

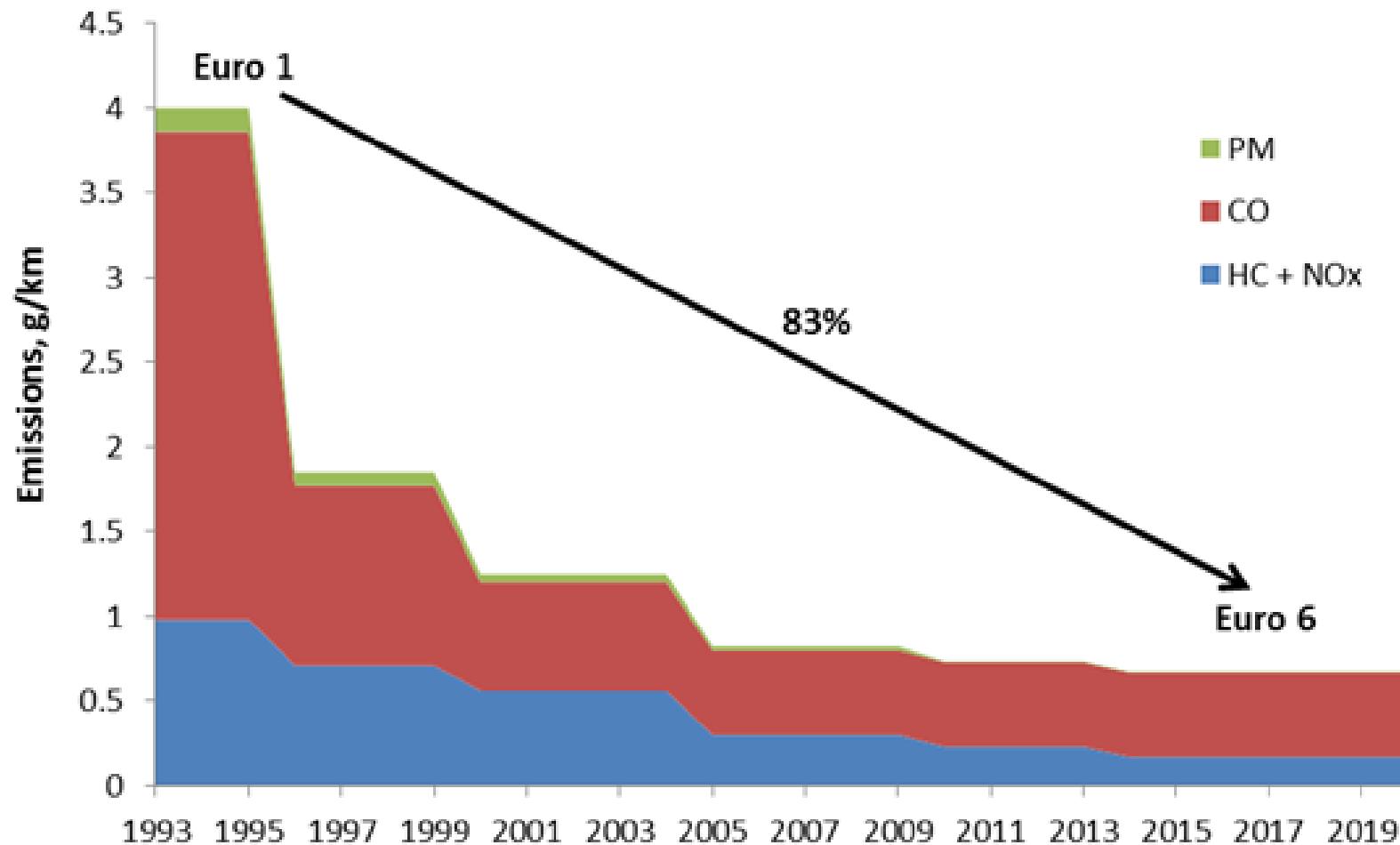
Investigation and Analysis of Ageing Mechanisms for Automotive Catalysts

