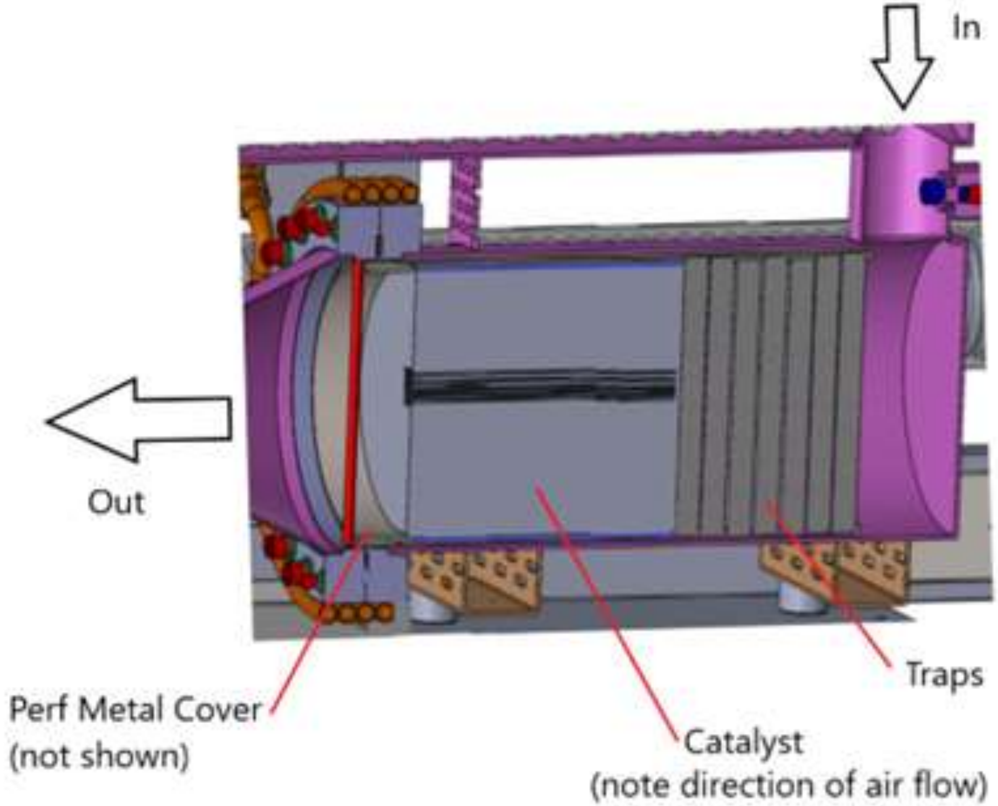
Heller Flux Reactor Overview
4-11-23

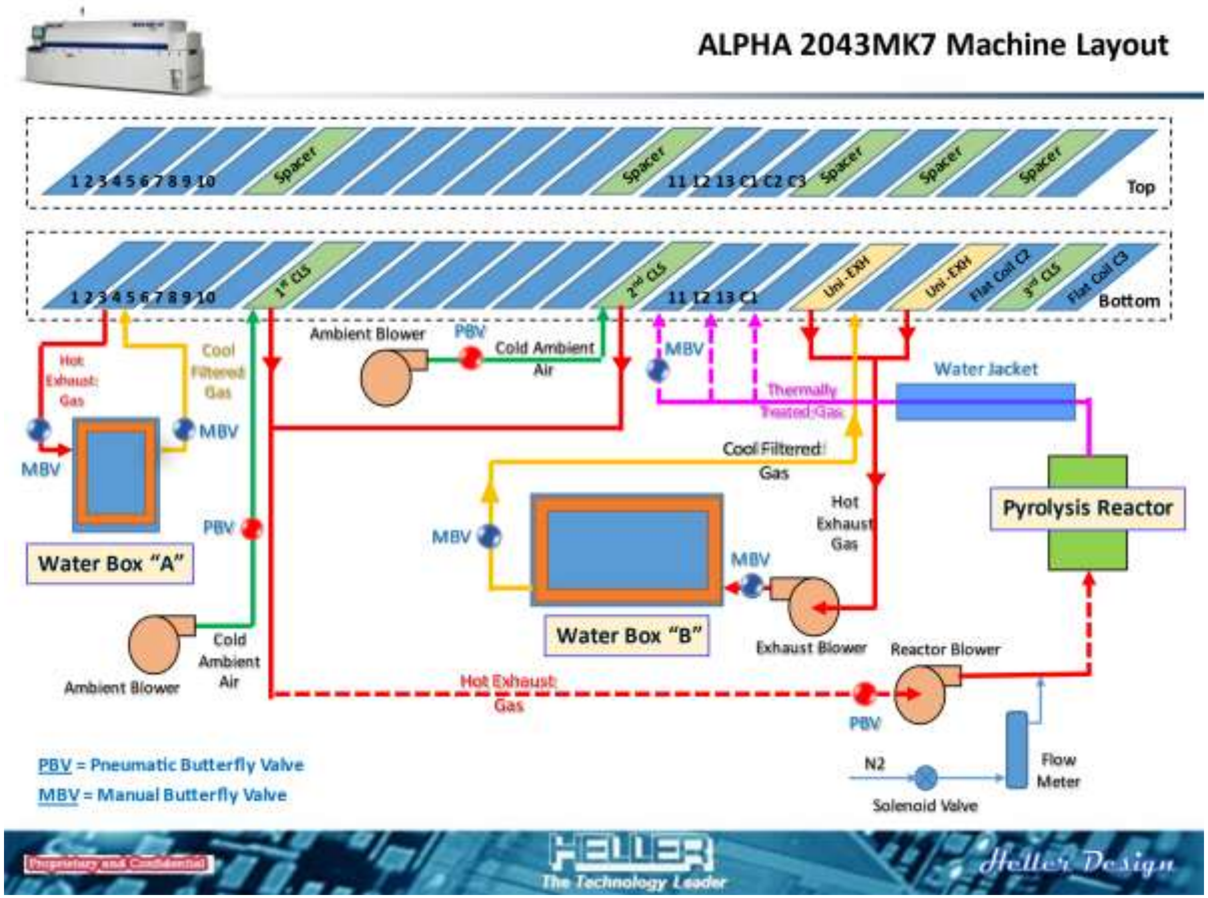
Operating Principle

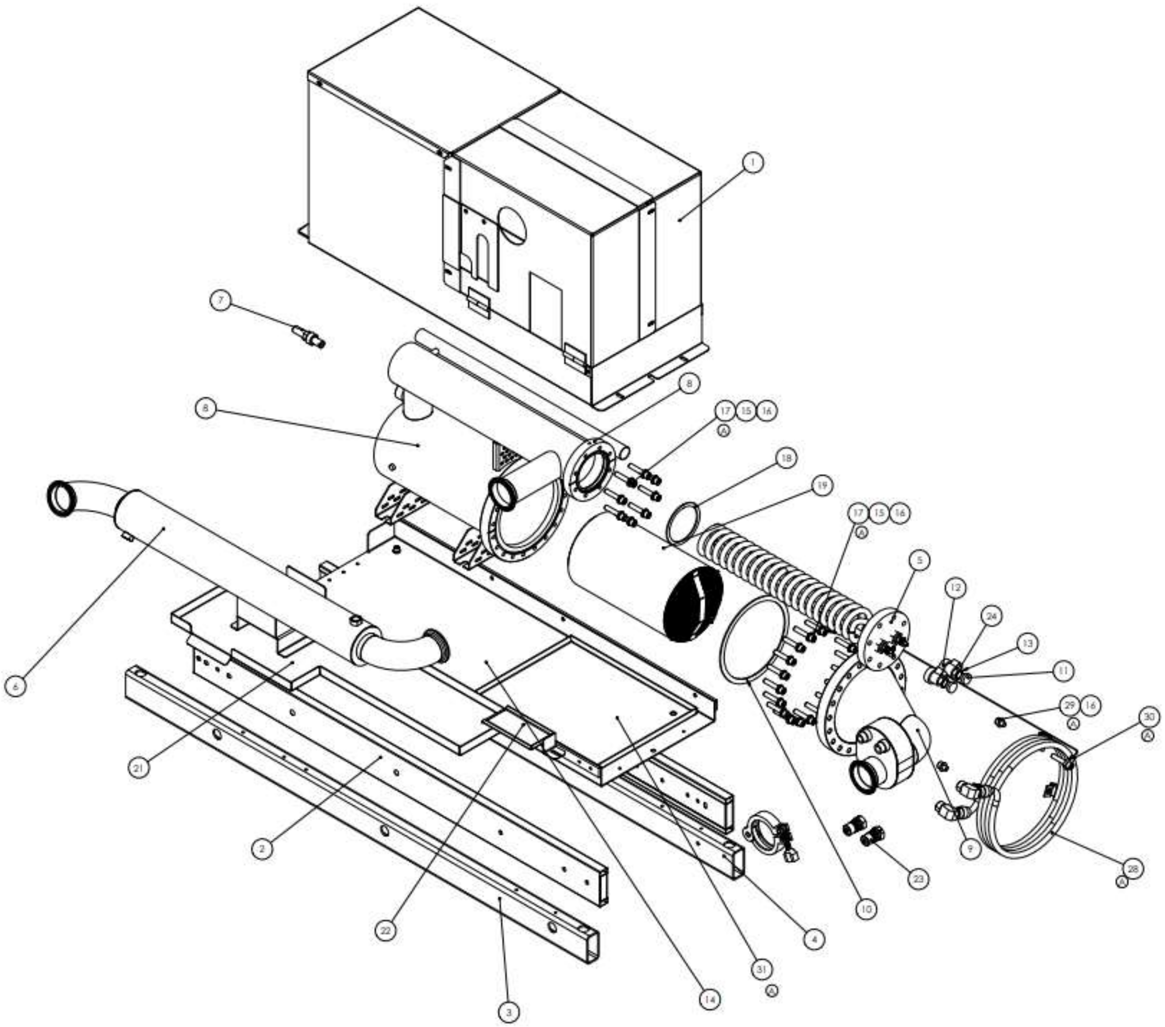
- Flux laden gas is exhausted from process chamber of a reflow oven.
- Gas is heated to approximately 500C.
- Heated gas is passed over wire mesh trap catalysts and then thru a ceramic honeycomb support /filter coated with non-precious or precious metal catalyst, with base metal promoters.

Cross Section Showing Configuration of Traps and Ceramic Substrate



Oven Diagram with Reactor





ITEM NO.	SIZE	PART NUMBER	DESCRIPTION	EXPLODED/QTY.
1	B	205030	REACTOR BOX	1
2		205025	SLIDING RAIL D2576-40 LOCK	1
3	B	205028-01	RAIL FIXED BEAM,REACTOR	1
4	B	205028-02	RAIL FIXED BEAM,REACTOR	1
5	B	205039-02	HEATER FLANGE ASSY	1
6	B	205042	RETURN DUCT	1
7	B	205041	TC TUBE ASSY	1
