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What progress in catalyst deactivation?

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Contents

- **Revisit some conclusions from Eurokin 2004 survey on 'Measurement and modelling of deactivation kinetics' and 2008 update at Eurokin Lyon meeting.** **Birtill (2004, 2007)**

- **Literature search from 2008-2018:** **'Catalyst' + 'Deactivation' : 11,453 references**

  'Catalyst + Deactivation + Model' : 1900 references

- **Many more references from other searches, citations, etc. Too many for comprehensive review.**

- **Focus in this talk on** **Test methods for catalyst deactivation under normal conditions.**

  Fitting simple models to test data.

  Accelerated decay.

- **Brief attention if time to**

  Monitoring the working catalyst.

  Insight into catalyst deactivation kinetics from mechanistic studies.

  Advances in reducing catalyst deactivation.

Selected lessons from Eurokin 2004 survey and 2008 update

- Empirical deactivation kinetics is usually adequate to make progress in early stage catalyst development and process design.
- Fundamental mechanistic models (‘coking’, sintering, etc.) need wide range of reaction and decay data and plausible relationship with activity. Too much time and effort for most practical purposes.
- Check for presence of axial decay gradient in fixed-bed reactor

  \- too easy to fit misleading decay models to integral data.
- Vary space-time in systematic manner to decouple reaction kinetics and decay kinetics.
  - Gradientless reactors are reliable but sequential testing over range of conditions is too slow.
  - More difficult to do reliably in a single fixed-bed reactor, and also too slow.
  - Parallel testing in multi-tubular integral reactor units is a productive approach.
- Obtain additional information from post mortem investigation of axial samples from fixed bed reactor combined with lifetime performance data - activity and characterization .
- Accelerated decay test procedures are useful, but caution. Risk of misleading results.

Reminder: Empirical deactivation kinetics. Power Law Expressions

$$a_t = \frac{\text{rate at which catalyst converts reactants at time t}}{\text{rate under same conditions with fresh catalyst}}$$

Deactivation kinetics	Concentration / conversion influence	Deactivation Rate -da / dt =	Activity –Time a =
Independent	None	$k_d\, a$	$\exp(-k_d\, t)$
Independent	None	$k_d\, a^m$	$(1 + (m-1)\, k_d\, t)^{-1/(m-1)}$ †
Parallel	Reactants A	$k_d\, f(C_A)\, a^m$	Complex
Series	Products B	$k_d\, f(C_B)\, a^m$	Complex

Levenspiel (1972, 1968)

† m≠ 1 Wojciechowski (1968)

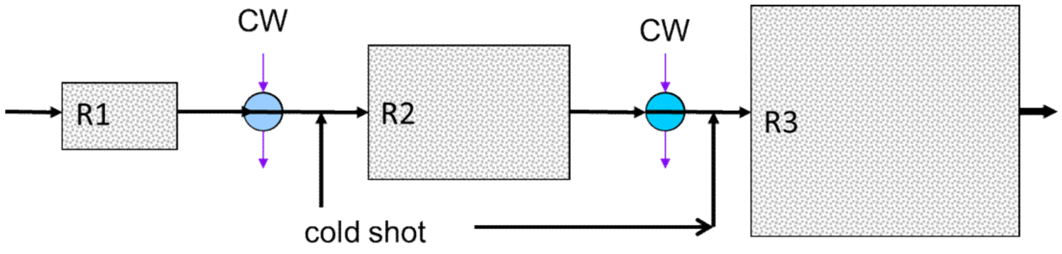
- Empirical fitting constants. Mechanistic origin unknown.

  k_d = decay rate constant, m = decay order. Also E_d = Temperature parameter

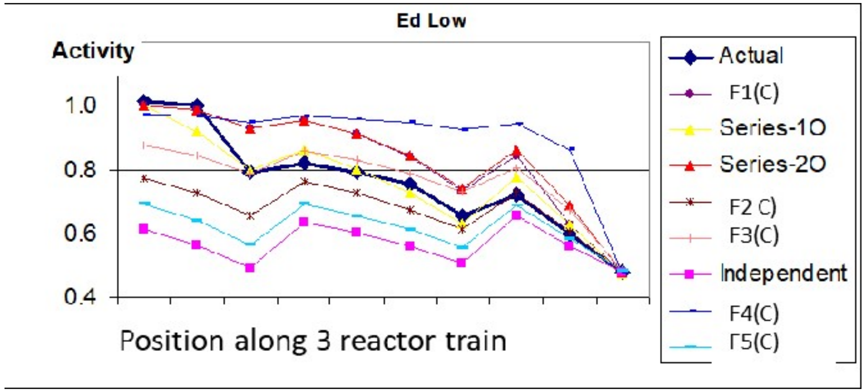
- Do not fit not activity-time expressions if there is evidence for composition dependence. Example found at 11th ISCD of fitting Wojciechowski formula to PFR data with parallel deactivation kinetics.