UnICEG – Emissions, Aftertreatment and RDE

Kurtis Irwin

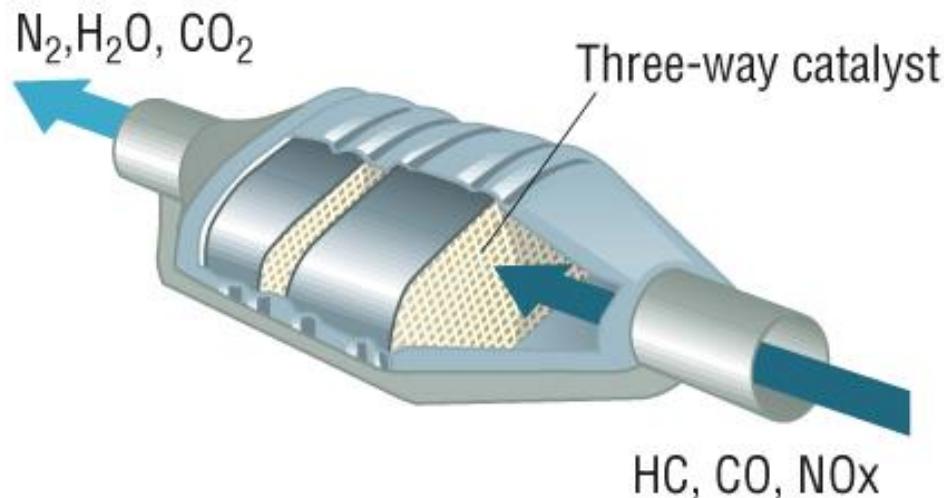
12/07/2019

Background/Issues faced



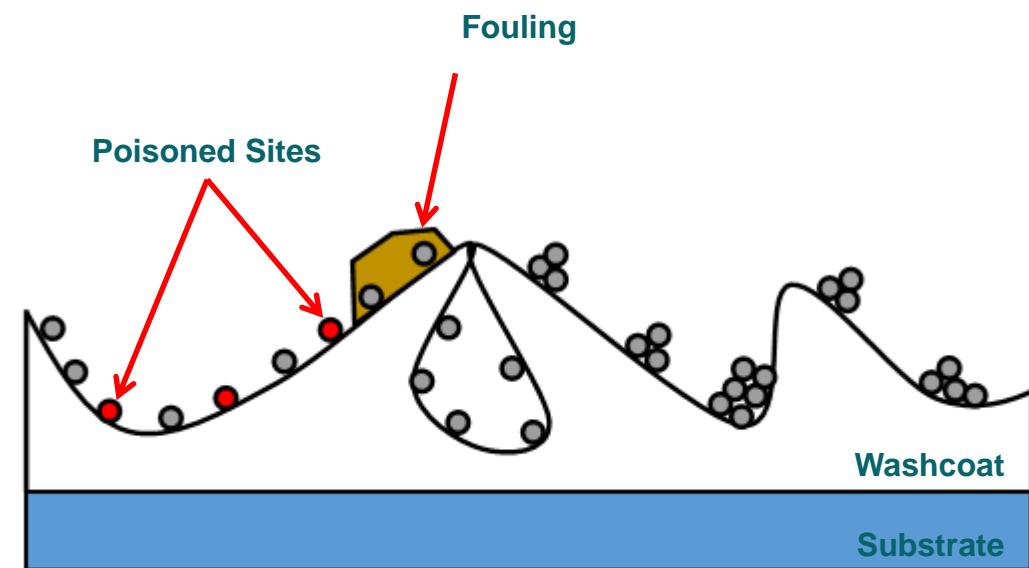
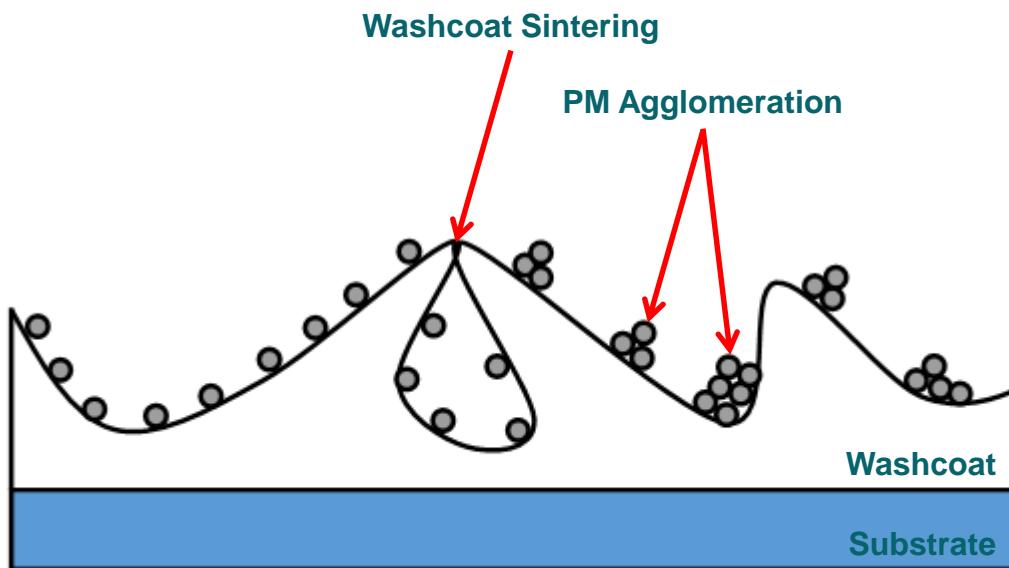
Project Aims & Objectives

- Developing a greater understanding of catalyst deactivation and ageing.
- Compare catalyst performance before and after ageing.
- Concentrating on the effects of oxygen on catalyst ageing.
- Ability to predict a change in dispersion of precious metals applying the kinetic model.
- Algorithms will be further developed to aid prediction of catalyst ageing.

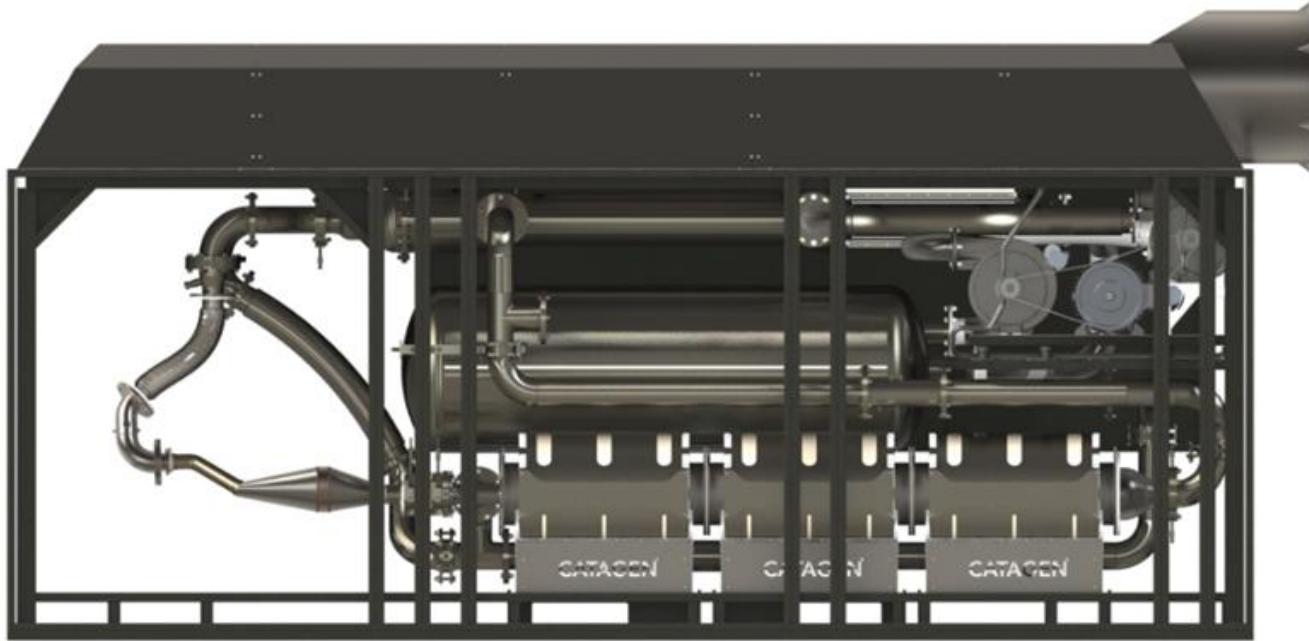


Catalyst Ageing

- Thermal Deactivation
 - Washcoat sintering/Phase changes
 - Precious metal agglomeration
- Poisoning
 - Selective
 - Fouling
- Mechanical