8	D	205038	REACTOR PIPE WELDMENT	1
9	D	205037	FLANGE WELDMENT W WATERJACKET	1
10	A	205020	6" CF Copper Gasket	1
11	A	295529	CERAMIC COVER, RING TERMINAL	2
12	A	205043	CERAMIC RING	2
13	CP	226359	WAVE WASHER (0.5"I.D. & 0.75"O.D.) - TUTCO	2
14	C	205029	REACTOR PLATE	1
15		95787M	M8 LOCK WASHER	27
16		95733M	M8 FLAT WASHER	30
17		96859	M8-1.0 X 40LG SHCS	28
18	A	205021	CF63 COPPER GASKET	1
19	B	205019	PYROLYSIS CAGE ASSY	1
20	CP	226227	CLAMP, 2" SANITARY FLANGE	1
21	D	205046	DRIP PAN	1
22	A	205047	DRIPPAN SMALL	1
23	CP	228170	QUICK DISCONNECT MALE, 3/8NPT	2
24	A	295528	CERAMIC SLEEVE, RING TERMINAL	2
25		95507M	M6X1.0 X 10mm SHCS	2
26		95592M	M6 WASHER LOCK	2
27		95591M	M6 FLAT WASHER	2
28	C	205464	FLANGE COIL ASSY, REACTOR	1
29	A	96861	M8-1.0 X 10MM SHCS	3
30	A	205467	PROBE T/C ASSY,BEND, REACTOR	1
31	C	205462	DRIP PAN , REACTOR INSIDE	1

