Supplemental Information for Apparatus for Efficient Utilization of Isotopically-Labeled Gases in Pulse Transient Studies of Heterogeneously Catalyzed Gas Phase Reactions

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Cost Breakdown of Pulse Injection Apparatus versus Typical SSITKA System

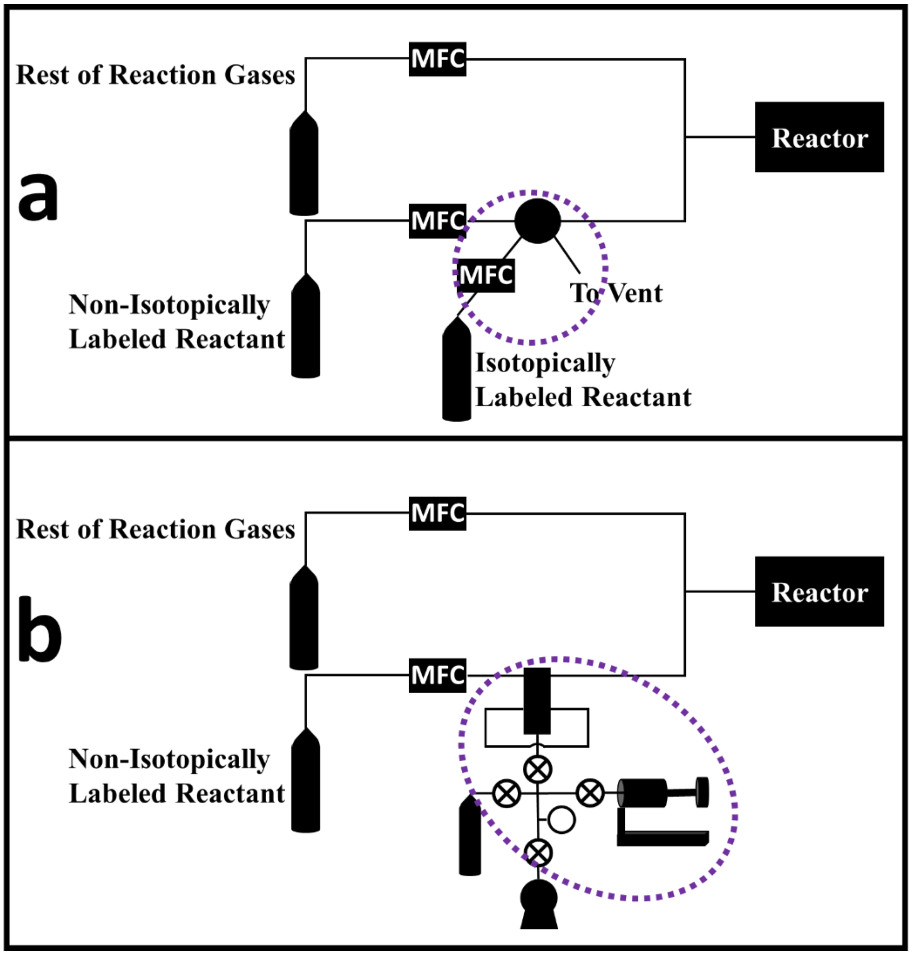

Figure S1: Block diagram of gas delivery systems for a) Typical SSITKA system, and b) Pulse Injection Apparatus described in this manuscript. The components considered in cost comparisons are circled with a purple dotted line.

Item	Size	Connections	Supplier	Price	#	Cost
VCR Gland	1/4"	Socket Weld	Swagelok	$8.30	6	$49.80
VCR Female Nut	1/4"	Nut	Swagelok	$5.40	4	$21.60
VCR Male Nut	1/4"	Nut	Swagelok	$4.60	2	$9.20
VCR Gaskets	1/4"	VCR	Swagelok	$1.40	6	$8.40
NTP-Socket Weld	1/4"	MNTP-Weld	Swagelok	$6.40	4	$25.60
SS Tubing 5ft.	1/4"	N/A	Swagelok	$16.60	1	$16.60
4 Port Valve	1/4"	4x FNPT	Sizto	$37.74	1	$37.74
Mass Flow Controller	1/4"	2x MVCR	MKS	$1,537.10	1	$1,537.10
					Total:	**$1,706.04**

Table S1: Cost estimate of typical SSITKA system.