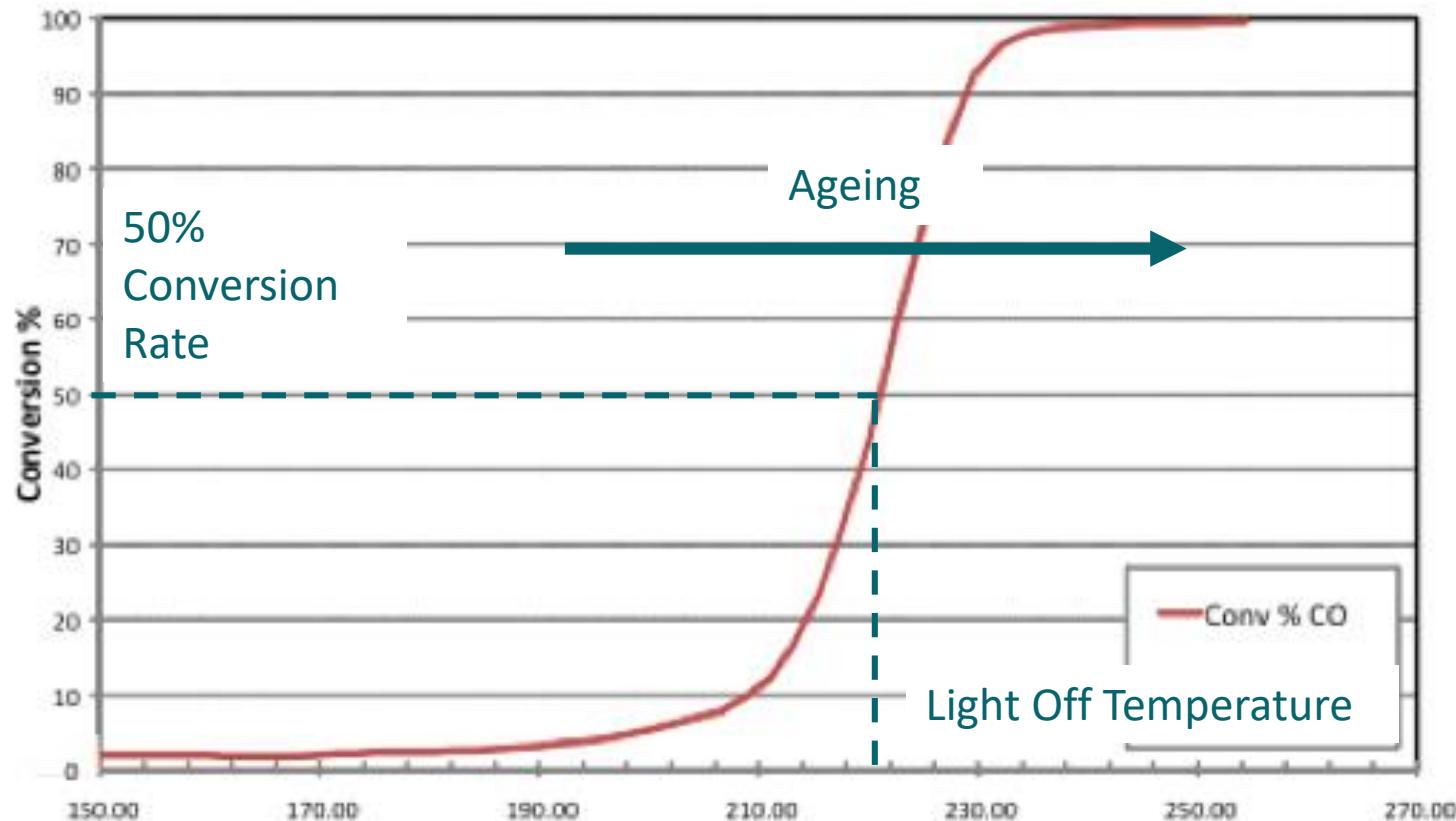


Testing Apparatus



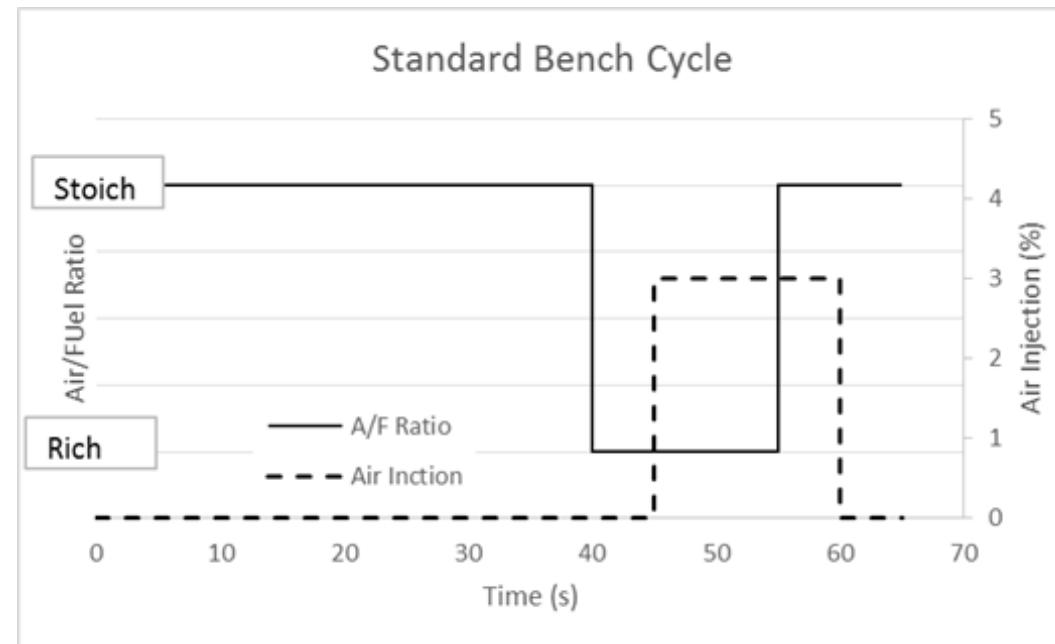
- Temperature control up to 1100°C
- Flow rates up to 100 g/s
- Industry standard emissions measurement
- Transient flow conditions (0 - 50 g/s in 6 seconds)
- Transient temperature conditions (0 - 800°C in 8 seconds)

Typical Characterisation Method – Light Off Test



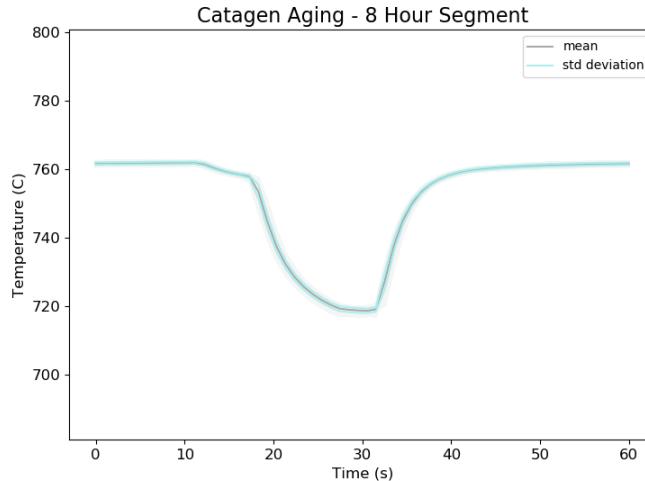
Ageing Environment

- **Standard Bench Cycle (SBC)**
 - Four distinct steps over 60 seconds
 - Stoichiometric – 40s
 - Rich – 5s
 - Rich with air injection – 10 s
 - Stoichiometric with air injection – 10s