NOTE:
1. NOT ALL SCREWS AND CLAMPS SHOWN
2. APPLY HIGH TEMPERATURE ANTI-SEIZURE OIL ON ALL SCREWS

NO DEVIATIONS, SUBSTITUTIONS OR EXCEPTIONS

REF:4147849

THIRD ANGLE PROJECTION

QUANTITY:
SO. No:
COMP. DATE:
NEXT ASSY QTY

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DIMENSIONS ARE IN MILLIMETERS

REACTOR ASSY

D 205027

A

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Wire Mesh Traps

Un-coated wire mesh trap

Coated trap

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Ceramic Substrate with Catalyst

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Focal Points

- Technical goals
- Flux Compound
- Reactor operation
- Catalyst & filter technology
- Contamination & characterization
- Reaction chemistry
- Novel aspects
- Summary

Technical Goals

1. Primary
   Reduce maintenance time & cost in the operation of a commercial flux reactor

2. Secondary
   Utilize O2 more effectively in the catalyst bed thereby minimizing unused O2 existing the reactor, while reducing catalyst cost

   Tertiary
3. Unify technology, if possible, for both formic and flux reactor tools

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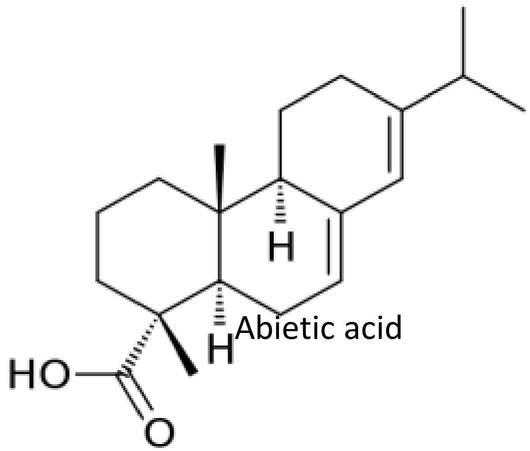
Analysis of flux reactor starting materials & contamination FTIR, Raman and GPC

Background: internal research indicates a typical flux composition may contain the following components



Abietic acid

- Rosin (resin) content is upward of 50-60% of a typical flux compound, eg, Abietic acid

- Abietic acid is a primary carboxylic acid in flux that serves to remove oxide formation from surfaces.

- Rheological modifiers & binders

- Solvent – linear glycols, + possibly some H20

- Small molecules, eg, ethers, alcohols, ketones

- Amines

Pyrolysis or devolatilization of flux occurs at elevated temperatures often in an inert or (02) deprived environment.
In general, heating flux compounds elutes lower molecular weight species that can undergo condensation producing small and larger molecular weight components that enter a reactor. Remaining materials in the crucible not volatilized are higher in aromatics content.
HC pyrolysis and oxidation are considered the early steps in the gasification of hydrocarbons.

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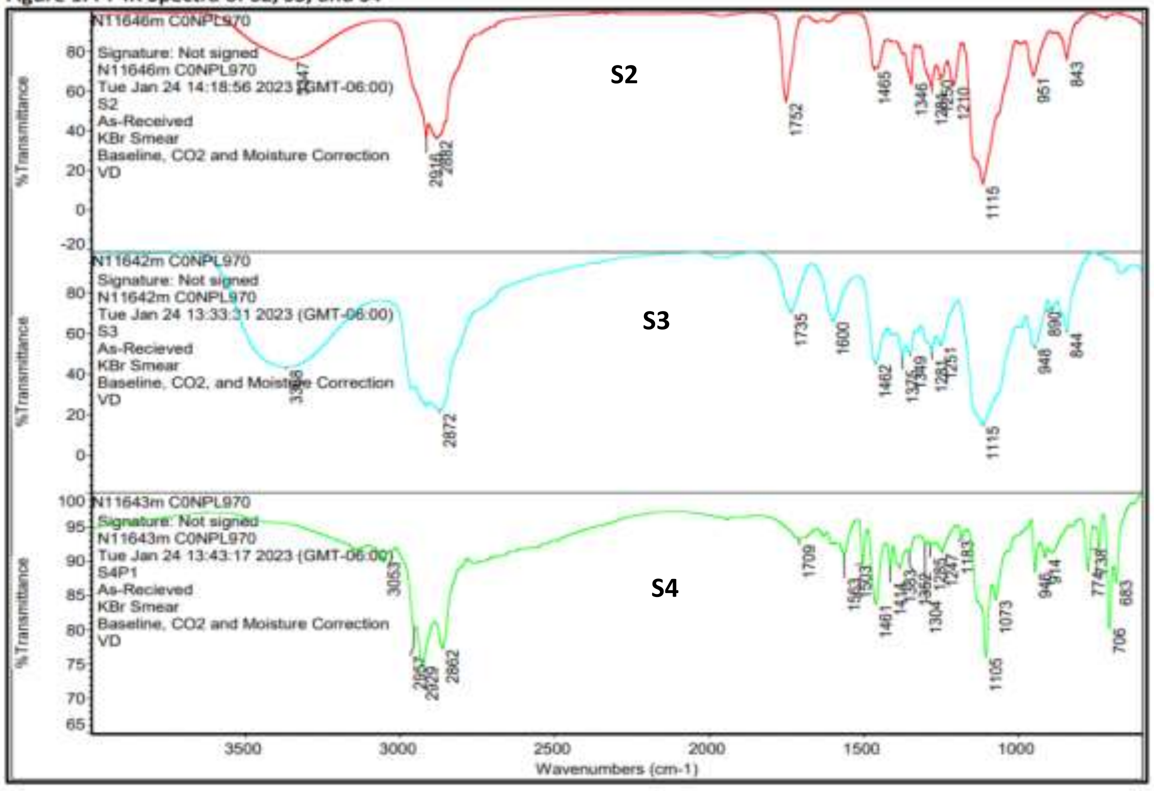
FTIR analysis of starting material flux, aged flux before and after the catalyst