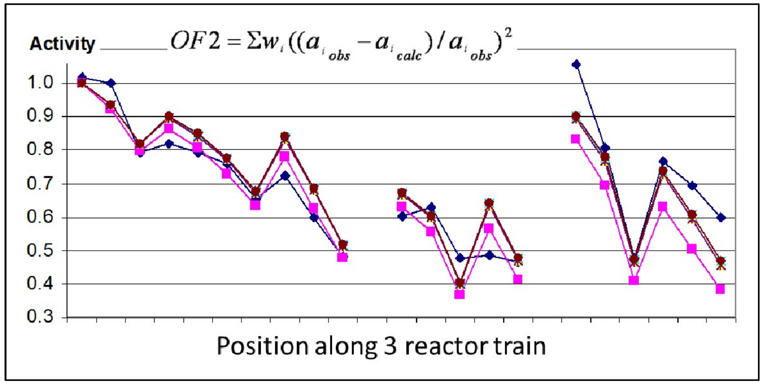
Empirical models are useful. Process design & optimisation

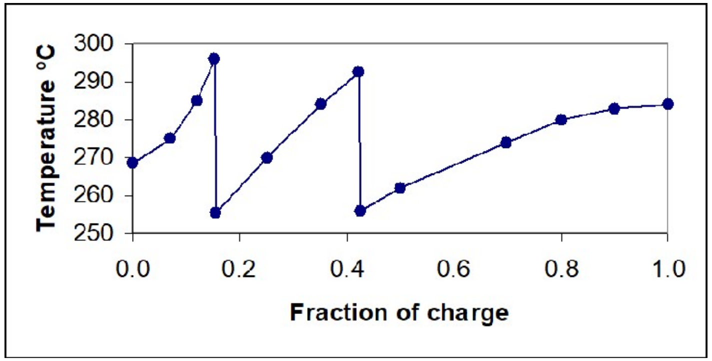
- 3 adiabatic reactors in series with intercooling. What is optimum temperature profile for catalyst life?



- Previous deactivation model - independent PLE, high E_d. Did not match observed performance.
- Reactor basket samples recovered from 10 locations. Known process history (T & X profiles). Measured activity in lab.
- Trial fitting of many PLEs to process history. High E_d would not fit. Only plausible fit = series deactivation with low E_d.
- Optimised fits over 3 plant discharges for best value of E_d.
- Used model to determine optimum SOL temperature profile.







Test equipment for catalyst decay

Birtill (2004, 2007) Updated

A= good capability
C= limited capability

† Additional studies published since 2004

Reactor type	With variation of space-time	With variation of feed composition	Decouple rxn & decay	Data range /period	% of exptl refs to 2004 †	Other pros and cons
Gradientless: Berty, Carberry, PFR + r/c	Yes	Yes	A	C	20	Commercial B, C units. Can test large pellets.
Fixed bed / plug-flow	No No	No Yes	C B	C C	54	Simple, inexpensive. Limited information.
	Yes	No	B	C	2	Slow sequential work
	Yes	Yes	A	C	0	
Fixed bed multi-port	Yes Yes	No Yes	B A	B B	4	Awkward construction. Take-off must be small.
Parallel multi-tube fixed bed reactors	Yes	Yes in parallel tests	A	A	1 †	Commercial multi-tube units. Can also vary τ
Coking μ-balance	Yes?	Yes	B?	C	5	By-passing?
Flow-thro' μ-balance	Yes	Yes	A	C	4	Commercial unit TEOM
Pseudo-adiabatic						Awkward construction.
single fixed-bed	No	Yes	B	B	2	Some information from
multi-zone fixed-bed	Yes	Yes	A	B	1	axial temperature gradient .
Pellet string (Temkin)	No	No	C	C	†	
Single-pellet diffusion	Diffusion	Yes	B	C		Awkward construction.

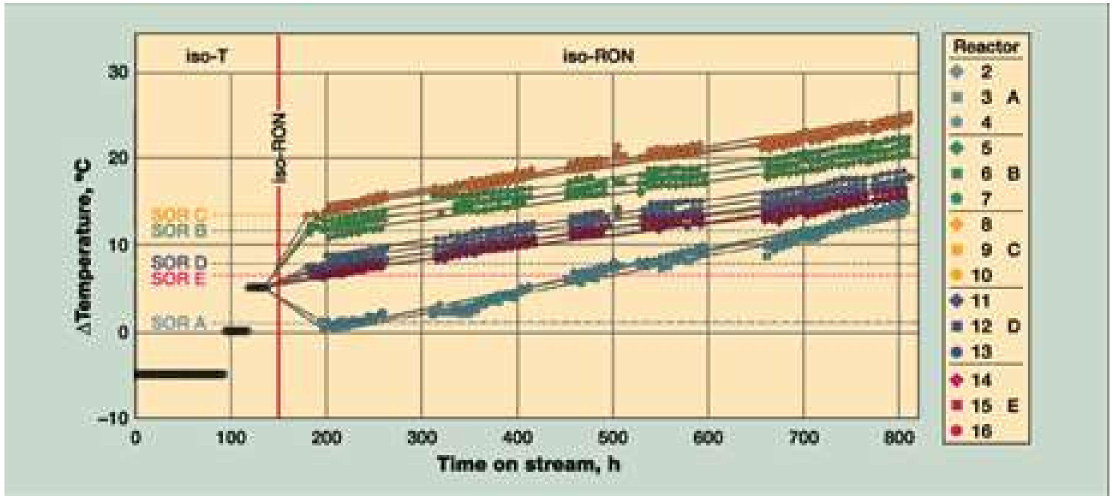
Parallel test reactors. Commercial facilities

- Avantium, hte, ILS, and others.
- Up to 64 reactors in parallel
- Gas and trickle-phase
- Need careful catalyst packing to avoid by-passing
  - Mears criteria (pellet and reactor dimensions), inert packing, evaluation tests
- Some decay studies claimed on websites of commercial test facilities but no examples found of Parallel Difference testing.

