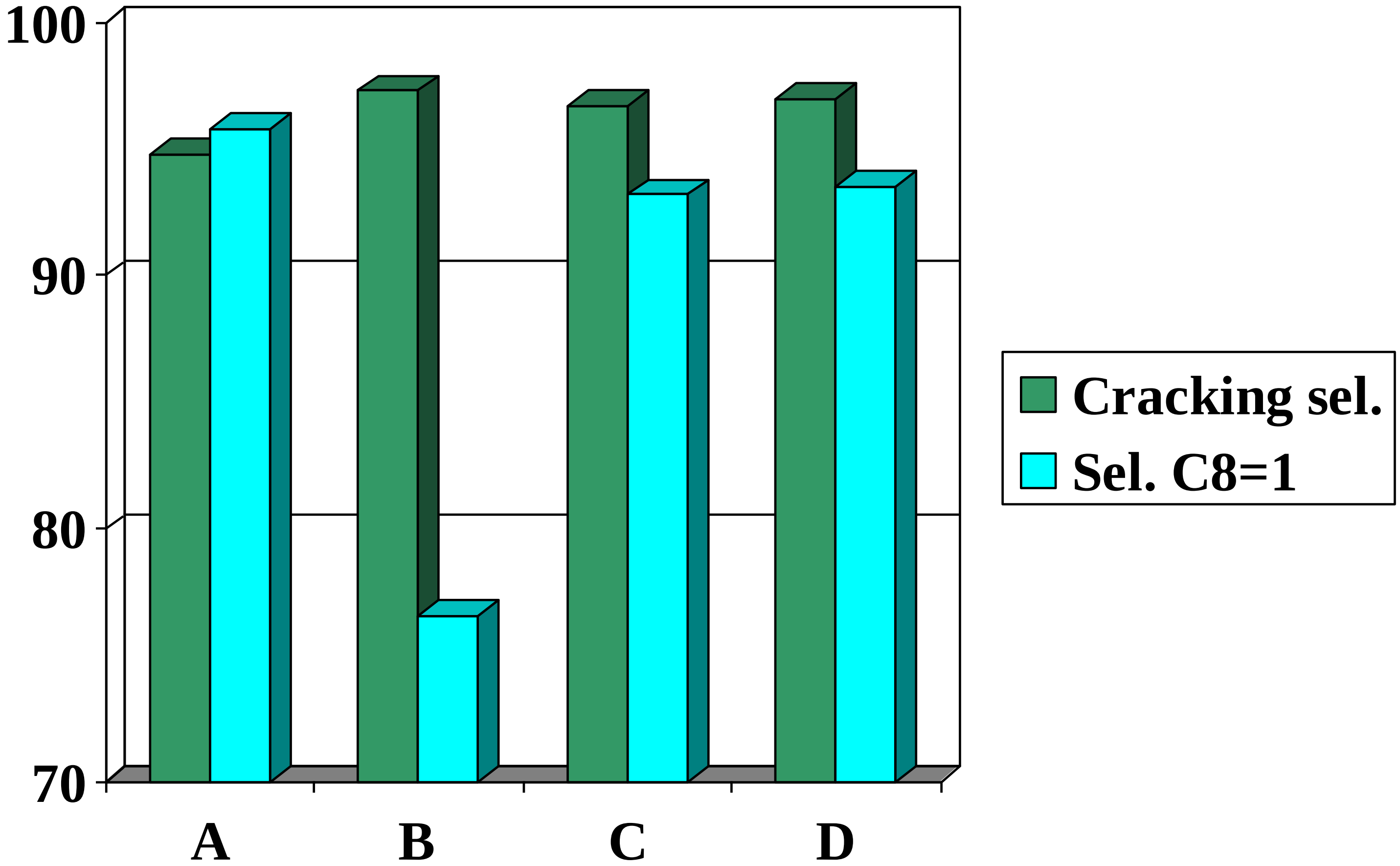
Hydrogenation



Hydrogenation - Conclusions

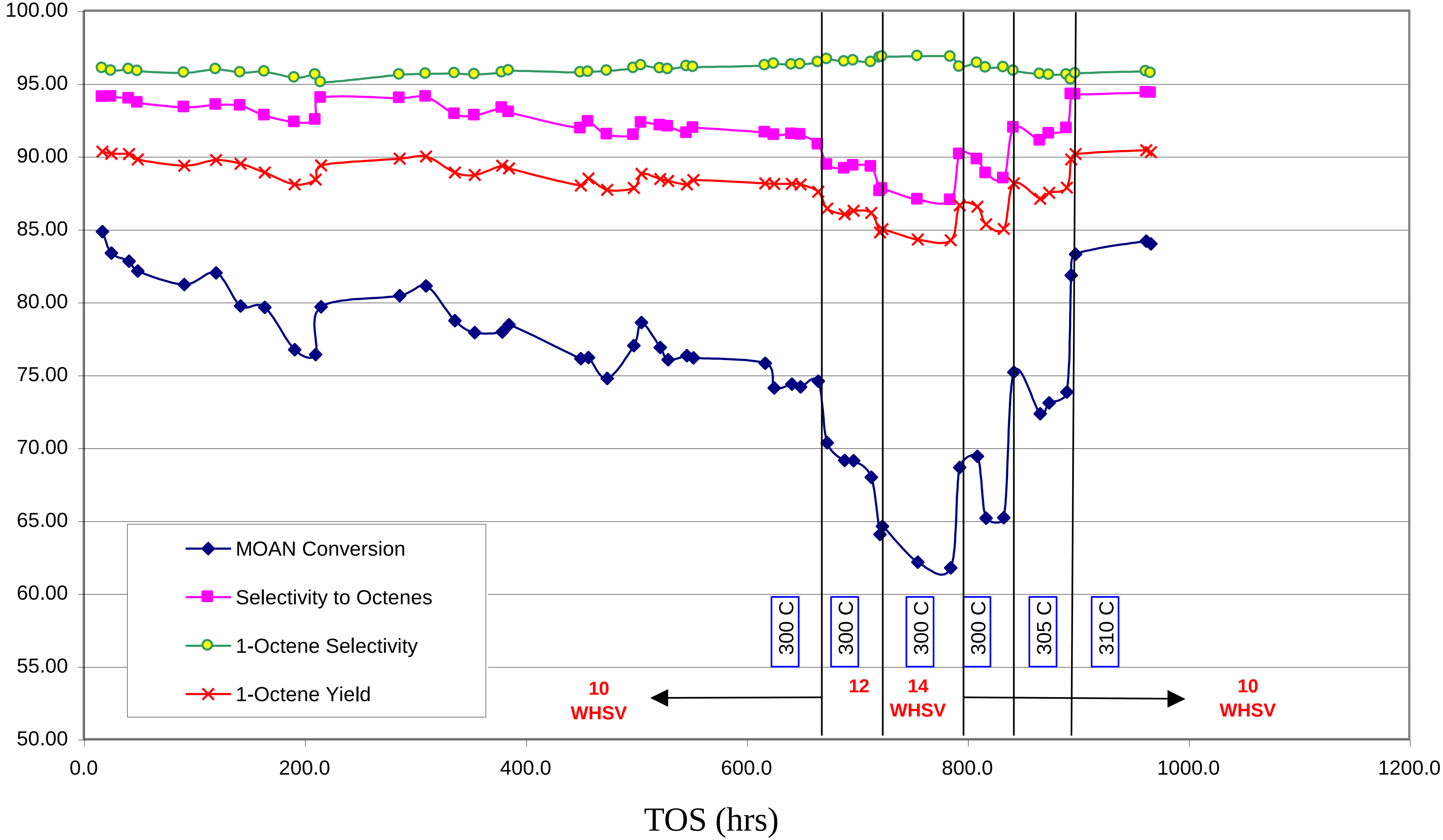
- **Hydrogenation of methoxy octadiene occurs readily over Ni containing commercial catalysts**
- **Ni containing catalysts maintain activity and selectivity over long period of time**
- **Hydrogenation takes place under relatively mild conditions in an adiabatic reactor system**
- **Separation of methoxy ethers after the hydrogenation step is easier (larger differences in boiling points)**