Figure 1. FT-IR Spectra of S2, S3, and S4



Result

Crucible sample, pre-catalyst after aging.
Aromatic structures, with H2O loss
More condensate compared to reference

Reference flux sample akin to a non-ionic surfactant

Base plate sample following Zeolite extrude aging, post reactor
Phenyl-imidazole detected at reactor inlet with lower molecular weight species, observed post reactor compared to the reference

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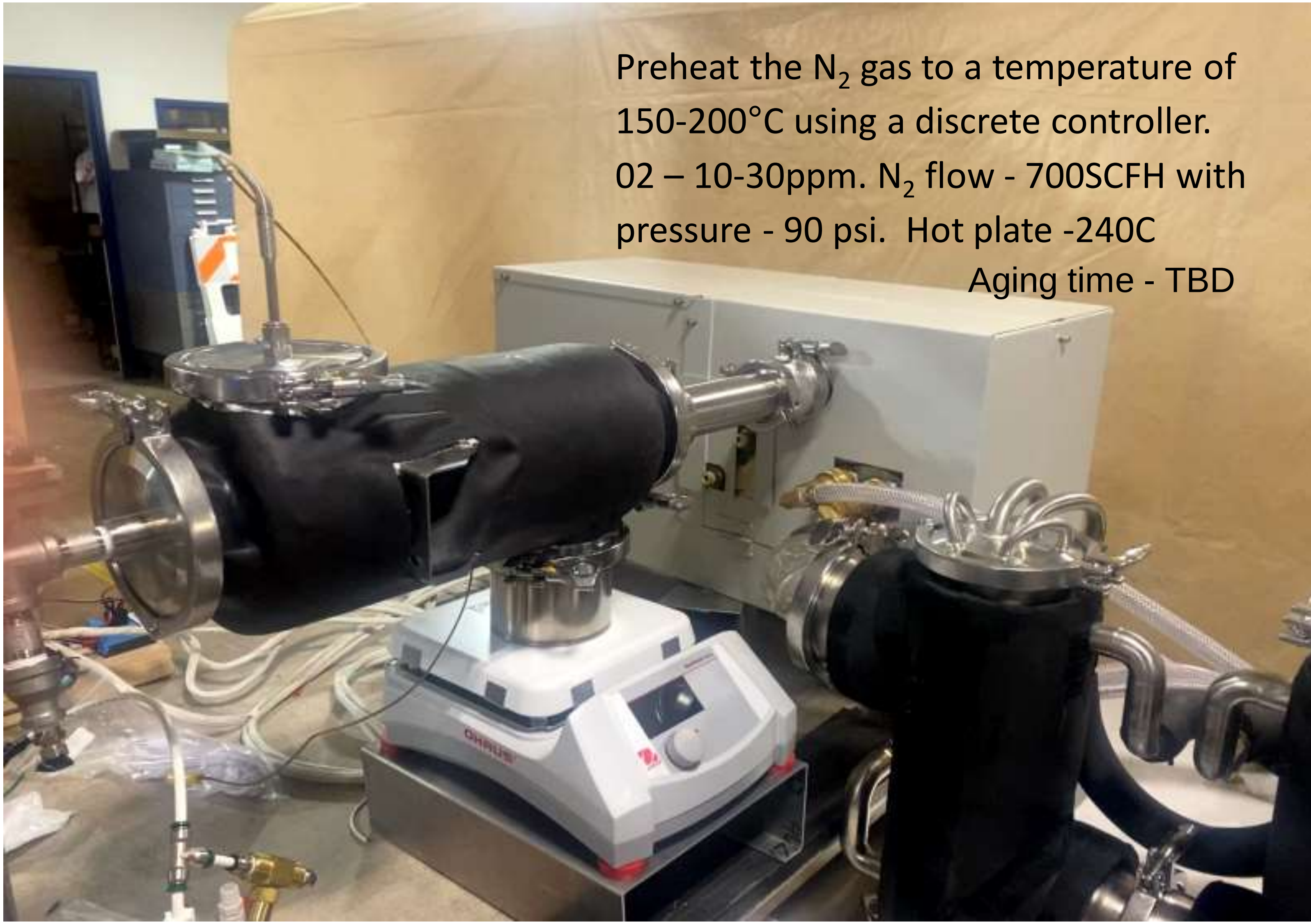
Flux Laboratory Reactor & Operating Conditions



Flux Test

C contamination poorly distributed on aged zeolite extrudate
GPF contamination more evenly distributed

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Result of a single aging cycle of zeolite extrudate

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GPF w/ Cu-Chabazite technology