‘Semi’-adiabatic parallel testing

Performance testing of Naphtha semi-regenerative reforming catalysts. Kirchmann et al (hte gmbh)

- 16-tube parallel test rig
- Endothermic reaction – multiple reaction zones with reheating to simulate commercial operational temperature profile – internal temperature monitored
- Increasing mean temperature to maintain iso-RON output
- Comparative performance of 5 different catalysts – full extrudates - tested in triplicate over 1000 h



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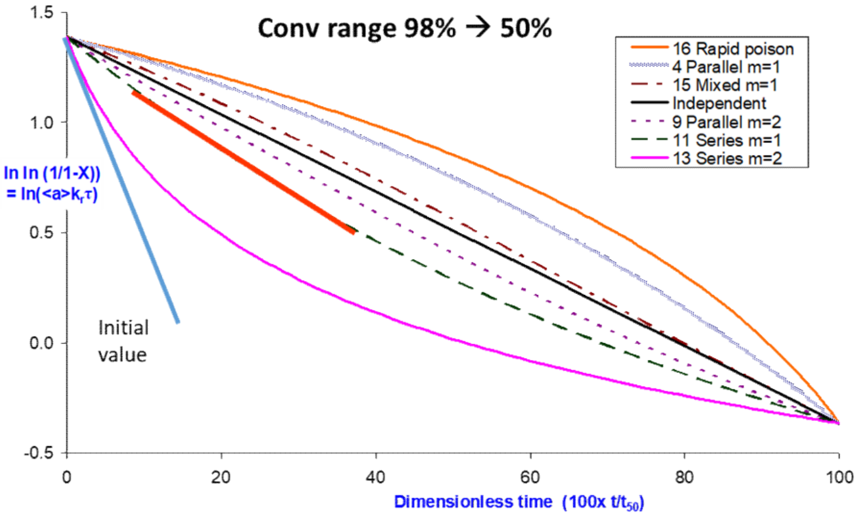
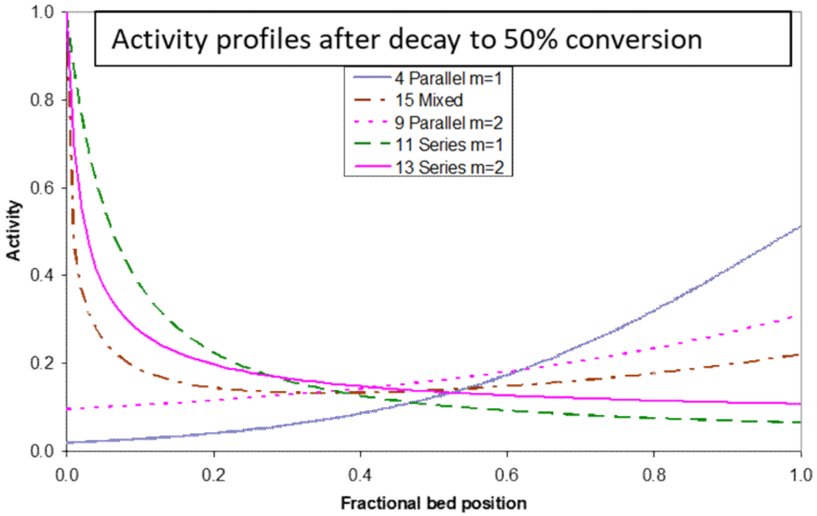
Deactivation in single PFR. Decreasing conversion, constant space-time. DCCST

- Can use linear plot ln <a> vs t to fit PFR data to independent 1st order decay model Levenspiel (1972).
- Unreliable in practice. How easy is it to fit a bogus straight line to deactivation data? Birtill (2011)
- Wide range of simulated cases. ~50% drop in conversion. Very different axial decay profiles.



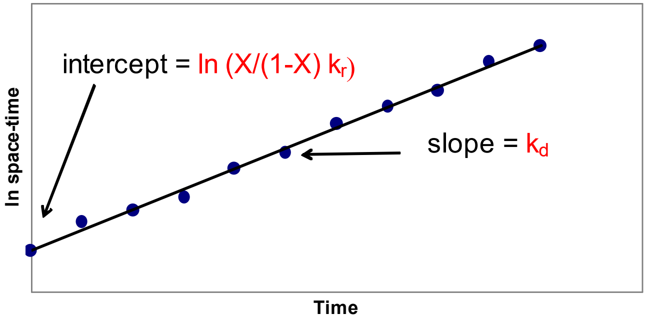
Note. LH figure. 1st order reaction kinetics and decay kinetics as indicated. Linear independent case with decay order m=1. For independent cases with m>1, plots will curve downward like series decay.



- Any non-linear deactivation plot can appear linear over short range, especially with noisy data.
- Easy to fit invalid independent decay kinetics or activity-time expressions to composition-dependent decay
  - Need to follow conversion drop over a wide range to confirm linearity.
- Determine initial values of deactivation rate with varying feedstock composition? Too many tests!