Item	Size	Connections	Supplier	Price	#	Cost
Fittings, tubing, and valves						
Ball Valve	1/4"	2x MVCR	Swagelok	$100.00	4	$400.00
Tee	1/4"	3x MVCR	Swagelok	$36.50	1	$36.50
4-way Cross	1/4"	4x MVCR	Swagelok	$48.90	1	$48.90
Female Union	1/4"	2x FVCR	Swagelok	$22.40	6	$134.40
Pressure Gauge Adapter	1/4"	MVCR - FNPT	Swagelok	$16.30	1	$16.30
NTP-Socket Weld	1/4"	MNTP-Weld	Swagelok	$6.40	5	$32.00
VCR Gland	1/4"	Socket Weld	Swagelok	$8.30	11	$91.30
VCR Female Nut	1/4"	Nut	Swagelok	$5.40	9	$48.60
VCR Male Nut	1/4"	Nut	Swagelok	$4.60	2	$9.20
SS Tubing - 10ft.	1/4"	N/A	Swagelok	$33.20	1	$33.20
VCR Gaskets	1/4"	VCR	Swagelok	$1.40	22	$30.80
Pressure Gauge	1/4"	MNPT	McMaster-Carr	$15.15	1	$15.15
5 Port Valve	1/4"	5x FNPT	Sizto	$49.32	1	$49.32
					Subtotal:	**$945.67**
Bellows Pump Component						
Ball Screw + Handle	N/A	N/A	McMaster-Carr	$58.55	1	$58.55
Ball Screw modification and fitting (labor)	N/A	N/A	N/A	$100.00	1	$100.00
Metal Supports (materials + labor)	N/A	N/A	McMaster-Carr	$165.00	1	$165.00
Linear guide bars and bushings	N/A	N/A	McMaster-Carr	$115.00	1	$115.00
Misc. Hardware	N/A	N/A	McMaster-Carr	$15.00	1	$15.00
Volume Reducing insert	N/A	N/A	McMaster-Carr	$28.00	1	$28.00
Bellows	2.75"x2.04"	CF-CF	Lesker	$634.00	1	$634.00
Movable End Cap	2.75"	CF	Lesker	$15.50	1	$15.50
Fixed End Cap	2.75-1/4"	CF-FVCR	Lesker	$86.00	1	$86.00
					Subtotal:	**$1,217.05**
					Total:	**$2,162.72**

Table S2: Cost breakdown of Pulse Injection Apparatus system.

Based on these comparisons, the Pulse Injection Apparatus costs **~$457** more than a typical SSITKA system. These calculations do not include: labor for assembling system, isotopically labeled gas cylinder, isotopically labeled gas regulator, or components common to both systems. If a higher quality 4- or 6- port valve is desired, a Valco 4-port valve (for the typical SSITKA system) would cost $1,220 (new total cost: **$2,888.30**), and a Valco 6-port valve (for Pulse Injection Apparatus system) would cost $1,275 (new total cost: **$3388.40**), bringing the difference between the Pulse Injection Apparatus and a typical SSITKA system to **$500**. Using a pre-fabricated linear shift mechanism from Lesker ($1770) instead of fabricating the Bellows Pump Component in-house ($1,217), adds an additional $553 to the cost of the Pulse Injection

Apparatus). Finally, we did not include the price of the mechanical pump, since many facilities have existing vacuum systems that can be utilized. Buying a new mechanical pump dedicated to the Pulse Injection Apparatus would cost an additional $700-$3,000, depending on the pump selected.

Estimates on Gas Use Efficiency

Using 1L @ STP of isotopically labeled gas in a 440mL sized lecture bottle, pressurized to 20.79 psig (according to Cambridge Isotope Laboratories, a common supplier of isotopically labeled gases). Assuming reaction is running at atmospheric pressure, using ideal gas law:

$$n_{total} = \frac{PV}{RT} = \frac{(1bar)(1L)}{(0.08314\ bar \cdot L \cdot mol^{-1} \cdot K^{-1})(273.15K)} = 0.04403\ mols$$

$$n_{recoverable} = \frac{PV}{RT} = \frac{(1.433bar)(0.440L)}{(0.08314\ bar \cdot L \cdot mol^{-1} \cdot K^{-1})(298.15K)} = 0.02544\ mols$$

$$\%_{recoverable} = \frac{n_{recoverable}}{n_{total}} = \frac{0.02544}{0.04403}(100\%) = 57.78\%$$

This is close to the rough approximation of 56% recoverable gas by assuming volume of lecture bottle is unrecoverable (440mL), leaving ~560mL out of 1L (i.e. 56%) recoverable.

If we assume ~10% gas loss due to venting and bottle change-out, the gas use efficiency becomes (0.9)(57.78%) = **52.00%**

If we assume ~10% gas loss using the Pulse Injection Apparatus from vacuuming and bottle change-out, the gas use efficiency of the Pulse Injection Apparatus becomes **90%**

This represents an improvement of **~1.7x** in gas use efficiency. This increases the amount of gas available to the researcher by **73%**.