Flux reactor Trap 1 upstream, ~25% volume wire mesh LPA-Cu catalyst

downstream, 75% volume Cu-Chabazite

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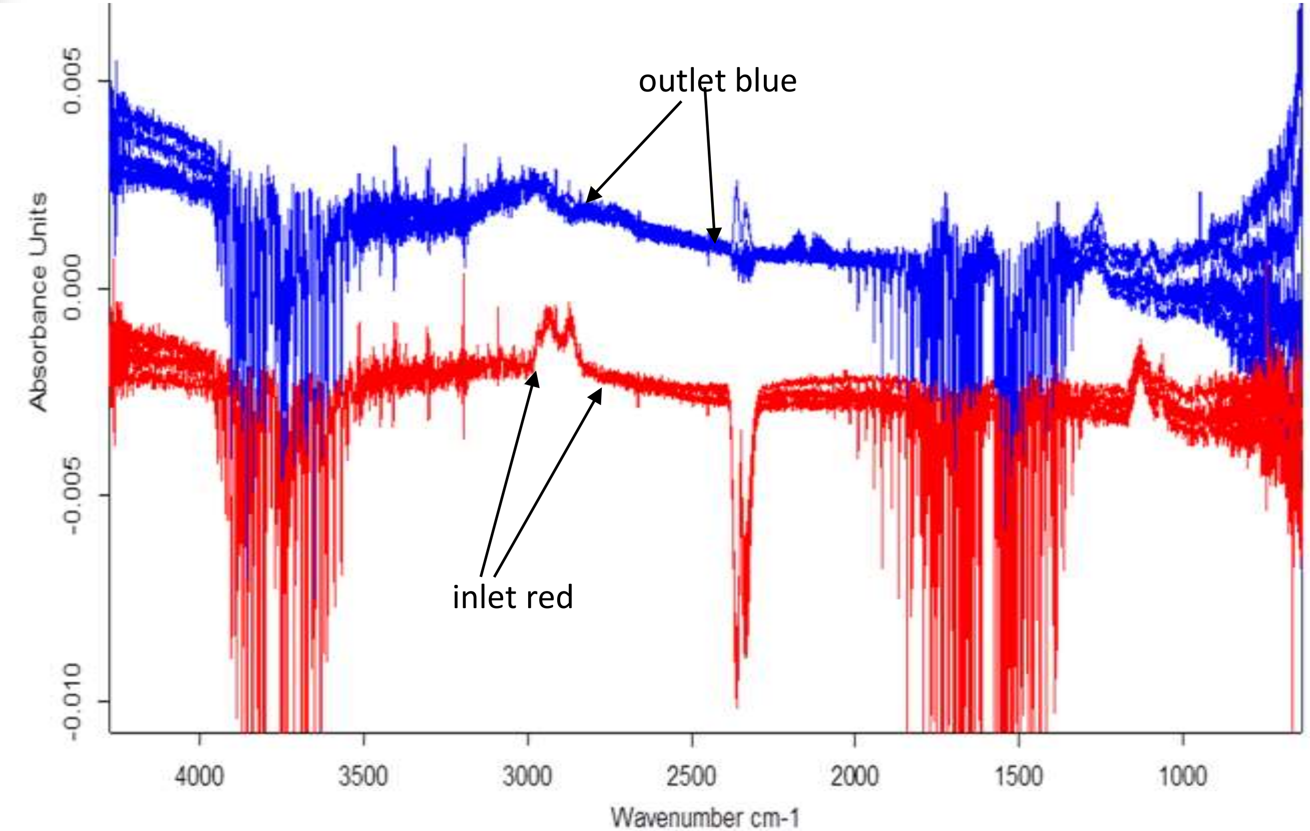
Full scale furnace

zeolite extrudate	GPF w/ Cu-Chabazite with pre-cats
Previous 10KG Flux Test Picture in 2020	**This time 10KG Flux Test Picture in 2023**

Cu-Chabazite A – beginning of run, 10% Cu -zeolite and wire mesh Cu coating on pre-catalysts

FTIR results show more CO, CO2 and water generated in outlet compared to the inlet



For A, inlet in red, water is detected as well as CO2 and some hydrocarbons.
For the outlet in blue, CO is forming and increasing and a new hydrocarbon at 1300cm-1. (unknown). CO2 is increasing at the outlet.

HC's – 2800cm-1
Water - 3750 & 1600cm-1
CO – 2100cm-1
CO2 – 2300cm-1

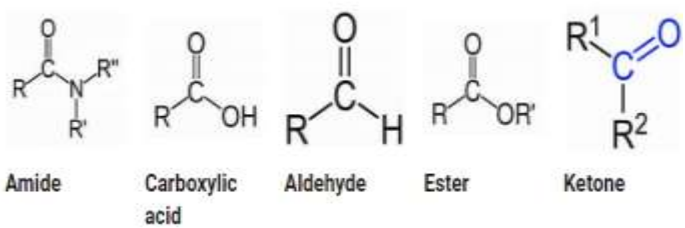
Reactive HC Species

Promyristyl-PM-3 $C_{23}H_{48}O_4$ (compound identified at reactor inlet)

<u>Physical properties</u>
BP 354 to 355C @ 760mm Hg
FP > 200F

Gas phase reactants eluted from crucible

Promyristyl-PM-3 $C_{23}H_{48}O_4$ formed at reactor inlet



+ **-Ether**
-Glycol
-Binder

$\longrightarrow$ HO----------[(C3H6)---O---------(CH2)13]$_n$--Me

~240C $\longrightarrow$ 200C
(crucible) (reactor inlet)

Condensation Rx (endothermic)

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O2 measurements before and after catalyst utilizing MFC & RapidOx Analyzer

O2 measurement on Cu-Chabazite on GPF, w/ no PM w/ 4 new wire mesh Cu catalyst traps, second aging

target	baseline	inlet	oulet	time
20	19.5	30	0	<1m
50	52	60.5	0	<1m
100	101	103.5	0	<1m
300	249.2	254	0	<2m
500				
high	1725	1731	1200+	

O2 measurement on DOC on DPF, 30.gPt/ft3 w/ 4 new wire mesh Cu catalyst traps, third aging

target	baseline	inlet	oulet	time
20	19.0	26.4	0	<1m
50	50.1	63.7	0	<1m
100	101.2	114.8	0	<1m
300	244.4	260.5	0	<1m
500				
high	1638	1646	42.1	1m

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Competing reaction chemistry, small chain volatile species formed in the gas phase in the crucible with larger chain species formed at catalyst inlet, not exclusive

1. Steam reforming - production of H2 and CO by reacting HC with H2O at temperatures above 400C
   CH4 + H2O (steam) $\longrightarrow$ CO + 3H2 (strongly endothermic)

2. Water-gas shift - reacting CO + H2O (steam) in the formation of CO2 + H2 (mildly exothermic)
   CO + H2O (steam) $\longrightarrow$ CO2 + H2

3. Partial oxidation with limited O2 in the feed (exothermic)
   2HC + O2 $\longrightarrow$ 2CO + H2

4. Condensation (polymerization) from reactor crucible to reactor inlet is exothermic
   (molecules losing potential and kinetic energy)

*The water-gas shift reaction (WGSR) describes the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen:
$\mathbf{CO + H_2O \rightleftharpoons CO_2 + H}$

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Aged Cu-LPA Wire Mesh Catalyst Traps

- 5 wire mesh Cu-catalysts in the
gas inlet position.