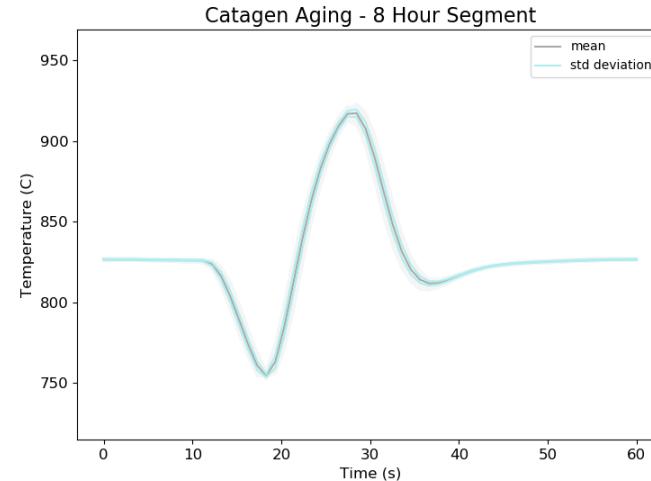


SBC Typical Profiles

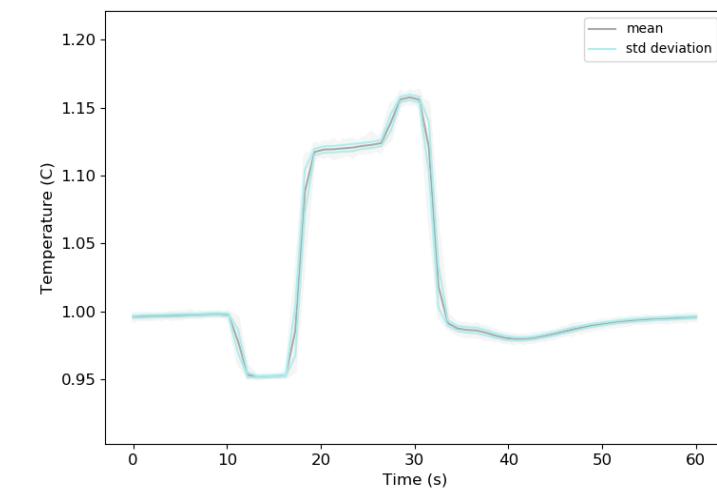
Inlet Temperature Profiles



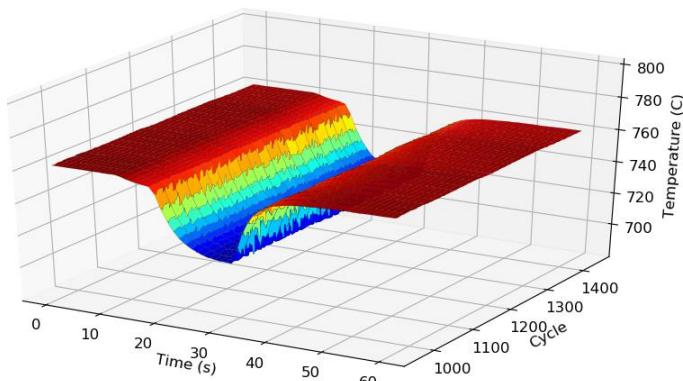
Bed Temperature Profiles



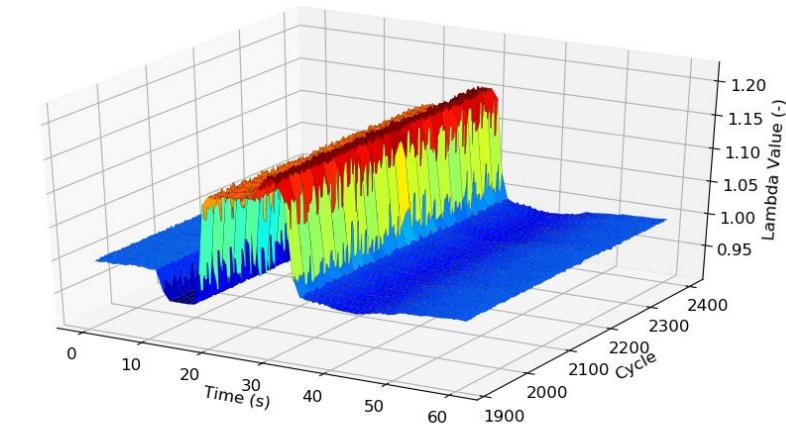
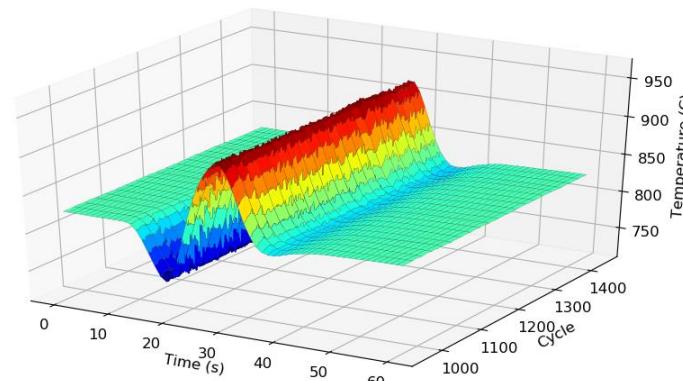
Lambda Temperature Profiles



