GENERAL MOTORS

EMISSION BENEFITS AND LIMITATIONS OF PASSIVE HYDROCARBON ADSORBER TECHNOLOGIES

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GM RESEARCH & DEVELOPMENT

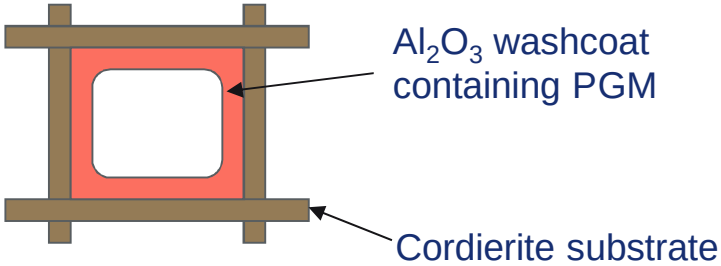
OVERVIEW

- Background – Passive HC Adsorbers
- Methods – Establishing Testing Protocol
  - HC selection
  - Reactor design
  - Sample information
- Results & Discussion
  - Controlling various HCs
  - Aging effects
  - Space velocity and Pd loading

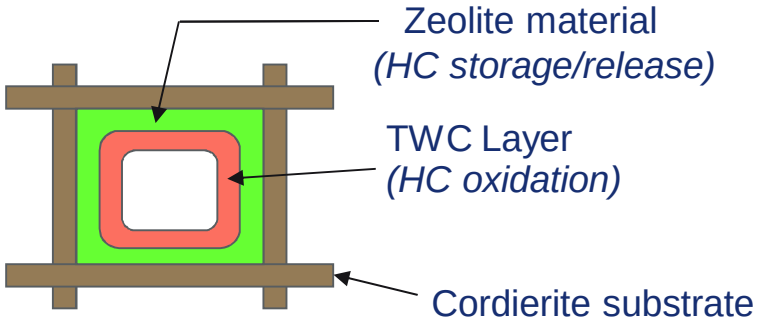
BACKGROUND - PASSIVE HC ADSORBER CATALYSTS

- As emission standards tighten, cold start emissions are the major contributor
  - Low-temperature (< 150°C) emission control is critical à STORAGE