- Black color throughout matrices suggesting C capture

- Mesh matrix remains open, not blocked

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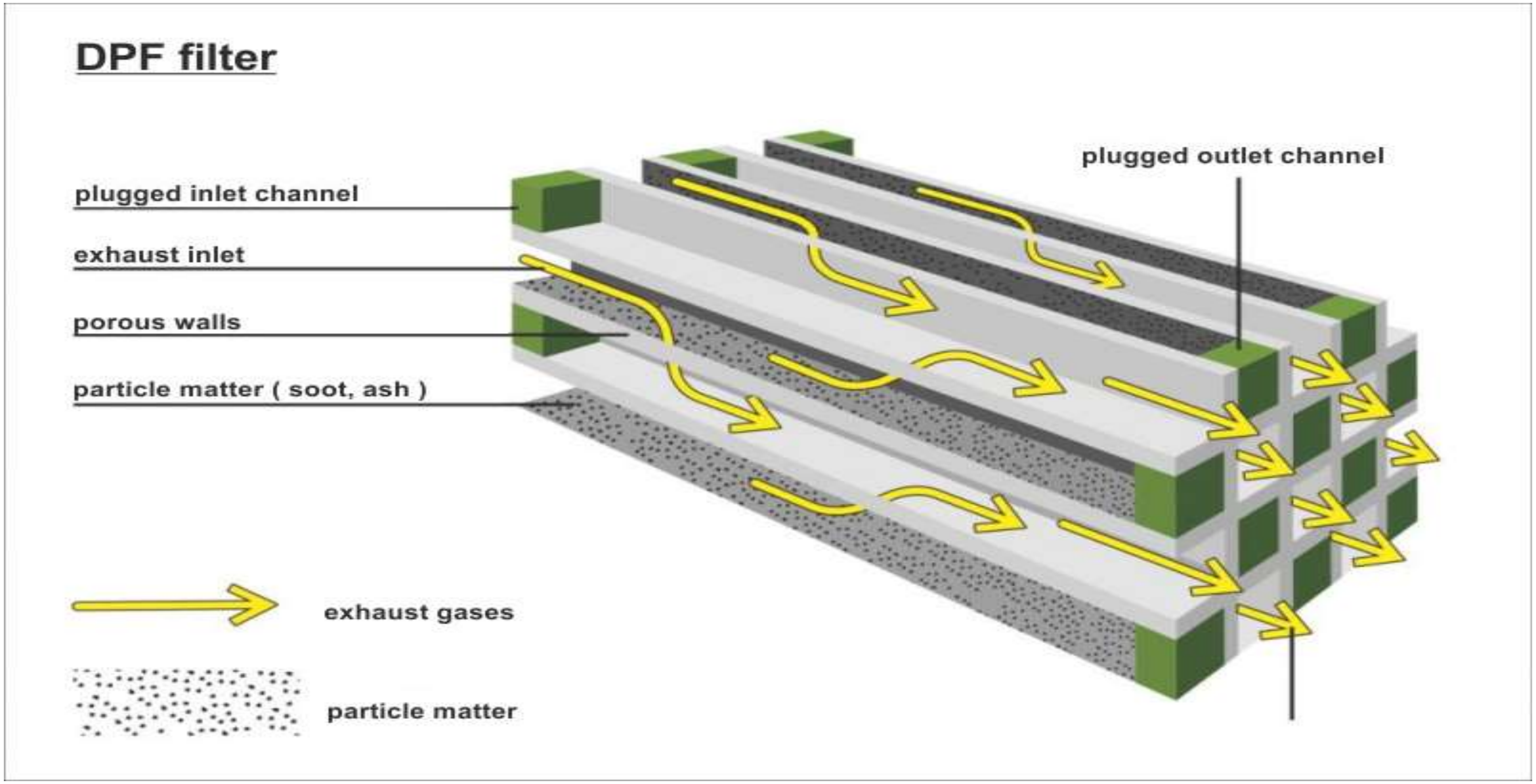
Catalytic Technologies to include - DOC, SCR, Zeolite and TWC
Substrates to include – SiC, metallic honeycomb and Cordierite, DPF & GPF

Material	Formula	Monolith Suppliers
Cordierite	$2MgO\text{-}2Al_2O_3\text{-}5SiO_2$	Corning, NGK, Denso, Hitachi Metals
Silicon carbide	SiC	Ibiden, NGK, Saint-Gobain, LiqTech
Aluminum titanate	Al_2TiO_5	Corning