Catagen Aging - 8 Hour Segment



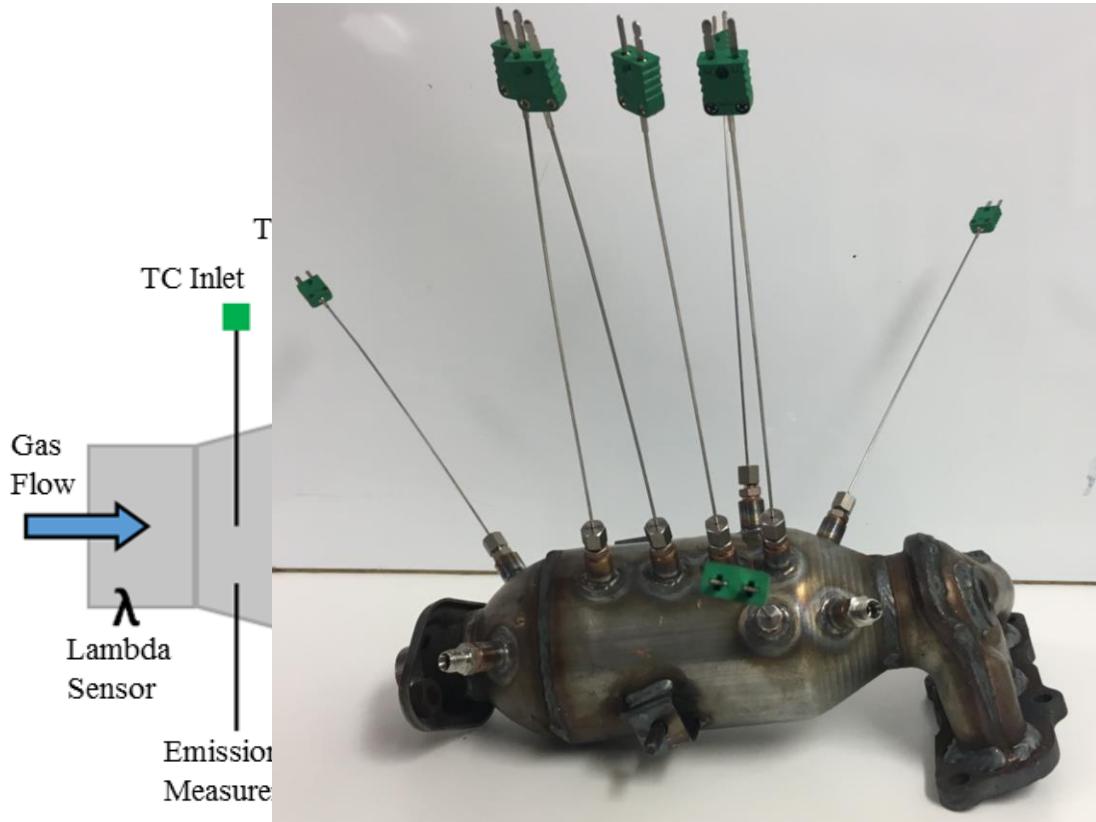
Catagen Aging - 8 Hour Segment



Effect of Oxygen on Catalyst Performance

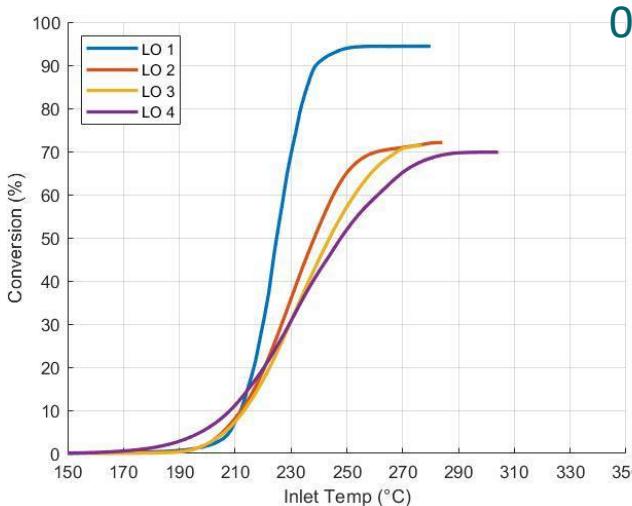
- **10 catalyst samples**
 - Range of different oxygen concentrations
 - Aged up to the equivalent of 100,000 miles
 - Controlled to 800°C average bed temperature
 - Flow rate of 25 g/s

	Average Oxygen Concentration (%)
Catalyst 0.5%	0.5
Catalyst 0%	0
Catalyst 0.75%	0.75
Catalyst 1%	1
Catalyst 1.5%	1.5
Catalyst 5%	5
Catalyst 0.5% 25K	0.5 (0-25k Miles)
Catalyst Fresh	Fresh

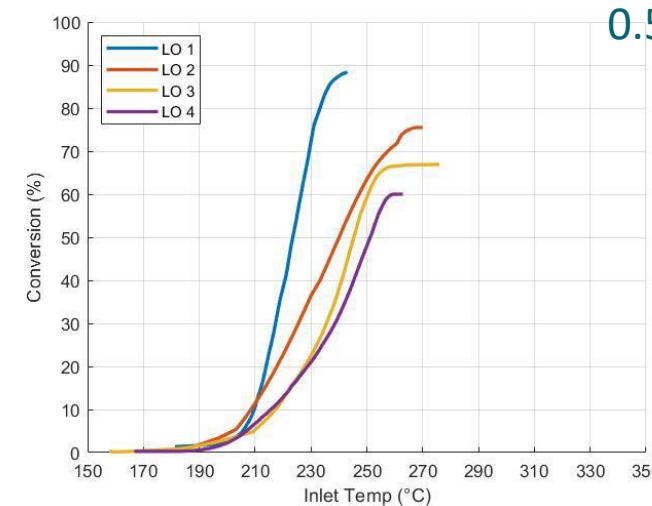


Results - Light-Off Curves

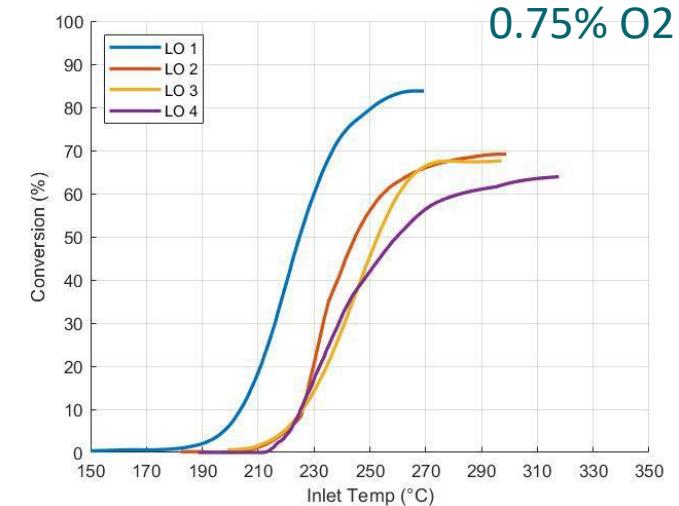
Full-scale light-off tests and results completed on the OMEGA reactor.



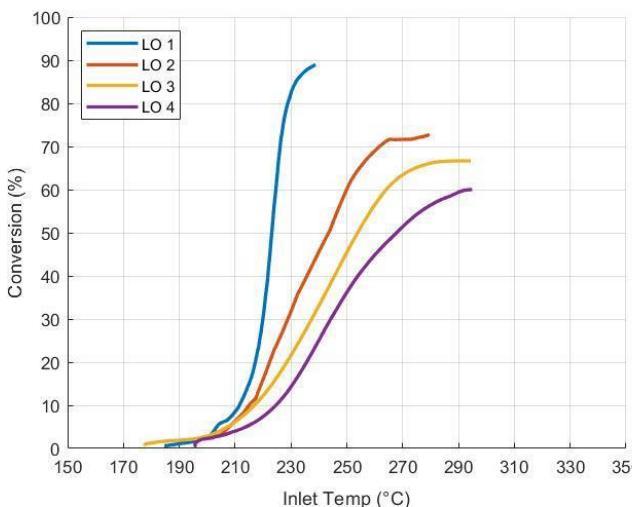
0% O₂



0.5% O₂



0.75% O₂



1% O₂

Conversion (%) vs Inlet Temp (°C) for 1.5% O₂. The graph shows four curves (LO 1, LO 2, LO 3, LO 4) starting at 0% conversion at 150°C. LO 1 reaches 100% conversion at approximately 235°C. LO 2 reaches 100% conversion at approximately 265°C. LO 3 reaches 100% conversion at approximately 275°C. LO 4 reaches 100% conversion at approximately 295°C.