Three-way catalyst coating



Typical HC adsorber coating

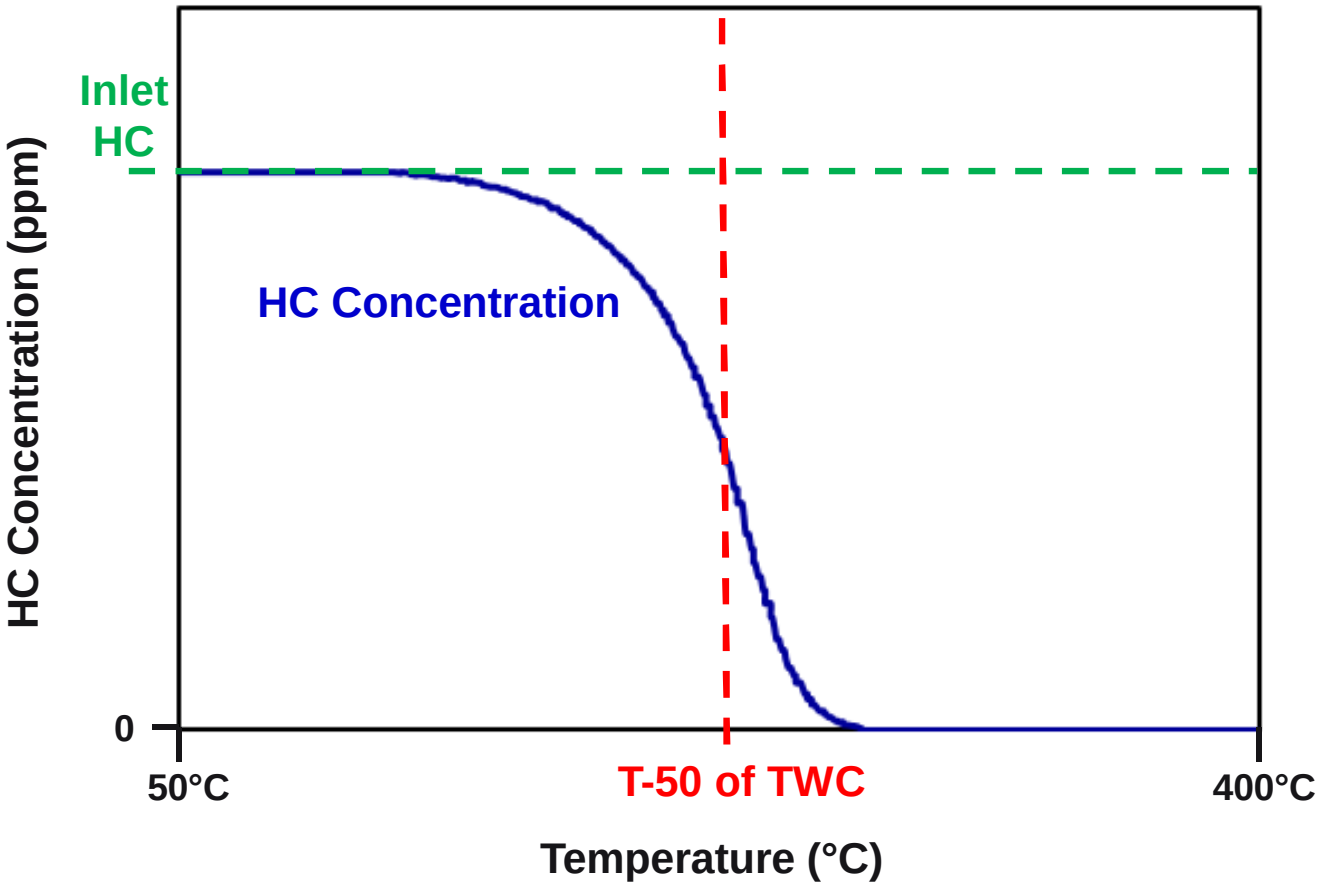


Source: Nissan, SAE Paper 2001-01-0892

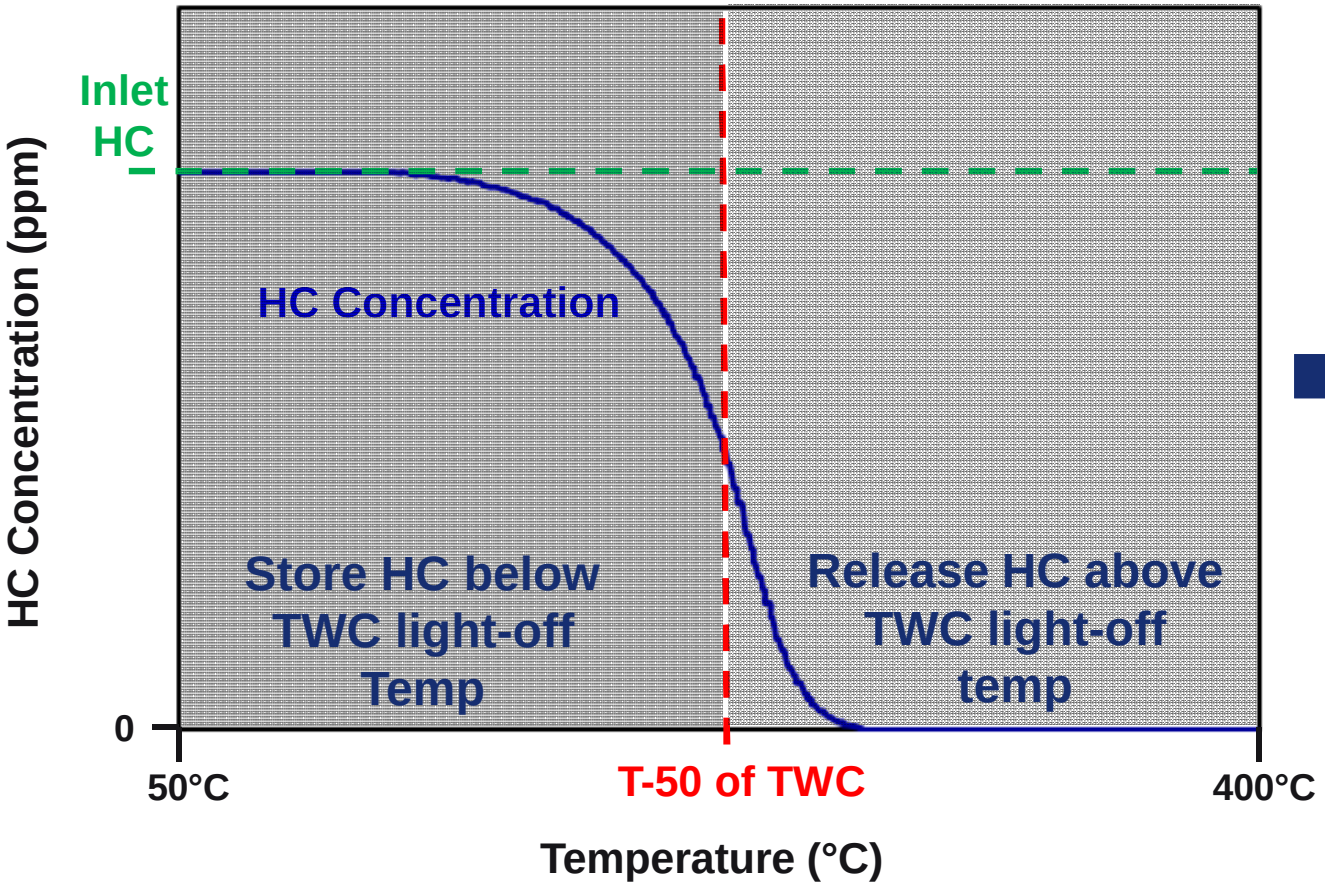
Desired Characteristics:

- Ability to store high concentrations of HCs during engine cold-start
- Ability to effectively convert (oxidize) stored HCs as they are released
- Good thermal durability

THREE WAY CATALYST HYDROCARBON LIGHT-OFF



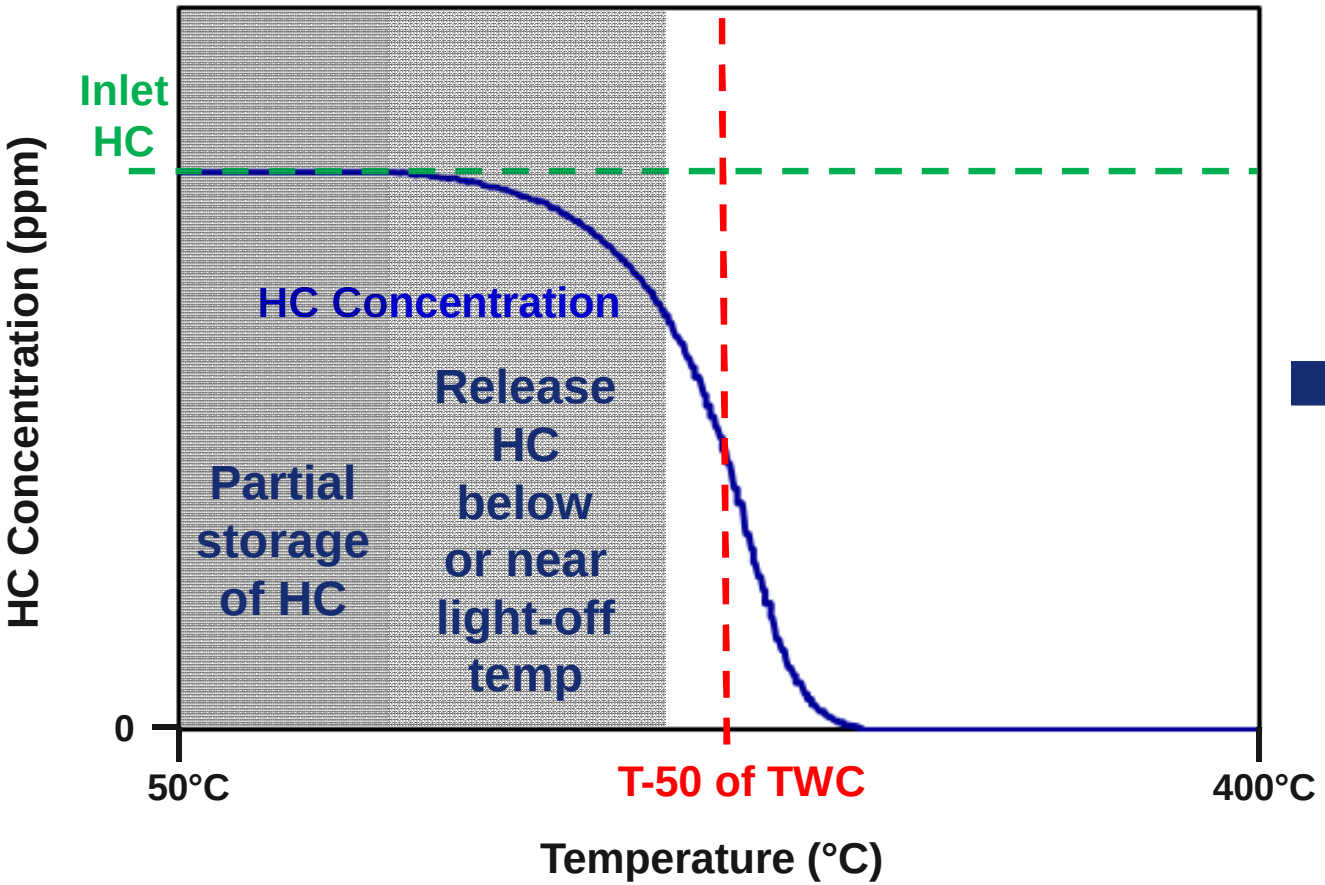
HC ADSORBER FUNCTION - IDEAL



IDEAL

Oxidize all stored HC

HC ADSORBER FUNCTION - REALITY



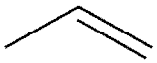
REALITY

Oxidize some portion of stored HC

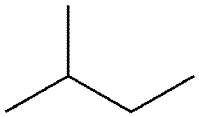
SIMULATED EXHAUST HYDROCARBON SELECTION

- Hydrocarbons common to gasoline exhaust:
  - Shorter chain *olefins* (C_2-C_6)
  - *i-pentane* is the major C_5 paraffin
  - *i-octane* is the major C_8 paraffin
  - Major *aromatic* components are C_7-C_9
- The concentration of normal paraffins is typically low