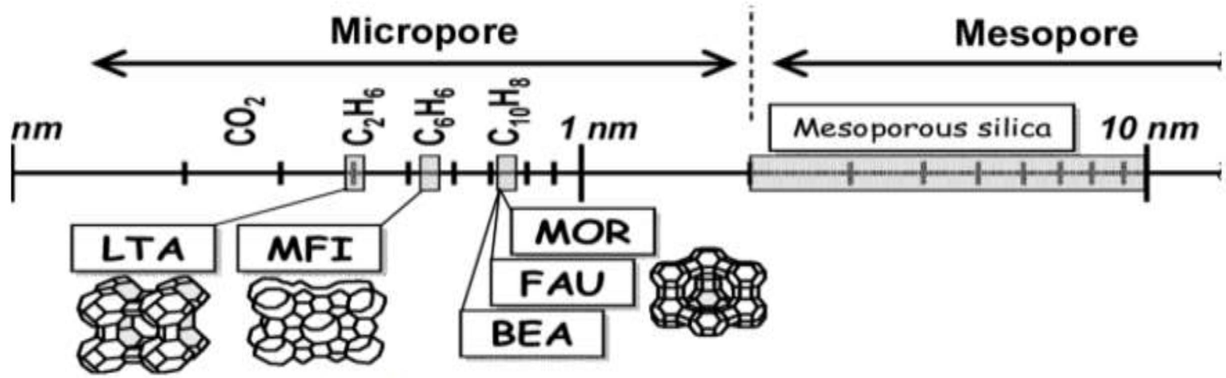


Zeolites – Pore Size

Pore Size	Number of Tetrahedra (MR [1])	Pore Diameter (Å)	Example
Small	8	4	PST-1 (NAT)
Medium	10	5.5	ZSM-5 (MFI)
Large	12	7.5	ZSM-12 (MTW)
Extra-large	>12	>7.5	CIT-5 (CFI)

[1] MR: Members of the ring.

Classification of zeolites according to their pore size.



Zeolite structure, pore size and molecular diameter of hydrocarbons.

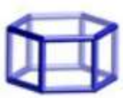
"some reactions can occur on the outer surface/pore mouth of a zeolite. reactive molecules don't always need to fit in the pore"

10% Cu-Chabazite Zeolite (ion exchange/impregnation)

Framework Type **CHA**

Framework

Cell Parameters:	trigonal	R -3 m (# 166)	
	a = 13.6750 Å	*b* = 13.6750 Å	*c* = 14.7670 Å
	α = 90.000°	β = 90.000°	γ = 120.000°
	Volume =	2391.6 $Å^3$	
	R_{DLS} =	0.0015	
Framework density (FD_{Si}):	15.1 T/1000 $Å^3$		
Topological density:	TD_{10} = 677	TD = 0.566667	
Ring sizes (# T-atoms):	8 6 4		
Channel dimensionality:	Topological (pore opening > 6-ring): 3-dimensional		
Maximum diameter of a sphere:			
that can be included	7.37 Å		
that can diffuse along	a: 3.72 Å	b: 3.72 Å	c: 3.72 Å
Accessible volume:	17.27 %		
ABC sequence	AABBCC sequence of 6-rings		
Secondary Building Units:	6-6 or 6 or 4-2 or 4		
Composite Building Units:			

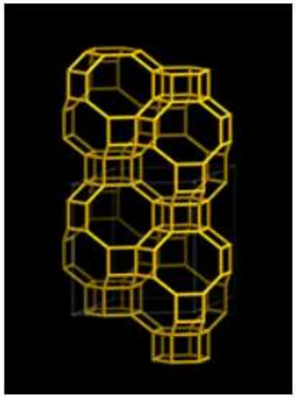


d6r (t-hpr)

cha (t-cha)

Natural Tiling *t-cha* *t-hpr*

Framework images
(click on icon for larger image)



Viewed normal to [001]

projection along [001]

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Summary & Remarks - Materials Characterization

1. Reference virgin flux sample characterization by FTIR suggests this material is chemically similar to a non-ionic surfactant

2. Aged flux from the reactor crucible shows the presence of aromatic rings, more condensate and less H2O compared to the reference

3. Post reactor sample shows the presence of lower molecular weight species compared to reference

4. Reference flux and aged flux collected from the reactor crucible show similar chemical properties to PEG, ethylene oxide, fatty acid condensate, alcohols and propylene

5. Reference flux material analysis by GPC shows light volatile fractions are ~ 4X as higher in concentration by number as compared to heavier molecular weight species

6. Aged crucible flux sample shows growth in size for the smaller and larger weight species

7. GPC analysis refinement of the reference flux, shows the lighter fraction exist over a range in molecular weight

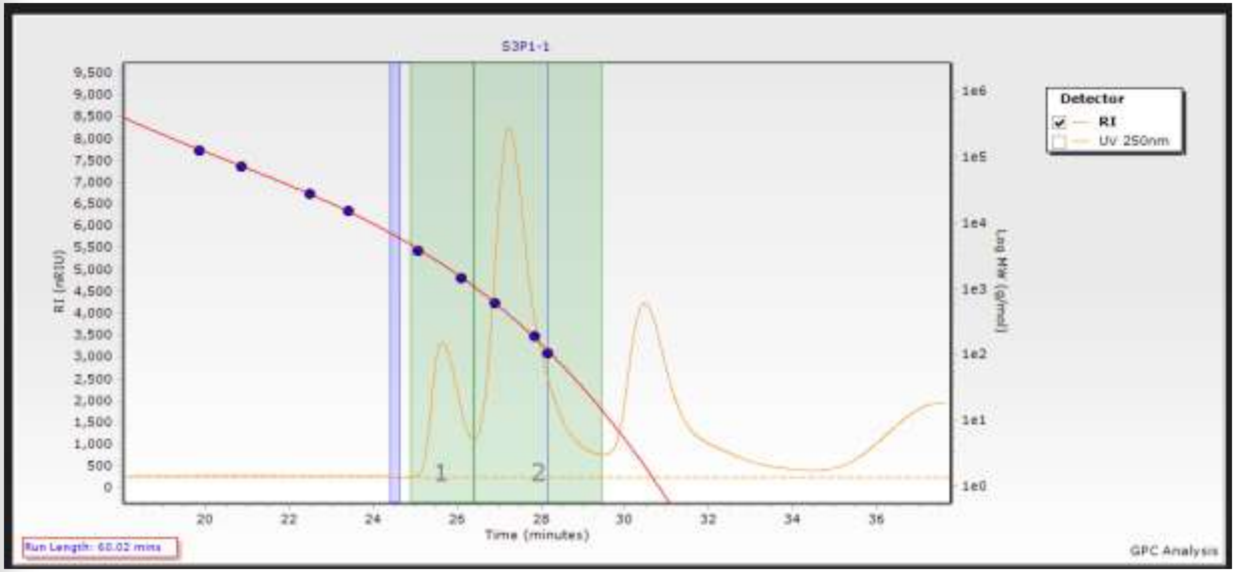
8. HC's exiting the reactor on base plate 1 are largely smaller molecular weight species, very possibly the species contaminating furnaces