Not including shipping costs for refilling the lecture bottle, 99% $^{13}CH_4$ is $264.00 for a 1L bottle.
Cost of unused gas in typical SSITKA system: (0.48)($264.00) = **$126.72**
Cost of unused gas in Pulse Injection Apparatus system: (0.1)($264.00) = **$26.40**
Difference per bottle = **$100.32**

Assuming the Pulse Injection Apparatus costs ~$500 more than a typical SSITKA system, the return on investment for building the Pulse Injection Apparatus is **~5 Bottles of $^{13}CH_4$** (or another equally priced isotopically labeled gas)

Theoretical Operation for VOC reactants

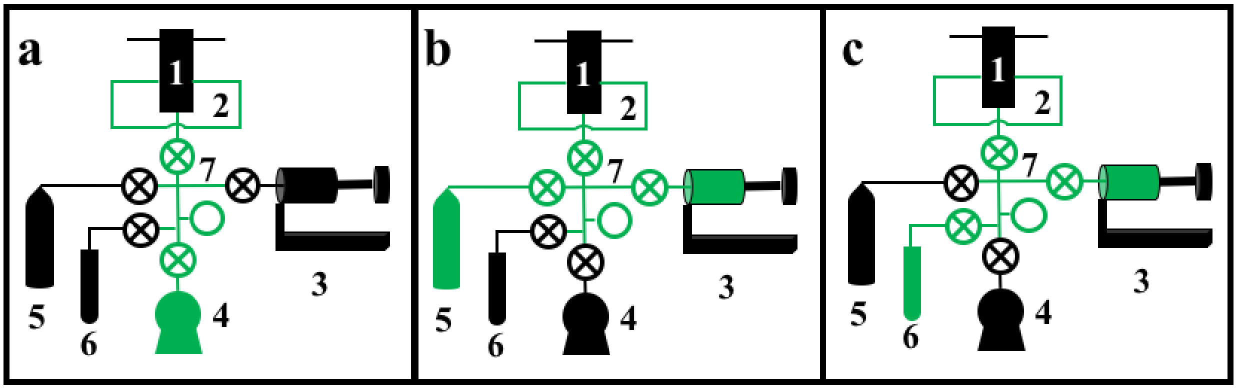

Figure S2: Theoretical operation for using VOC isotopically labeled reactants; A) Sample loop evacuation; B) Carrier gas filling; C) VOC reactant filling; Labeled components: 1) 5-port valve, 2) Sample loop, 3) Bellows pump; 4) Vacuum pump, 5) Carrier gas, 6) Isotopically labeled VOC, 7) Valve manifold

Theoretically, this apparatus could be used to inject a pulse of isotopically labeled VOC + carrier gas, that could be placed in line after a VOC saturator. Similar to a saturator, the partial pressure of the VOC is controlled by heating the VOC to a temperature such that: $X_{VOC} = \frac{VP_{VOC}}{P_{reactor}}$, where X_{VOC} is the mole fraction of the VOC in the saturator line, VP_{VOC} is the vapor pressure of the VOC at the temperature the vial of VOC is heated to, and $P_{reactor}$ is the pressure of the reaction (or pressure of the saturator line). In our design, Figure S1 depicts the way to obtain a pulse of isotopically labeled VOC:

a) Evacuate the sample loop with the vacuum pump
b) With the bellows pump partially compressed, fill the bellows pump and sample loop with a low pressure of the carrier gas used in the saturator line
c) Open the vial of VOC to the bellows pump and sample loop. Expand and adjust the bellows pump until the total pressure equals $P_{reactor}$. This requires waiting for the VOC to reach vapor-liquid equilibrium, and iterating the bellows pump compression to reach $P_{reactor}$.

We stress that this is merely a theoretical design, and have not explored the practical feasibility of this design. The biggest impediment will likely be the time required to let the VOC reach vapor-liquid equilibrium at $P_{reactor}$ as well as time required to let the VOC and carrier gases mix thoroughly. Since the main benefit of the Pulse Injection Apparatus is the ability to recover the sub-atmosphere gas in the isotopically labeled gas cylinder, the same benefit may not extend to VOC samples. However, this design does not have a practical minimum of isotopically labeled VOC requirement, the way a saturator may (for example, a minimum liquid level required to let the carrier gas sparge effectively). Finally, this design would require the bellows pump, valve manifold, sample loop, and 5-port valve to be heated to a temperature above the VOC saturator temperature in order to avoid VOC condensation in other parts of the system.