propylene

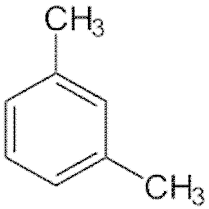


i-pentane

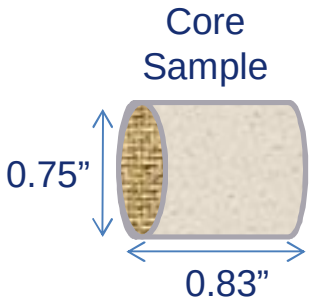


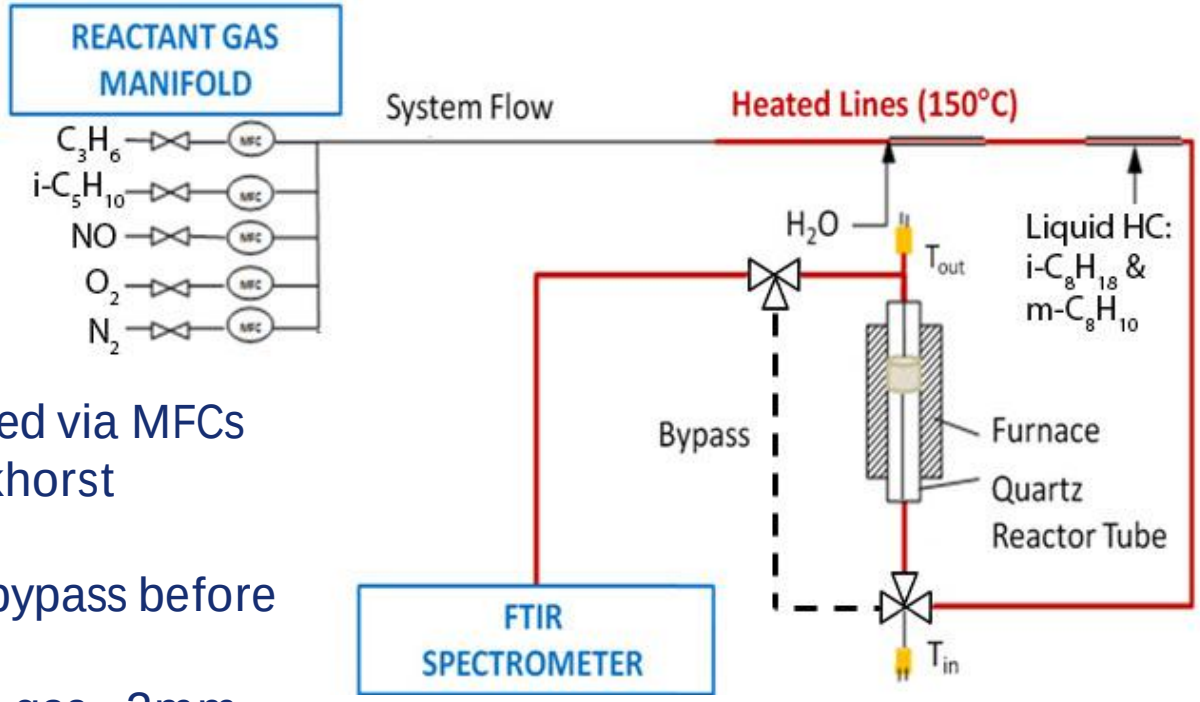
i-octane

m-xylene



REACTOR SYSTEM





- Gaseous components fed via MFCs
- Liquid HC fed via Bronkhorst evaporator
- Feed was stabilized in bypass before switching over catalyst
- T_{in} and T_{out} measured in gas ~2mm from sample

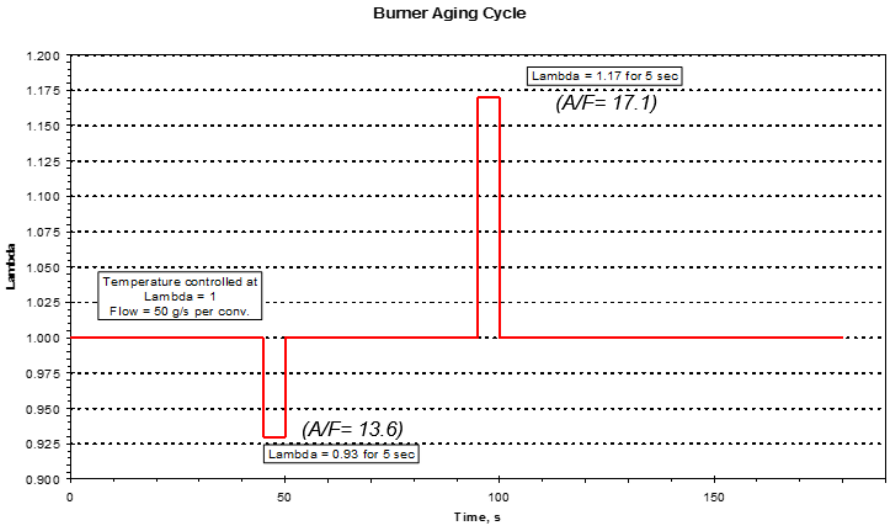
HC ADSORBER SAMPLES AND AGING

HC Adsorber	Pd:Rh (g/ft³)	50h/800°C	50h/850°C	50h/900°C
A-10	10:2	X		
A-50	50:2	X	X	X
A-100	100:2	X		
B-50	48:2	X		
B-70	68:2	X	X	X
B-100	98:2	X		

X = Tested

Main focus of this study

Aging performed in lab reactor with L/R cycling - 5s 3% CO, 5s 3% O_2; N_2 all other times; always with 10% H_2O, 10% CO_2