Single PFR. Constant Conversion Increasing Space-Time method. CCIST Birtill 2007, 2011

- 1st order reaction - constant fluid density - 1st order independent decay kinetics: $-da/dt = k_d a$
- Increase space-time (decrease flowrate F) to maintain constant integral conversion over time.
  Flow 'deactivation-compensation'
- $\ln \tau = k_d\, t + \text{constant}$ Levenspiel 1972
- Linear plot of $\ln \tau$ against time is consistent with independent 1st order decay but it does not prove it.
- Wide range of simulated cases. Plots are linear or almost linear for composition-dependent decay.
- General solution (Leibniz integral rule). PA Kirwan
- Ψ'(X), Λ' (X) describe composition dependence of reaction kinetics and decay kinetics. Condition of linearity is that integral is not a function of time. True only in special case m=1

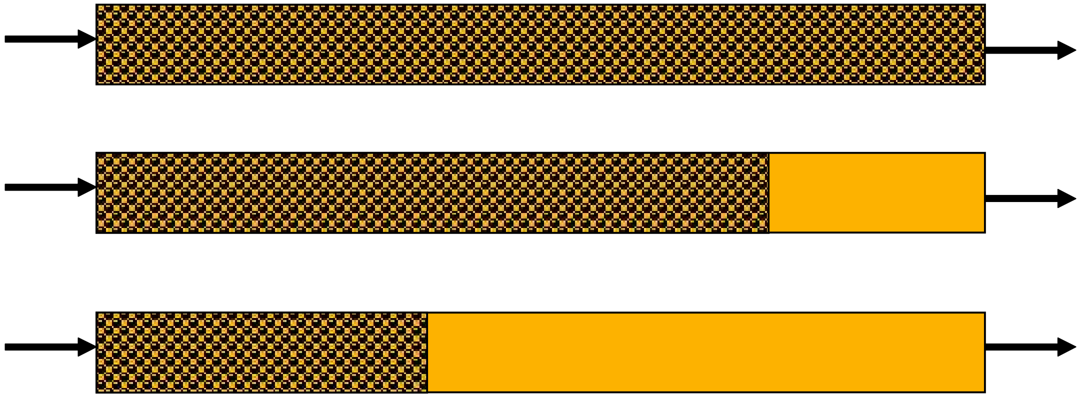


$$\int_0^1 \frac{\Psi'(X)}{\Lambda'(X)^m}\left(\frac{\partial X}{\partial z}\right)^m dz$$

- Need systematic variation of feedstock to apply this method to composition-dependent decay. Awkward and slow.
- Parallel Difference Testing with constant feed composition is much easier

Fixed bed reactors: parallel difference testing

Birtill 2003

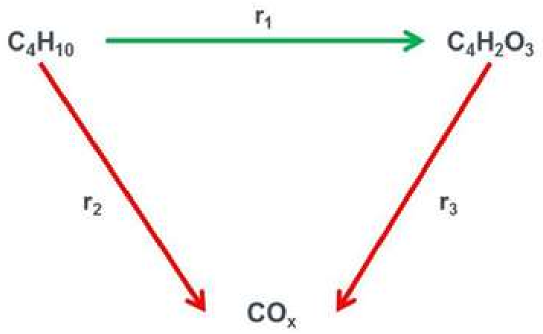


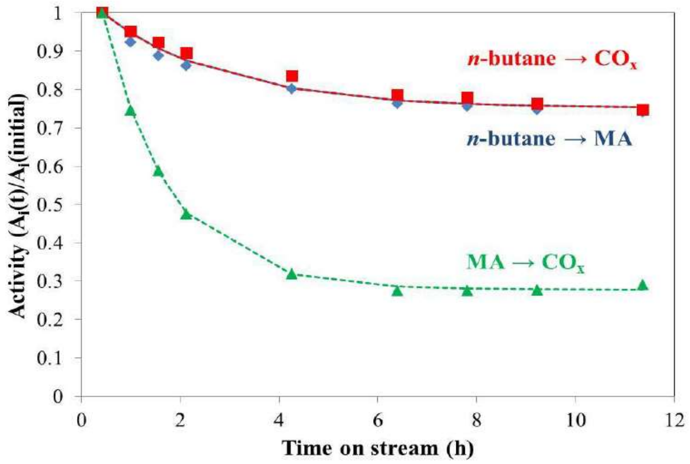
- 8-tube reactor units used in ICI from 1970s for catalyst screening.
- 1980. Parallel difference tests to estimate segmental catalyst decay
- Different catalyst mass W, fixed feedrate F (i.e., different W/F)
- Same temperature in all beds
- Operate with
  - either constant temperature/ decreasing conversion in all beds
  - or same increasing temperature in all beds so as to maintain constant conversion in just the full bed
    - deactivation-compensation
- Determine integral performance in each segment by difference.
- Can determine mean segmental activity using reliable reaction kinetic model if known.
  - Reliable model will show same activity in all segments at t=0. Any deviation will be exposed.
- Can carry out additional tests, varying temperature and feed composition.
  - generate lots of data simultaneously, covering decay over entire bed and over range of reaction conditions!

Parallel difference testing. Oxidation of n-butane to maleic anhydride.