MOAN Cracking

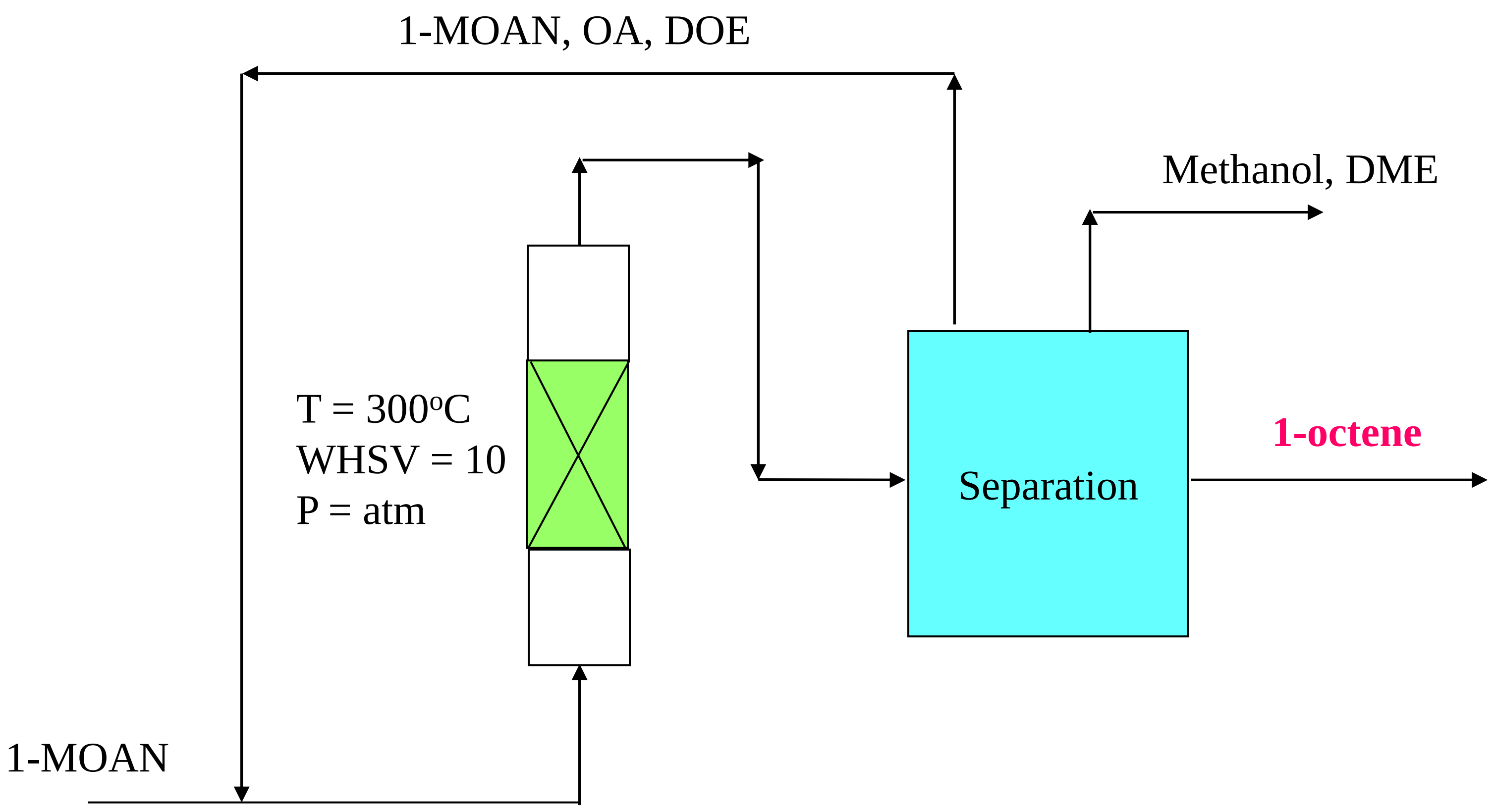


(T = 300°C, WHSV = 10, TOS = 7 hrs)

Cracking Catalyst Ageing Test



Cracking


1-MOAN, OA, DOE
Methanol, DME
T = 300°C
WHSV = 10
P = atm
Separation
1-octene
1-MOAN

Cracking - Conclusions

- **The 1-methoxy-octane cracking step has been a major challenge regarding the selection of the best alumina catalyst**
- **Commercial large pore alumina is the catalyst of choice**
- **Catalyst selectivity to 1-octene is above 95%**
- **Selected catalyst maintains its catalytic properties over long period of time**

Conclusions

- **Butadiene from the C4 fraction could be transformed into 1-octene with relatively high conversion and selectivity using solid catalyst only**
- **Corresponding selectivities of the three consecutive process steps are: 62%, 99% and 95+%**
- **Use of heterogeneous catalysts makes the process simpler and more cost effective**
- **Need for solvents, catalyst recovery, and complex separation sections were eliminated**