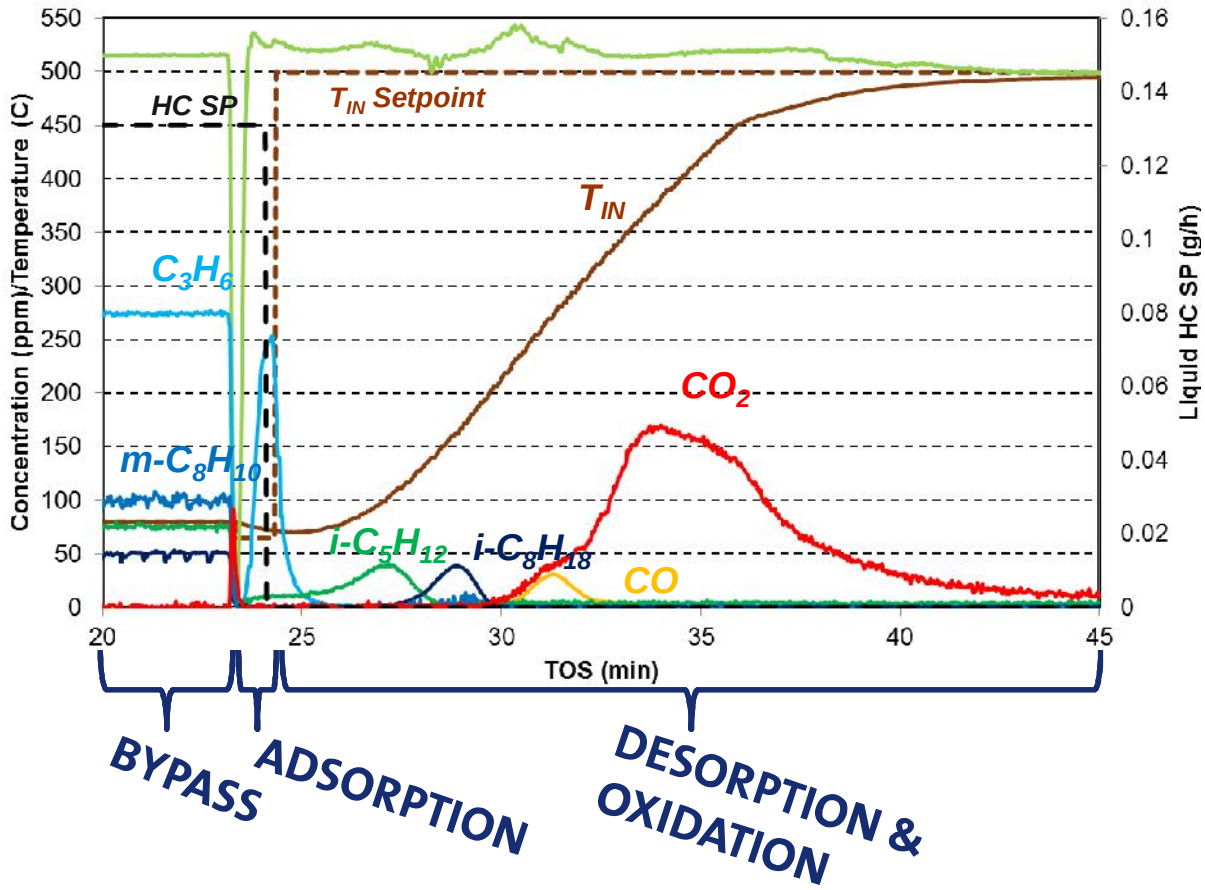


- Two different passive HC adsorber technologies (each with varied PGM loadings)
- Three different aging temps: 800, 850, 900°C

EXAMPLE RUN – SAMPLE A-50, 800°C AGED

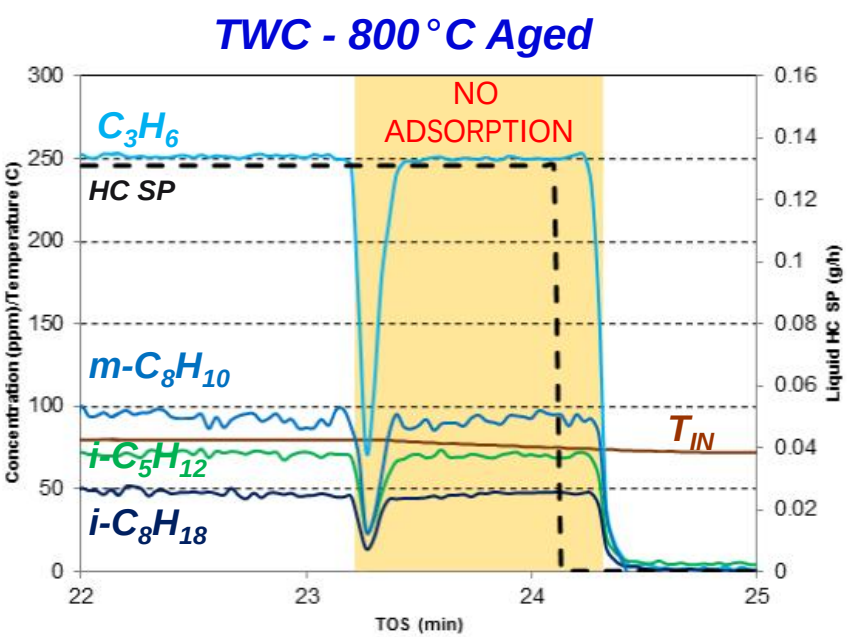
1. Pretreat 30 min/500°C with O_2 & H_2O
2. Stabilize feed in BYPASS
3. Switch feed over catalyst at 75°C – ADSORPTION
4. Cut off HC flow after 1 minute
5. Immediately set inlet gas temp to 500°C and begin ramping(~40 °C/min) – DESORPTION & OXIDATION

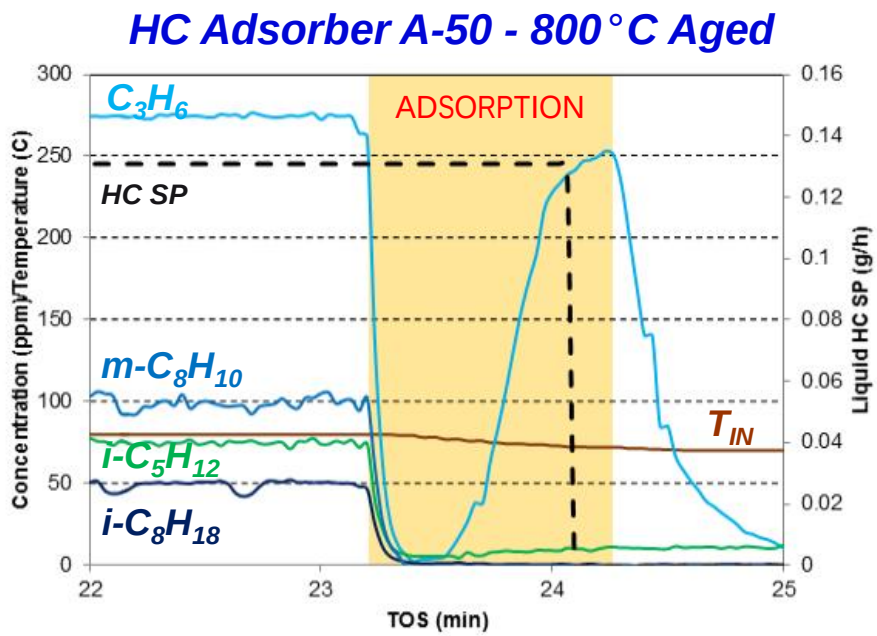
	PRETREAT.	ADS.	DES. & OX.
iso-pentane	0	70 ppm	0
iso-octane	0	50 ppm	0
m-xylene	0	100 ppm	0
propylene	0	250 ppm	0
NO	0	500 ppm	500 ppm
O_2	10%	5610 ppm	5610 ppm
H2O	5%	5%	5%



Note: No CO_2 in feed so that it could be used for carbon balance; 2300 ppm C1 HC during Ads.