Wilkinson SK (PhD thesis, Birmingham, 2014), Wilkinson et al, (2013) sponsored by Johnson Matthey

- VPO catalyst. Triangular mechanism
- Studied ‘conditioning’ after start-up to near steady state.
- Parallel tests. Charge W fractions **0.25, 0.5, 0.75, 1.0.**
- Additional test with **0.075W** – X <10%
  - pseudo-differential conditions
- Data at t=0 used to determine best kinetic model
- Activity values derived over time on stream
- Initial activity deactivation/conditioning is independent of axial composition and also T
- Data imply 2 types of active site
  - **Site 1: n-Bu oxidation to both MA and CO/CO2**
  - **Site 2 for MA → CO/CO2**
    Big decline and so catalyst becomes more selective

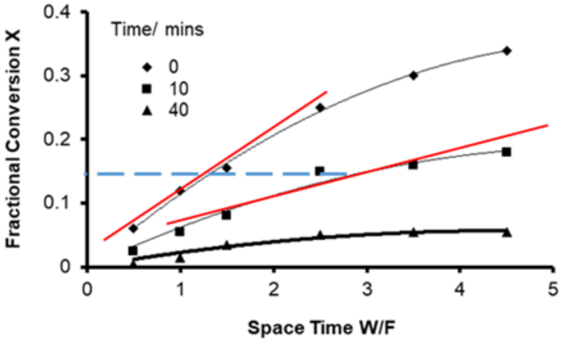


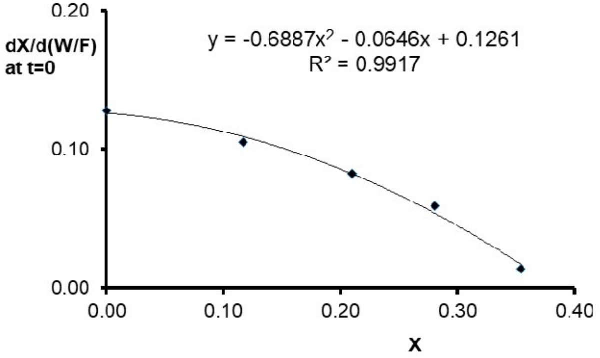


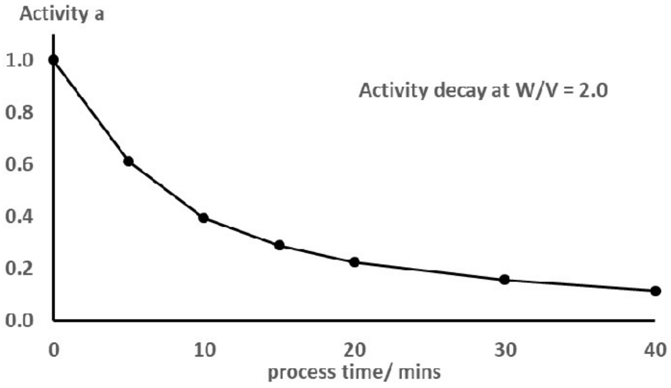
Sequential tests at different space time

Corella et al (1980)

- $C_6H_5CH_2OH \xrightarrow{\text{supported Cu/Cr2O3}} C_6H_5CHO + H_2$ Sequential tests. Plug flow reactor. 6 values of $W/F = \tau$
- Plot conversion vs τ at set times. Determine gradients $dX/d\tau_{X,\,t}$ at selected values of τ.
  - Done by visual inspection in the paper. Alternative method is to fit $X - \tau$ polynomial, then differentiate.
- Determine point activity a at selected value of τ at time t relative to fresh catalyst at same conversion
  $dX/d\tau_{X,\,t} / dX/d\tau_{X,\,t=0}$ Visual inspection.
- Alternative method: plot $dX/d\tau_{X,\,t=0}$ vs X – a reaction model for fresh catalyst. See middle figure below.
- Plot point activity at selected τ against time to derive decay rate at selected τ.
- Problems. (1) Too many sequential tests. Impractical for slow decay. (2) Feedstock variation. (3) Error from $X - \tau$ curve-fits.

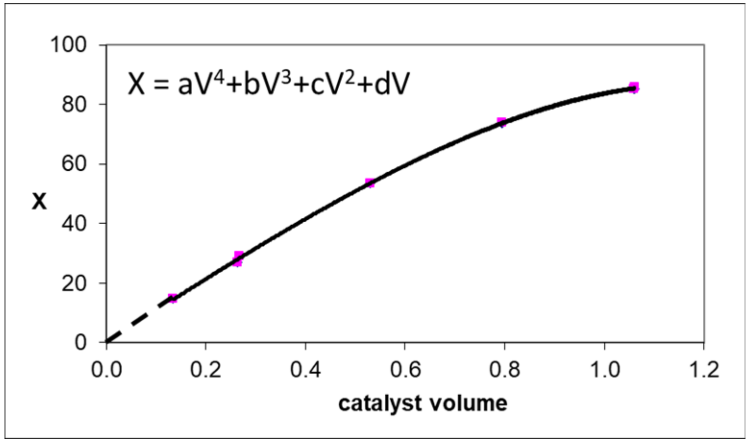






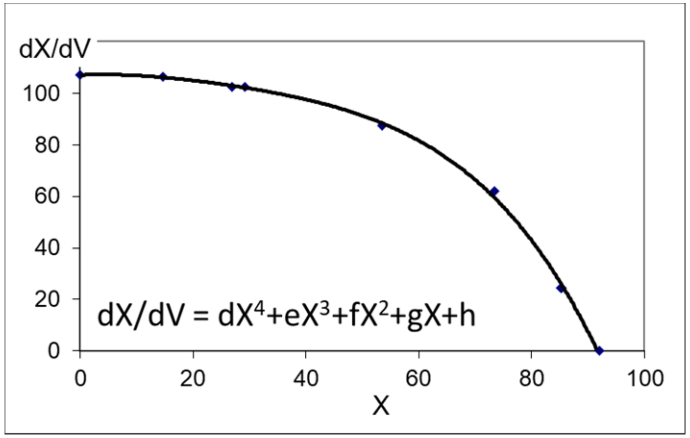
Parallel Difference testing with initial reference plot. I