Inlet Temp (°C)	LO 1 (%)	LO 2 (%)	LO 3 (%)	LO 4 (%)
150	0	0	0	0
170	0	0	0	0
190	0	0	0	0
210	5	5	5	5
230	30	25	20	15
250	65	55	45	35
270	90	75	65	55
290	98	70	60	50
310	98	70	60	50
330	98	70	60	50
350	98	70	60	50

1.5% O₂

Conversion (%) vs Inlet Temp (°C) for 5% O₂. The graph shows four curves (LO 1, LO 2, LO 3, LO 4) starting at 0% conversion at 150°C. LO 1 reaches 100% conversion at approximately 235°C. LO 2 reaches 100% conversion at approximately 270°C. LO 3 reaches 100% conversion at approximately 280°C. LO 4 reaches 100% conversion at approximately 300°C.

Inlet Temp (°C)	LO 1 (%)	LO 2 (%)	LO 3 (%)	LO 4 (%)
150	0	0	0	0
170	0	0	0	0
190	0	0	0	0
210	5	5	5	5
230	30	25	20	15
250	65	55	45	35
270	90	75	65	55
290	98	70	60	50
310	98	70	60	50
330	98	70	60	50
350	98	70	60	50

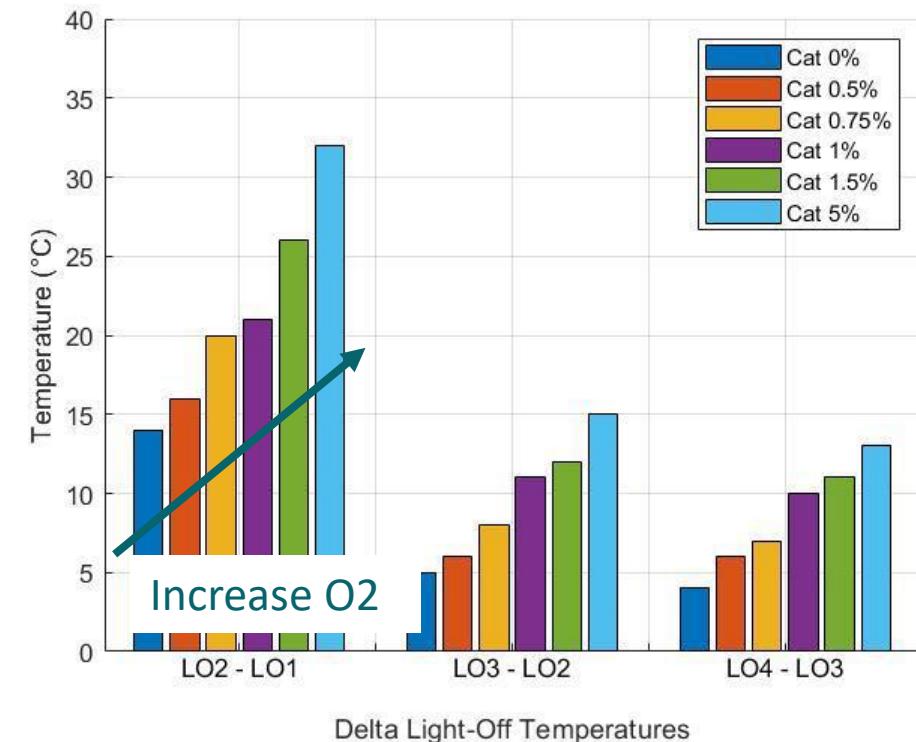
5% O₂

+44 (0) 28 90 455 100 info@catagen.co.uk catagen.co.uk

Results - Light-Off Temperatures

Full-scale light-off differences throughout the ageing.

	Ageing Distance (Equivalent Miles)			
Catalyst Sample	0	25,000	50,000	100,000
Catalyst 0% LO Temperature (°C)	225	239	244	248
Catalyst 0.5% LO Temperature (°C)	224	240	246	252
Catalyst 0.75% LO Temperature (°C)	225	245	253	260
Catalyst 1% LO Temperature (°C)	223	244	255	265
Catalyst 1.5% LO Temperature (°C)	219	245	257	268
Catalyst 5% LO Temperature (°C)	228	260	275	288



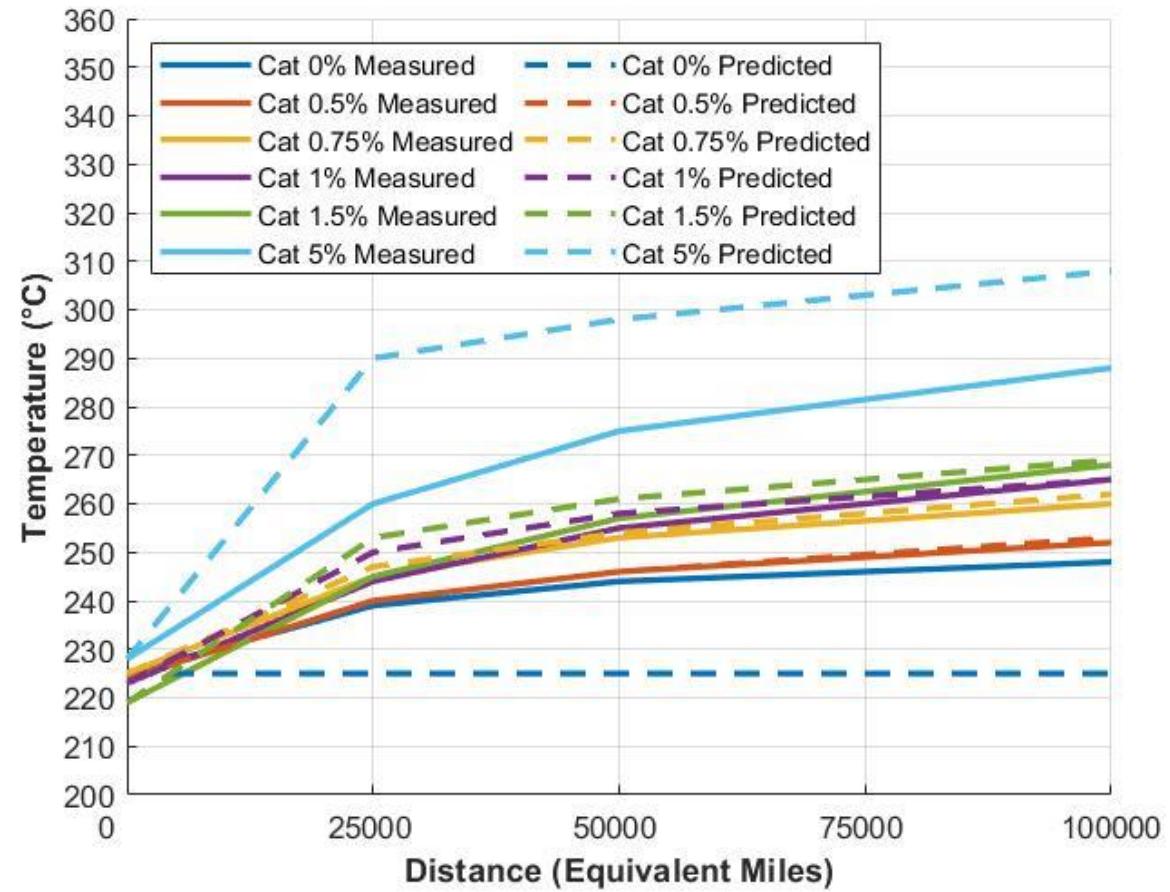
Analysis - Light-Off Temperatures

Measured LO Temps (°C)