ADSORPTION PHASE



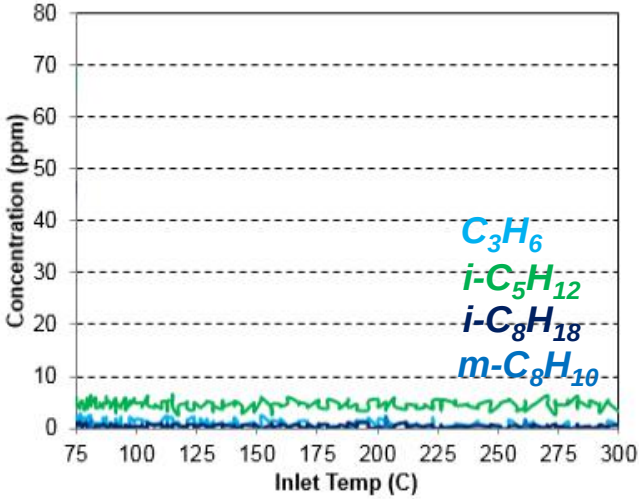


- TWC case comparable to empty reactor à no adsorption
- Adsorption of HC is real, not artifact of valve switching
- Case without adsorption integrated to determine total HC exposure

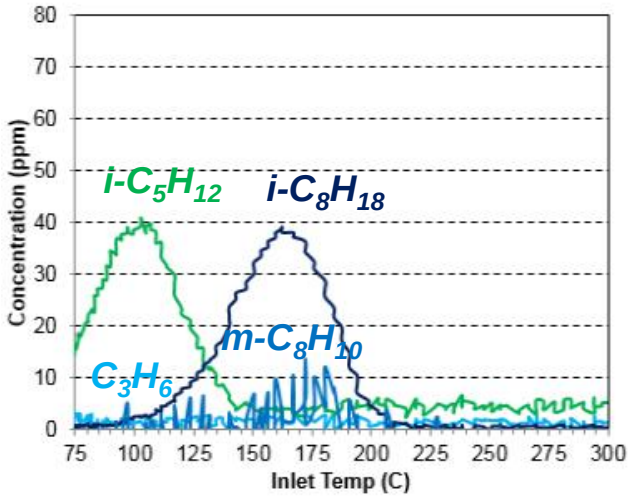
	% Storage Efficiency			
	C3H6	m-C8H10	i-C8H18	i-C5H12
A-50 800°C	38%	100%	100%	84%

DESORPTION AND OXIDATION PHASE

TWC - 800°C Aged



HC Adsorber A-50 - 800°C Aged

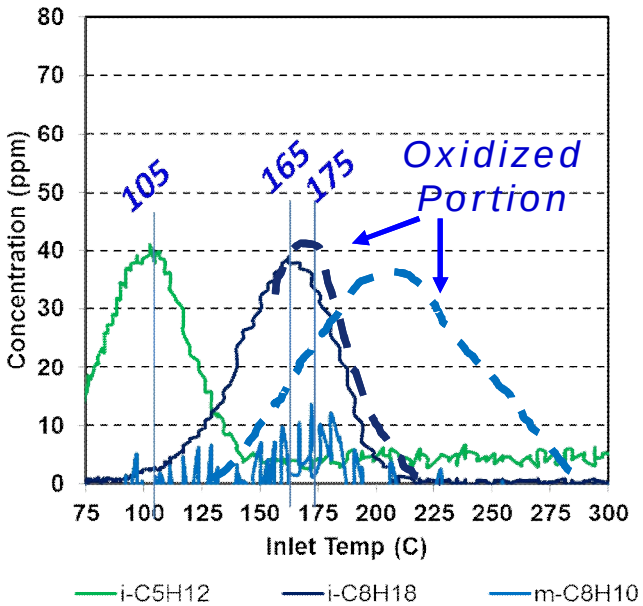


	% Storage Efficiency				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
A-50 800°C	38%	100%	100%	84%	100%	94%	6%	11%

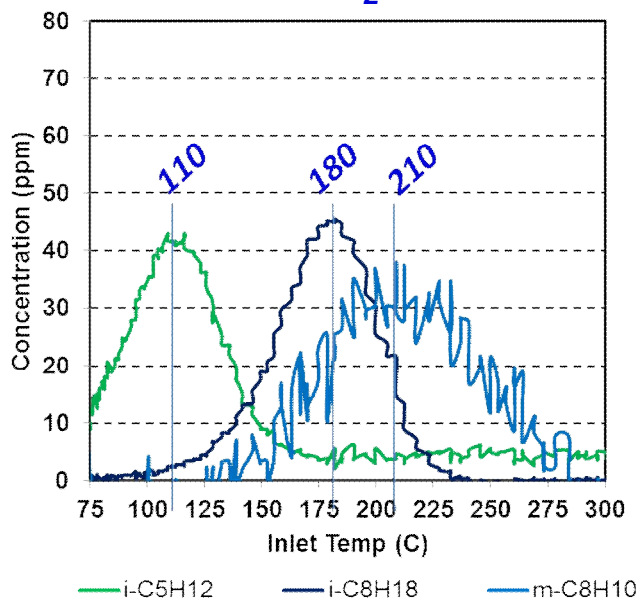
- TWC stores no HC
- Order of release: i-pentane, i-octane, m-xylene (No propylene release)
- m-xylene is almost entirely oxidized here à cannot determine true desorption temperature of m-xylene