- Parallel tests with charge volume fractions 0.125, 0.25, 0.5, 0.75, 1.0 Segmental performance by parallel difference method. Duplicate tests if possible to reduce inconsistency.
- **Use short (1/8) bed to measure front end performance more precisely (near differential conditions).**
- **X-V curve-fitting for fresh catalyst. Determine reference plot of $(dX/dV)_{t=0}$ vs X.**
  A reaction model for fresh catalyst.



$$a_{\Delta z} = \frac{\left(\frac{\Delta X}{\Delta V}\right)_{\Delta z,Xm,t}}{\left(\frac{\Delta X}{\Delta V}\right)_{Xm,t=0}}$$

$$a_{\Delta z} = \frac{\left(\frac{\Delta X}{\Delta V}\right)_{\Delta z,Xm,t}}{\left(\frac{dX}{dV}\right)_{Xm,t=0}}$$



- Determine mean activity values for each segment **Δz** by normalising **ΔX/ΔV** at each time on stream against equivalent values for fresh catalyst at same mean conversion **Xm** for segment from **X-V** plot for fresh catalyst (preferred) or **dX/dV** at **Xm** from derivative plot.

Parallel Difference testing with initial reference plot. II

- Method works well in practice.
- Illustrated with industrial example. Ester hydrogenation. Birtill & Deeley
- Short 1/8 bed was especially useful for detecting fast (poison-driven) decay localised in this segment.
- Comparable segmental deactivation plots against time-on-stream using (a) pre-determined reaction model or (b) initial X-V reference plot.
- Activation phase could only be seen after subtraction of fast decay at front of bed.
- Similar deactivation rate in all segments except front. Composition independent.

Modelling Co F-T Catalyst Deactivation using GPLEs. Argyle, Frost & Bartholomew, (2014)

Activity-time plot with asymptotic behaviour can be fitted to *'Simple' Power-Law Expression* with high order m or *'Generalised' Power-Law Expression* with '*steady state*' term a_{ss} and low order m' = 1 or 2. Fuentes (1985)

$$-\frac{da}{dt} = k_d a^m \quad vs \quad -\frac{da}{dt} = k'_d (a - a_{ss})^{m'}$$

- Examined 10 sets of published data on cobalt catalyst deactivation in Fischer-Tropsch process. †
- Fast initial deactivation, but plots do not reach a steady state.
- Data interpreted in terms of 2 principal regimes of deactivation:
  (1) early, rapid loss of activity associated with sintering
  and/or (?) cobalt aluminate formation in different cases
  (2) later, slow loss of activity typically due to carbon formation.
- De-convolution of 'rapid' and 'slow' deactivation curves, BOTH fitted to composition-independent 1st or 2nd order GPLEs.
- 4 parameters and 2 coefficients. ***Data can be fitted this way but too many variables for empirical model? Need direct characterisation evidence. Would a combination of high order fast process + linear slow process fit just as well?***

† No data for effect of composition (CO, H2, H2O).

In situ / In Operando characterisation

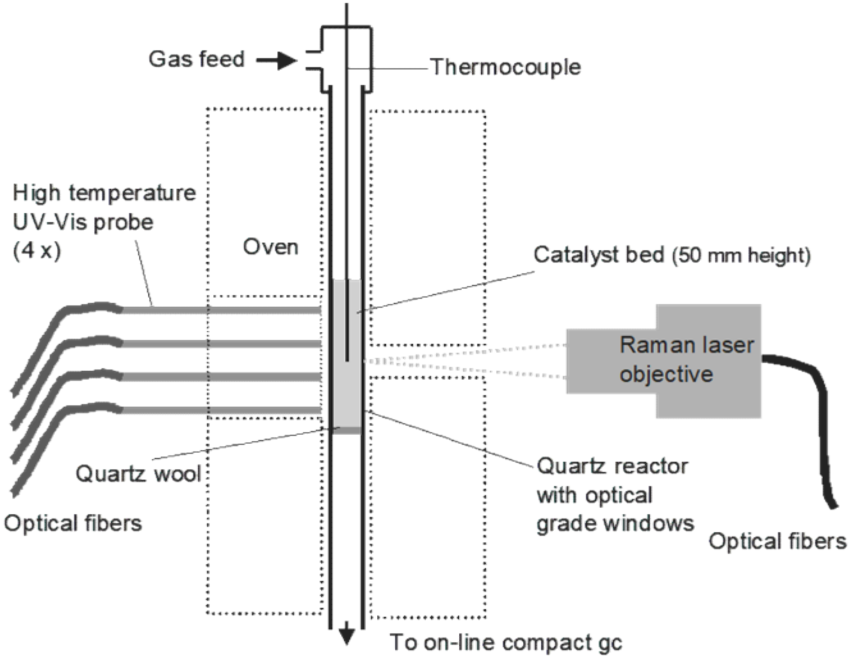
- Large number of publications since 2008, mainly on reaction mechanisms
- Eurokin sponsored review on in-situ characterization techniques for reaction kinetics.
  Tsakoumis et al (2015).
- Catalyst sintering. HRTEM. Rapid loss of catalyst activity in the earliest stages of catalyst sintering from Ostwald ripening rather than particle migration and coalescence DeLaRiva et al (2013).