Pulse Functions at Different Flowrates

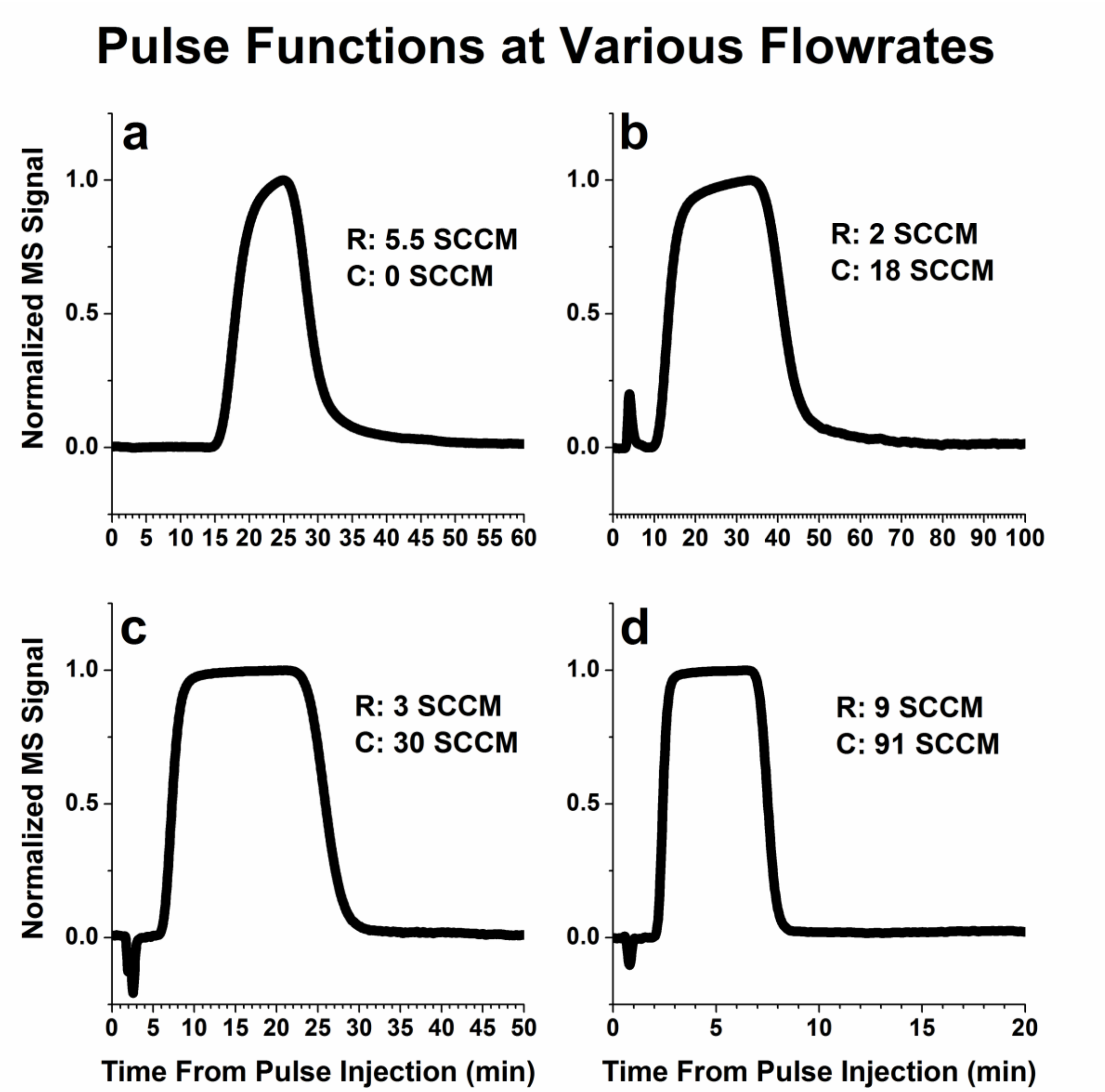

Figure S3: Shape of the pulse functions at various flowrates of the isotopically-labeled/non-isotopically-labeled reactant gas ("R") and the total flowrate of the remaining gases ("C" for generic "carrier gas"). a) 5.5 Standard Cubic Centimeters (SCCM) reactant gas, 0 SCCM Carrier Gases; b) 2 SCCM reactant gas, 18 SCCM carrier gases; c) 3 SCCM reactant gas, 30 SCCM carrier gases; d) 9 SCCM reactant gas, 91 SCCM carrier gases.

Figure S3 demonstrates the effect on flowrate (and therefore time for diffusion and other mass transfer effects to occur) on the pulse function. The ¼" tubing we used has a volume of ~16.4mL per meter. Relevant reactor system tubing lengths:

Pulse Injection Apparatus to connection joining with other gases (i.e. connection where "R" and "C" join): 99cm

Connection joining "R" and "C" to reactor: 286cm

Reactor to Mass Spectrometer: 51cm