PINPOINTING DESORPTION TEMP – TESTING IN ABSENCE OF O_2

Full Feed



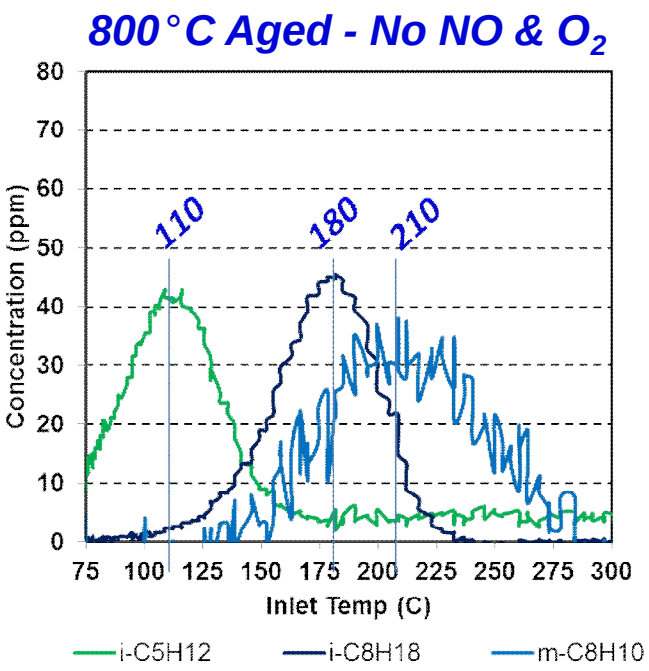
No NO & O_2 in Feed

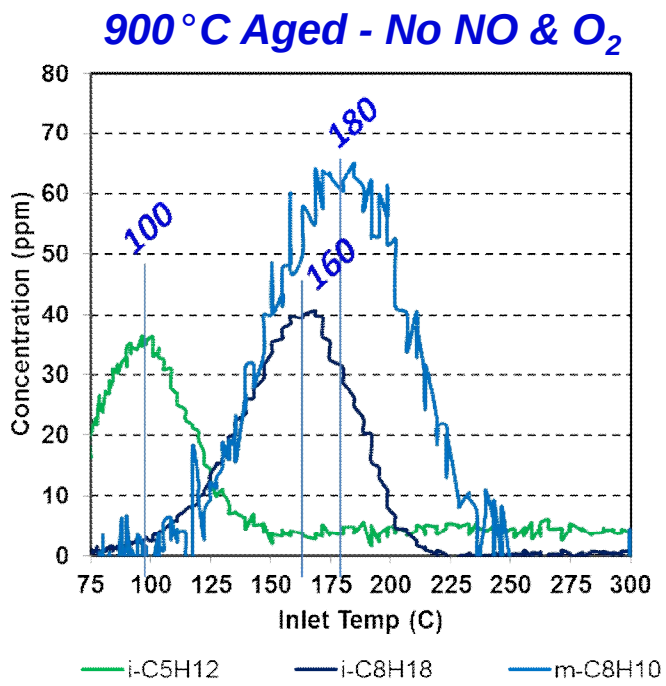


- Peak desorption temperatures appear lower due to oxidation
- A significant portion of m-xylene and smaller portion of i-octane are oxidized on the 800°C aged adsorber
- i-pentane desorbs well before light-off

Both aged 50h/800°C/10%H_2O

EFFECT OF AGING ON DESORPTION TEMPERATURES – SAMPLE A-50

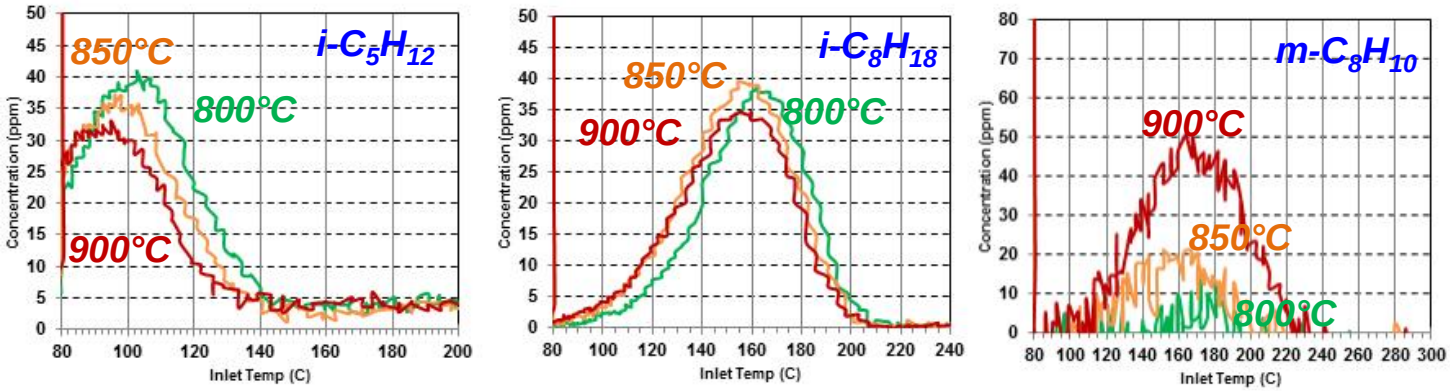




- After 900°C aging all desorption peaks shift to lower temperature (10-30°C shift)
- Desorption peak temperature of m-xylene is 30°C lower

IMPACT OF AGING – SAMPLE A-50

Temperature Programmed Desorption/Oxidation



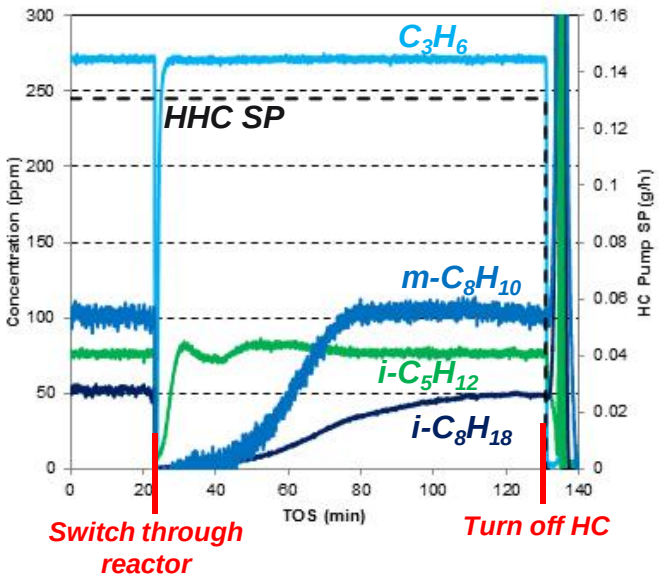
	% Storage Efficiency				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
A-50 800°C	38%	100%	100%	84%	100%	94%	6%	11%
A-50 850°C	0%	100%	100%	71%	n/a	72%	0%	2%
A-50 900°C	0%	100%	100%	62%	n/a	22%	4%	0%

- Propylene storage deteriorates after aging at 850°C or higher
- i-octane and m-xylene storage are maintained with aging, but desorption shifts to lower temperature
- Less i-pentane stored with aging and desorption shifts to lower temperature

EFFECT OF AGING ON ADSORPTION CAPACITY AND LIGHT-OFF TEMPERATURE – SAMPLE A-50

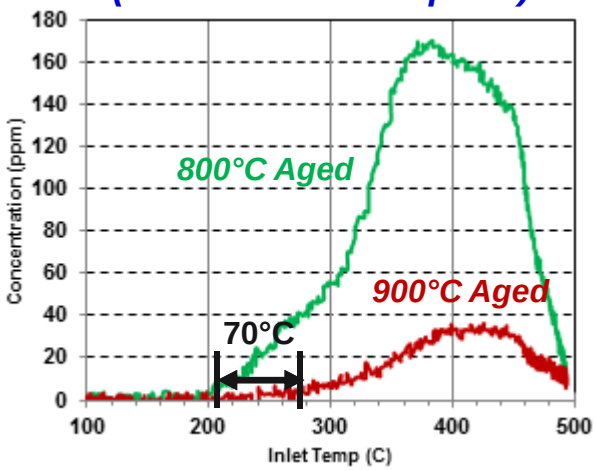
1. PRETREAT 30 min with O_2 & H_2O
2. Cool RCTR to 75°C and stabilize feed in bypass
3. Switch feed over catalyst, 2h ADSORPTION at 75°C