Weckhuysen & co-workers.

- Coking of $CrOx/Al_2O_3$ catalyst in propane dehydrogenation. Cyclic reaction and oxidative regeneration.
- Combined operando UV/vis–Raman spectroscopic study.
- Two UV/vis and a single Raman optical fibre probe used to study catalyst bed under true reaction conditions with on-line GC analysis.
- 2007: Lab reactor 0.3g. Diagram Xander Nijhuis

  2015: Pilot plant 500g. Sattler et al (2014)

Is commercialisation in sight yet?



Eurokin Decay Study 2004
Birtill (2003-2007)

Accelerated Decay Risk Index: 1 - 625

Risk Factor	1	3	5
Catalyst type & composition X	Single type. Single source.	Moderate range of composition.	Different types. Several sources.
Decay mechanism X	Well known / characterized	Qualitatively characterized	Unknown / not characterized
Test conditions / Severity X	Range : low to medium severity.	Single condition. Medium severity.	Single condition. High severity.
Reason for test	Selection for further evaluation.	Plant selection. Verification of vendor claims.	Plant selection. No vendor info.

Which decay process are you accelerating?

Are you causing some different damage?

How can you check?

Catalysis Benchmarking survey, US DOE Bligaard et al (2016)

"Accelerated catalyst aging tests can be expeditious, but these tests are risky unless the causes of deactivation are known and extrapolations justified on the basis of experiments."

Accelerated decay tests: diesel hydroprocessing, Co-Mo catalyst.

Vogelaar et al (2010). 11th ISCD (2009). Albemarle

- Comparative characterisation of samples of catalyst from
  - (a) commercial unit, long time under normal conditions (more deactivated) and
  - (b) pilot plant with accelerated decay under "extreme process conditions".
    - Extreme conditions not specified: high temperature, low pressure, high conversion.
- TGA peaks for both samples show maximum at 450°C, but combustion starts and finishes 50°C higher for sample (a). 'Soft coke converts to 'hard coke' over extended time on stream.
- STEM-EDX analysis. Compared uniform metal dispersion in sample (a) from normal operation with severe metal agglomeration in sample (b). Clusters of Co-Mo-S
- Author conclusion: "*artificial aging treatment resulted in a completely different deactivation behavior of the catalyst, as compared to the normal operation cycle. … difficult to mimic industrial life cycle .. at lab scale, especially when conditions strongly deviate from typical process operation*"
- Sintering shows that temperature was too high in this (extreme?) accelerated decay procedure
- Can accelerated coking be a valid predictor of catalyst performance?

Accelerated coking for hydrotreating catalysts. Pacheco (Petrobras) et al (2011)

- Feed: diesel-based mix. Two-step accelerated deactivation sequence:
  - (A) higher temp to increase coke formation: Normal T 360 °C, test range 380-420 °C, mostly 400 °C
  - (B) at same high T, lower H2/oil to "age" the coke by increasing its aromaticity.
- Measured total carbon content and its chemical nature but not metal dispersion.
- Test reaction sequence to determine rate constants, E_A, and degree of deactivation ΔT.
  - Constant reaction order and E_A interpreted to mean that deactivation is caused by simple loss of active sites by coking rather than fundamental change in their nature.
- Similar procedure, but now no measurement of coke or metal dispersion. Novaes, Pacheco et al (2017)
- Combination of kinetic approach with measurement of quantity and nature of coke and metal dispersion would be more convincing.

- An alternative approach to accelerated decay. Incorporate within Parallel Difference test sequence.
  - Include additional conditions with higher severity.
- Conclusion. Accelerated decay can be a valuable approach … but be careful

Mechanistic coking decay models

- Detailed survey is beyond the scope of this work. Multi-level complexity.
  - Refinery processes with complex feedstocks coupled with complex reaction networks.
  - Blockage to pore networks - Micro – Meso - Macro
- Eurokin Survey. Part II. Conclusions. Birtill (2004)

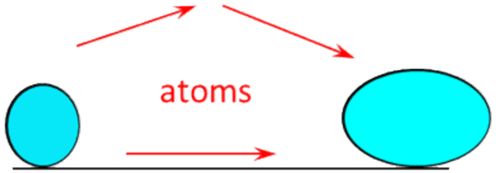
  (vii) The determination of coking kinetics and empirical activity-coke relationship is more demanding on time and resources than simple PLE but is justified in some situations, e.g., to define the axial coke profile.