9. Four distinct retention volumes visualized. Overlay results suggest the aged crucible sample have the highest molecular weight species while those detected post catalyst have the lowest molecular weight

Novel - Unique Features

- None-PM solution demonstrated
- Pre-cat wire mesh base metal catalyst
- SOF capture on wire mesh catalysts
- Surface and bulk chemistry
- Minimal bypass
- Ready access to active sites
- Regenerable
- Cost effective
- Acceptable operating back pressure
- Different substrate types
- Flexibility in integration
- Wider choice in catalytic materials
- Multiple coatings
- Layering, zone and gradient coating
- Higher surface areas, (materials & substrates)
- Substrate wall filtration

S3 – <u>reference flux</u> – virgin material analysis by GPC shows light volatile fractions are ~ 4X as high in concentration by number as heavier molecular weight species



			Peak 1					Peak 2				
Sample Description	**Preparation**	**Injection**	**Mp**	**Mn**	**Mw**	**Mz**	**PD**	**Mp**	**Mn**	**Mw**	**Mz**	**PD**
S3	1	1	2,376	2,000	2,166	2,328	1.08	395	165	346	475	2.10
		2	2,376	1,991	2,164	2,334	1.09	395	166	346	475	2.08
	2	1	2,393	2,001	2,176	2,349	1.09	399	169	351	479	2.08
		2	2,376	1,996	2,170	2,340	1.09	395	172	353	478	2.05
	Average		2,380	1,997	2,169	2,338	1.09	396	168	349	477	2.08
	Standard Deviation		9	5	5	9	0.00	2	3	4	2	0.02
	% RSD		0	0	0	0	0	1	2	1	0	1

$\overline{M}_p$ – peak average molecular weight; $\overline{M}_n$ – number average molecular weight; $\overline{M}_w$ – weight average molecular weight; $\overline{M}_z$ – z-average molecular weight; PD – polydispersity index; Molecular weight (M) units = Dalton (g/mol).

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GPC results S2 crucible sample following aging

Figure 4. Representative GPC Chromatogram of S2

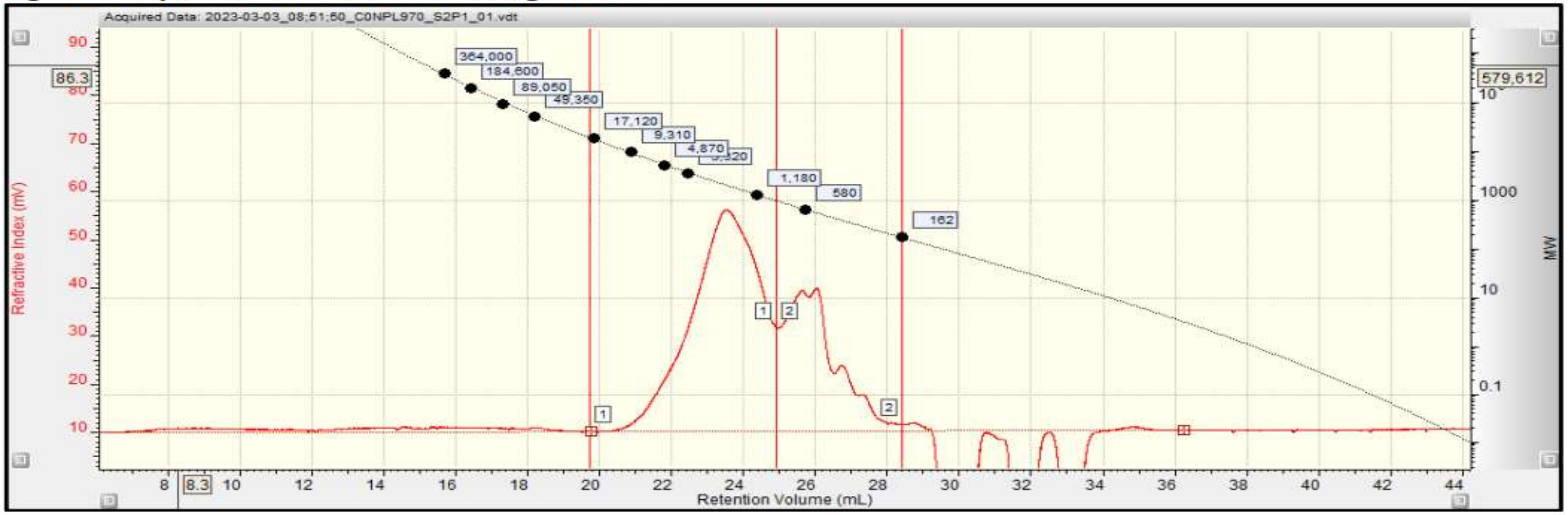

Table 2. Molecular Weight Distribution of S2

Sample Description	Peak	Preparation	Injection	$\bar{M}_P$	$\bar{M}_N$	$\bar{M}_W$	$\bar{M}_Z$	PD
C (S2)	1	1	1	1,946	1,870	2,390	3,251	1.28
			2	1,955	1,877	2,406	3,265	1.28
		2	1	1,958	1,894	2,436	3,397	1.29
			2	1,944	1,878	2,434	3,382	1.30
		Average		1,951	1,880	2,417	3,324	1.29
		Std. Dev.		7	10	22	76	0.01
		% RSD		0	1	1	2	1
	2	1	1	532	491	560	618	1.14
			2	534	502	566	619	1.13
		2	1	645	496	567	626	1.14
			2	648	492	560	618	1.14
		Average		590	495	563	620	1.14
		Std. Dev.		66	5	4	4	0.01
		% RSD		11*	1	1	1	1