Adsorption to Saturation – 800°C Aged



Sample A-50	Quantity Adsorbed (g/L)
800°C Aged	15.8
900°C Aged	15.4

CO_2 Generation during TPD (after 1 min Adsorption)

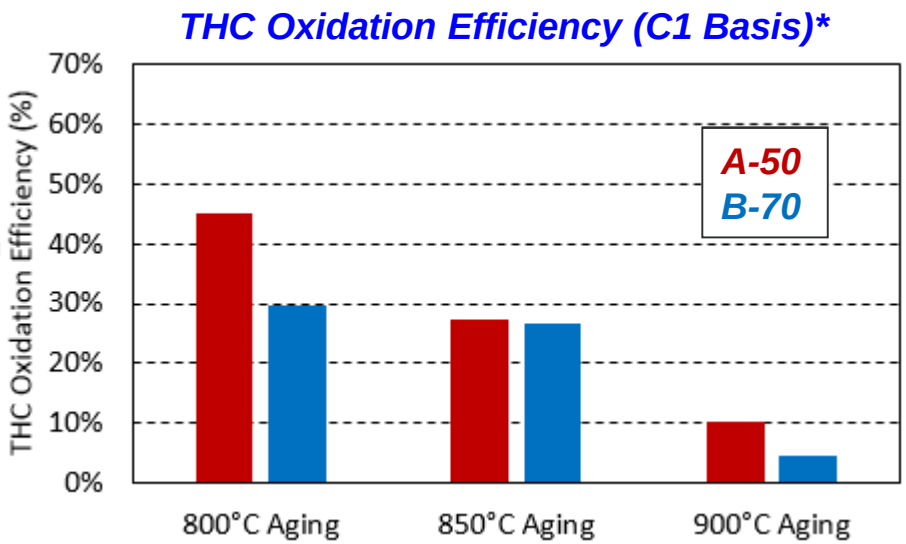


Deactivation mechanisms at 900°C:

- Desorption peaks shift to lower temperature
- Oxidation (T-50) shifts to higher temperature
- Propylene storage capability is lost

Total storage capacity is unaffected

OVERALL OXIDATION EFFICIENCY (% OF EXPOSED HC OXIDIZED) COMPARED TO ADSORBER B



** THC Oxidation Efficiency Calculated as Average of:*

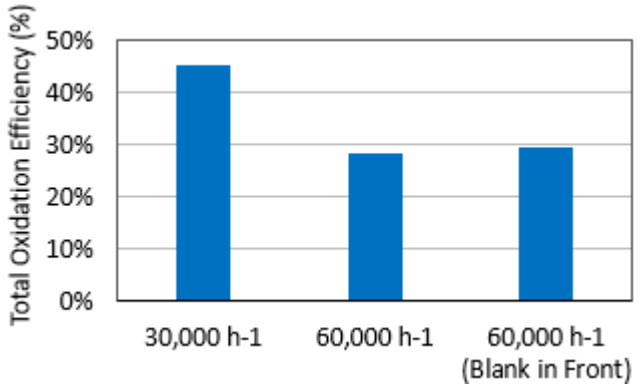
$$\frac{\text{(Exposed C1 HC - Released C1 HC)}}{\text{(Exposed C1 HC)}}, \quad \frac{\text{(CO+CO}_2\text{ Measured)}}{\text{(Exposed C1 HC)}}$$

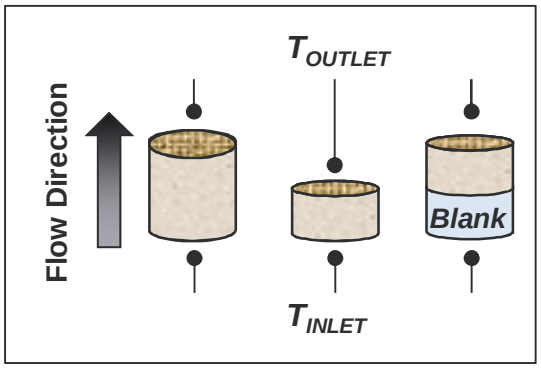
- ~45% of exposed HC are oxidized on A-50 aged at 800°C
- Adsorber B has significantly lower performance (30%)
- After 850°C both < 30%, after 900°C both < 10%
- For 800°C aged samples, significant differences in propylene and m-xylene performance (otherwise similar)

	% Storage Efficiency				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
A-50 800°C	38%	100%	100%	84%	100%	94%	6%	11%
A-50 850°C	0%	100%	100%	71%	n/a	72%	0%	2%
A-50 900°C	0%	100%	100%	62%	n/a	22%	4%	0%
B-70 800°C	8%	100%	100%	76%	100%	74%	8%	1%
B-70 850°C	8%	100%	100%	71%	100%	66%	3%	0%
B-70 900°C	0%	96%	86%	45%	n/a	20%	0%	0%

SPACE VELOCITY EFFECT – SAMPLE A-50

THC Oxidation Efficiency at 30k vs 60k h^{-1}





Full-size (30k h^{-1}) vs. Half-size (60k h^{-1})

** THC Oxidation Efficiency Calculated as Average of:*

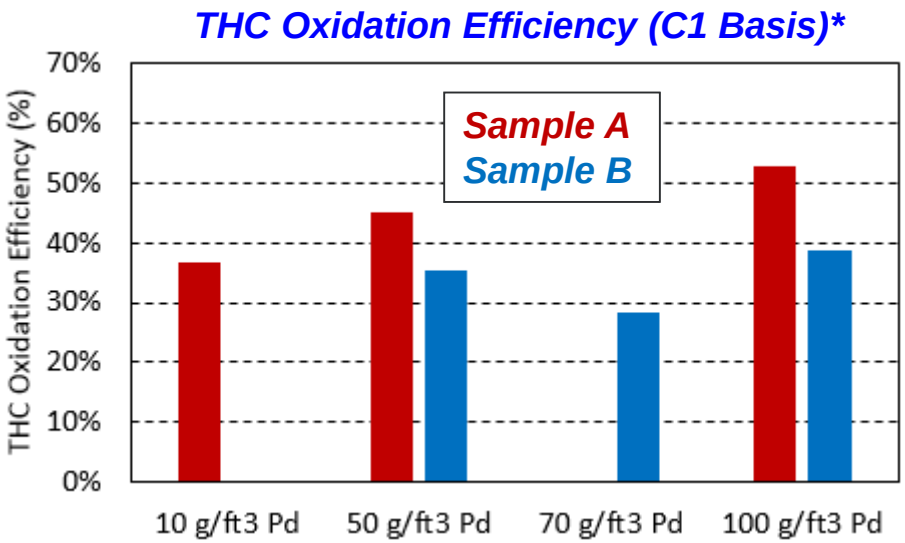
$$\frac{\text{(Exposed C1 HC - Released C1 HC)}}{\text{(Exposed C1 HC)}}, \quad \frac{\text{(CO+CO}_2\text{ Measured)}}{\text{(Exposed C1 HC)}}$$