Catalyst Sample	Ageing Distance (Equivalent Miles)			
	0	25,000	50,000	100,000
Catalyst 0% LO Temperature (°C)	225	239	244	248
Catalyst 0.5% LO Temperature (°C)	224	240	246	252
Catalyst 0.75% LO Temperature (°C)	225	245	253	260
Catalyst 1% LO Temperature (°C)	223	244	255	265
Catalyst 1.5% LO Temperature (°C)	219	245	257	268
Catalyst 5% LO Temperature (°C)	228	260	275	288

Predicted LO Temps (°C)

Catalyst Sample	Ageing Distance (Equivalent Miles)			
	0	25,000	50,000	100,000
Catalyst 0% LO Temperature (°C)	225	225	225	225
Catalyst 0.5% LO Temperature (°C)	224	240	246	253
Catalyst 0.75% LO Temperature (°C)	225	247	254	262
Catalyst 1% LO Temperature (°C)	223	250	258	265
Catalyst 1.5% LO Temperature (°C)	219	253	261	269
Catalyst 5% LO Temperature (°C)	228	290	298	308



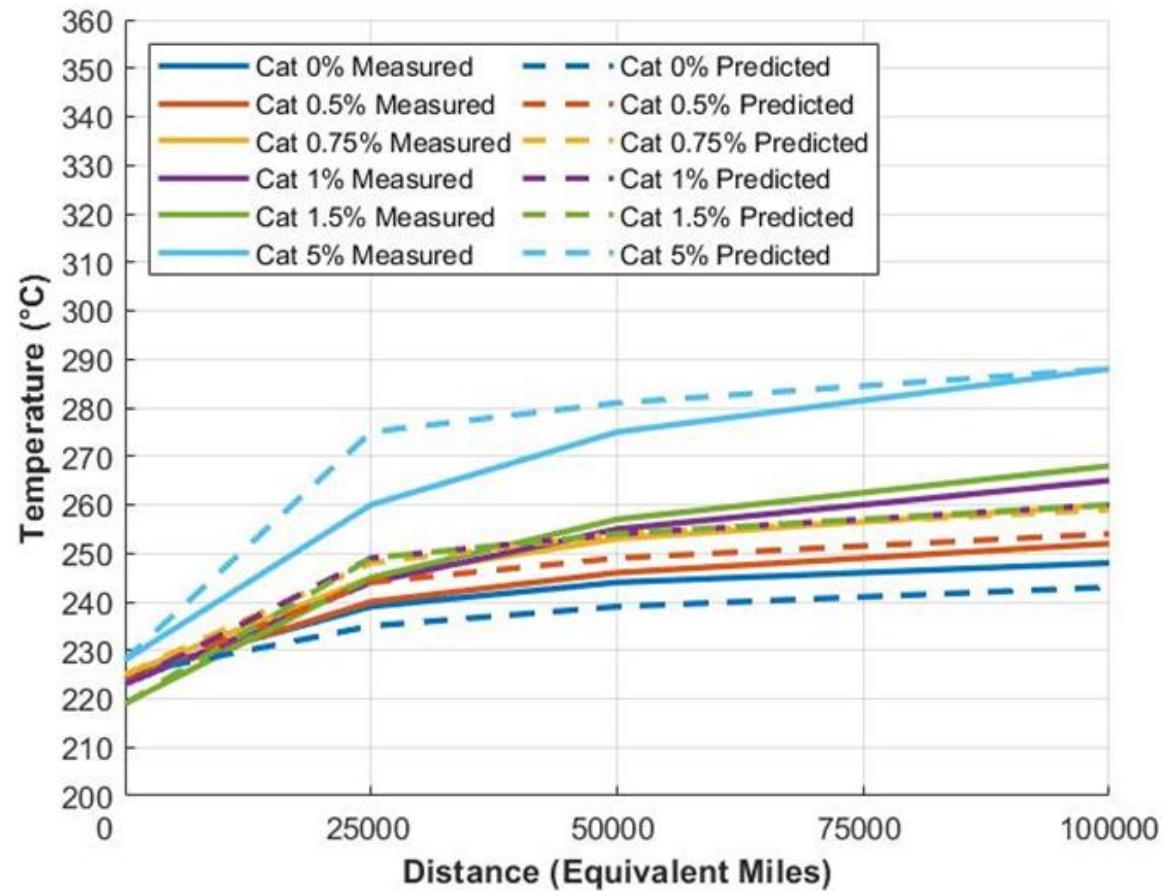
Analysis - Light-Off Temperatures

Measured LO Temps (°C)

Catalyst Sample	Ageing Distance (Equivalent Miles)			
	0	25,000	50,000	100,000
Catalyst 0% LO Temperature (°C)	225	239	244	248
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Predicted LO Temps (°C)