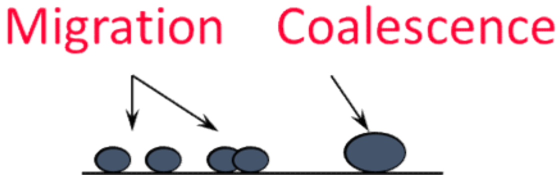
  (xxvii) The problems of catalyst decay coupled with intra-particle diffusion resistance and changes to the catalyst pore structure … require dedicated, custom research strategies for progress to be made on a rational basis.
- Combination of coking kinetics with an empirical activity-coke relation can be expressed more simply by an activity PLE. Birtill (2007)
- Parametric sensitivity analysis. Some mechanistic models are overcomplicated.
- Some mechanistic coking decay models can be reduced down to simple PLEs.
- Valuable insight from specialist kinetic studies.
  "the deactivating agent is not an inert substance but is involved in reactions, sometimes of the same type as those leading to the main products of the process." Froment (2008)

Mechanisms of sintering

Supported metal particles

- ‘Ostwald ripening’ (OR)
    - vapour-transport of atoms or atom-complexes (high temp)
    - migration of atoms or atom-complexes across surface
- Particle migration across surface followed by coalescence (PMC)





In situ TEM DeLaRiva et al (2013) and simulation Hansen et al (2013)

Rapid sintering of nanoparticles in phase I: OR >> PMC
Slower sintering of crystallites in phase II: PMC + OR

Sintering of supported Ni steam reforming catalysts

Sehested et al (2003-2014)

- Systematic fundamental study of sintering mechanism – density functional theory (DFT).
- Particle Migration/ Coalescence (PMC) dominant mechanism < 600 °C
  - Induced by adsorbate-metal complexes with low formation energies and/or low diffusion barriers
  - Rate depends on distance between metal particles, diffusivities and concentration of transport species at metal surface
- Recent work – revised calculations - surface NiOH rather than Ni_2OH is the most prominent transport species in presence of H_2O/H_2 - lowest combined energy of formation and diffusion at Ni surface.

- Constant b depends on K_{eq} and D for NiOH, Ni wt%, support SA, $\text{đ}_{Ni,t=0}$
- Numerical modelling of PMC to extract DNi-OHKNi-OH (effective mass diffusion constant) from experimental catalyst sintering data.

$$\frac{d_{Ni}}{d_{Ni0}} = \left(b\,t\left(\frac{P_{H2O}}{P_{H2}^{\ 0.5}}\right) + 1\right)^{1/7}$$

- Note. Activity of Ni steam reforming catalysts correlates better with Ni step density rather than Ni particle size Sehested (2006).
- Still useful to understand sintering kinetics and mechanism. Sintering kinetics lead to Dispersion PLE with natural order m ~8. Hence ‘rational’ causes for high m.

Two-step agglomeration model. Finney & Finke (2017)

- 'Bimolecular' agglomeration (sintering) of nanoparticles B to form bigger nanoparticles C.
- Autocatalytic agglomeration (small B + bigger C) to form larger particles '1.5C'.

$$B + B \xrightarrow{k3} C$$

$$B + C \xrightarrow{k4} 1.5C$$

- Particle types C and 1.5C defined with 'average' variable size.
- 'Average' rate-constants k_3 and k_4 used to fit kinetics for 'average' nanoparticle with wide size range.
- 'Mechanism' has some similarity to Particle Migration & Coalescence but does not explain why the particles move about.
- Pretentious claims for general physical significance. 'Ockham's razor' (cited 7x) and 'disproof-based' (cited 13x). 'Simplicity' and 'falsifiability' confused with mechanistic rigour.
- Two-step agglomeration model does fit some observed (sigmoidal) data sets better than some PLEs but not others. Just a number-fitting exercise with $k_4 >> k_3$?
- Generally dismissive of Ostwald Ripening. Yet some cases do involve atomic complexes with CO or OH
- Authors imply that users of empirical models don't realise that they are empirical. Irritating.

Some strategies for reducing catalyst decay.

Extracts from Eurokin survey Birtill (2004). Some recent advances (2012-2018) have been inserted.

- Catalyst composition
- Formulation
  - Stabilising nanoparticles
    - Design the metal-support interface to slow down sintering
      Lu et al (2012)
    - Control of precursor nanoparticle size distribution
      Various authors incl. Grillo, Moulijn et al (2018)
    - ‘Core-Shell Nanostructured Catalysts’. Zhang et al (2013)
    - Sacrificial Coating Strategy - Enhancement of Metal-Support Interaction. Zhan et al (2016)
  - Add protective components to counteract fouling, promote re-oxidation, etc
  - Avoid undesirable trace support impurities which migrate over life
  - Design storage capacity within pellet for poisons and foulants
  - Design pellet architecture to preserve activity within pores

'Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition'.

Lu et al, Science, 335 (2012)

$$C2H6 + O2 \xrightarrow{650\ ^{\circ}C} C2H4 + H2O$$

- Stabilisation of Pd nanoparticles on alumina.
    - Controlled overcoating with 45 layers of alumina using multiple sequences of Atomic Layer Deposition of Me_3Al / hydrolysis.
    - Development of microporosity by subsequent thermal treatment.
- Some reduction in catalytic activity. Great reduction in coking and sintering.

- 320 citations since 2012
- ALD method too expensive for large commercial scale? Shows a way forward. Revisiting SMSI.
- Many subsequent examples of NP stabilisation to high temperatures
- Wet chemical approaches to 'core−shell structures' – nanoparticles + porous oxide shells

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