All aged 50h/800°C/10%H_2O

	% of Exposed HC Stored				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
30,000 h-1	38%	100%	100%	84%	100%	94%	6%	11%
60,000 h-1	24%	92%	85%	57%	100%	67%	2%	5%
60,000 h-1 (Blank in Front)	23%	92%	85%	56%	100%	76%	0%	5%

- At 30k h-1 HC exposure is only 5% of the storage capacity (10% at 60k)
- Adsorption and oxidation rates are space velocity sensitive
- Longer sample may be able to re-adsorb HC downstream

PALLADIUM LOADING EFFECT



- Increasing Pd loading of Sample A improves:
  - Propylene storage
  - M-xylene oxidation
- Effect of increased Pd is minor for Sample B

** THC Oxidation Efficiency Calculated as Average of:*

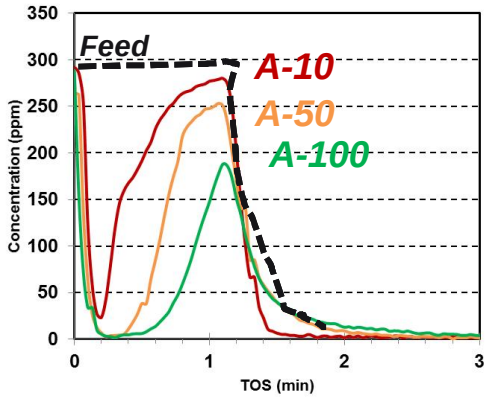
$$\frac{(\text{Exposed C1 HC - Released C1 HC})}{(\text{Exposed C1 HC})}, \quad \frac{(CO+CO_2 \text{ Measured})}{(\text{Exposed C1 HC})}$$

All aged 50h/800°C/10%H_2O

	% Storage Efficiency				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
A-10	13%	100%	100%	78%	100%	84%	0%	5%
A-50	38%	100%	100%	84%	100%	94%	6%	11%
A-100	61%	100%	100%	80%	100%	100%	15%	8%
B-50	15%	100%	100%	73%	100%	84%	2%	3%
B-70	17%	100%	100%	79%	100%	74%	8%	14%
B-100	26%	100%	100%	78%	100%	88%	8%	18%

PROPYLENE STORAGE TRENDS – SAMPLE A

Adsorption of Propylene



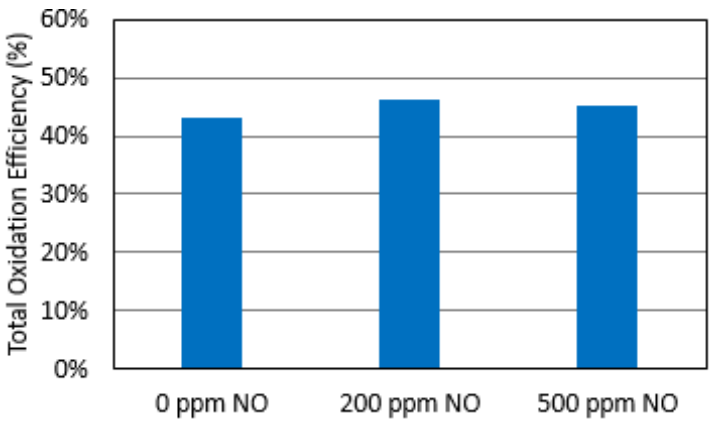
All aged 50h/800°C/10%H_2O

	% Storage Efficiency				% Oxidation Efficiency of Stored HC			
	C3H6	m-C8H10	i-C8H18	i-C5H12	C3H6	m-C8H10	i-C8H18	i-C5H12
A-10	13%	100%	100%	78%	100%	84%	0%	5%
A-50	38%	100%	100%	84%	100%	94%	6%	11%
A-100	61%	100%	100%	80%	100%	100%	15%	8%

- Relatively high storage of propylene on adsorber A (always completely oxidized)
- Propylene storage seems to be linked to Pd content

EFFECT OF NO - PROPYLENE VS. M-XYLENE

THC Oxidation Efficiency (C1 Basis)*



All aged 50h/800°C/10%H_2O

** THC Oxidation Efficiency Calculated as Average of:*
(Exposed C1 HC - Released C1 HC) / (Exposed C1 HC), (CO+CO_2 Measured) / (Exposed C1 HC)

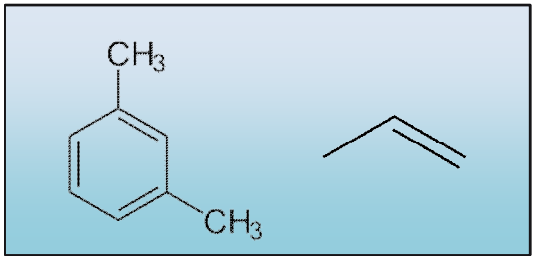
	% of Exposed HC Stored		% Oxidation Efficiency of Stored HC	
	C3H6	m-C8H10	C3H6	m-C8H10
0 ppm NO	69%	100%	100%	56%
200 ppm NO	57%	100%	100%	89%
500 ppm NO	38%	100%	100%	94%

- As NO concentration increases:
  - Less C_3H_6 stores
  - More m-xylene is oxidized
  - Overall % C1 HC oxidized is constant
- NO may inhibit adsorption of propylene
- Less propylene desorbing allows more m-xylene to be oxidized (similar T-50)

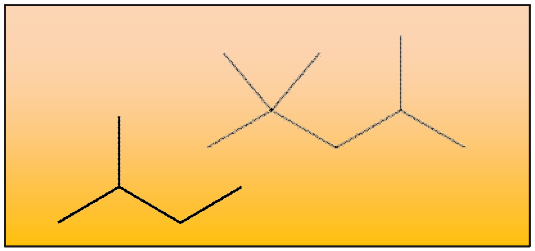
CONCLUSIONS

- Hydrocarbon make-up critical to overall HC adsorber performance
- Olefins and aromatics à controlled to some degree
- Alkanes à difficult to control
  - i-octane stores but releases before T-50
  - i-pentane stores <70% and releases well before T-50
- 900°C aging destroys performance of all adsorbers tested, but zeolite does not collapse
  - Total storage capacity is unaffected
  - Oxidation (T-50) shifts to higher temperature
  - Desorption peaks shift to lower temperatures
- Propylene storage appears to be linked to Pd sites

Controllable



Improvement Needed



Durability
≥ 850°C

GENERAL MOTORS

THANK YOU FOR YOUR ATTENTION!

Questions?

GM RESEARCH & DEVELOPMENT