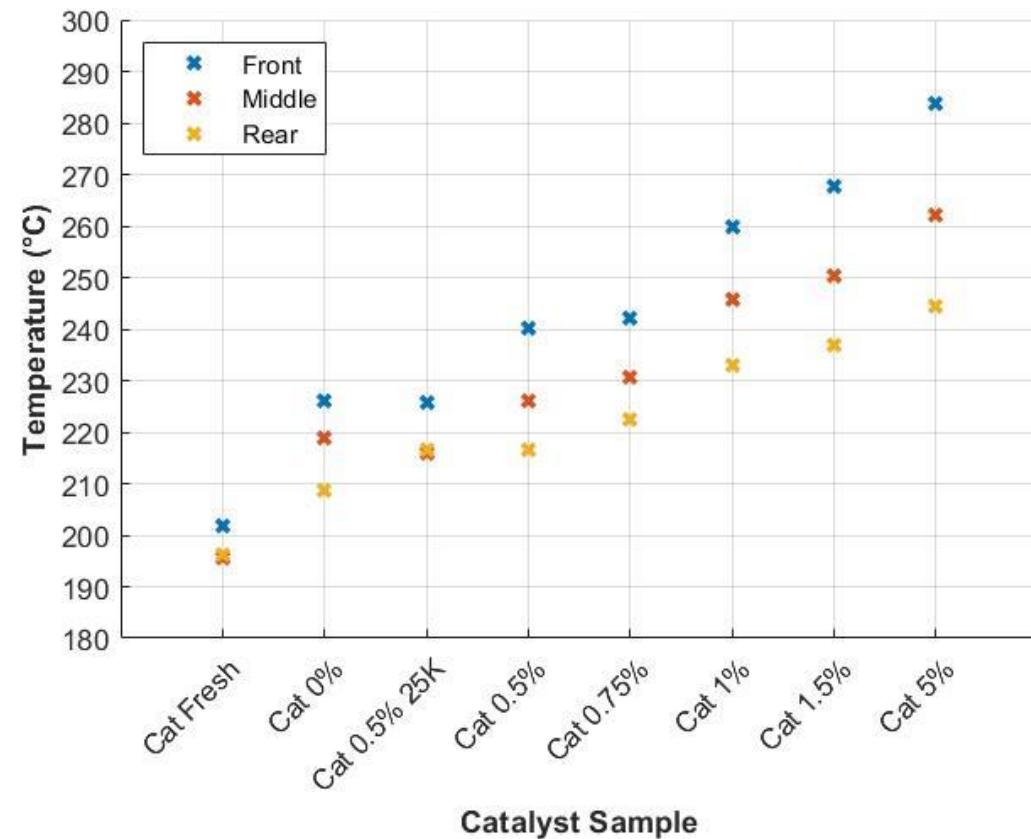
Catalyst Sample	Ageing Distance (Equivalent Miles)			
	0	25,000	50,000	100,000
Catalyst 0% LO Temperature (°C)	225	235	239	243
Catalyst 0.5% LO Temperature (°C)	224	244	249	254
Catalyst 0.75% LO Temperature (°C)	225	248	254	259
Catalyst 1% LO Temperature (°C)	223	249	254	260
Catalyst 1.5% LO Temperature (°C)	219	249	254	259
Catalyst 5% LO Temperature (°C)	228	275	281	287



Analysis - Light-Off Temperatures

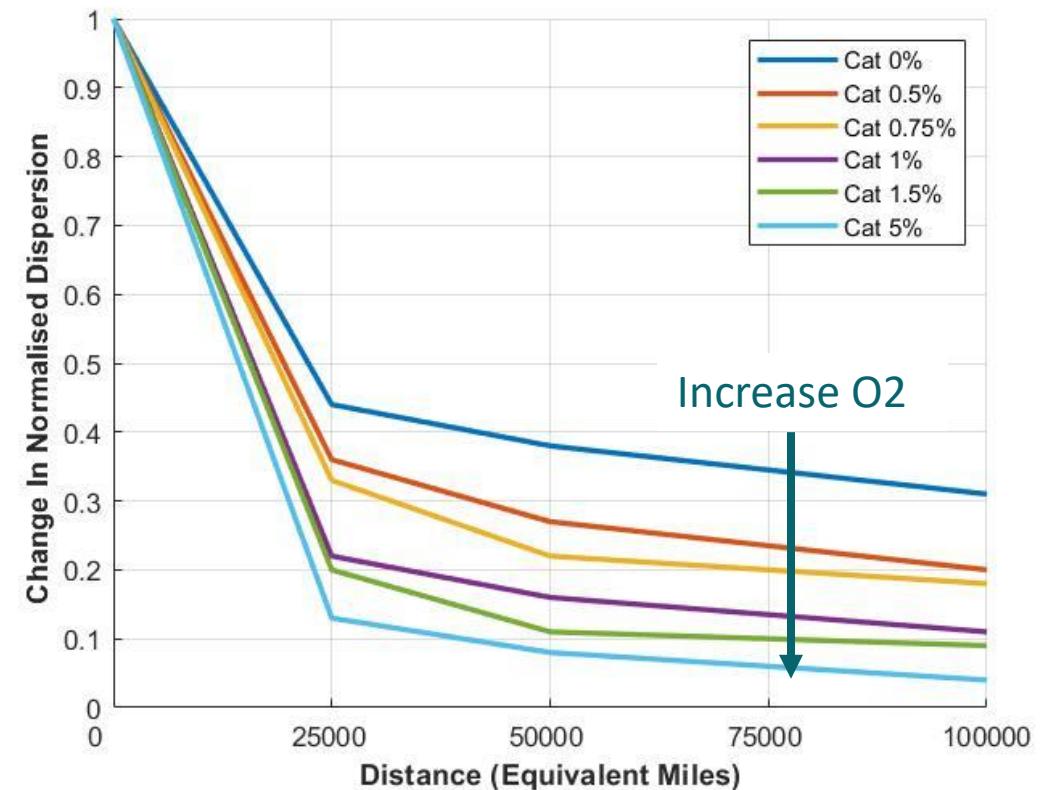
Cored light-off results, showing ageing throughout the catalyst brick.

Catalyst Sample	Front	Middle	Rear
Catalyst 0% LO Temperature (°C)	226	219	209
Catalyst 0.5% LO Temperature (°C)	240	226	216
Catalyst 0.75% LO Temperature (°C)	242	231	223
Catalyst 1% LO Temperature (°C)	260	246	233
Catalyst 1.5% LO Temperature (°C)	268	250	237
Catalyst 5% LO Temperature (°C)	284	262	245
Catalyst 0.5% 25K LO Temperature (°C)	226	216	216
Catalyst Fresh LO Temperature (°C)	201	196	196



Analysis - Change in Dispersion Throughout Ageing

Catalyst Sample		Ageing Distance (Equivalent Miles)			
		0	25,000	50,000	100,000
Catalyst 0%	Light-Off Temperature (°C)	225	238	243	250
	Normalised Dispersion (%)	1.00	0.44	0.38	0.31
Catalyst 0.5%	Light-Off Temperature (°C)	224	240	245	252
	Normalised Dispersion (%)	1.00	0.36	0.27	0.20
Catalyst 0.75%	Light-Off Temperature (°C)	225	245	252	259
	Normalised Dispersion (%)	1.00	0.33	0.22	0.18
Catalyst 1%	Light-Off Temperature (°C)	223	245	255	265
	Normalised Dispersion (%)	1.00	0.22	0.16	0.11
Catalyst 1.5%	Light-Off Temperature (°C)	220	245	256	267
	Normalised Dispersion (%)	1.00	0.20	0.11	0.09
Catalyst 5%	Light-Off Temperature (°C)	229	260	276	290
	Normalised Dispersion (%)	1.00	0.13	0.08	0.04



Conclusions

- Oxygen has a significant effect on degradation of catalyst performance and efficiency.
- It is not a linear relationship between an increase in oxygen and increase in deactivation.
- More severe ageing during the initial stages of deactivation.
- Current ageing theory does not accurately correlate with varying oxygen concentrations for palladium catalysts.
- Cored light-off tests concluded that the front of the catalysts were experiencing more ageing.
- Oxygen also has a significant effect on the change in dispersion on the catalyst.

**Thank you for your attention.
Questions?**